MSCPH-552

M. Sc. IVth Semester

Material Science

DEPARTMENT OF PHYSICS

SCHOOL OF SCIENCES

UTTARAKHAND OPEN UNIVERSITY

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UNIT 1 OVERVIEW OF MATERIALS

Structure

1.1 INTRODUCTION

The branch of physics which deal with the properties of materials is known as Material Science. Any physical substance that can be used for the preparation of a thing can be called material. We are living in a world of materials and the maximum of it is in solid form. Many things used by humans are made up of different types of solid materials. Human civilization can be distinguished on the basis of the material that they used. Transportation, housing, clothing, utensils, communication, food production, every segment of our life is influenced by materials. Historically humans had been designed by the level of their ability to develop materials and called as Stone Age, Bronze Age, Iron Age, etc. The earliest human knew few of the naturally occurring materials like stone, wood, clay, bone, silica, and so on. With the passing of time, they developed techniques for producing more materials of utility such as pottery and various metals. Later on, humans discover heat treatment of clay and pots or metals for superior properties. After a long journey of human society, finally, they have developed many technologies that make our life so comfortable. In our contemporary era, sophisticated composite materials, and semiconductor-based devices are being made that highly influence human society.

The field of material science deals with investigating the structure, properties, synthesis of the material, performance, development, etc. On the other hand, material engineering deals with the designing of the material for desired requirements. Properties like strength, modulus, and electrical, thermal, and chemical properties of solids depend on their atomic and molecular structures. To study materials, first, we have to understand the structure of solid materials. Previously, solid-state physics is concerned with crystalline solids and their properties. Later on, the study of materials has been extended, and many new materials like nanocrystalline, amorphous, glasses, liquid crystals, polymer, composite materials, and many other new materials are included in this branch. This new and comparatively wider field is known as Condensed Matter Physics. It is a new and largest area of Physics that is useful to understand the nature of matter ranging from fundamental particles to matter in the universe.

1.2 OBJECTIVE

After reading this unit, we will be able to understand:

1. Basic idea about atomic structure

2. Different types of bonds
3. Basic idea Crystal structure
4. Classification of materials
5. Advanced materials
6. Significance of material science

1.3 FUNDAMENTAL CONCEPTS OF ATOMIC STRUCTURE:

In this unit, we are going to start with some fundamental concepts of atomic structures and their interatomic bonding. So first, let us know why it is required to study atomic structures and interatomic bonding. Generally, there is a relationship between structure and the properties of materials and they give a particular essence of how the material will behave. Some properties in solids strongly depend on the type of atomic structures and interatomic bonding. Every material has some atomic structures and interatomic bonding because the atoms are closely packed with some bonding, otherwise, the atoms can go randomly anywhere, so there should be some force that can act in between the atoms. Thus, the atomic level structure can strongly influence material performance, so this is a vital point in material science.

Now we will discuss the material performance. Generally, we talk about the modulus, melting point, and coefficient of expansion of the materials. Material performance directly defines the properties of materials; of course, from that particular point of view, we can get information about the materials. Carbon exists in different structural forms. We can consider carbon as diamond and graphite from a material point of view. Different structures of carbon are shown in Figure 1.1.

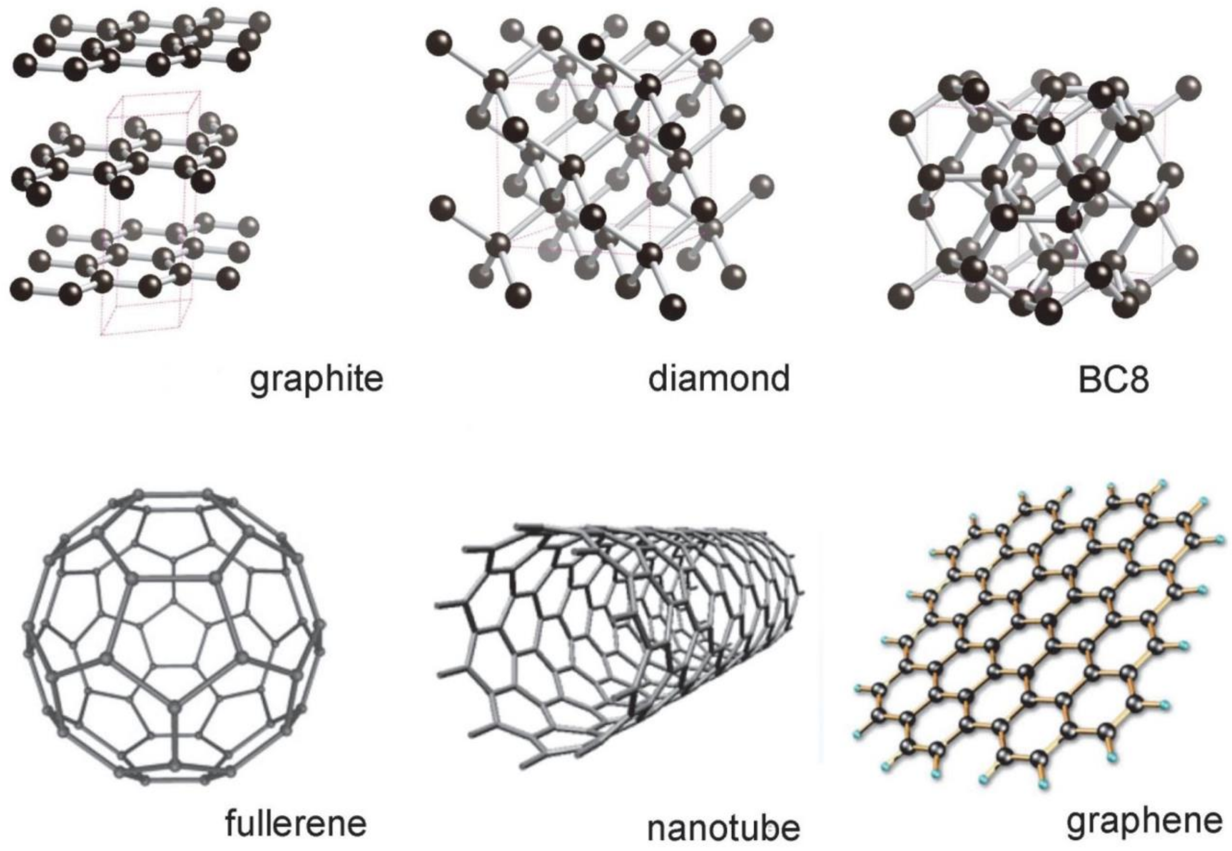

Figure 1.1: Different forms of carbon.

In Figure 1.1, some forms of carbon are illustrated like graphite, diamond, fullerene, carbon nanotube, etc. Graphite looks dull, opaque, and soft and the common materials mean easily available, when we are talking about the diamond it is very brilliance and transparent, and it is having some glittering, or maybe some kind of reflection in nature, it is very hard and it is alsothe rear earth materials because it is not easily available, you can prepare it some kind of artificial diamond, but with some help of high-end equipment. Generally, we can see the crystal structure of the graphite and the crystal structureof the diamond also, there is some crystal structure of the graphite that is layer-by-layer stacking, and in the diamond, it is a closed-packed carbon atom. Now we briefly review atomic structure. Generally, atoms are made of two things nucleus and electrons. Further, the nucleus is constituted by two things that are the protons and the neutrons. The electrons revolve around the nucleus. So, the atom is divided into two groups, one is the nucleus, and the other is electrons. The electrons are negatively charged particles, protons are positively charged particles and neutrons are electrically neutrons. The atomic structure is shown in Figure 1.2. The magnitude of the charge on electron and protons are 1.6 x 10^{-19} coulombs, and the protons and neutrons masses are 1.67 x10^{-27} kg, for electron it is 9.11 x10^{-31} kg.

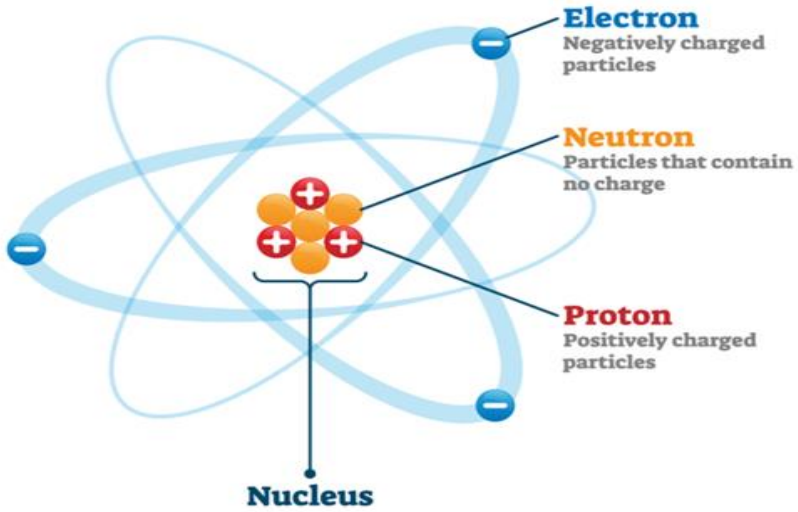

Figure 1.2: Atomic Structure

Now we review atomic mass as this term will appear frequently in this course. The atomic mass unit or maybe theAMU is equal to 1/12 the mass of the carbon atom. Generally, it's the proton mass and the neutron mass. A mole is the amount of matter that has a mass in grams equal to the atomic mass in AMU of atoms, so the number of atoms in a mole is called the Avogadro number, and the Avogadro number is 6.023 x 10^{23} atoms. Now let us know the behavior of electrons, generally, it's a wavelike behavior as shown in Figure 1.3.

Quantum mechanically we can only give the probability of an electron being in a particular position or in volume, more accurately presentation of an electron is as a cloud. Quantum mechanics is used to describing the wave behavior of electrons, generally, the electronic structure of isolated atoms, characteristics of the electron's wavelike nature, electrons are in orbitals, and each orbital is at a discrete energy level determined by its quantum numbers. The quantum number originated by applying quantum mechanics in the hydrogen atom which represents the simplest atomic structure.

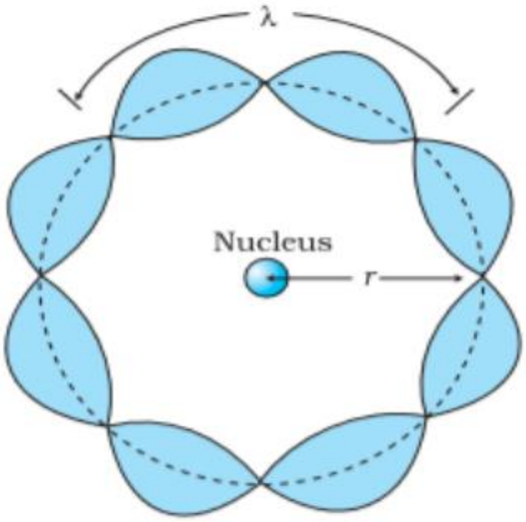

Figure 1.3: Wave-like behavior of electron

Principal ***qatum numbers*** n = 1, , 3,… The energy of an electron a shell is given by Equation $E_n = -\frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n^2}\right)$. Since, the energy eigen values depend only on quantum number n, they were in excellent agreement experimental values based on with Bohr model. Hence, n is said to be known as "a *Principal Quantum Number*". The second is orbital quantum number l= 0, 1, 2, 3,… (n-1). l varies from *0, 1, 2, 3,…(n-1)*, this proves that the electron can have discrete values of angular momentum. Finally, the total energy E is also quantized like the orbital angular momentum and it remains conserved. And this is just demonstrated by the quantization of l. Hence, l is termed as the 'orbital' quantum number. The expression for angular momentum was obtained through the theory of Born-Sommerfield, wher k was relaced by $\sqrt{(l(l+1)}$. For example, a state with n = 2 with l = 0 is shown as *2s* state. Similarly, another state with n = 3 and l=1 is written as *3p*.

Third is as magnetic quantum number. $m_l, \pm1, \pm2, \pm3, \dots, \pm l$. The analysis of m_l originates when the atom is placed in an external magnetic field. You can imagine that when an electron is revolving around the nucleus, it behaves like a small loop of current having a magnetic dipole when placed in an external magnetic field. Its potential energy depends upon its magnetic moment and its orientation with respect to the field. But here, the magnitude and direction of the magnetic moment depend upon the magnitude and direction of angular momentum $\vec{L}$ of the electron. This also determines the magnetic potential energy. Since the direction of L is also quantized with respect to the external magnetic field. If the field is along the z-axis, the component of $\vec{L}$can be defined as

$$L_z = m_l \frac{h}{2\pi}, \text{ where } \qquad m_l = 0, \pm1, \pm2, \pm3, \dots, \pm l.$$

Since we can observe that m_l describes the quantization of $\vec{L}$in magnetic field (known as space quantization), and finally, the discretization of magnetic energy of the electron. Therefore, m_l is known as a magnetic quantum number. Therefore, *n, l*, and m_l are the three quantum numbers used to specify each of the eigenfunctions of a single electron atom here n specifies the total energy (the eigenvalue), *l* specifies the angular momentum and m_l determines the z-component of the angular momentum of the electron. For a given value of n, there are different values of *l* and for every different value of *l*, we have several values of m_l. Hence, several different eigenfunctions resemble exactly the same eigenvalue E_n. And this property of eigenfunctions is said to be a 'degenerate' state. The last is spin quantum number s which shows the spin state of an electron in the orbit.

The electron configuration is stable only for the noble gases, except for noble gases the outer shell is not completely filled, because there is somevacancy, so one or more electrons may be lost or gained to form an ion or shared in a covalent bond, have complete S and P subshells, tend to be very, very unreactive, so here you can see theelement and atomic number and the electronic configurations, so for hydrogen generally it is 1S1, for helium it is 1S2 because an atomic number is 2, so when we are talking about the say post carbon so it is 6 that means 1S2, 2S2, and 2P2 so it's total 6, when you are talking about the magnesium it's 12, 1S2, 2S2, 2P6 and the 3S2, when we are talking about the argon it is having 18 like 1S2, 2S2, 2P6, 3S2, 3P6 so it's show on.

1.4 PERIODIC TABLE:

Now we are going to discuss the periodic table. The elements are arranged with increasingatomic number, and elements in groups or columns have similar valence electrons and physiochemical properties (Figure 1.4). For example, the elements in group 8A, are particular case of inert gases which have stable electron configurations and the examples are helium, neon, argon, krypton, xenon, radon. In group 7A there are halogens that have one or two electrons deficiency, like for fluorine, chlorine, bromine, iodine. like that, in group 1A and 2A, so when we are talking about 1A and 2A alkali and the alkaline earth metals 1 or 2 electrons in excess like hydrogen, lithium, sodium, potassium, like beryllium, magnesium, calcium like that. In group 3B and 2B so generally here is that 3B and here is the 2B so in this particular case thisall are that transition metals, like strontium, like zinc, like cadmium, like mercury so and so on,in group 3A, 4A, and 5A so in this particular case the 3A, 4A, and 5A so this group so it is the intermediates between metals and non-metals like boron, carbon, nitrogen or maybe aluminum,silicon, phosphorous, gallium, germanium, arsenide, so on.

Electronegativity is the tendency of an atom to accept electrons that’s why it became negative, so electropositive elements readily give up electrons to become positive ions, so it losing the electrons. Electronegative elements readily acquired the electrons to become the negative ions, so it is accepting the electrons, it increases in moving from left to right and top to bottom, so it increases in the moving from left to right, and from the top to bottom.

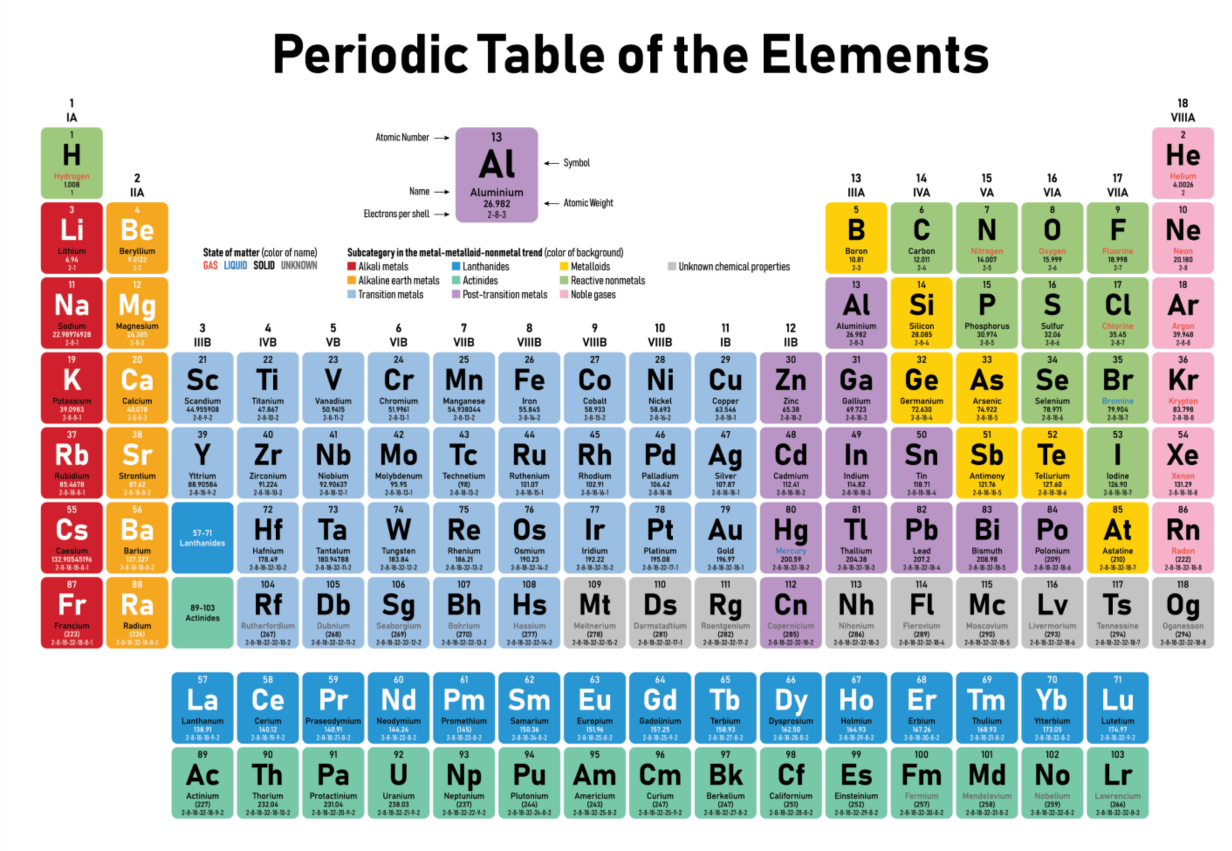

Figure 1.4: Periodic table

1.5 ATOMIC BONDING IN SOLIDS:

Now we will briefly discuss the atomic bonding in solids. Atoms are bound to each other by a number of bonds as we already know which made the atomic cluster together and atoms are arranged. we are having so many atoms so there should be some bonding, then only the atoms can come close together and give a compact shape. The principle of atomic bonding is considered as the interactions between two isolated atoms as they are brought into close proximity from an infinite separation. Solids are basically aggregates of atoms. For the existence of a solid, there is a binding force that binds the atoms in molecules and molecules in a solid. In solids, the interatomic forces are of two types, one is repulsive to prevent the atoms from merging with each other, and the other is attractive to keep them close. Both the attractive and repulsive forces depend on the interatomic separation (generally denoted by r). At a particular separation called equilibrium separation r_0, the force of repulsion is equal to the force of attraction. At this position, the potential energy of the system becomes minimum and the crystal becomes stable. Figure 3.1 show the variation of interatomic force (denoted by F) with interatomic separation r. The potential energy or internal energy of a solid or material is the sum of all individual energies of atoms plus their interaction energies. The potential energy is the sum of repulsive and attractive energy of atoms which again depends on the interatomic separation r. At equilibrium position $r= r_0$ the potential energy U(r) becomes minimum as shown in Figure 1.5 and the solid becomes stable. For example, the NaCl crystal is more stable than Na and Cl atoms. Thus, the energy of the NaCl crystal is less than the individual energy of Na and Cl atoms. This means the energy of the crystal is less than the energy of individual free atoms. The difference in the energies is nothing but binding energy. Thus binding energy is defined as the energy required to keep the atoms or molecules in a solid to an infinite separation.

Similarly, the cohesive energy of a crystal is also defined as the energy required for separating its components (ion or molecule) into neutral free atoms at infinite separation with some electronic configuration. For example, the cohesive energy of nitrogen solid is the energy required to separate nitrogen molecules from nitrogen solids as nitrogen molecules are the component of solid nitrogen. Similarly, in the case of NaCl crystal, the cohesive energy of NaCl is the energy required to separate the NaCl solid into isolated Na^+ and Cl^- ions, instead of atoms, as ions are the components of NaCl crystal. In the case of metallic solids, the cohesive energy of metallic solids is the energy required to separate their components (neutral atoms) into neutral atoms of metals. Sometimes we use the term binding energy defined as the energy required to separate a particle from a system of particles. This term is generally used in sub-atomic particle line electron (e), proton (p) or neutron (n), etc. in atomic nuclei. In the crystal, the binding energy is energy which includes cohesive energy and ionization energy. For example, in magnesium, cohesive energy is 1.51eV/atom, ionization energy is 22.67eV/atom and binding energy is 24.18 eV/atom.

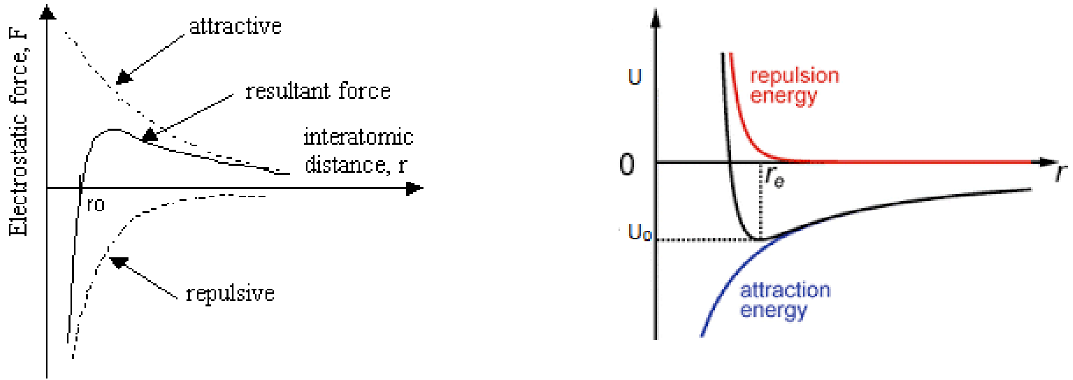

Figure 3.1: Variation of interatomic force to interatomic separation

Figure 3.2: Variation of Potential Energy and interatomic separation

Figure 1.5: Variation of interatomic force and potential energy

1,5.1 Cohesive Energy

The potential energy between two atoms in solid varies greatly with interatomic spacing r and generally given by

$$U(r) = \frac{a}{r^m} + \frac{b}{r^n} \qquad (1)$$

Where n and m are integer numbers.

The individual atoms in a solid must be hold together by interatomic forces and known as bond. However, there are repulsive forces which provide elasticity to crystal and avoid the atoms to collapse on each other. The attractive forces among the constituent particles are basically electrostatic and depend on the electronic configuration of atoms. Depending on the configuration of atoms, different types of bonding occur as Vander Waal bonding, ionic bonding, coordinate bonding and metallic bonding etc. Based on different types of bonding different kinds of solids come into existence as discussed in next steps.

Classification of Atomic Bonds:

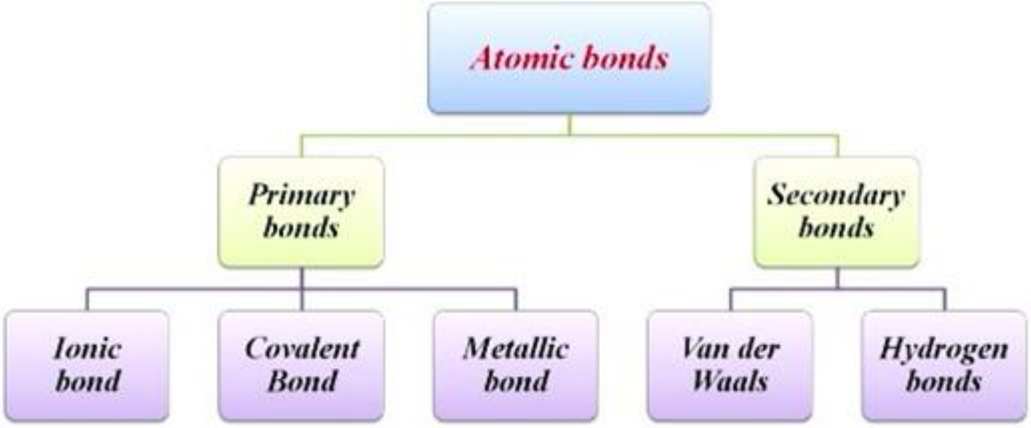

Figure 1.6: Classification of Bonding.

We have already study about the different types of bonding in solids. So now we are going to discuss about the effects of bonding on the properties of materials and how it effects. Two important factors contributing to properties of materials is the nature of bonding and the atomic structure. First we are going to discuss the covalent bond, in this case bond energy is 5 electron volt melting point is high, hardness in terms of ductility it is hard, and ductility is very, very poor, electrical conductivity is very low, and the examples diamond, graphite, germanium, silicon. In ionic bond, generally the bond energy is 1, 2, 3, melting point is high,it's hardness is hard, ductility is very very poor, electrical conductivity is low like sodium chloride, zinc sulfite and the CACL. In metallic bonds, it's energy is 0.5 electron volt, it's melting point varies, hardness also varies and electrical conductivity is very very high like iron, copper, silver, etc. In case of Van der Waals force it varies from 0.001 to 0.1, melting point islow, then hardness is soft but ductility is also very poor, electrical conductivity is also low like neon, argon, krypton. The last one is the hydrogen, it's melting point is very very low, hardness is soft, and ductility is poor, usually low and generally the example is the ice or maybe the water. The comparison is shown in figure 1.7.

Bond	Bond Energy (eV)	Melting point	Hardness (Ductility)	Electrical Conductivity	Examples
Covalent	5 (8×10^{-19} J)	High	Hard (poor)	Usually Low	Diamond, Graphite, Ge, Si
Ionic	1-3	High	Hard (poor)	Low	NaCl, ZnS, CsCl
Metallic	0.5	Varies	Varies	High	Fe, Cu, Ag
Van der Waals	0.001-0.1	Low	Soft (poor)	Low	Ne, Ar, Kr
Hydrogen		Low	Soft (poor)	Usually Low	Ice

Figure 1.7: Comparison of different types of Bonding.

1.6 Material properties:

As we know materials means any physical substance which is used to make things, material. The material word come from actually it’s aLatin word, means a material which means relating to the matter, the matter from which a thing is or can be made so that means from materials we can make something, some product. On the basis of microstructure,there are two properties one is called the sensitive properties, another one is called the microstructure insensitive properties. Microstructures’ sensitive properties are yield stress, hardness, and magnetic properties. And microstructure insensitive properties mean density, and elastic modulus which cannot be directly get from that particular material, but we can calculate by some other input parameters. Important parameters to understand the properties, the first is known as the atomic structure, the second one is known as the electromagnetic structure or maybe the interatomic bonding, and the third one is known as the microstructure.

1.7 Classification of Materials:

Now we discuss the classification of materials. On the basis of phase, the material can be gas, liquid, or maybe solid. Based on structure, structure means the arrangement of atoms or maybe the molecules or maybe the ions, materials can be classified as crystalline, semi-crystalline, quasi-crystalline, or amorphous. Similarly, based on band structure materials can be classified as metals, semi-metals, semiconductors, and insulators. But in general solid materials are conventionally classified as metals, ceramics, polymers, and composite materials. The classification of material is shown in Figure 1.8.

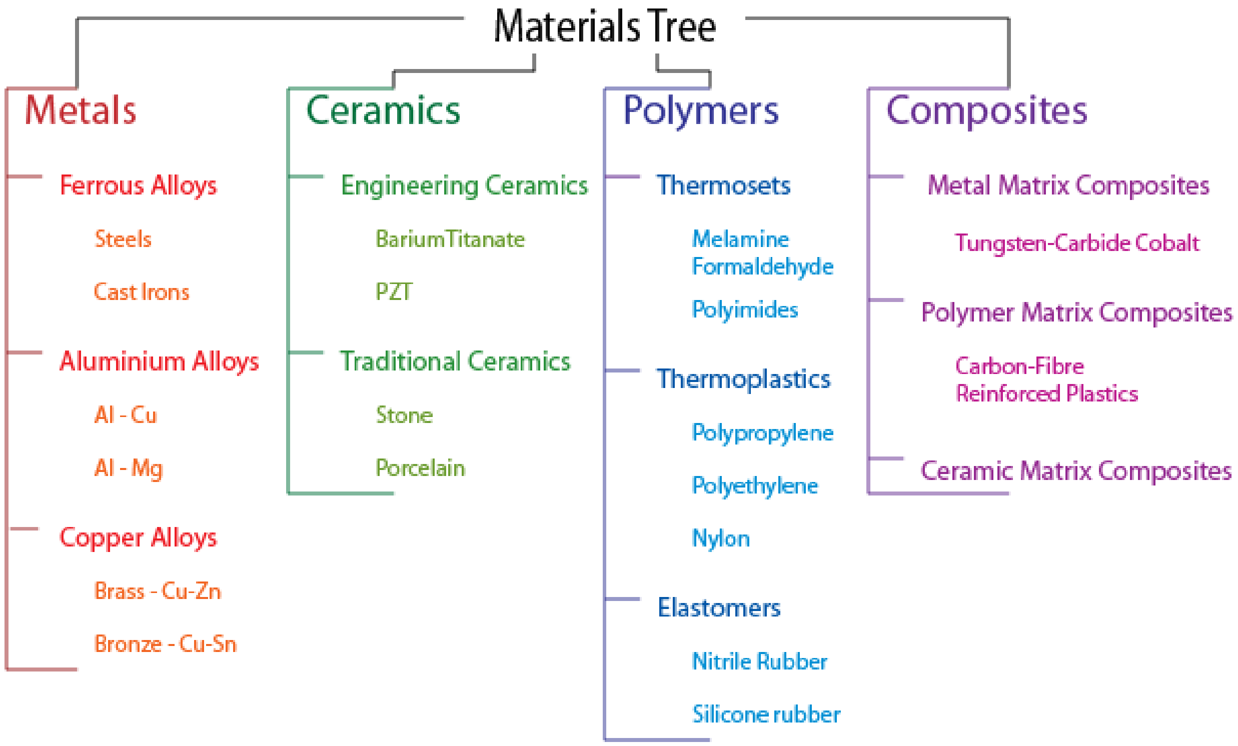

Figure 1.8: Classification of materials.

Another classification is based on advanced materials used in advanced technologies such as semiconductors, biomaterials, smart materials, nanomaterials etc. This classification is known as the Functional Classification of Materials and is given as

1-Aerospace

2-Biomedical

3-Electronic Materials

4-Energy and Environmental Technology material

5-Magnetic Materials

6-Photonic or Optical Materials

7-Smart Materials

8-Structural Materials

1.7.1 Metals:

Metals are basically some elements available in the periodic table (iron, aluminum, gold, silver, copper, nickel, etc.) and available in nature in different forms. About 91 of the 118 elements in the periodic table are metals, so if we carefully see the periodic table of materials, we can find that blue in color all are generally metals, so there are a total of 91 elements that are metals. Metal may be a material or element, compound, or alloy. Typically, metals are hard when in the solid state, opaque and shiny. Metals are generally malleable and ductile. Due to specific mechanical and electrical and other properties of metals, these are highly useful for human society. So, copper, copperis used for electrical wiring, because it is a very good conductor of electricity and malleable. Iron is used to make cars, and bridges, generally we can understand or know that generally iron we are used for structural applications, so because it is too hard with high tensile strength. We will study the metals in detail in the next unit. The metals have also high density as shown in Figure 1.9. Regarding Mechanical properties, these materials are relatively strong. The tensile strength of metals with different materials is shown in Figure 1.10.

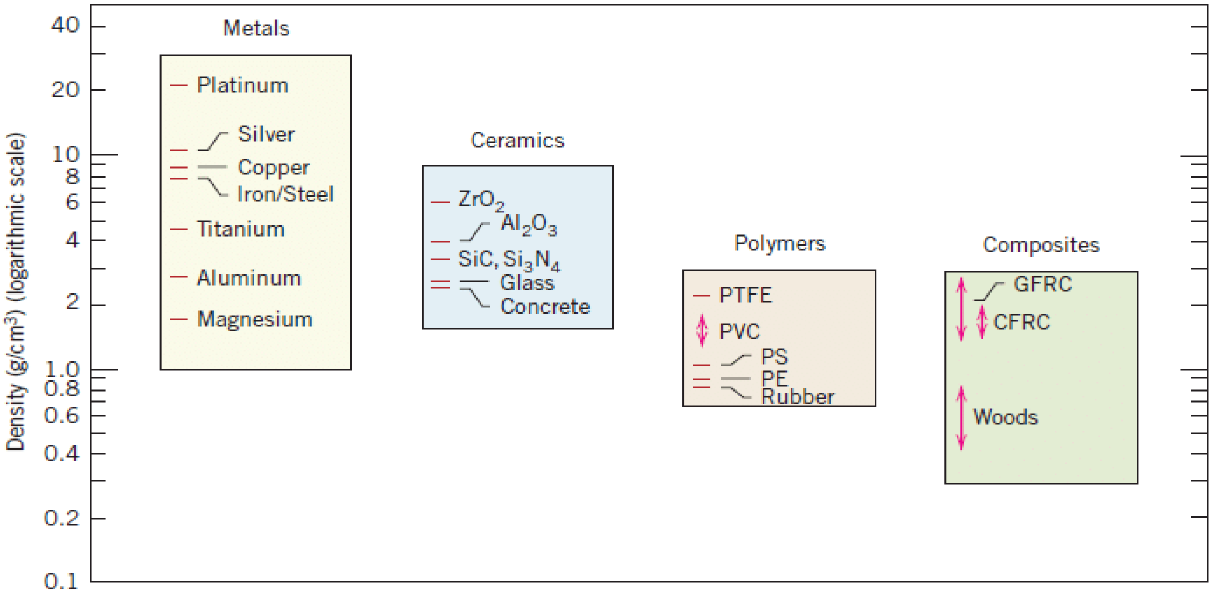

Figure 1.9: Density of different materials

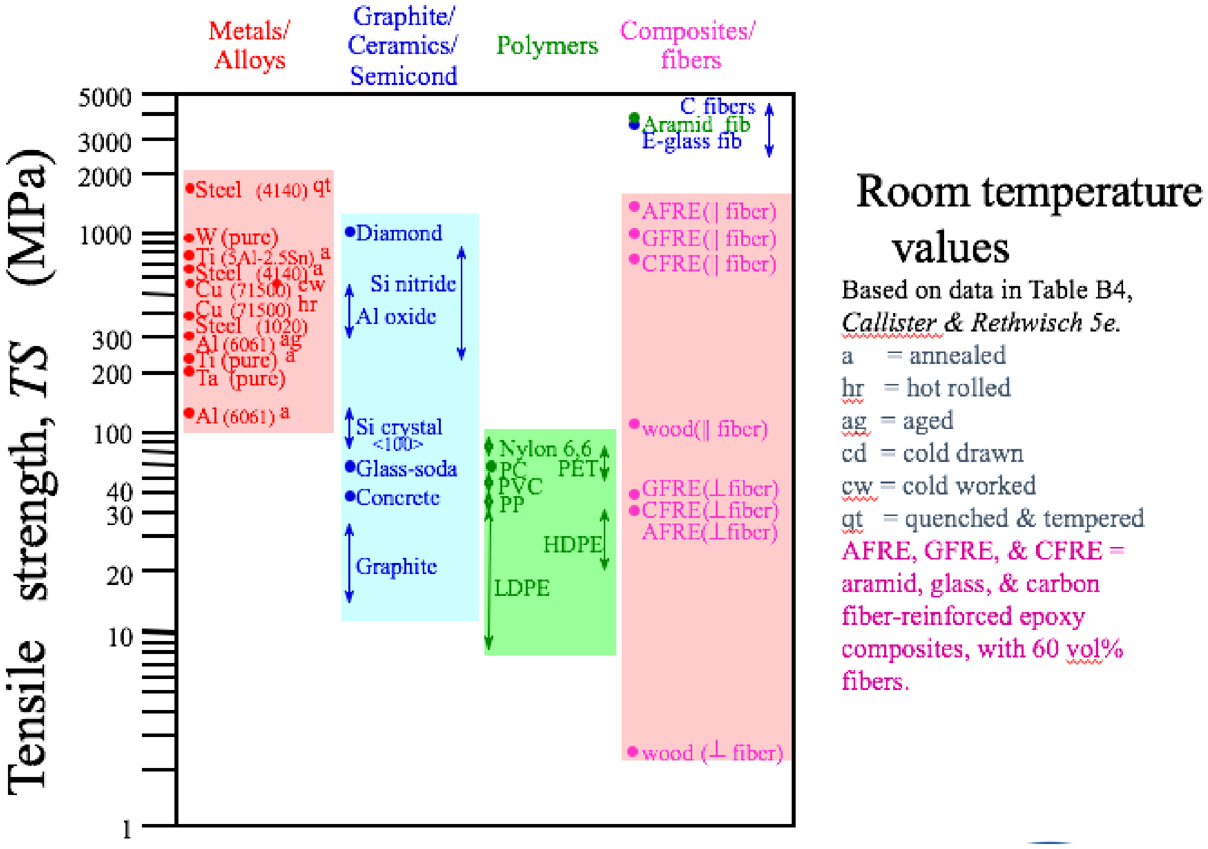

Figure 1.10: Tensile strength of different materials

Figure 1.11: Some examples that are made of metals and metal alloys

1.7.2 Ceramics:

Ceramic materials are inorganic, non-metallic solids which are generally oxide, nitride, or carbide materials. Some elements, such as carbon or silicon, may also be considered ceramics. Some of the common ceramic materials are aluminum oxide (alumina Al_2O_3), Silicon dioxide (silica SiO_2) silicon carbide (SiC), silicon nitride (Si_3N_4), etc. Ceramics are compounds between metallic and nonmetallic elements. Other common examples are earthenware, porcelain, and brick. Ceramic materials are brittle, hard, strong in compression, heat-resistant, corrosion-resistant materials, and weak in shearing and tension. A ceramic is made by shaping and then firing an inorganic, nonmetallic material, such as clay, at a high temperature. The earliest ceramics made by humans were pottery objects (pots, vessels, or vases) or figurines made from clay, either by itself or mixed with other materials like silica, hardened and sintered in the fire. Later, ceramics were glazed and fired to create smooth, colored surfaces, decreasing porosity through the use of glassy, amorphous ceramic coatings on top of the crystalline ceramic substrates. Ceramics now include domestic, industrial, and building products, as well as a wide range of materials developed for use in advanced ceramic engineering, such as in semiconductors. They withstand chemical erosion that occurs in other materials subjected to acidic or caustic environments. Ceramics generally can withstand very high temperatures, ranging from 1,000 °C to

1,600 °C (1,800 °F to 3,000 °F). These materials are typically insulative in nature and do not pass heat and electricity. Figure 1.12 shows the electrical conductivity of ceramics and other different types of materials.

These materials may be optically transparent or opaque and some oxide ceramic material show magnetic properties also.

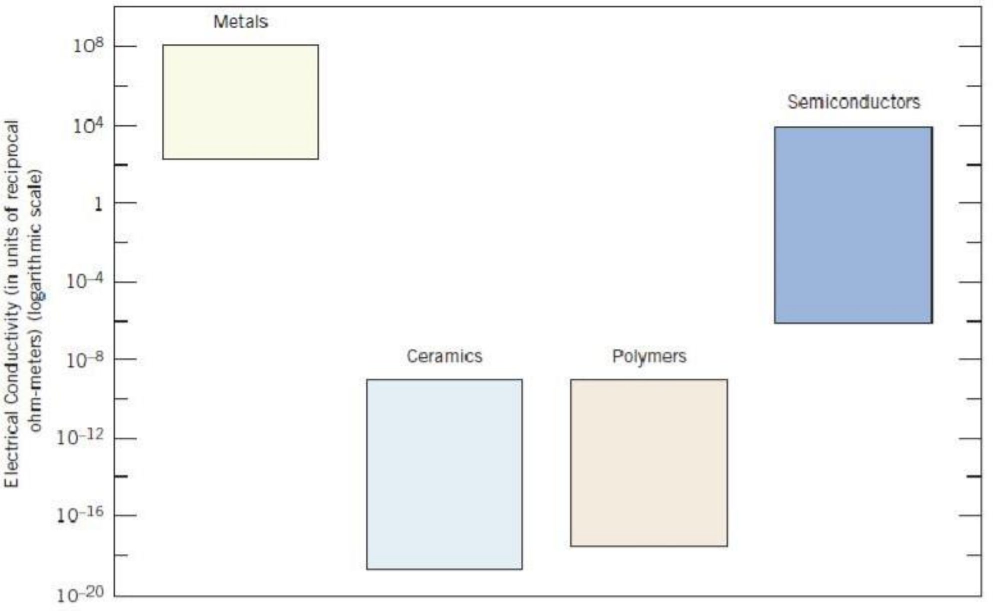

Figure 1.12: Electrical conductivity of different materials

The crystalline structure of ceramic materials varies widely. Most often, fired ceramics are either vitrified or semi-vitrified as is the case with earthenware, stoneware, and porcelain. Varying crystallinity and electron composition in the ionic and covalent bonds cause most ceramic materials to be good thermal and electrical insulators. With such a large range of possible options for the composition/structure of a ceramic (nearly all of the elements, nearly all types of bonding, and all levels of crystallinity), the breadth of the subject is vast and identifiable attributes (hardness, toughness, electrical conductivity) are difficult to specify for the group as a whole. General properties such as high melting temperature, high hardness, poor conductivity, high moduli of elasticity, chemical resistance, and low ductility are the norm, with known exceptions to each of these rules (piezoelectric ceramics, glass transition temperature, superconductive ceramics). Many composites, such as fiberglass and carbon fiber, while containing ceramic materials are not considered to be part of the ceramic family. Many ceramics experts do not consider materials with amorphous (noncrystalline) character (i.e., glass) to be ceramics even though glassmaking involves several steps of the ceramic process and its mechanical properties are similar to ceramic materials. However, heat treatments can convert glass into a semi-crystalline material known as glass-ceramic.

Figure 1.13: Some examples of ceramics.

1.7.3 Polymers:

Polymers include the familiar plastic and rubber materials. Many of them are organic compounds that are chemically based on carbon, hydrogen, and other nonmetallic elements (viz. O, N, and Si). Furthermore, they have very large molecular structures, often chain-like in nature that have a backbone of carbon atoms. Some of the common and familiar polymers are polyethylene (PE), nylon, poly(vinyl chloride) (PVC), polycarbonate (PC), polystyrene (PS), and silicone rubber. These materials typically have low densities (Figure 1.9), whereas their mechanical characteristics are generally dissimilar to the metallic and ceramic materials—they are not as stiff nor as strong as these other material types (Figures 1.10). However, on the basis of their low densities, many times their stiffnesses and strengths on a per mass. In addition, many polymers are extremely ductile and pliable (i.e., plastic), which means they are easily formed into complex shapes. In general, they are relatively inert chemically and unreactive in a large number of environments. One major drawback to the polymers is their tendency to soften and/or decompose at modest temperatures, which, in some instances, limits their use. Furthermore, they have low electrical conductivities (Figure 1.12) andare nonmagnetic. The photograph in Figure 1.14 shows several articles made of polymersthat are familiar to the reader. Several common objects that are made of polymeric materials: are plastic tableware (spoon, fork, and knife), billiard balls, a bicycle helmet, two dice, a lawnmower wheel (plastic hub and rubber tire), and a plastic milk carton.

Polymers exhibit a wide range of stress-strain behaviors as shown in the figure below. The brittle polymer (red curve) elastically deforms and fractures before deforming plastically. The blue curve is a plastic polymer and is similar to curves for many metals. Its behavior begins in the linear elastic deformation region. As the curve transitions from elastic to plastic deformation typically there is a peak stress. For polymer materials, this peak stress is identified as the yield stress. As the material is pulled further, fracture occurs. The stress value when a fracture occurs is defined as the tensile strength of polymer materials. The tensile strength can be greater than, equal to, or less than the yield strength. The green curve is a class of polymers known as elastomers. These materials exhibit rubber-like elasticity and will return to their original shape and form unless they are extended to the point of fracture.

Polymers exhibit a wide range of stress-strain behaviors as shown in figure 1.15 below. The brittle polymer (red curve) elastically deforms and fractures before deforming plastically. The blue curve is a plastic polymer and is similar to curves for many metals. Its behavior begins in the linear elastic deformation region. As the curve transitions from elastic to plastic deformation typically there is a peak stress. For polymer materials, this peak stress is identified as the yield stress. As the material is pulled further, fracture occurs. The stress value when a fracture occurs is defined as the tensile strength of polymer materials. The tensile strength can be greater than, equal to, or less than the yield strength. The green curve is a class of polymers known as elastomers. These materials exhibit rubber-like elasticity and will return to their original shape and form unless they are extended to the point of fracture.

Figure 1.14: Some examples of polymer

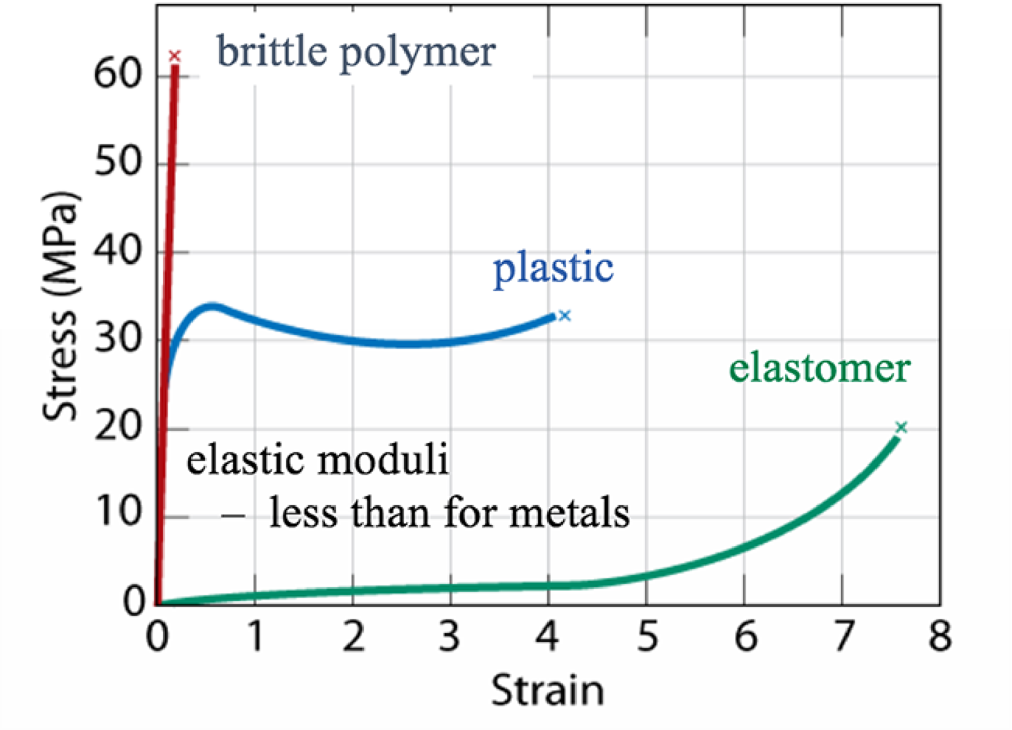

Figure 1.15: Stress-strain behaviors of polymer

1.7.4 Composites:

A composite is made of two (or more) individual materials, which come from the categories discussed above—viz., metals, ceramics, and polymers. The design goal of a composite is to achieve a combination of properties that is not obtained by any single material, and also to incorporate the best characteristics of each of the component materials. A large number of composite types exist that are represented by different combinations of metals, ceramics, and polymers. Furthermore, some naturally-occurring materials are also considered to be composites—for example, wood and bone. Wood and many other plant tissues contain the cellulose chain polymer in a matrix of lignin, phenol polymer, and other organic compounds. However, most of those we consider in our discussions are synthetic (or man-made) composites. One of the most common and familiar composites is fiberglass, in which small glass fibers are embedded within a polymeric material (normally epoxy or polyester). The glass fibers are relatively strong and stiff (but also brittle), whereas the polymer is ductile (but also weak and flexible). Thus, the resulting fiberglass is relatively stiff, strong, (Figure 1.8) flexible, and ductile. In addition, it has a low density (Figure 1.7). Another of these technologically important materials is the “carbon fiber reinforced polymer” (or “CFRP”) composite—carbon fibers that are embedded within a polymer. These materials are stiffer and stronger than glass fiber-reinforced materials, yet they are more expensive. The CFRP composites are used in some aircraft and aerospace applications, as well as high-tech sporting equipment (e.g., bicycles, golf clubs, tennis rackets, and skis/snowboards).

8. ADVANCED MATERIALS:

Materials that are utilized in high-technology (or high-tech) applications are sometimes termed advanced materials. By high technology we mean a device or product that operates or functions using relatively intricate and sophisticated principles; examples include electronic equipment (camcorders, CD/DVD players, etc.), computers, fiber-optic systems, spacecraft, aircraft, and military rocketry. These advanced materials are typically traditional materials, whose properties have been enhanced, and, also newly developed, high-performance materials. Furthermore, they may be of all material types (e.g., metals, ceramics, polymers), and are normally expensive. Advanced materials include semiconductors, biomaterials, and what we may term “materials of the future” (that is, smart materials and nanoengineered materials), which we discuss below. The properties and applications of a number of these advanced materials—for example, materials that are used for lasers, integrated circuits, magnetic information storage, liquid crystal displays (LCDs), and fiber optics—are also discussed in subsequent chapters. Examples of some advanced materials are shown below in Figure 1.16.

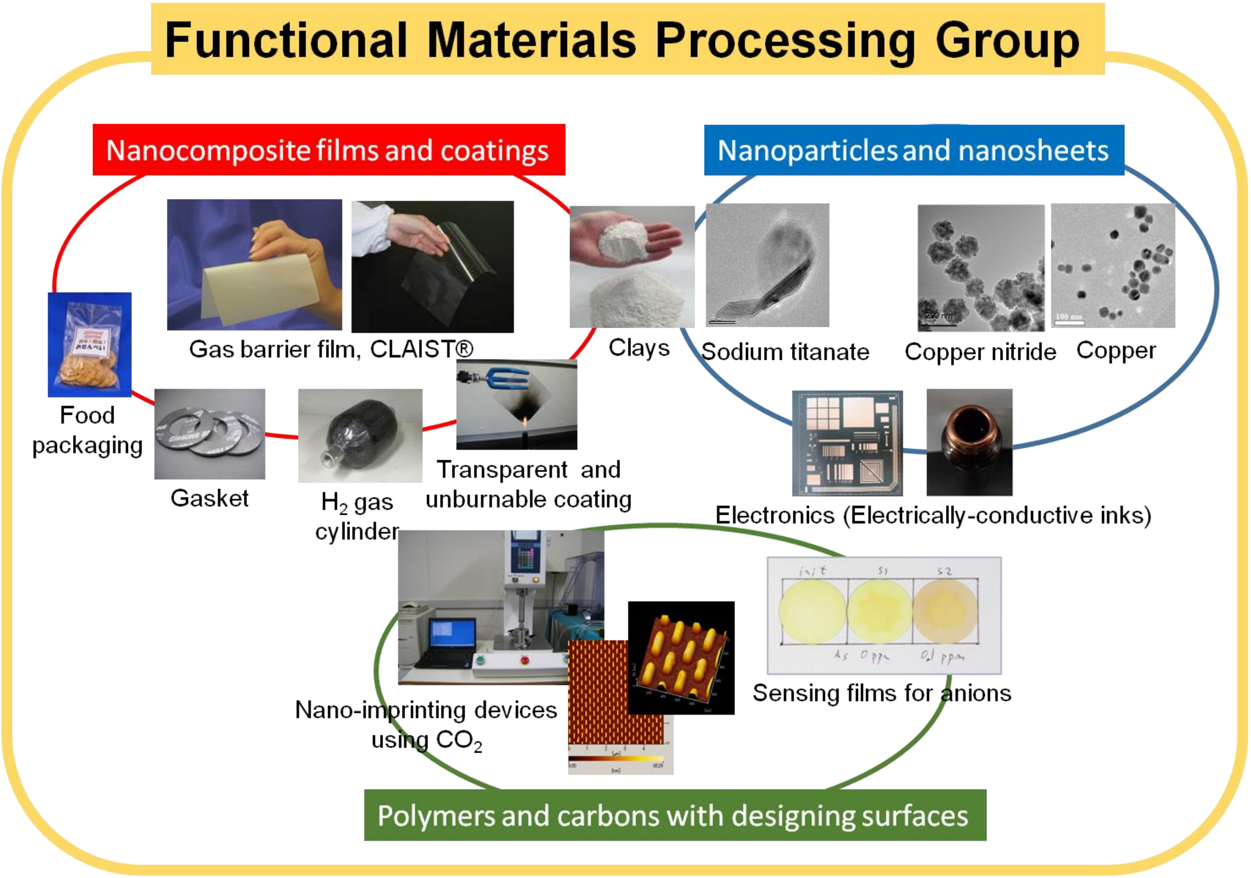

Figure 1.16: Example of some advanced materials.

1.8.1 Semiconductors Materials:

Semiconductors have electrical properties that are intermediate between the electrical conductors (viz. metals and metal alloys) and insulators (viz. ceramics and polymers)—Figure 1.5. Furthermore, the electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of impurity atoms, for which the concentrations may be controlled over very small spatial regions. Semiconductors have made possible the advent of integrated circuitry that has totally revolutionized the electronics and computer industries (not to mention our lives) over the past three decades.

The history of the understanding of semiconductors begins with experiments on the electrical properties of materials. The properties of the time-temperature coefficient of resistance, rectification, and light sensitivity were observed starting in the early 19th century. Karl Ferdinand Braun developed the crystal detector, the first semiconductor device, in 1874. Thomas Johann Seebeck was the first to notice an effect due to semiconductors, in 1821. In 1833, Michael Faraday reported that the resistance of specimens of silver sulfide decreases when they are heated. This is contrary to the behavior of metallic substances such as copper. In 1839, Alexandre Edmond Becquerel reported observation of a voltage between a solid and a liquid electrolyte, when struck by light, the photovoltaic effect. A unified explanation of these phenomena required a theory of solid-state physics, which developed greatly in the first half of the 20th century. In 1878 Edwin Herbert Hall demonstrated the deflection of flowing charge carriers by an applied magnetic field, the Hall Effect. By 1931, the band theory of conduction had been established by Alan Herries Wilson and the concept of band gaps had been developed. Walter H. Schottky and Nevill Francis Mott developed models of the potential barrier and of the characteristics of a metal–semiconductor junction. By 1938, Boris Davydov had developed a theory of the copper-oxide rectifier, identifying the effect of the p–n junction and the importance of minority carriers and surface states. Figure 1.17 shows the silicon semiconductor material. The semiconductor materials have a number of applications as shown in figure 1.18.

Figure 1.17 silicon semiconductor materials.

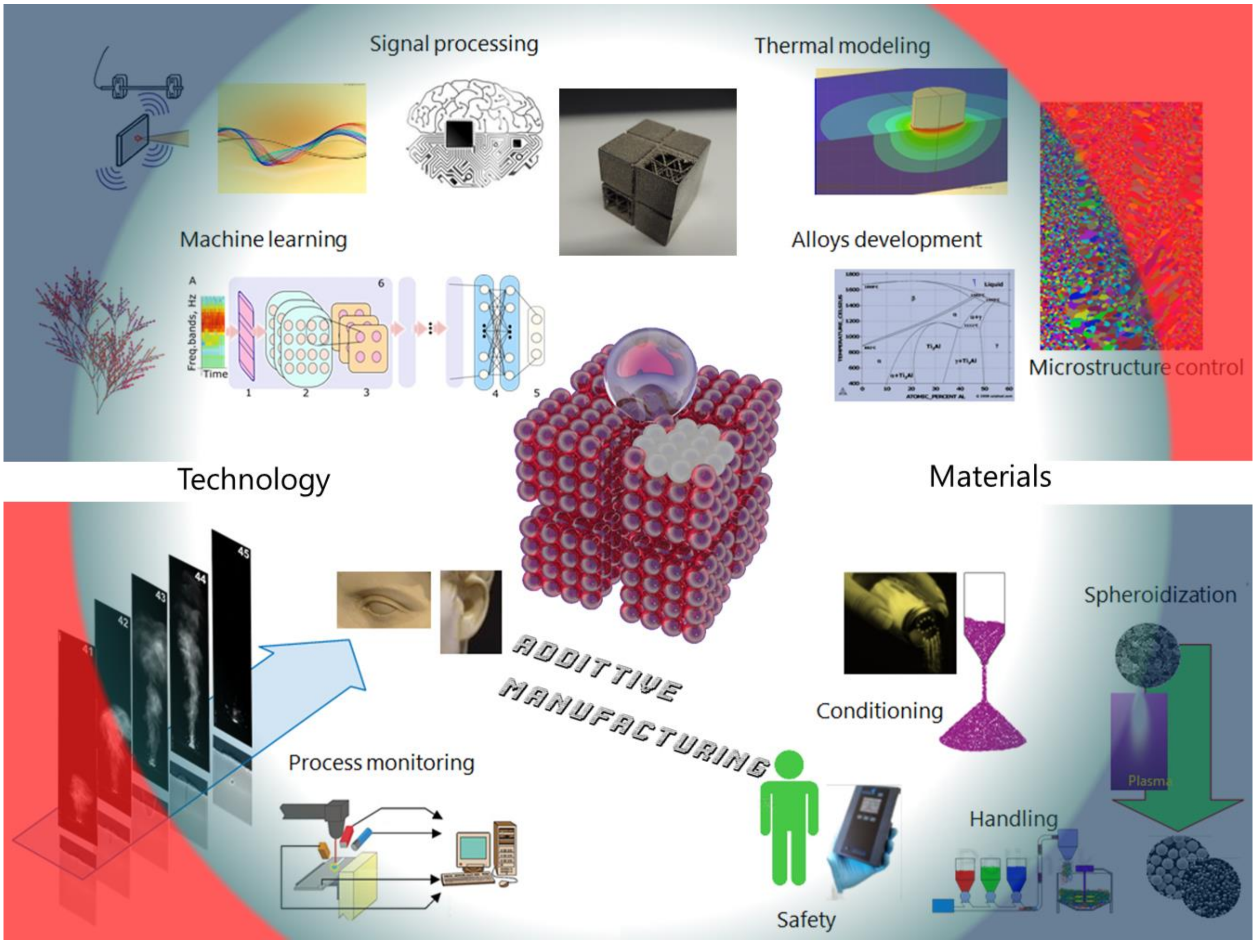

Figure 1.17 Applications of semiconductor materials.

1.8.2 Biomaterials:

Biomaterials are employed in components implanted into the human body for the replacement of diseased or damaged body parts. These materials must not produce toxic substances and must be compatible with body tissues (i.e., must not cause adverse biological reactions). All of the above Materials such as metals, ceramics, polymers, composites, and semiconductors—may be used as biomaterials. biomaterial is a substance that has been engineered to interact with biological systems for a medical purpose, either a therapeutic (treat, augment, repair, or replace a tissue function of the body) or a diagnostic one. As a science, biomaterials are about fifty years old. The study of biomaterials is called biomaterials science or biomaterials engineering. It has experienced steady and strong growth over its history, with many companies investing large amounts of money into the development of new products. Biomaterials science encompasses elements of medicine, biology, biophysics, chemistry, tissue engineering, and materials science. Biomaterial is different from biological material, such as bone, that is produced by a biological system. A hip implant is an example of an application of biomaterials as shown in figure 1.18.

Figure 1.18: A hip implant biomaterials

1.9 MATERIALS OF THE FUTURE:

1.9.1. Smart Materials:

Smart (or intelligent) materials are a group of new and state-of-the-art materials now being developed that will have a significant influence on many of our technologies. The adjective “smart” implies that these materials are able to sense changes in their environments and then

respond to these changes in predetermined manners—traits that are also found in living organisms. In addition, this “smart” concept is being extended to rather sophisticated systems that consist of both smart and traditional materials. Components of a smart material (or system) include some type of sensor (that detects an input signal), and an actuator (that performs a responsive and adaptive function). Actuators may be called upon to change shape, position, natural frequency, or mechanical characteristics in response to changes in temperature, electric fields, and/or magnetic fields. Four types of materials are commonly used for actuators: shape memory alloys, piezoelectric ceramics, magnetostrictive materials, and electrorheological/magnetorheological fluids. Shape memory alloys are metals that, after having been deformed, revert back to their original shapes when the temperature is changed. Piezoelectric ceramics expand and contract in response to an applied electric field (or voltage); conversely, they also generate an electric field when their dimensions are altered. The behavior of magnetostrictive materials is analogous to that of piezoelectric, except that they are responsive to magnetic fields. Also, electrorheological and magnetorheological fluids are liquids that experience dramatic changes in viscosity upon the application of electric and magnetic fields, respectively. Materials/devices employed as sensors include optical fibers, piezoelectric materials (including some polymers), and microelectromechanical devices (MEMS). For example, one type of smart system is used in helicopters to reduce aerodynamic cockpit noise that is created by the rotating rotor blades. Piezoelectric sensors inserted into the blades monitor blade stresses and deformations; feedback signals from these sensors are fed into a computer-controlled adaptive device, which generates noise-canceling antinoise.

1.9.2 Nanoengineered Materials:

Until very recent times the general procedure utilized by scientists to understand the chemistry and physics of materials has been to begin by studying large and complex structures, and then to investigate the fundamental building blocks of these structures that are smaller and simpler. This approach is sometimes termed “top-down” science. However, with the advent of scanning probe microscopes which permit observation of individual atoms and molecules, it has become possible to manipulate and move atoms and molecules to form new structures and, thus, design new materials that are built from simple atomic-level constituents (i.e., “materials by design”). This ability to carefully arrange atoms provides opportunities to develop mechanical, electrical, magnetic, and other properties that are not otherwise possible. We call this the “bottom-up” approach and the study of the properties of these materials is termed “nanotechnology”; the “nano” prefix denotes that the dimensions of these structural entities are on the order of a nanometer (10-9 m)—as a rule, less than 100 nanometers (equivalent to approximately
500 atom diameters). One example of a material of this type is the carbon nanotube, discussed in Section 12.4. In the future, we will undoubtedly find that increasingly more of our technological advances will utilize these nanoengineered materials.

1.10 India’s achievement of metallurgy in the past:

An example of Indian metallurgical brilliance is the Iron Pillar of Delhi. The Iron Pillar of Delhi is a structure 7.21 meters (23 feet 8 inches) high with a 41-centimeter (16 in) diameter that was constructed during the reign of Chandragupta II (375–415 AD), and referred to as Chandra in the oldest Gupta-Brahmi inscription on the pillar. The pillar carries a number of inscriptions of different dates, some of which have not been studied systematically despite the pillar's prominent location and easy access. It is assumed that it was originally erected perhaps outside the Udayagiri Caves and moved to its present location by Ittotmish in 1233 AD. This pillar now stands in the Quwwat-ul-Islam mosque in the Qutub Minar complex in India (Figure 1.19).

The pillar has attracted the attention of archaeologists and materials scientists because of its high resistance to corrosion and has been called a "testimony to the high level of skill achieved by the ancient Indian iron smiths in the extraction and processing of iron". The corrosion resistance results from an even layer of crystalline iron (III) hydrogen phosphate hydrate forming on the high-phosphorus-content iron, which serves to protect it from the effects of the Delhi climate. It is famous for the rust-resistant composition of the metals used in its construction. The pillar weighs more than 6 tonnes. Delhi Iron pillar is one of the examples of India’s marvelous achievement of metallurgical in the past.

Figure 1.19: Delhi Iron Pillar and inscription of King Chandragupta II

1.10 Summary

1. Any physical substance that can be used for the preparation of a thing can be called material. Transportation, housing, clothing, utensils, communication, food production recreation, every segment of our life is influenced by materials.

2. The field of material science deals with investigating the structure, properties, synthesis of the material, performance, development, etc. On the other hand, material engineering deals with the designing or engineering of the material to produce a material of specific need.

3. Two important factors contributing to the properties of materials are the nature of bonding and the atomic structure. Important parameters to understand the properties are atomic structure, interatomic bonding, and microstructure.

4. The covalent bond, in this case, bond energy is about 5 electron volt melting point is high, hardness in terms of ductility it is hard, and ductility is very poor, and electrical conductivity is very low. Examples are diamond, graphite, germanium, and silicon.

5. In ionic bonds, generally the bond energy is about 1 eV, the melting point is high,its hardness is hard, ductility is very poor, and electrical conductivity is low like sodium chloride, zinc sulfite, and the CACL.

6. In metallic bonds, its energy is 0.5 electron volt, its melting point varies, hardness also varies and electrical conductivity is very high like iron, copper, silver, etc.

7. In the case of Van der Waals force it varies from 0.001 to 0.1, melting point islow, then hardness is soft but ductility is also very poor, and electrical conductivity is also low like neon, argon, and krypton.

8. The hydrogen bond, its melting point is very low, hardness is soft, and ductility is poor, usually low, and generally the example is the ice or maybe the water.

9. On the basis of microstructure materials have two properties one is called the sensitive properties another one is called the microstructure insensitive properties. Microstructures' sensitive properties

are yield stress, hardness, and magnetic properties. And microstructure insensitive properties mean density, and elastic modulus which cannot be directly get from that particular material, but we can calculate by some other input parameters.

10. In general solid materials are conventionally classified as metals, ceramics, polymers, and composite materials.

11. Functional Classification of Materials is as Aerospace, Biomedical, Electronic Materials, Energy Materials, Environmental Materials, Magnetic Materials, Photonic or Optical Materials, Smart Materials, etc.

12. Metals are basically some elements available in the periodic table (iron, aluminum, gold, silver, copper, nickel, etc.) and available in nature in different forms. About 91 of the 118 elements in the periodic table are metals. Typically, metals are hard when in the solid state, opaque and shiny. Metals are generally malleable and ductile.

13. Ceramic materials are inorganic, non-metallic solids that are generally oxide, nitride, or carbide materials. Some elements, such as carbon or silicon, may also be considered ceramics. Some of the common ceramic materials are aluminum oxide (alumina Al_2O_3), Silicon dioxide (silica SiO_2) silicon carbide (SiC), silicon nitride (Si_3N_4), etc. Other common examples are earthenware, porcelain, and brick. Ceramic materials are brittle, hard, strong in compression, heat-resistant, corrosion-resistant materials, and weak in shearing and tension.

14. Polymers include the familiar plastic and rubber materials. Many of them are organic compounds that are chemically based on carbon, hydrogen, and other nonmetallic elements (viz. O, N, and Si). Furthermore, they have very large molecular structures, often chain-like in nature that have a backbone of carbon atoms. Some of the common and familiar polymers are polyethylene (PE), nylon, poly(vinyl chloride) (PVC), polycarbonate (PC), polystyrene (PS), and silicone rubber.

15. A composite is made of two (or more) individual materials, which come from the categories discussed above—viz., metals, ceramics, and polymers. The design goal of a composite is to

achieve a combination of properties that is not obtained by any single material, and also to incorporate the best characteristics of each of the component materials.

1.11 Glossary

Cohesive energy: Cohesive energy is the energy gained by arranging the atoms in a crystalline state, as compared with the gas state.

Bond: This made the atoms cluster together and atoms are arranged.

Stress: stress is the force acting on the unit area of a material.

Tensile strength:, the *maximum load that a material can support without fracture when being stretched.*

Hardness: Hardness is the ability of a material to resist deformation,

Ceramics: A *ceramic* is any of the various hard, brittle, heat-resistant, and corrosion-resistant materials made by shaping and then firing an inorganic, nonmetallic material.

Polymer: A class of natural or synthetic substances composed of very large molecules, called macromolecules, which are multiples of simpler chemical units called monomers. Polymers make up many of the materials in living organisms, including, for example, proteins, cellulose, and nucleic acids.

Composite: A material is a material that is produced from two or more constituent materials.

Biomaterial: A substance that has been engineered to interact with biological systems for a medical purpose (treat, augment, repair, or replace a tissue function of the body) or a diagnostic one.

Smart Materials: Materials that have properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, moisture, electric or magnetic fields, light, temperature, pH, or chemical compounds.

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3.14 SUGGESTED READIN

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1.15 Terminal Questions

1. What do you mean by atomic bonding in solids?
2. Give a classification of different type of materials.
3. What are composite materials?

UNIT 2 BASIC PROPERTIES OF METALS

Structure

2.1 INTRODUCTION

A metal is a material in the form of an element, compound, or alloy that is typically hard when in a solid state, opaque and shiny, and generally malleable and ductile. About 91 of the 118 elements in the periodic table are metals. In physics, metal is generally regarded as any substance capable of conducting electricity at a temperature of absolute zero. Many elements and compounds that are not normally classified as metals become metallic under high pressures. For example, the nonmetal iodine gradually becomes a metal at a pressure of between 40 and 170 thousand times atmospheric pressure. Equally, some materials regarded as metals can become nonmetals. In chemistry, two elements that would otherwise qualify (in physics) as brittle metals—arsenic and antimony—are commonly instead recognized as metalloids due to their chemistry (predominantly non-metallic for arsenic, and balanced between metallicity and nonmetallicity for antimony). In astrophysics, the term "metal" is cast more widely to refer to all chemical elements in a star that are heavier than helium, and not just traditional metals. In this sense, the first four "metals" collected in stellar cores through nucleosynthesis are carbon, nitrogen, oxygen, and neon, all of which are strictly non-metals in chemistry. A star fuses lighter atoms, mostly hydrogen, and helium, into heavier atoms over its lifetime.

Metals, as chemical elements, comprise 25% of the Earth's crust and are present in many aspects of modern life. The strength and resilience of some metals have led to their frequent use in, for example, high-rise building and bridge construction, as well as most vehicles, many home appliances, tools, pipes, and railroad tracks. Copper, copperis used for electrical wiring, because it is a very good conductor of electricity and malleable. Iron is used to make cars, and bridges, generally you can understand or maybe you know that generally iron we used for structural applications, so because it is too hard with high tensile strength. Precious metals were historically used as coinage, but in the modern era, coinage metals have extended to at least 23 chemical elements. The history of refined metals is thought to begin with the use of copper about 11,000 years ago. Gold, silver, iron (as meteoric iron), lead, and brass were likewise in use before the first known appearance of bronze in the 5th millennium BCE.

2.2 OBJECTIVE

After reading this unit we will able to understand:

1. Basic idea of metals
2. Classification of metals
3. Mechanical Properties of metals
4. Materials

2.3 Different types of metals:

Now we classify metals as base metals, noble metals, then precious metals, heavy metals, ferrous metals, nonferrous metals, etc. The classification is shown in Figure 2.1.

2.3.1 Base metals:

Base metals are easily oxidized or corroded and react easily with dilute hydrochloric acid to form the metal chloride and hydrogen. Generally, the base metal can react with some other acids or maybe the base. Some examples of base metals are copper, lead, nickel, tin, aluminum, zinc, iron, and their alloys

2.3.2 Noble metals:

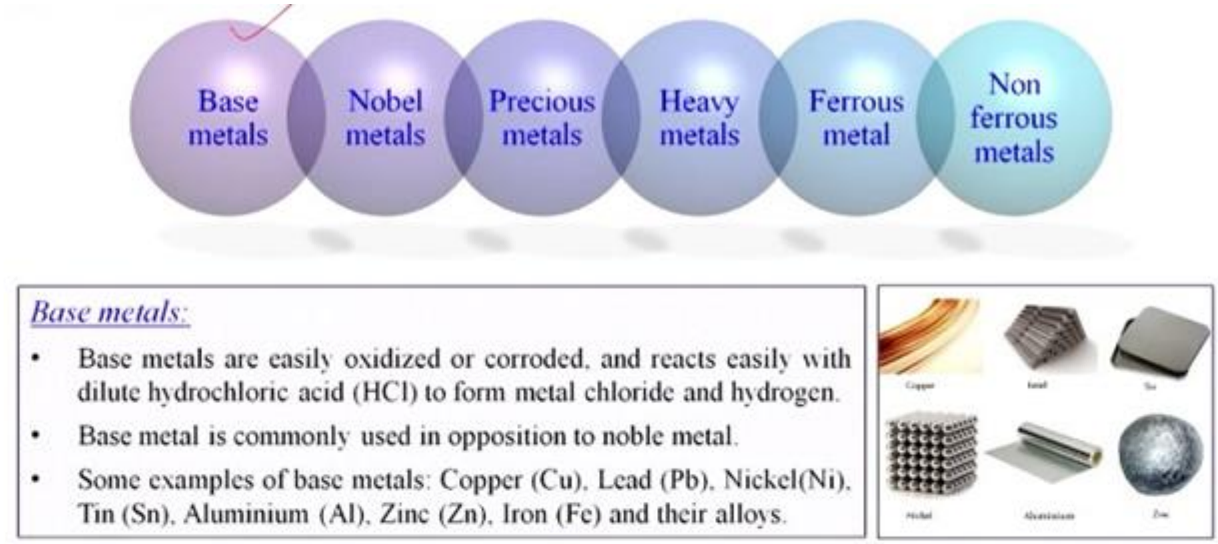
The Noble metals are resistant to corrosion and oxidation in moist air, unlike most base metals. So the noble metals generally don’t react with the air or maybe the environmental moisture. Examples of noble metals are gold, platinum, silver, rhodium, iridium, etc. Base metal is commonly used in opposition to noble metal.

2.3.2 Precious metals:

Precious metals are rare, natural or correct metallic chemical elements of high economic value, and very expensive as their name indicates. Precious metals are less reactive than noble metals. Precious metals are not easily available. Precious metals are usually ductile and have a high luster means the shininess of that material.

2.3.2 Heavy metals:

Heavy metals are very dense metals and metalloids. metalloids are nothing but a mixture of metals and non-metals, for example, boron, silicon, germanium, arsenic, antimony, etc.



Base metals:

- Base metals are easily oxidized or corroded, and reacts easily with dilute hydrochloric acid (HCl) to form metal chloride and hydrogen.
- Base metal is commonly used in opposition to noble metal.
- Some examples of base metals: Copper (Cu), Lead (Pb), Nickel(Ni), Tin (Sn), Aluminium (Al), Zinc (Zn), Iron (Fe) and their alloys.

Figure 2.1: Different types of metals

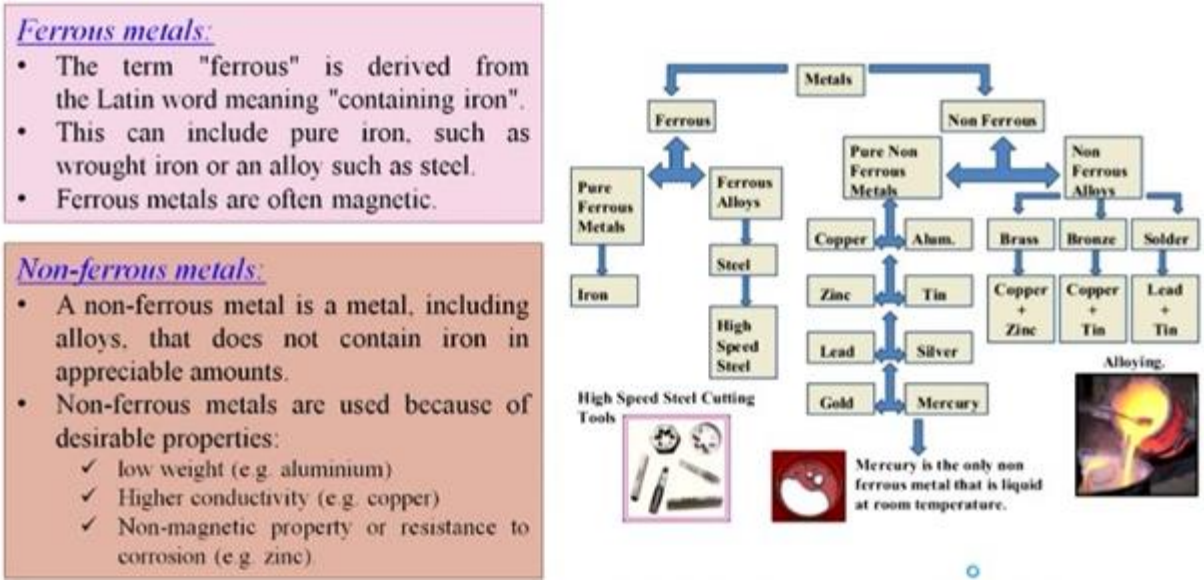
As iron is one of the most available metals in the earth’s crust, therefore, the most common classification is based on iron content. When we look at iron content, we can divide metals into three categories:

- Ferrous (contains iron)
- Nonferrous (contains no iron)

All types of metal contain unique properties and depending on their melting point, density, and malleability, some are better suited to certain purposes than others.

Ferrous metals: Ferrous metals means the iron content is there, so the term ferrous is derived from the Latin word meaning containing iron, this can include pure iron such as wrought iron, or an alloy such as steel, because steel the iron percentage is more. Ferrous metals are often magnetic in nature

Nonferrous metals: Metal including alloys that do not contain iron in appreciable amounts, we are not telling that ironwill be not present over there, maybe a near amount of iron may be present but that is very, very negligible. Nonferrous metals are used because of desirable properties like low weight, like aluminum, so that's why we are using aluminum for aerospace applications, higher conductivity of copper that's why we are making any kind of electrical wiring or maybe wire this copper. The next one is called the nonmagnetic property or resistance to the corrosion, zinc, so that's why we are doing the zinc plating so that, that material can, the service life of that material can increase.



Ferrous metals:

- The term "ferrous" is derived from the Latin word meaning "containing iron".
- This can include pure iron, such as wrought iron or an alloy such as steel.
- Ferrous metals are often magnetic.

Non-ferrous metals:

- A non-ferrous metal is a metal, including alloys, that does not contain iron in appreciable amounts.
- Non-ferrous metals are used because of desirable properties:
  - ✓ low weight (e.g. aluminium)
  - ✓ Higher conductivity (e.g. copper)
  - ✓ Non-magnetic property or resistance to corrosion (e.g. zinc)

Mercury is the only non ferrous metal that is liquid at room temperature.

Figure 2.2: Ferrous and non-ferrous metals

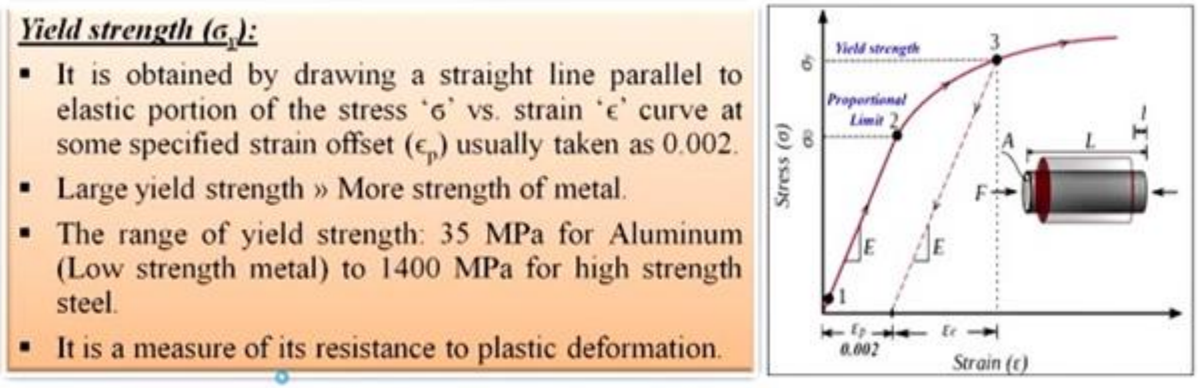
2.4 Properties of metals:

Now we discuss the physical properties as mechanical properties, thermal properties, electrical properties, and magnetic properties of metals, and chemical properties as reactivity, toxicity, and corrosion. The first type, physical properties are the lustrous shine, which means it is very, very reflective in nature. For example, gallium crystal has lustrous. Another property is hardness, metals are mostly harder to cut because their strength is too high; however, some metals like sodium, potassium, and magnesium are easy to cut. High density is another property of metal it varies from less than water, like sodium to very dense like lead. Metals have high melting and boiling points because metallic bonds are strong and a lot of energy is needed to break them except the mercury. Metals are generally good conductors of heat and electricity. Metals on being hammered can be beaten into thinner sheets, this is called malleability, and this is one good property of the metals, so this is known as the malleability. Gold and silver metals are the most malleable metals and are used for making very precious ornaments or maybe a very small size of ornaments.

2.5. Mechanical properties:

Now we discuss the mechanical properties. Some mechanical properties are significant for metal. Some important mechanical properties of the metals are brittleness, creep, ductility, elasticity, fatigue, hardness, malleability, plasticity, resilience, and toughness, yield strength. These combinations are known as the mechanical properties of the metals.

2.5.1 Yield strength: So first we will discuss the yield strength of the metals. The yield strength is obtained by drawing a straightline parallel to elastic portions of the stress (σ) versus strength (ε) curve at some specified strength offset ε_P usually taken as 0.002. The point at which the straight line cut the stress-strain curve gives yield strength σ_Y. In Figure 2.3 we can see that the X axis is denoting the strength, and the Y axis is denoting the stress and we are getting a stress-straincurve of the metals. If we give the spaceof 0.002 and then we are just drawing a parallel line, just along with this one and then this line is touching the stress-strain curve at this particular point, and that is known as the yield strength of particular metals. Large yield strength means more strength of the metal. The range of yield strength for aluminum is 35 megapascal, which is known as low-strength metal, to 1400 megapascal called high-strength steel. Yield strength is a measure of its resistance to plastic deformation.



Yield strength (σ_y):

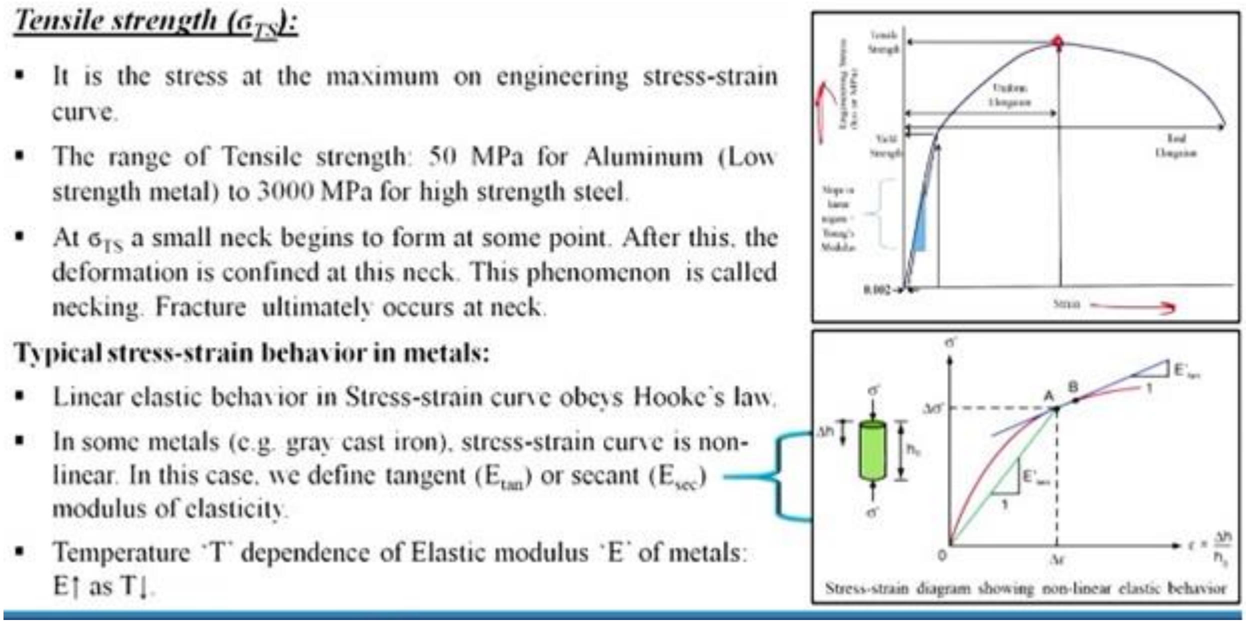
- It is obtained by drawing a straight line parallel to elastic portion of the stress 'σ' vs. strain 'ϵ' curve at some specified strain offset (ϵ_p) usually taken as 0.002.
- Large yield strength » More strength of metal.
- The range of yield strength: 35 MPa for Aluminum (Low strength metal) to 1400 MPa for high strength steel.
- It is a measure of its resistance to plastic deformation.

Figure 2.3: stress-strain curve and yield strength σ_Y

2.5.2 Tensile strength:

Tensile strength is the stress at the maximum on the engineering stress-strain curve. , so if you see this particular figure the same, the strain is denoting into the X axis and the elastic engineering stress is denoting the Y axis, and if you plot the stress-strain curve, so as per the definitions so it is the maximum value on engineering stress-strain curve is known as the tensile strength of that particular metals, so the range of tensile strength generally 50 megapascal for aluminum, low strength metal to 3000 megapascal for high strength steel.

At Sigma TS a small neck begins to form at some point after this the deformation is confined at this neck, this phenomenon is called the necking, so when we are trying to stress the materials after a certain time the diameter is going to decreases so that is known as the necking, fracture ultimately occurs at the neck, because it depends upon the elastic properties, so after a certain time when that neck is going to be bigger and bigger and then after that, the material will fell at that particular point. Typical stress-strain behavior in metals so linear elastic behavior in stress-strain curve obeys Hooke's law because it is normal that, generally all the metals follow Hooke's law, in some metals like gray cast iron, stress-strain curve is nonlinear, in this case, we define the tangent or secant so if you see this picture so first we are getting that E prime tan and E prime secant, so generally we define it as a tangent or secant, modulus of elasticity, so if the temperature dependence on the elastic modulus of metals if elastic modulus will increase so automatically the temperature is going down, in the opposite word if I can say that if we increase the temperature of any metals, so automatically the elasticity of the metals is going down.



Tensile strength (σ_{TS}):

- It is the stress at the maximum on engineering stress-strain curve.
- The range of Tensile strength: 50 MPa for Aluminum (Low strength metal) to 3000 MPa for high strength steel.
- At σ_{TS} a small neck begins to form at some point. After this, the deformation is confined at this neck. This phenomenon is called necking. Fracture ultimately occurs at neck.

Typical stress-strain behavior in metals:

- Linear elastic behavior in Stress-strain curve obeys Hooke's law.
- In some metals (e.g. gray cast iron), stress-strain curve is non-linear. In this case, we define tangent (E_{tan}) or secant (E_{sec}) modulus of elasticity.
- Temperature 'T' dependence of Elastic modulus 'E' of metals: E↑ as T↓.

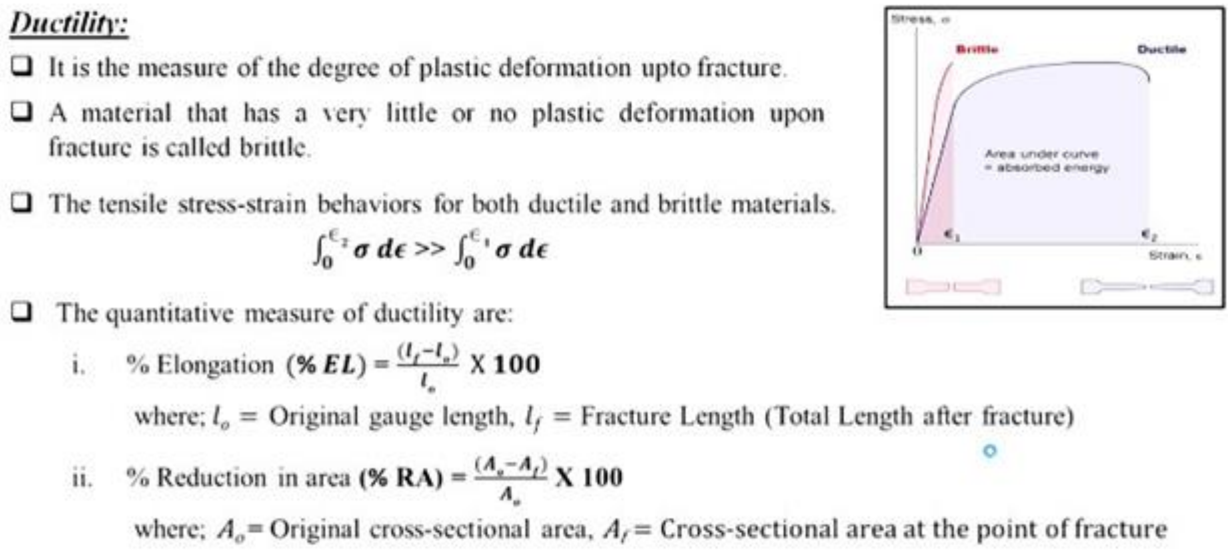
Stress-strain diagram showing non-linear elastic behavior

Figure 2.4: Tensile strength

2.5.3 Ductility:

Ductility it is the major of the degree of plastic deformations up to fracture, material that has a very little or no plastic deformation upon fractureis called the brittle, so generally the ductility means when we are trying to stretch that materials the material is stretching, if the material is stretching up to certain point we can say that the ductility of the material is very good, but if we are going to stretch that materials and at the time of stretching, initial stretching if the material will break generally we are calling it as a brittle material, so the tensile stress strain behavior for both ductile and brittle materials is integration 0 to epsilon to sigma DE always greater than integrations 0 to epsilon 1 sigma DE, so in this particular graphic you can see that the epsilon 1 is denoting the brittle materials and epsilon 2 is denoting the ductile materials, the quantitative measure of ductility are percentage elongations, generally we are defining as a percent EL = LF – L0/L0 x 100, so where L0 is the original gauge length LF is the fracture length, total length after the fracture, so in this particular graph we can see that at epsilon 2 the, after that the material has failed.

Now we will discuss the percentage reduction in area, generally, we are denoting it by the percentage RA = A0 – AF/A0 x 100, so where A0 is the original cross-sectional area, AF is the cross-sectional area at the point of fracture, so of course at the time of point of fracture your cross-sectional area is going to be narrow down which is nothing but known as the necking.



Ductility:

- ☐ It is the measure of the degree of plastic deformation upto fracture.
- ☐ A material that has a very little or no plastic deformation upon fracture is called brittle.
- ☐ The tensile stress-strain behaviors for both ductile and brittle materials.

$$\int_0^{\epsilon_2} \sigma\, d\epsilon >> \int_0^{\epsilon_1} \sigma\, d\epsilon$$

- ☐ The quantitative measure of ductility are:
  - i. % Elongation $(\% EL) = \frac{(l_f - l_o)}{l_o}$ X 100
    where; l_o = Original gauge length, l_f = Fracture Length (Total Length after fracture)
  - ii. % Reduction in area **(% RA)** = $\frac{(A_o - A_f)}{A_o}$ **X 100**
    where; A_o = Original cross-sectional area, A_f = Cross-sectional area at the point of fracture

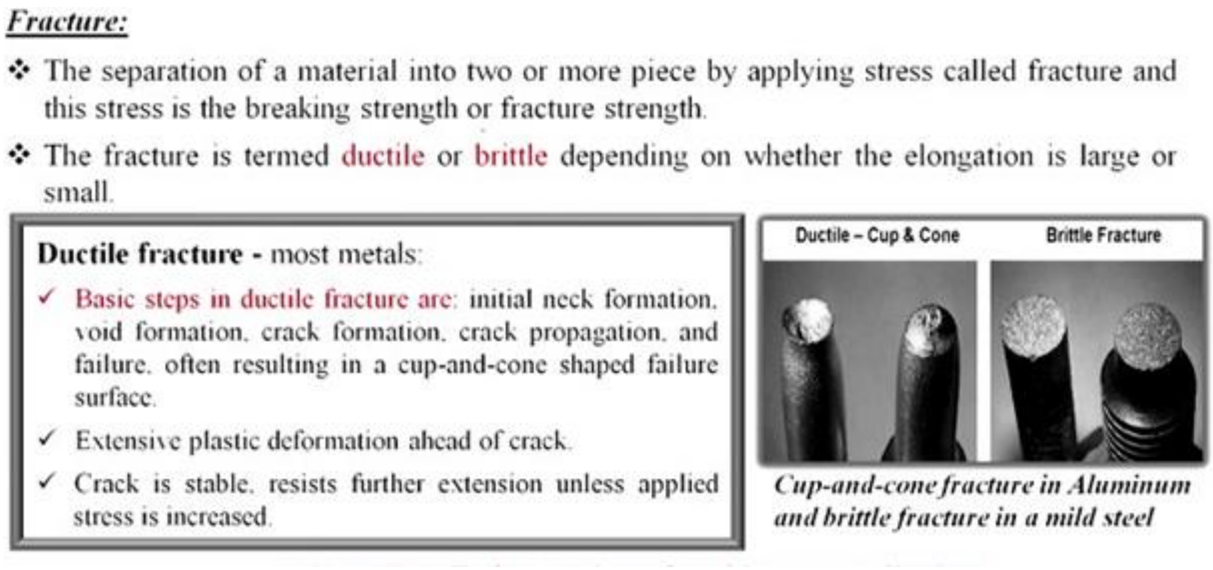
Figure 2.5: Ductility of metals

2.5.4 Fracture:

The separation of a material into two or more piecesby applying stress is called the fracture, and this stress is the breaking strength or maybe known as the fracture strength, the fracture is termed ductile or brittle, depending on whether the elongation is large or small.

Now we will talk about ductile fracture, generally, we pray for ductile fracture for most metals, basic steps in ductile fracture are initial neck formations, void formations, crack formations, crack propagations, and failure often resulting in a cup and cone-shaped failure surface, so in this particular figure you can see that cup and cone structure has been formed, so from this particular picture we can assume that this material is ductile in nature, extensive plasticdeformation ahead of crack, crack is stable resist further extension unless applied stress is increased.

Note ductile fracture is preferred in most applications as I already discussed, but when you are talking about brittle fracture you find that it’s a simple type of cracking, there will not be, there are no formations of any cup or cone shape, so simple the material will break at a certain point.



Fracture:

- The separation of a material into two or more piece by applying stress called fracture and this stress is the breaking strength or fracture strength.
- The fracture is termed ductile or brittle depending on whether the elongation is large or small.

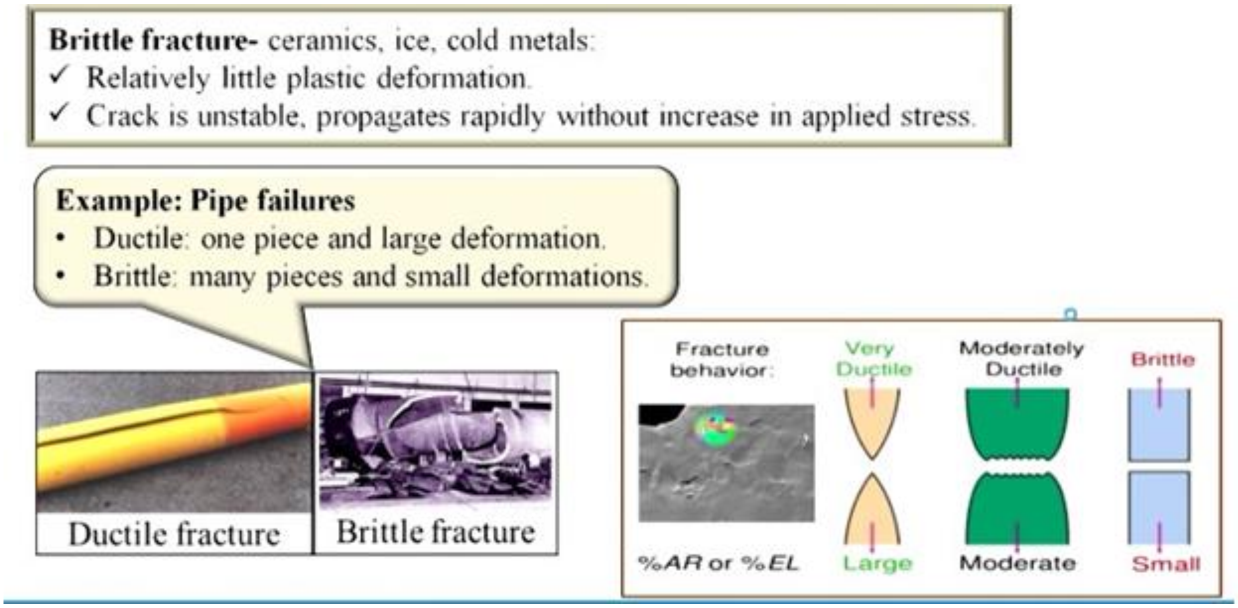
Ductile fracture - most metals:

- ✓ Basic steps in ductile fracture are: initial neck formation, void formation, crack formation, crack propagation, and failure, often resulting in a cup-and-cone shaped failure surface.
- ✓ Extensive plastic deformation ahead of crack.
- ✓ Crack is stable, resists further extension unless applied stress is increased.

Cup-and-cone fracture in Aluminum and brittle fracture in a mild steel

Figure 2.6: Fracture in metals

Now we will discuss brittle fracture, brittle fracture ceramics, ice, cold metals, relatively little plastic deformations, and unstable cracks propagating rapidly without an increase in applied stress, examples we are giving pipe failures, generally most of the pipes we are making it by the castiron, so ductile 1 piece and large deformations, brittle many pieces and the small deformations,so if the material or maybe the pipe is made by any ductile materials, so you can find that there a crack formation has been taken place, but if it has been made by some kind of brittle materials, so after fracture, you can find that has been broken into very small, small, small, small parts. Herewhen you are talking about the fracture behavior so you can find that there are different types of fracture taking place, so area reductions and elongation break is taking place, so if it is very ductile you can find a very sharp cup and cone type of structure over there, if it is moderately ductile you can find a very less area of cup and cone as structure, but if it is brittle you can find that there is a sharp break of that particular metals.



Brittle fracture- ceramics, ice, cold metals:

- ✓ Relatively little plastic deformation.
- ✓ Crack is unstable, propagates rapidly without increase in applied stress.

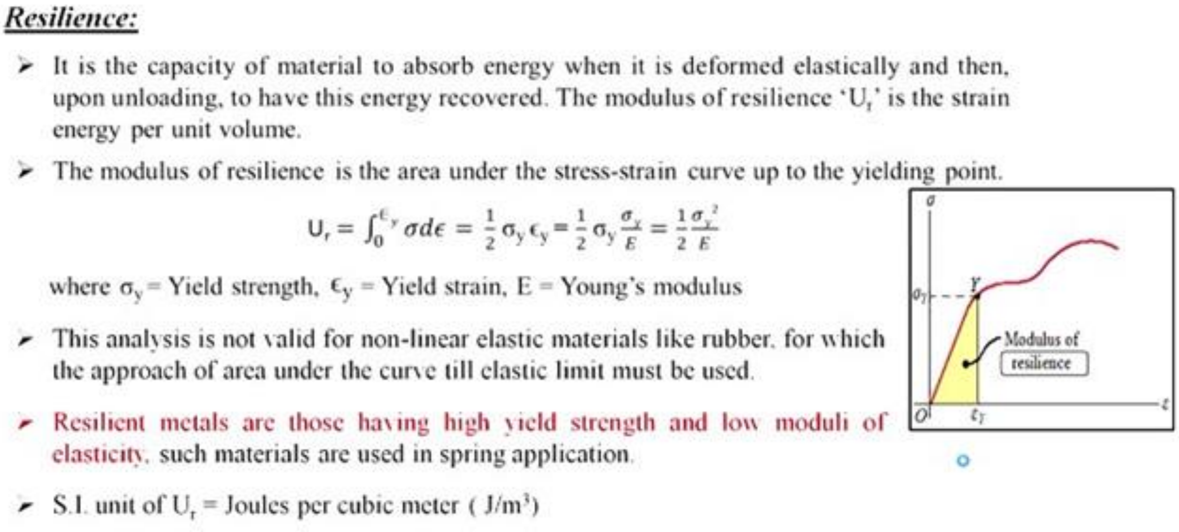
Example: Pipe failures

- Ductile: one piece and large deformation.
- Brittle: many pieces and small deformations.

Figure 2.7: Different types of Fracture in metals

2.5.5 Resilience:

Resilience is the capacity of a material to absorb energy when it is deformed elastically and then upon unloading to have this energy recovered. The modulus of resilience is generally denoted by capital U, subscript Ur is the strain energy perunit volume, the modulus of resilience in the area under the stress-strain curve up to the yielding point, so in this particular graph you can see the yielding point is here at Y, so Ur = integration 0 to epsilon Y, sigma D epsilon = 1/2 sigma Y epsilon Y = 1/2 sigma Y/E = 1/2 sigma Y square/E,so here the sigma Y is the yield strength, epsilon Y is the yield strength and E is nothing but the Young modulus, this analysis is not valid for nonlinearly elastic materials like rubber, because rubber is an amorphous material for which the approach of the area under the curve till elastic limit must be used, resilient metals are those having high yield strength and low moduli of elasticity, such materials are used in spring applications, because they are having some damping factor, so SI unit of the resilience is joule per cubic meter.



Resilience:

- It is the capacity of material to absorb energy when it is deformed elastically and then, upon unloading, to have this energy recovered. The modulus of resilience 'U_r' is the strain energy per unit volume.
- The modulus of resilience is the area under the stress-strain curve up to the yielding point.

$$U_r = \int_0^{\epsilon_y} \sigma d\epsilon = \frac{1}{2}\sigma_y \epsilon_y = \frac{1}{2}\sigma_y \frac{\sigma_y}{E} = \frac{1}{2}\frac{\sigma_y^2}{E}$$

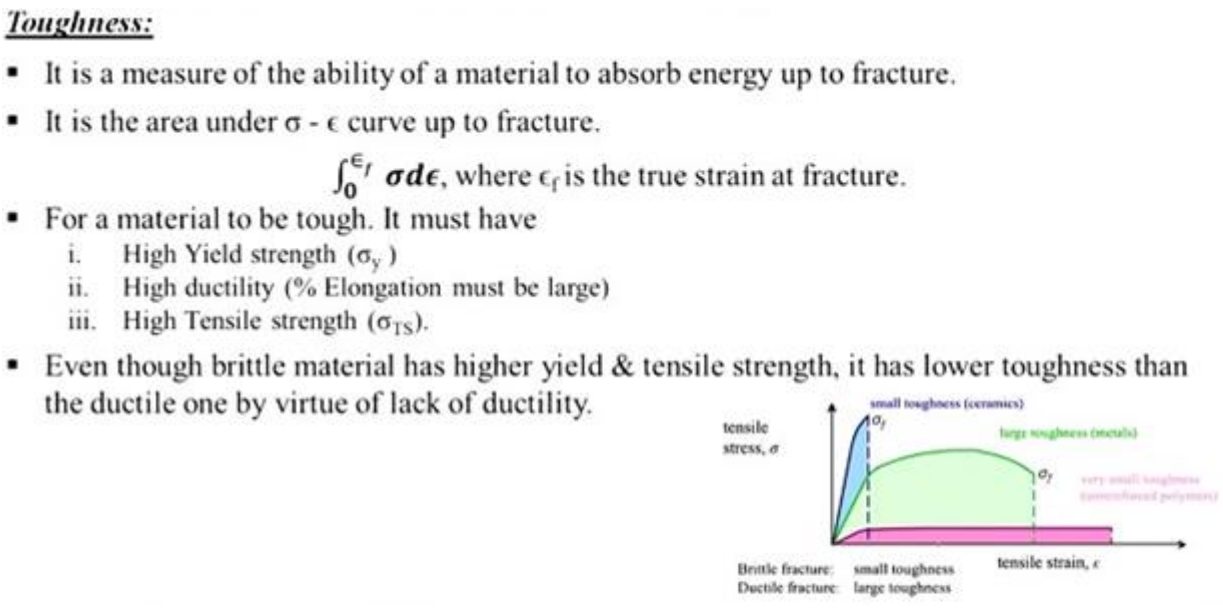
where σ_y = Yield strength, ϵ_y = Yield strain, E = Young's modulus

- This analysis is not valid for non-linear elastic materials like rubber, for which the approach of area under the curve till elastic limit must be used.
- Resilient metals are those having high yield strength and low moduli of elasticity, such materials are used in spring application.
- S.I. unit of U_r = Joules per cubic meter (J/m^3)

Figure 2.8: Resilience in metals

2.5.6 Toughness:

Toughness is a measure of the ability of a material to absorb energy up to fracture. It is the area under the sigma to epsilon curve up to fracture, so generally we are talking about the area. Now it is a formula is integrations 0 to epsilon F, sigma D epsilon where epsilon if is the true strain at fracture, for a material to be tough it must have high yield strength, high ductility percentage elongation must be very very large, high tensile strength even though brittle materials has higher yield and tensile strength it has lower toughness than the ductile, one by lack of ductility.



Toughness:

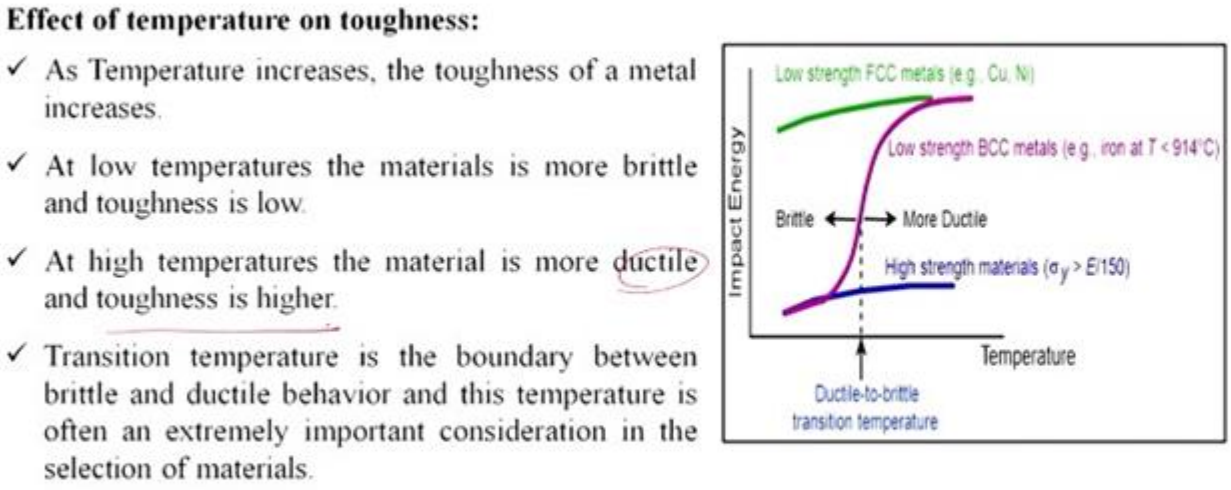
- It is a measure of the ability of a material to absorb energy up to fracture.
- It is the area under σ - ϵ curve up to fracture.

$$\int_0^{\epsilon_f} \sigma d\epsilon, \text{ where } \epsilon_f \text{ is the true strain at fracture.}$$

- For a material to be tough. It must have
  - i. High Yield strength (σ_y)
  - ii. High ductility (% Elongation must be large)
  - iii. High Tensile strength (σ_{TS}).
- Even though brittle material has higher yield & tensile strength, it has lower toughness than the ductile one by virtue of lack of ductility.

Figure 2.8: Toughness in metals

Now we will discuss about the effect of temperature on toughness, as temperature increases the toughness of a metal increases, at low temperatures the material is more brittle and toughness is low, at high temperatures the material is more ductile and toughness is higher, transition temperature is the boundary between the brittle and ductile behavior and this temperature is often an extremely important considerations in the selection of materials, in the right hand side if you see this particular graph you can find that X axis is denoting the temperature, Y axis is denoting the impact energy, and if we are talking about any materials, so say suppose at normal temperature the material is showing the brittleness, but when we are increasing the temperature, so automatically it is crossing the transient line or maybe the transit temperature and it is going into the ductile side, so in this particular case we are rising the temperature up to 940 degree centigrade, so when we are rising the temperature from room temperature to more than 900 degree centigrade so automatically the material is converting from brittle to ductile in nature, andthe toughness of the material is also going to be increased.



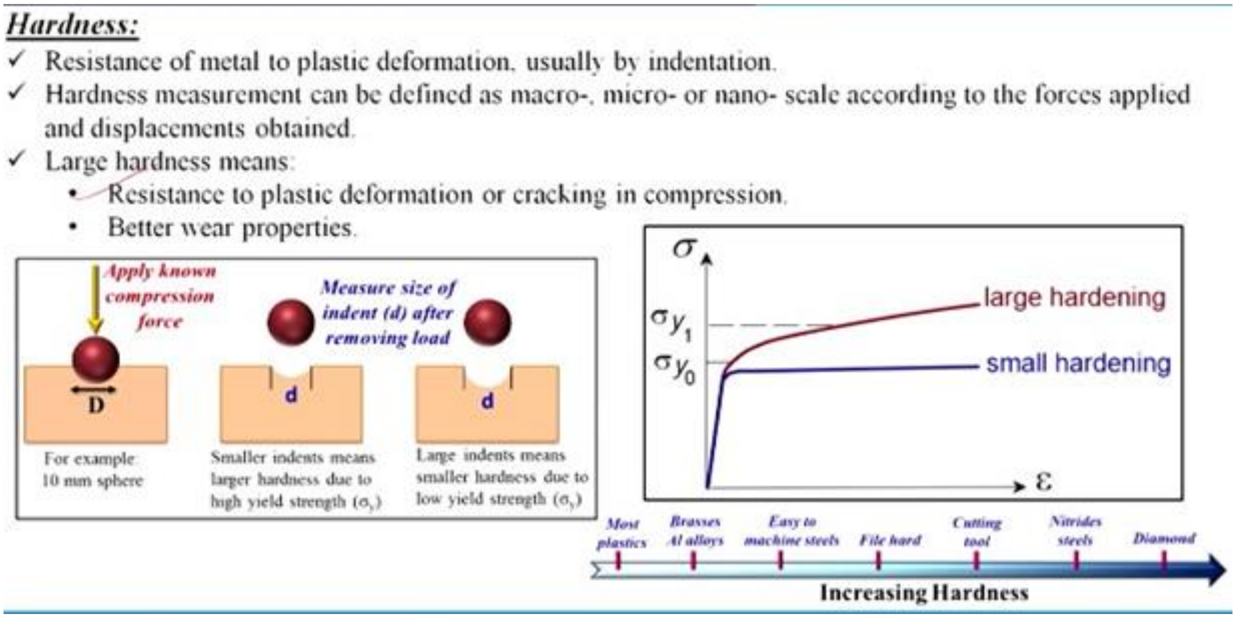
Effect of temperature on toughness:

- ✓ As Temperature increases, the toughness of a metal increases.
- ✓ At low temperatures the materials is more brittle and toughness is low.
- ✓ At high temperatures the material is more ductile and toughness is higher.
- ✓ Transition temperature is the boundary between brittle and ductile behavior and this temperature is often an extremely important consideration in the selection of materials.

Figure 2.9: Effect of temperature on toughness

2.5.7 Hardness:

The hardness of the metals is defined as the resistance of metal to plastic deformations usually by indentation. Indentation is nothing but it is one kind of method or maybe it’s one kind of thing by which we are making any indent onto the metal itself, hardness measurement can be defined as macro, micro, or nano-scale according to the forces applied and displacements obtained. Large hardness means resistance to plastic deformation or cracking in compression, and better wear properties, so for this particular image if you see that weare having a metal and then we are putting a compressive force by a ball having 10-millimeter diameter it’s a sphere in shape and we are giving a just impact or indent onto the metal itself. Then a smaller indent means larger hardness due to the high yield strength because it is not allowing that ball to go inside, and if some larger indents mean smaller hardness due to the low yield strength, the same thing has been proven over here also, so when you are talking about the large hardening so automatically the hardness of that particular material is going to be increased, and then small hardening means the hardness of that particular material is going to be decreased, if you see the material wise hardness so first the plastics are the lesser hardness as well as the diamond is the most harder materials in the material series, so it’s followed like plastics, then brasses, aluminum alloys easy to machine steels, file hard, cutting tool, nitrate steels, and the last one is the diamond which is the most harder one.



Hardness:

- ✓ Resistance of metal to plastic deformation, usually by indentation.
- ✓ Hardness measurement can be defined as macro-, micro- or nano- scale according to the forces applied and displacements obtained.
- ✓ Large hardness means:
  - Resistance to plastic deformation or cracking in compression.
  - Better wear properties.

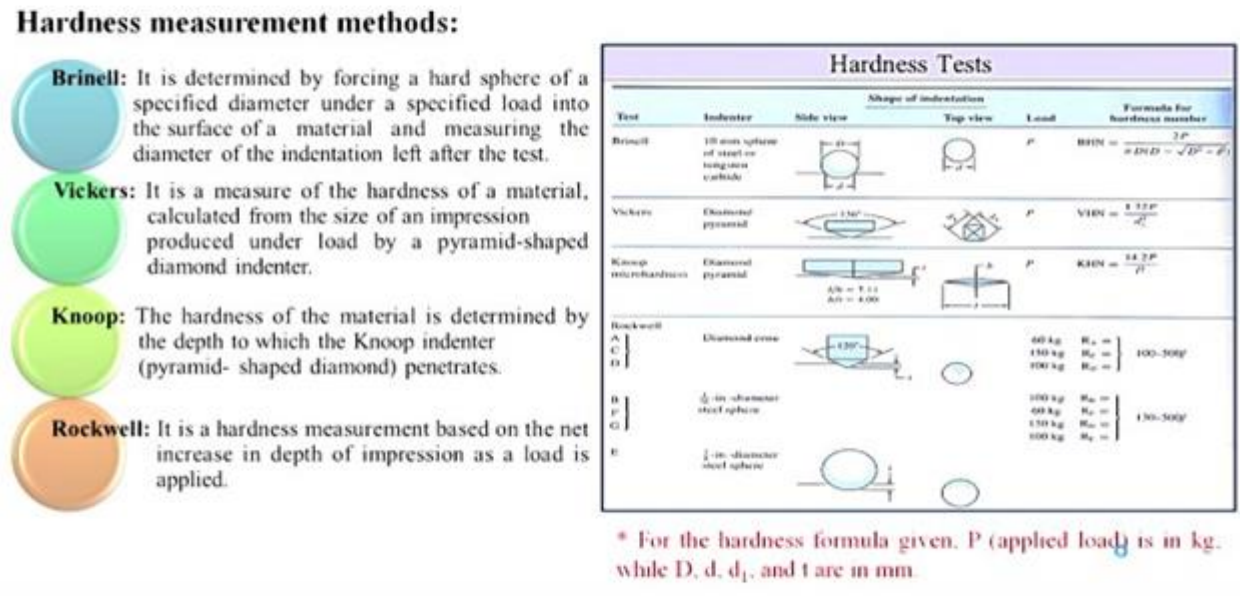
Figure 2.10: Hardness of metal

Now we will discuss techniques for the hardness measurement, there are four types of techniques generally we are using to measure the hardness of any kind of metal, first one is known as the Brinell, followed by Vickers, Knoop, Rockwell, so Brinell is determined by forcing a hard sphere of a specified diameter under a specified load into the surface of a material and measuring the diameter of the indentation left after the test, so in this particular case generally we are using a round shape ball and we are following that ball from a particular height and after that, just we are checking that how much depth, how much depth it has gone inside the material.

Vickers, is the measure of the hardness of a material calculated from the size of an impression produced under load by a pyramid-shaped diamond indenter, in this particular case we are using one pyramid-shaped diamond indenter.

Knoop, the hardness of the material is determined by the depth to which the Knoop indenter pyramid-shaped diamond penetrates, so in this particular case, we are going to do it by the diamond pyramid shape.

And the last one is known as the Rockwell, so it is a hardness measurement based on the net increase in depth of impression as a load is applied, so for the hardness formula given P is the applied load over here is in KG, while capital DD, small d1 and t are all in the millimeter, so by getting this value, by putting those value in this particular equations you can easily calculate what is the hardness value of different metals.



Hardness measurement methods:

Brinell: It is determined by forcing a hard sphere of a specified diameter under a specified load into the surface of a material and measuring the diameter of the indentation left after the test.

Vickers: It is a measure of the hardness of a material, calculated from the size of an impression produced under load by a pyramid-shaped diamond indenter.

Knoop: The hardness of the material is determined by the depth to which the Knoop indenter (pyramid- shaped diamond) penetrates.

Rockwell: It is a hardness measurement based on the net increase in depth of impression as a load is applied.

Hardness Tests

* For the hardness formula given, P (applied load) is in kg, while D, d, d_1, and t are in mm.

Figure 2.11: Hardness measurement methods

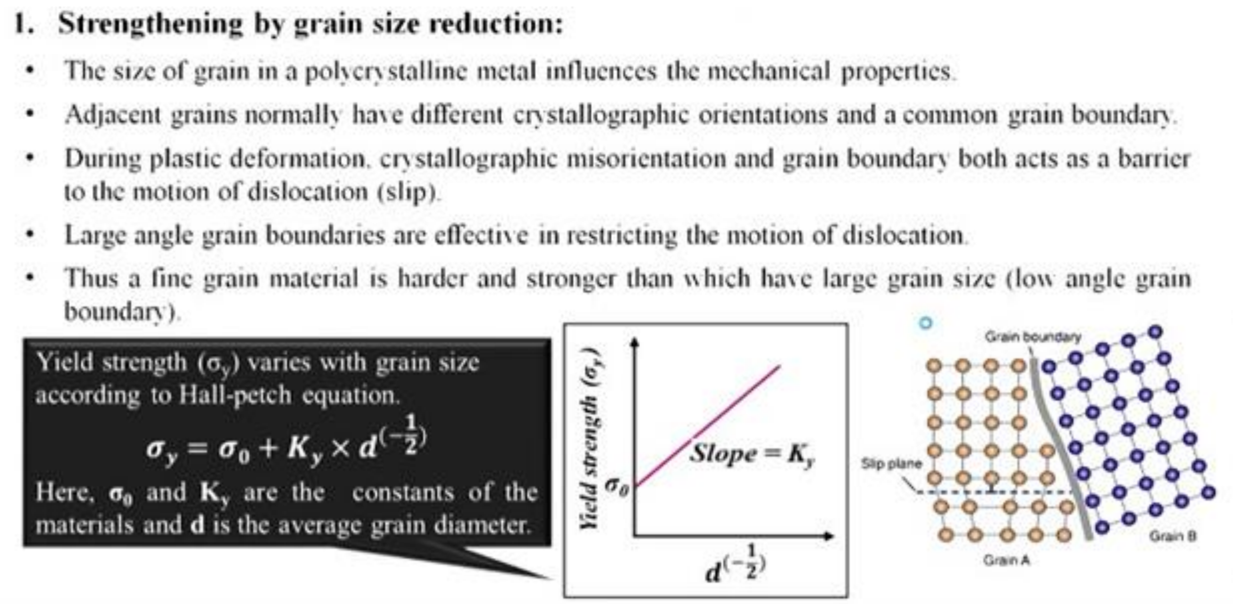
2.6 Strengthening of metals:

Strengthening of metals, that are also an important parameter, so strengthening of metals means increasing the yield strength, tensile strength, and hardness at the cost of ductility. When we are going to increase the strength so automatically the ductility of that metal is going to be decreased, all metals and alloys contain some dislocation that where introduced during solidification, during plastic deformation, and from rapid cooling, strengthening occurs because of dislocation movements like slips within the crystal structure of materials, strengtheningmechanism in metals, first restricting or hindering the motion of dislocations, this can be carried out by reducing grain size in polycrystalline materials and by making a solid solution of metals, and the second one is that strain hardening which is nothing but known as the cold working process.

2.6.1 Strengthening by grain size reduction

So first we will discuss the strengthening by grain size reduction, so the size of grain in a polycrystalline metal influences the mechanical properties, adjacent grains normally have different crystallographic orientations and a common grain boundary, so from this particular image you can

find that there are two different grain structure and this is known as the grain boundary.
During plastic deformation, crystallographic misorientation, and grain boundary both act as a barrier to the motion of dislocations or maybe the slips, so this is known as the slip plane over there. Large angle grain boundaries are effective in restricting the motion of dislocation, thus a fine grain material is harder and stronger than have large grain size, low angle grain boundary, so yield strength generally sigma Y varies with grain size according to the Hall-Petch equation, sigma Y = sigma 0 + KY x D to the power -1/2, where sigma 0 and KY are the constants of the material and D is the average grain diameter.



1. Strengthening by grain size reduction:

- The size of grain in a polycrystalline metal influences the mechanical properties.
- Adjacent grains normally have different crystallographic orientations and a common grain boundary.
- During plastic deformation, crystallographic misorientation and grain boundary both acts as a barrier to the motion of dislocation (slip).
- Large angle grain boundaries are effective in restricting the motion of dislocation.
- Thus a fine grain material is harder and stronger than which have large grain size (low angle grain boundary).

Yield strength (σ_y) varies with grain size according to Hall-petch equation.

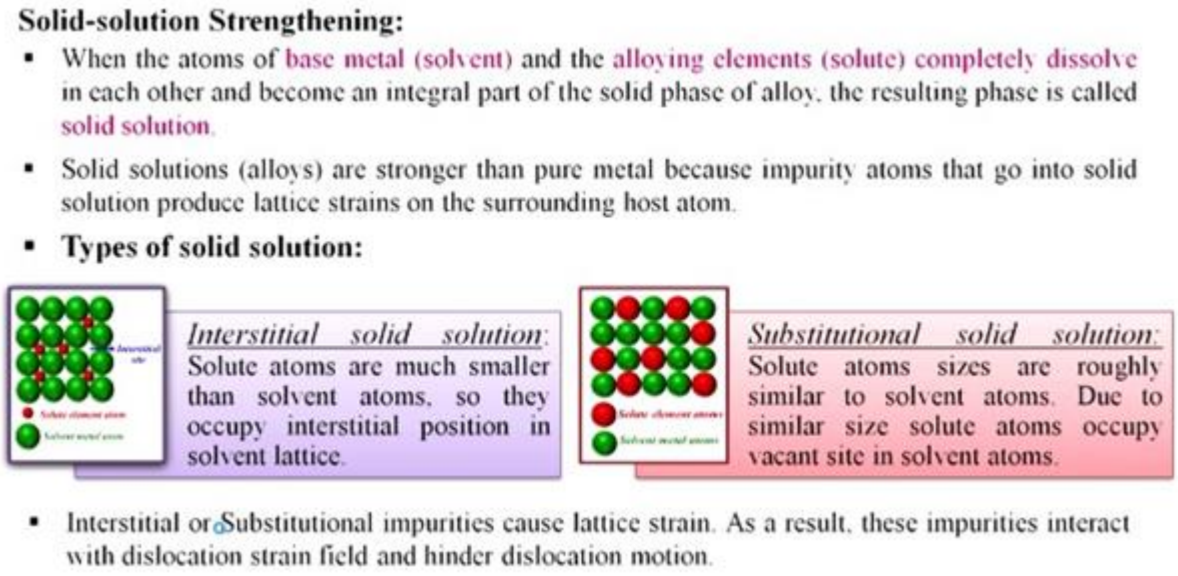
$$\sigma_y = \sigma_0 + K_y \times d^{\left(-\frac{1}{2}\right)}$$

Here, $\boldsymbol{\sigma_0}$ and $\mathbf{K_y}$ are the constants of the materials and **d** is the average grain diameter.

Figure 2.12: Strengthening by grain size reduction

2.6.2 Strengthening by solid solution

Now we will discuss solid solution strengthening, so when the atoms of base metals like a solvent and the alloying elements like solute completely dissolve in each other and become an integral part of the solid phase of alloy, the resulting phase is called the solid solution. Solid solutions generally, it's a alloy because it are a mixing of two different materials that are stronger than pure metal because impurity atoms that go into solid solution produce the lattice strains on the surrounding host atom, so there are two types of solid solutions, first one is called the interstitial solid solutions, second one is called the substitutional solid solutions, when you are talking aboutthe interstitial solid solutions, solid atoms are much smaller than solvent atoms, so they occupy the interstitial position in the solvent lattice, so from this particular case you can find that this is known as the interstitial site where the solute atoms are going and staying over there, and when you are talking about the substitutional solute solutions, solute atom sizes are roughly similar to solvent atoms, due to similar size solute atoms occupy the vacant site in the solvent atoms, so simple this site was initially vacant and that place has been taken care by the solute atoms.



Solid-solution Strengthening:

- When the atoms of base metal (solvent) and the alloying elements (solute) completely dissolve in each other and become an integral part of the solid phase of alloy, the resulting phase is called solid solution.
- Solid solutions (alloys) are stronger than pure metal because impurity atoms that go into solid solution produce lattice strains on the surrounding host atom.
- **Types of solid solution:**

Interstitial solid solution: Solute atoms are much smaller than solvent atoms, so they occupy interstitial position in solvent lattice.

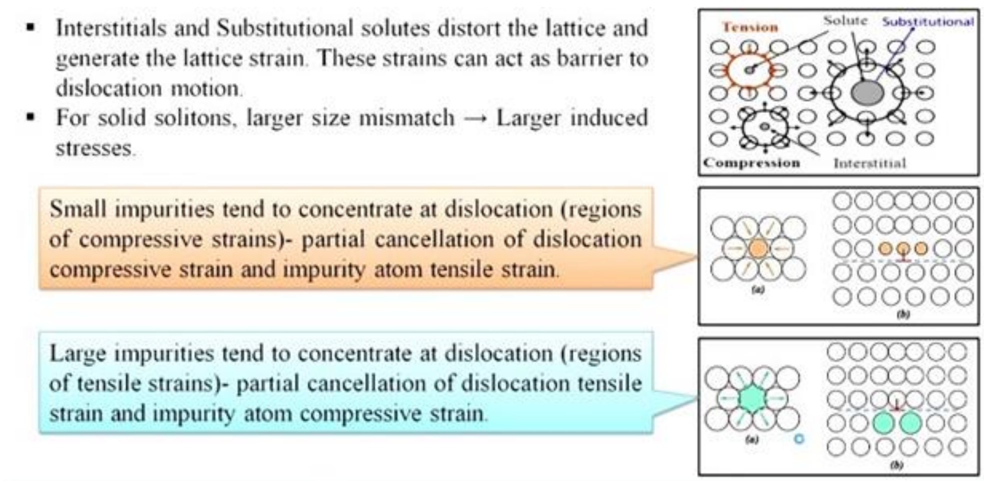
Substitutional solid solution: Solute atoms sizes are roughly similar to solvent atoms. Due to similar size solute atoms occupy vacant site in solvent atoms.

- Interstitial or Substitutional impurities cause lattice strain. As a result, these impurities interact with dislocation strain field and hinder dislocation motion.

Figure 2.13: Strengthening by solid solution

Interstitial or substitutional impurities cause the lattice strains, as a result, these impurities interact with the dislocation strain field and hinder the dislocation motion of the metals, interstitial and substitutional solutes distort the lattice and generate the lattice strain, how? These strains can act as barriers to dislocation motion, for solute solutions with larger size mismatches, and larger induced stresses.

So now we will discuss that how it is happening, so small impurities tend to concentrate at dislocation here if you see this image dislocation, regions of the compressive strains, partial cancellation of dislocation compressive strains, and impurity atom the tensile stress. Large impurities tend to concentrate at dislocations, regions of tensile, here you can see the size of the atoms is much bigger than the interstitial site space, so what happened? Partial cancellation of dislocation tensile strain and impurity atom compressive strain, so here the impurity atom is giving the compressive strain to the surroundings, and in this particular case, the impurity atom isgetting the tensile strain from the surroundings.



- Interstitials and Substitutional solutes distort the lattice and generate the lattice strain. These strains can act as barrier to dislocation motion.
- For solid solitons, larger size mismatch → Larger induced stresses.

Small impurities tend to concentrate at dislocation (regions of compressive strains)- partial cancellation of dislocation compressive strain and impurity atom tensile strain.

Large impurities tend to concentrate at dislocation (regions of tensile strains)- partial cancellation of dislocation tensile strain and impurity atom compressive strain.

Figure 2.14: lattice strains by Interstitial or substitutional impurities

Increasing the concentrations of the impurity results in an attendant, increase in tensile and yield strength and decrease in percentage elongations which is nothing but known as the ductility, so now we are trying to give one example so that you can better understand, for example variation with nickel content of a tensile strength, yield strength and ductility for copper nickel alloys showing the strengthening, so in this particular case you can find that the, it is starting with the copper and then it is going with the nickel 100%, so copper 0, 20, 40, 60, 80 and 100, and nickel in this particular case is 0, and nickel percentage is going to be increased in this particular directions, so in this particular case you can find the maximum tensile strength in this particular zone, that means it is more or less 60% of the copper, and 40% of the nickel, the same thing we are getting for the yield strength also, so for the yield strength, generally we are getting it for the 80% of the copper, and the 20% for the nickel, and the elongation at break we are getting generally for the 58% of copper, and rest maybe the 42% of the nickel.

- Increasing the concentration of the impurity results in an attendant increase in tensile and yield strength and decrease in % elongation (ductility).
- For example: Variation with nickel content of (a) tensile strength, (b) yield strength and (d) ductility (% EL) for copper-nickel alloys, showing strengthening.

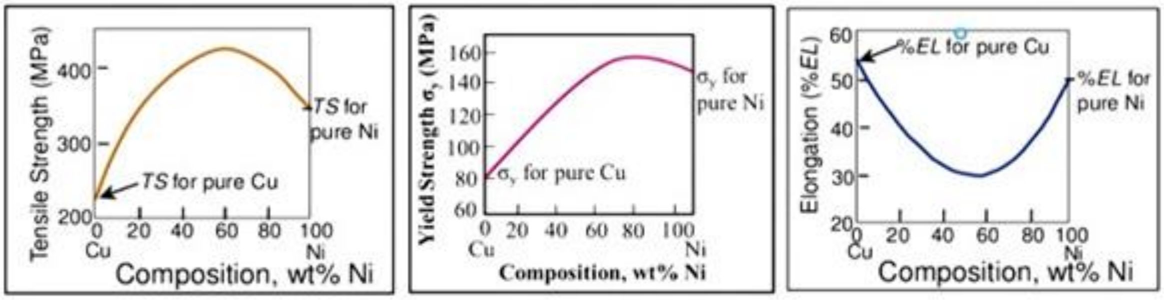
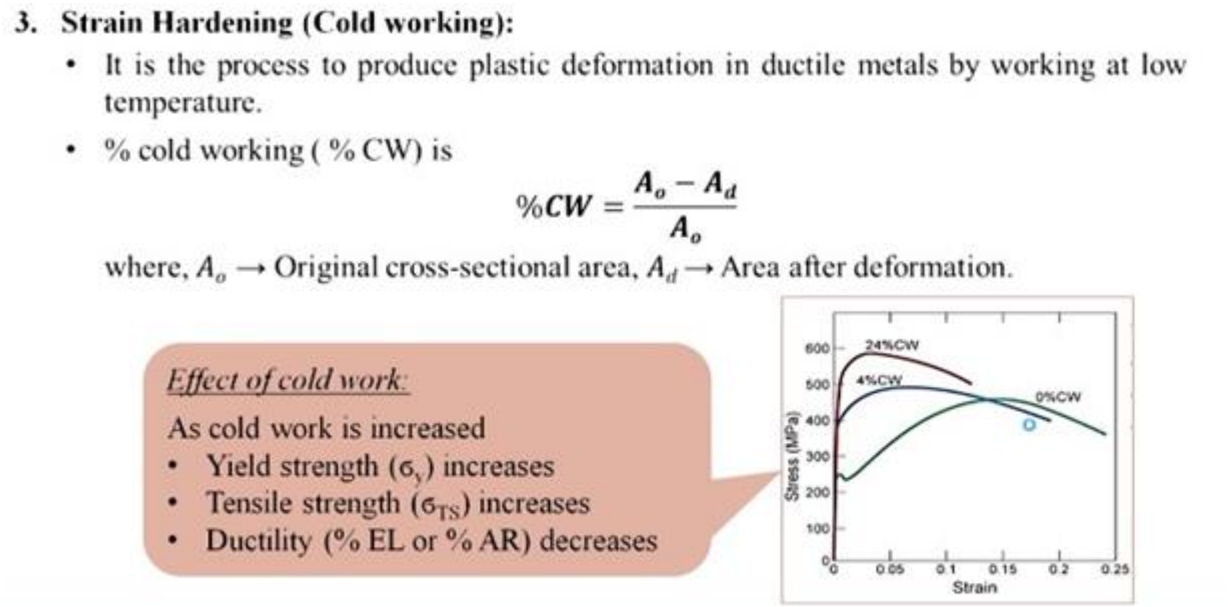


Figure 2.15: variation with a nickel content of a tensile strength, yield strength

2.6.3 Strain hardening or cold working:

Now we'll discuss strain hardening which is nothing, already told you is known as cold cracking, so or maybe the cold working, so is the process to produce plastic deformation in ductile metals by working at low temperatures, so percentage cold working is known as the A0 – AD/A0, where A0 is the original cross-sectional area, AD is the area after deformations, so generally from this particular stress-strain curve you can see that when you are doing the 24% cold working, so automatically the strength of that particular material is going to be increased, but when we are doing the less cold working or maybe the no cold working, so automatically that strength of that particular material is going to be decreased. So the effect of cold work, as cold work is increased yield strength increases, tensile strength increases, and ductility decreases is the main parameter.



3. Strain Hardening (Cold working):

- It is the process to produce plastic deformation in ductile metals by working at low temperature.
- % cold working (% CW) is

$$\%CW = \frac{A_o - A_d}{A_o}$$

where, $A_o \rightarrow$ Original cross-sectional area, $A_d \rightarrow$ Area after deformation.

Effect of cold work:

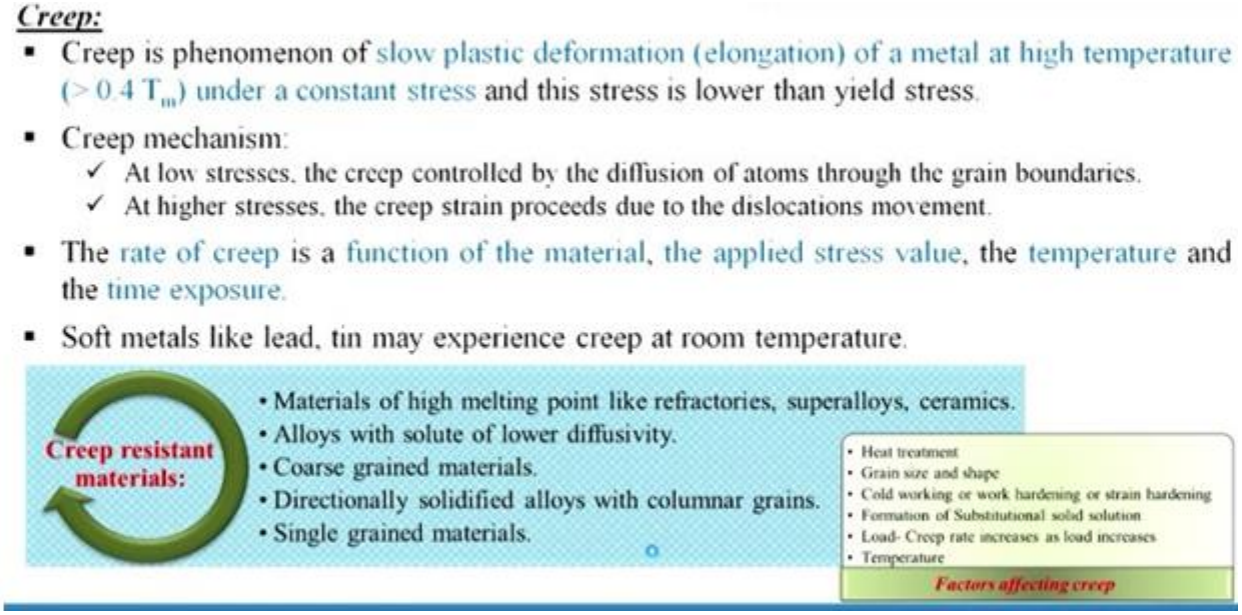
As cold work is increased

- Yield strength (σ_y) increases
- Tensile strength (σ_{TS}) increases
- Ductility (% EL or % AR) decreases

Figure 2.16: Strain hardening or cold working

2.7 Creep:

Creep is the phenomenon of slow plastic deformations or maybe the elongations of a metal at high temperatures. Generally, it is more than 0.4 times the melting temperature under constant stress, and this stress is lower than the yield stress. Now we try to understand the creep mechanism. At low stresses, the creep is controlled by the diffusion of atoms through the grain boundaries. At higher stresses, the creep strain proceeds due to the dislocation movement. The rate of creep is a function of the material the applied stress value the temperature and the time of exposure. Soft metals like lead and tin may experience creep at room temperature, so there are some creep-resistant materials also, materials of high melting points like refractories, superalloys, ceramics, alloys with solutes of lower diffusivity, coarse-grained materials, directionally solidified alloys with columnar grains, single grained materials, so what are the factors which affect the creep? The first one is known as the heat treatment, then grain sizeand shape, cold working or work hardening or strain hardening, formation of substitutional solid solutions, load-creep rate increase as load increases, and the last one is known as the temperature.



Creep:

- Creep is phenomenon of slow plastic deformation (elongation) of a metal at high temperature (> 0.4 T_m) under a constant stress and this stress is lower than yield stress.
- Creep mechanism:
  - ✓ At low stresses, the creep controlled by the diffusion of atoms through the grain boundaries.
  - ✓ At higher stresses, the creep strain proceeds due to the dislocations movement.
- The rate of creep is a function of the material, the applied stress value, the temperature and the time exposure.
- Soft metals like lead, tin may experience creep at room temperature.

Creep resistant materials:

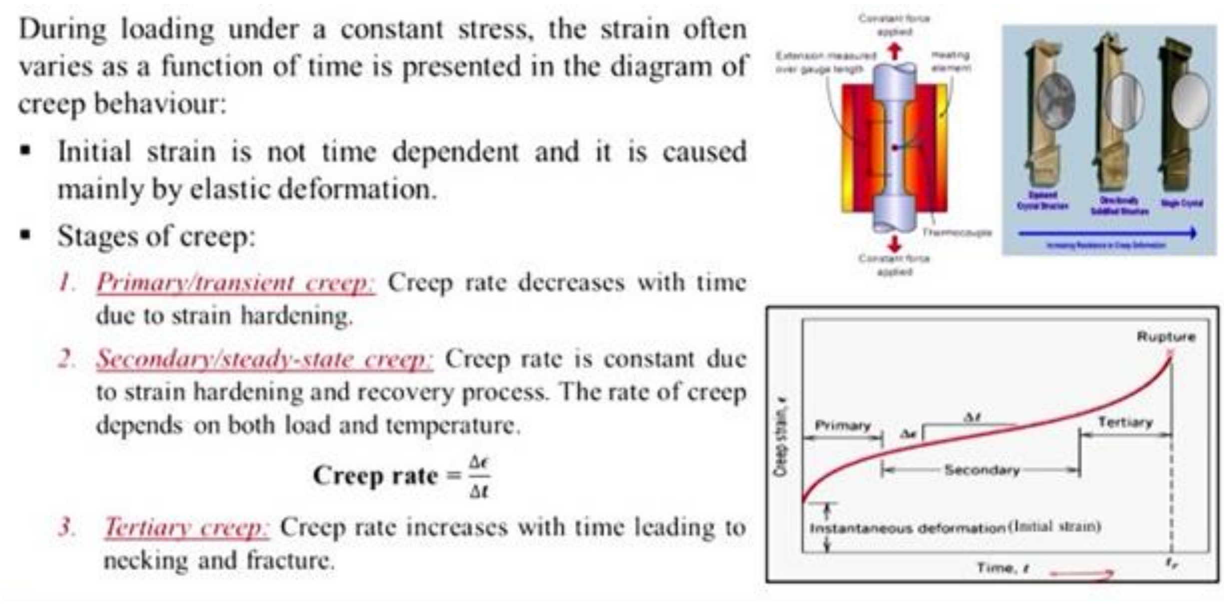
- Materials of high melting point like refractories, superalloys, ceramics.
- Alloys with solute of lower diffusivity.
- Coarse grained materials.
- Directionally solidified alloys with columnar grains.
- Single grained materials.

- Heat treatment
- Grain size and shape
- Cold working or work hardening or strain hardening
- Formation of Substitutional solid solution
- Load- Creep rate increases as load increases
- Temperature

Factors affecting creep

Figure 2.17: Creep mechanism

During loading under constant stress, the strain often varies as a function of time is presented inthe diagram of creep behavior, so generally, the creep strain is denoted into the Y axis, and the time is denoted at the X axis. Initial strain is not time-dependent and it is caused mainly by elastic deformation, so there are three stages of creep, first one is called the primary or maybe the transient creep, creep rate decreases with time due to the strain hardening, in this particular case so here het time as it is increasing the creep rate is decreasing, secondary or maybe the study state creep, creep rate is constant due to strain hardening and recovery process, the rate of creep depends on both load and temperature, so here the creep rate is known as the del epsilon by delT, so in this particular case you can find that it is almost like a proportion, and last one is known as the tertiary, creep rate increases with time leading to necking and the fracture, so in this particular case again it is increasing very rapidly.



During loading under a constant stress, the strain often varies as a function of time is presented in the diagram of creep behaviour:

- Initial strain is not time dependent and it is caused mainly by elastic deformation.
- Stages of creep:
  1. *Primary/transient creep:* Creep rate decreases with time due to strain hardening.
  2. *Secondary/steady-state creep:* Creep rate is constant due to strain hardening and recovery process. The rate of creep depends on both load and temperature.

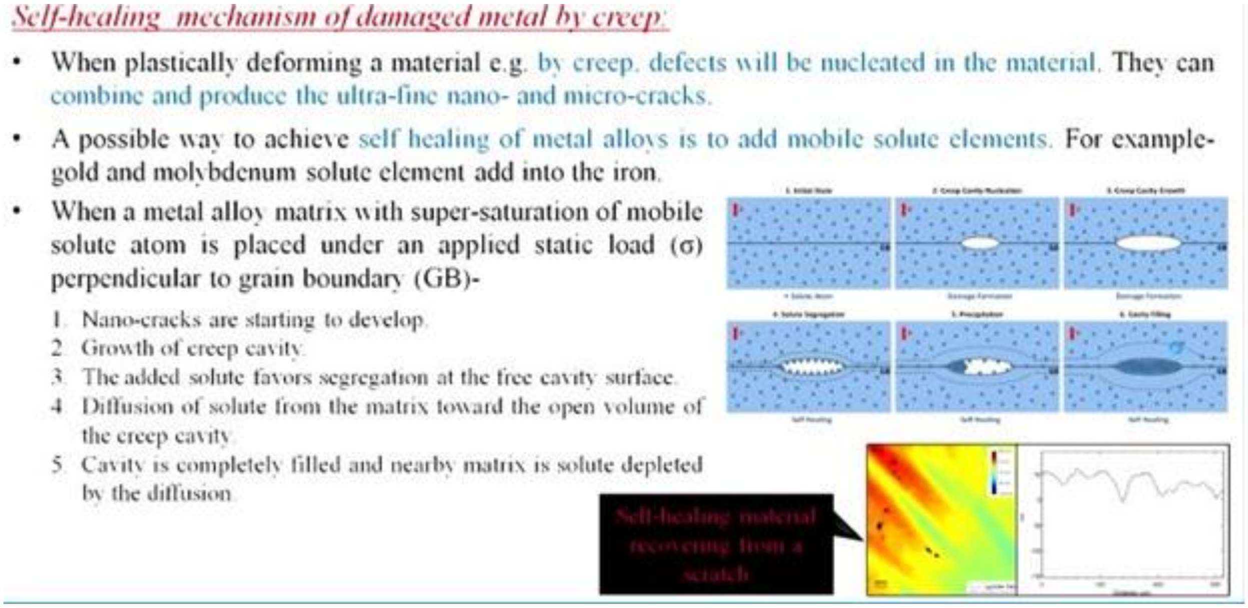
     $$\textbf{Creep rate} = \frac{\Delta\epsilon}{\Delta t}$$
  3. *Tertiary creep:* Creep rate increases with time leading to necking and fracture.

Figure 2.17: Creep behavior

2.7.1 Self-Healing Mechanism by Creep:

Now we will discuss the self-healing mechanisms of some damaged metal by creep, so plastically deforming material, for example by creep defects will be nucleated in the material, they can combine and produce the ultra-fine nano or maybe the micro-cracks, a possible way to achieve self-healing of metal alloys is to add mobile solute elements. For example, generally, we are using gold and molybdenum solute elements added to the iron. When a metal alloy matrix with supersaturation of mobile solute atom is placed under an applied static load, perpendicular to the grain boundary what happens? Nano-cracks are starting to develop, so in this particular case,you can find that the nano-cracks have been started. Growth of the creep cavity is taking place, the added solute favors the segregation at the free cavity surface, in this particular case, you can find that diffusion of the solute is taking place.

Now diffusion of solute from the matrix towards the open volume of the creep cavity, so full diffusion has taken place, now after a certain time you can find that completely, the cavity is filled and the nearby matrix is solute depleted by the diffusion, so in this particular graph, you can find the self-healing material requiring from a scratch, so after a certain time you can find that the how the creep is going to be decreased.



Self-healing mechanism of damaged metal by creep:

- When plastically deforming a material e.g. by creep, defects will be nucleated in the material. They can combine and produce the ultra-fine nano- and micro-cracks.
- A possible way to achieve self healing of metal alloys is to add mobile solute elements. For example- gold and molybdenum solute element add into the iron.
- When a metal alloy matrix with super-saturation of mobile solute atom is placed under an applied static load (σ) perpendicular to grain boundary (GB)-

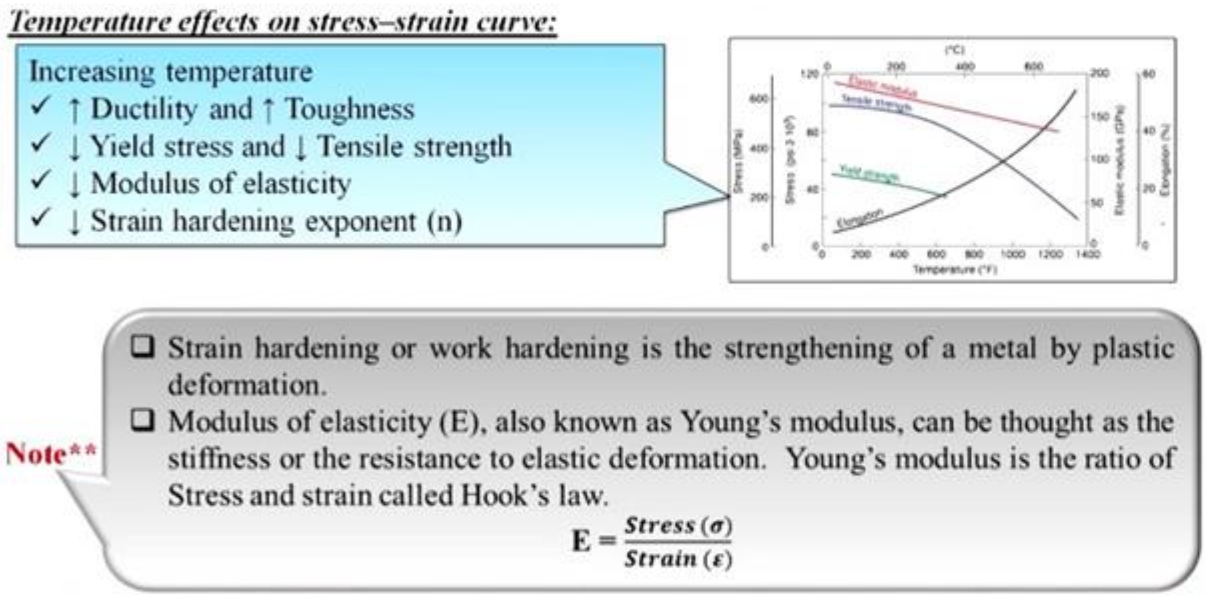
1. Nano-cracks are starting to develop.
2. Growth of creep cavity.
3. The added solute favors segregation at the free cavity surface.
4. Diffusion of solute from the matrix toward the open volume of the creep cavity.
5. Cavity is completely filled and nearby matrix is solute depleted by the diffusion.

Self-healing material recovering from a scratch

Figure 2.18: Self-Healing Mechanism by Creep

2.8. Temperature effects on the stress-strain curve

Temperature affects on stress-strain curve, so if we increase the temperature so ductility and toughness will increase, yield stress and the tensile strengths are going to be decreased, modulus of elasticity is going to be decreased. Strain hardening exponent is also going to be decreased, so in this particular graph you can find that, for example so when we are trying to increase the temperature its elongation is going to be increased, but its elastic modulus is going to be decreased, tensile strength is also going to be decreased, and the yield strength is also going to bedecreased, so strain hardening or maybe the work hardening is the strengthening of a metal by plastic deformation, modulus of elasticity also known as the Young modulus can be thought as stiffness or the resistance to elastic deformation, the Young modulus is the ratio of stress and strain called the Hooke’s law which I have already discussed earlier. So generally the Young modulus or maybe the modulus of elasticity which is denoted by the capital E is known as the stress by strain.



Temperature effects on stress–strain curve:

Increasing temperature

- ✓ ↑ Ductility and ↑ Toughness
- ✓ ↓ Yield stress and ↓ Tensile strength
- ✓ ↓ Modulus of elasticity
- ✓ ↓ Strain hardening exponent (n)

Note**

☐ Strain hardening or work hardening is the strengthening of a metal by plastic deformation.

☐ Modulus of elasticity (E), also known as Young's modulus, can be thought as the stiffness or the resistance to elastic deformation. Young's modulus is the ratio of Stress and strain called Hook's law.

$$\mathbf{E} = \frac{\textit{Stress}\ (\sigma)}{\textit{Strain}\ (\varepsilon)}$$

Figure 2.19: Temperature effects on the stress-strain curve

2.9 Summary

1. A metal is a material in the form of an element, compound, or alloy that is typically hard when in solid state, opaque and shiny, generally malleable and ductile.

2. Base metals are easily oxidized or corroded and react easily with dilute hydrochloric acid to form the metal chloride and hydrogen. Generally, the base metal can react with some other acids or maybe the base.

3. Noble metals are resistant to corrosion and oxidation in moist air, unlike most base metals. So the noble metals, generally don't react with the air or maybe the environmental moisture. Examples of noble metals are gold, platinum, and silver.

4. Precious metals are rear, natural, or correct metallic chemicalelements of high economic value, and very expensive as their name indicates. Precious metals are less reactive than noble metals. Precious metals are not easily available.

5. heavy metals are very dense metals and metalloids. metalloids are nothing but a mixture of metals and non-metals, examples are boron, silicon, germanium, arsenic etc.

6. Ferrous metals mean the iron content is there as wrought iron or an alloy such as steel because steel the iron percentage is more. Nonferrous metals: Metal including alloys that do not contain iron in appreciable amounts.

7. The yield strength is obtained by drawing a straightline parallel to elastic portions of the stress (σ) versus strength (ε) curve at some specified strength offset ε_P usually taken as 0.002.

8. Tensile strength is the stress at the maximum on the engineering stress-strain curve.

9. Ductility is the major degree of plastic deformations up to fracture, material that has very little or no plastic deformation upon fractureis called brittle. Generally, ductility means when we are trying to stretch that material the material is stretching.

10. The separation of a material into two or more piecesby applying stress called the fracture, and this stress is the breaking strength or maybe known as the fracture strength, the fracture is termed ductile or brittle, depending on whether the elongation is large or small.

11. Resilience, is the capacity of a material to absorb energy when it is deformed elastically and then upon unloading to have this energy recovered.

12. Toughness is a measure of the ability of a material to absorb energy up to fracture. It is the area under the sigma to epsilon curve up to fracture, so generally we are talking about the area.

13. The hardness of the metals is defined as the resistance of metal to plastic deformations usually by the indentation.

14. Strengthening of metals means increasing the yield strength, tensile strength, and hardness at the cost of the ductility, of course when we are going to increase the strength so automatically the ductility of that metal is going to be decreased.

15. Creep is the phenomenon of slow plastic deformations or maybe the elongations of a metal at high temperature

16. Temperature affects on stress-strain curve, so if we increase the temperature so ductility and toughness will increase, yield stress and the tensile strengths are going to be decreased, modulusof elasticity is going to be decreased.

2.10 Glossary

Metal - Material in the form of an element, compound, or alloy that is typically hard when in solid state, opaque and shiny, generally malleable and ductile.

Noble metals- resistant to corrosion and oxidation in moist air

Heavy metals- very dense metals and metalloids

Metalloids - the mixture of metals and the non-metals

Ferrous – a material with iron content

Nonferrous metals- Metal including alloys that do not contain iron in appreciable amounts

Yield strength - obtained by drawing a straightline parallel to elastic portions of the stress (σ) versus strength (ε) curve at some specified strength offset ε_P usually taking as 0.002.

Tensile strength- the stress at the maximum on the engineering stress-strain curve.

Ductility- the major degree of plastic deformations up to fracture, material that has very little or no plastic deformation upon fractureis called brittle. Generally, ductility means when we are trying to stretch that material the material is stretching.

Fracture- The separation of a material into two or more piecesby applying stress called the fracture

Fracture strength- stress is the breaking strength or the fracture strength.

Resilience- capacity of a material to absorb energy when it is deformed elastically and then upon unloading to have this energy recovered.

Toughness- a measure of the ability of a material to absorb energy up to fracture

Hardness- resistance of metal to plastic deformations usually by the indentation.

Creep- the phenomenon of slow plastic deformations or maybe the elongations of a metal at high temperature

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2.12 SUGGESTED READING

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2.13 Terminal Questions

1. What do you mean by metals? Give the classification of metals.
2. Give a classification of different types of metals.
3. What are the physical properties of metals?
4. Why mechanical properties of metals are significant? Give some important mechanical properties of metals.
5. Define yield strength and draw the stress-strain curve for a metal.
6 What is the tensile strength? With the help of a stress-strain curve explain the behavior of metals.
7. Explain the ductility in terms of elastic deformation in metals.
8. Define fracture in the case of metals. How many types of fractures are possible in metals?
9 Define resilience and modulus of resilience of metals.
10. Define the hardness and toughness of the metals.
11. Explain the Strengthening of metals. Give the different methods of Strengthening metals.
12. What is the Creep phenomenon? Explain different creep mechanisms.

UNIT 3 CERAMICS

Structure

3.1 INTRODUCTION

In previous units we have discussed abut different material as metals, ceramics, polymer composites etc. In this unit we study the ceramics. Ceramic materials are inorganic nonmetallic compounds which are hard, brittle, heat-resistant and corrosion-resistant, strong in compression, and weak in shearing and tension. Ceramics materials are generally formed by the action of heat and subsequent cooling. They can withstand very high temperatures, ranging from 1,000 °C to 1,600 °C. Most ceramics are compounds between metallic and nonmetallic elements for which the interatomic bonds areeither totally ionic bond or predominantly ionic but having same covalent character. They may be crystalline or may be partially crystalline. They are non-metallic oxide, nitride, or carbide material. Some elements, such as carbon or silicon, may be considered as ceramics. Common examples are brick, earthenware, porcelain, pottery objects (pots, vessels, vases), figurines made from clay, either by itself or mixed with other materials like silica. Some advance examples are silicon carbide for the cutting disk, carbon ceramics for the disk brakes, semiconductors, electrical insulators, composites such as fiberglass and carbon fiber etc.

Figure 3.1: Some examples of different types of ceramics

3.2 History of ceramics:

Now we are going to discuss about the history of the ceramics. It has been started very long back, in 26,000 BC early man discovers that clay consisting of mammoth fat and bone mixed with bone action and local loess can be molded and dried in sun to form brittle and heat resistant materials. In 4,000 BC glass was discovered in ancient Egypt, this glass consisted of a silicate glaze over a sintered quartz body. It was initially used in jewelry purpose. Then from 50 BC to 50 AD, production of optical glasses, lenses, and mirrors, window glasses begins in Rome, Italy.

In 600 AD, porcelain first ceramic composite was created by the Chinese. This material was made by firing clay along with feldspar and quartz. Then we are moving to mid-1800's. Thomas Edison tried various type ceramics for resistivity towards his newly discovered carbon microphone, discovery of porcelain electrical insulations and incandescent light bulb. In 1960, discovery of fiber optic cable which allows laser light pulse to carry large amount of information with extremely low energy loss. Then in 1965, the development of photovoltaic cells which convert light into electricity opens a new way to access the solar energy.In 1987, discovery of semiconducting ceramic oxide with a critical temperature of 72 kelvin, a potential application of ceramic superconductor is in integrated circuit, in new high speedcomputers. In 1992, certain ceramics known as smart materials are discovered, these materials can sense and react to variables surface conditions much like a living organism, and till today whatever the ceramics has been discovered for advance applications, everything will cover in this particular lecture.

Table 3.1: History of ceramics

28,000 BC	Early man discovers that clay consisting of mammoth fat and bone mixed with bone can be molded and dried in sun to form brittle and heat resistant materials, Ceramic figurines are used for ceremonial purposes.
18,000 BC	Chinese pottery appears.
14,000 BC	Ceramic pottery spreads in Eastern Asia.
9,000 BC	Ceramic products, such as vases, bricks, and tiles, become popular in the Middle East and Europe.
3,500 BC	Simple glass items are fabricated in Mesopotamia and Egypt.
3,500 BC	The wheel is invented, which will later be applied in wheel-forming of pottery.
3,000 BC	Glazed pottery is produced in Mesopotamia.
1,500 BC	Egyptians start building factories for production of glassware.
600 AD	600 CE Chinese introduce porcelain.
1400AD	High-temperature furnaces are developed in Europe for metallurgical use.

1500 AD	High-temperature refractory materials are introduced to build furnaces for making steel, glass, ceramics, and cements, leading the way to the industrial revolution.
1800 AD	Porcelain electrical insulators and incandescent light bulbs are invented.
1920 AD	High-strength quartz-enriched porcelain for insulators, alumina spark plugs, glass windows for automobiles, and ceramic capacitors are introduced.
1940 AD	Research on oxide magnetic materials (ferrites) and ferroelectric materials begins.
1950 AD	Ceramic capacitors based on barium titanate are developed.
1960 AD	Alumina insulators for voltages over 220 kV are introduced and applications for carbides and nitrides are developed. The first yttria-based transparent ceramic is invented. Bioglass is also discovered.
1970 AD	Partially stabilized zirconia is developed. High-performance cellular ceramic substrates for catalytic converter and particulate filters for diesel engines are commercialized.
1980 AD	Ceramic high-temperature superconductors are developed.
1990 AD	Nanotechnology initiatives begin proliferating worldwide.
1990 AD	The robocasting process for 3D printing of ceramics is developed.

3.3 Objectives:

After reading this unit we will able to understand:

1. Basic idea ceramics
2. Classification of ceramics
3. Preparations of traditional and advanced ceramics
4. Properties of ceramics
5. Advantage of ceramics
6. 11 Applications of ceramics

3.4 Different types of ceramics:

Now we classify the ceramics. Generally ceramics can be classified in two categories as traditional ceramics and the advanced ceramics. Advanced ceramics also has been divided into two sub categories, one is called the electro ceramics, and another one is called the advanced structural ceramics.

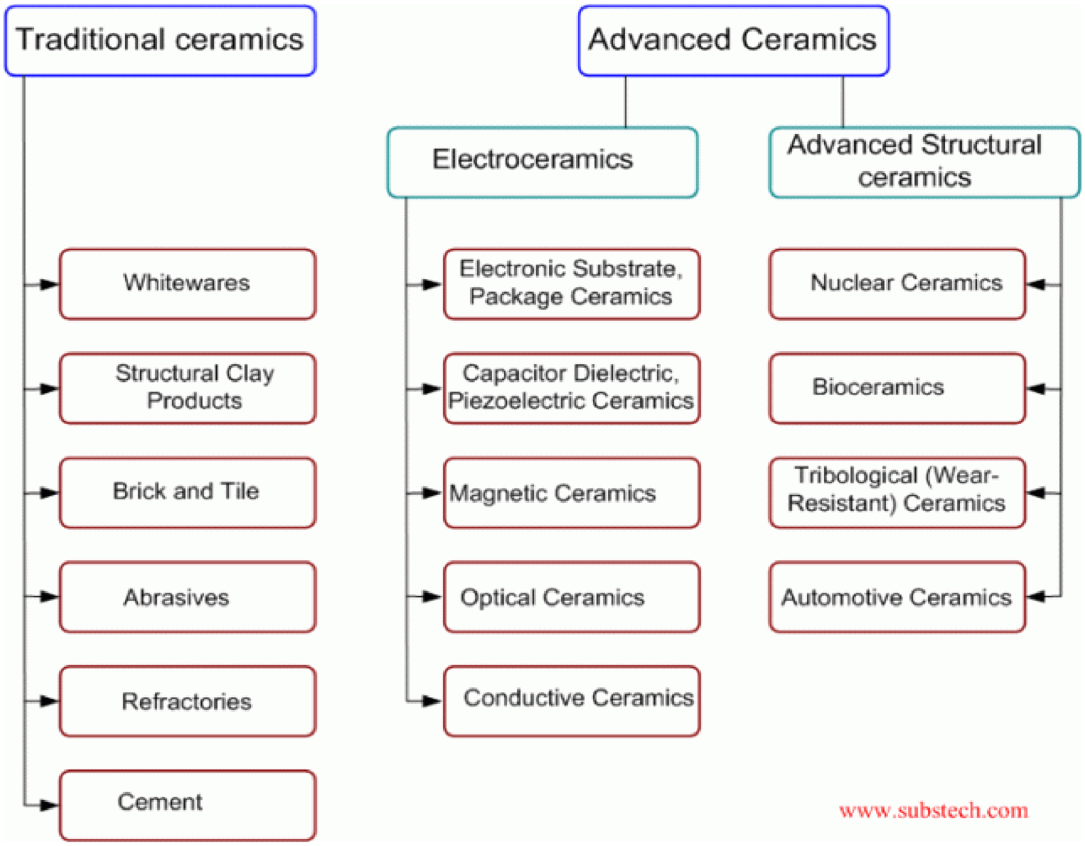


Figure 3.2: Classification of ceramics

3.4.1 Traditional ceramics:

Traditional ceramics are made from natural raw materials which can be get from the environment of clay or maybe clay silicates. It contains categories of pottery like earthenware, stoneware and porcelain. The composition of the clays used type of additives and firing temperatures determine the nature of the end product. General applications are, building materials like bricks, clay pipe, glass, household goods like pottery, cooking ware, manufacturing like abrasives materials, electrical devices, fibers, etc. as shown in figure 3.2

3.4.2 Whitewares:

Whitewares are ceramic products that are white to off- white in appearances. These materials have different properties which includes imperviousness to fluids, low conductivity of electricity, chemical inertness and an ability to be formed into complex shapes. They are differentiated according to their degree of vitrifications. Vitrifications is the full or partial transformation of a substance into a glass. In the production of ceramics, vitrification is responsible for their impermeability to water. The whiteware may be porous, semi-vitreous, vitreous and the non-vitreous. Vitrification is usually achieved by heating materials until they liquidize, then cooling the liquid, often rapidly, so that it passes through the glass transition to form a glassy solid. Certain chemical reactions also result in glasses. The example of e whiteware products are china dinnerware, crockery set, floor and wall tiles, sanitary ware, dental implants, electrical porcelain and the decorative ceramics. Whiteware products are frequently used in our day to day life.

Figure 3.3: White ware products used in our day to day life

3.4.3 Clay Products:

Clay is a finely grained natural rock or soil material that combines one or more clay minerals with traces of metal oxides and the organic matter. They are plastic due to their water content and become hard brittle and non-plastic upon drying. Depending on the soils content in which it is found, clay can appear in various colours like white, dull grey, brown or deep orange red. Main groups of clays are kaolinite, montmorillonite-smectite, illite and chlorite.

Figure 3.4: Clay Products

3.4.4 Bricks and Tiles:

Brick and tile are structural clay products used in building construction. The brick, first produced in a sun-dried form at least 6,000 years ago and the forerunner of a wide range of structural clay products used today. Brick is a small building unit in the form of a rectangular block, formed from clay or shale or mixtures and burned (fired) in a kiln or oven, to produce strength, hardness, and heat resistance. Structural clay tile, also called terra-cotta, is a larger building unit, containing many hollow spaces (cells), and is used mainly as backup for brick facing or for plastered partitions. Structural clay-facing tile is often glazed for use as an exposed finish. Wall and floor tile is a thin material of fireclay with a natural or glazed finish. Quarry tile is a dense pressed fireclay product for floors, patios, and industrial installations in which great resistance to abrasion or acids is required.

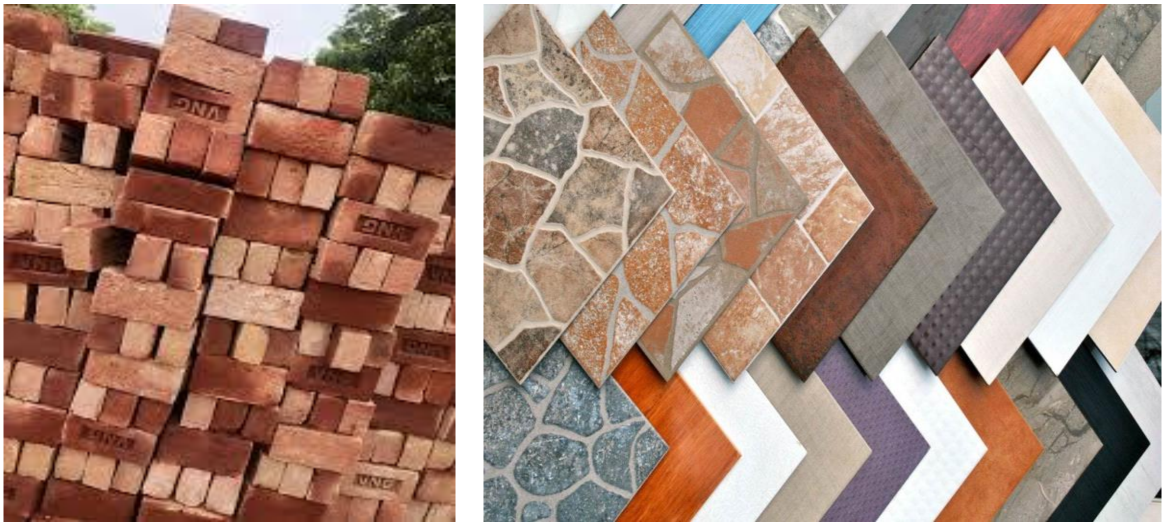


Figure 3.5: Bricks and Tiles

3.4.5 Abrasives:

Abrasive are sharp and hard material used to wear away the surface of softer and less resistant materials. Abrasives are very hard substances used for grinding, shaping or polishing the other materials, generally the emery paper or maybe for any kind of polishing or maybe the lapping or for the hunting methods generally we are using this kind of abrasive materials. They are also able to cut materials which are too hard, for other tools and give better finishes and hold the closer tolerance. So abrasive particles are used to give the final shape of a products. Abrasive are both natural and synthetic substances, ranging from the relatively soft particles used in household cleansers and jeweler's polish to the hardest known material, the diamond. Common abrasives include silicon carbide, tungsten carbide, aluminum oxide and the silica sand. It has different properties such as high melting point, chemically inert and high abrasive power.

Figure 3.6: Abrasives

3.4.6 Refractories:

Refractories are materials that are resistant to high temperature, used predominantly as furnace linings for elevated temperature materials processing and other applications in which thermomechanical properties are critical. Refractories are generally the material as brick or maybe any kind of high temperature materials made from the ceramics. So refractories ceramics are insulating materials, design to withstand high stresses and the temperature. They are produced from natural and synthetic materials usual in nonmetallic or combinations of compounds and minerals such as aluminum, fire clays, bauxite, chromite, dolomite, magnetite etcetera. They have high content of silicon, or aluminum oxide.

Figure 3.7: Refractories Ceramics

3.4.7 Cements:

Cements are also one kind of ceramics. Cement is a binder used for construction that sets hardens and adheres to other materials binding them together, generally for the building operations or maybe the structure applications. It is made by grinding together a mixture of limestone and clay, which is then heated at a temperature of 1450 degree centigrade. It has adhesives and cohesive properties, so common application of cements are using it for the buildings like floor, beams, roofing, piles and bricks. Cement is also used for making the roads, pathways, bridges, parking for transport and for the pipes, drains, dams, tanks and pools for water. Civil works like docks, retaining walls, warehousing etc. Cement has a very versatile application.

Figure 3.8: Cement Ceramics

3.4.8 Glasses or amorphous ceramics:

Glass is a solid material with amorphous structure which means that atoms are not organized according to a well-ordered, repeating arrangement as in crystals. Glass-ceramics are made of small grains surrounded by a glassy phase, and have properties in between those of glass and ceramics. The main ingredient in glasses or amorphous ceramics is the silica SiO_2. when it is cooled very slowly it will form crystalline structure, if cooled more quickly it will form amorphous structure consisting of disordered and linked chains of silicon and the oxygen atoms. It can be tempered to increase its toughness and resistance to cracking, its depends upon your applications. For example the car wind shield is made of the tempered glasses or may be some glasses which have the high temperature applications. There are different types of glasses, generally soda-lime glasses, it includes 95% of all glass, so this is the pictorial view of soda-lime glass, then lead glass it contains lead oxide to improve the refractive index, borosilicate it contains the boron oxide known as the pyrex, so generally all our chemical, petri dish or maybe the pipette or burette, generally we are making it from the boron silicate.

Next we are discussing about the flat glasses, generally we are using for the windows for our household purposes, container glasses, bottles, then pressed and blown glasses generally dinner ware and the glass fibers for the home insulations for generally for the high temperature resistance we are using this kind of glass wools or maybe the glass fibers.

Figure 3.8: Glass Ceramics

3.5 Advanced ceramic materials:

The advanced ceramic materials have been developed over the past half century, because these all are the generally the research based or maybe the application based ceramic materials. The type of ceramic exhibits a high degree of industrial efficiency. This ceramics often have simple chemical compositions but they are difficultto manufacture. so this classifications of the advanced ceramics based on chemical compositions,first it will come the nitrate ceramics, generally the silicon nitrate or maybe the aluminum nitrate,silicate ceramics like porcelain, magnesium silicate, mullite etcetera, carbide ceramics like silicon carbide, boron carbide, tungsten carbide. This kind of carbides we are using for cutting tool materials, oxides ceramics like aluminum oxide, aluminum, titanate, magnesium oxide, sometimes we are using this kind of materials for enhancing the strength of that particular material also.

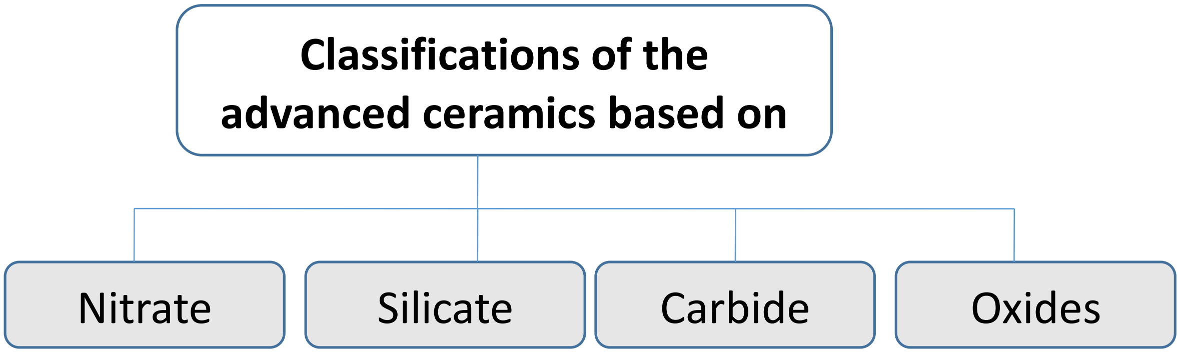


Figure 3.9: classifications of the advanced ceramics based on chemical compositions

Based on applications, advanced ceramics can be Classified into two parts, one is known as the electro ceramics, another is known as the advanced structural ceramics. In case of electro ceramics, first is the coating ceramics, then conducting ceramics, magnetic ceramics, and the optical ceramics. In case of the advanced structural ceramics, first is the nuclear ceramics, bio ceramics, tribological ceramics and the automotive ceramics.

Advanced ceramics plays a vital role in increasing the safety, cost-effectiveness and comfort in vehicle and automotive engineering. As per our own desire we are making this kind of ceramics as per our own requirement. Ceramics substrates, circuit carriers, core materials and many other components arein use throughout the electronics industries. Nowadays we are using this ceramics in a versatile manner for the electronics applications. A ceramic material enables safe, low wear process control, reduce emissions and ensure efficient use of resource in many areas of energy supply and the environmental technology. These are some applications but Ceramics nowadays we are using for our day to day life.

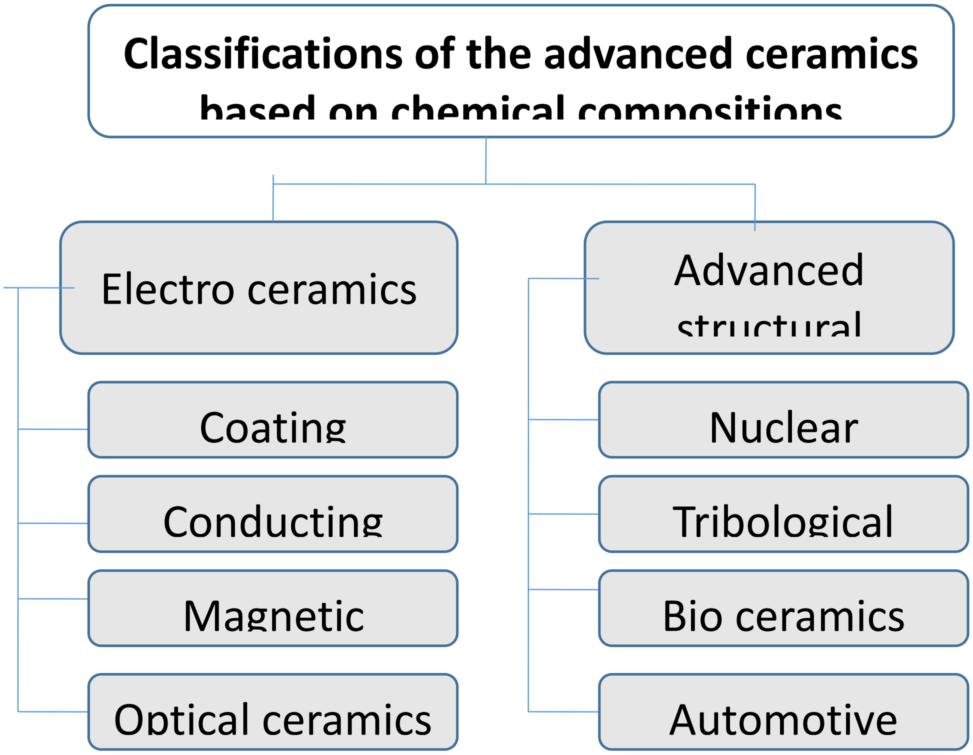
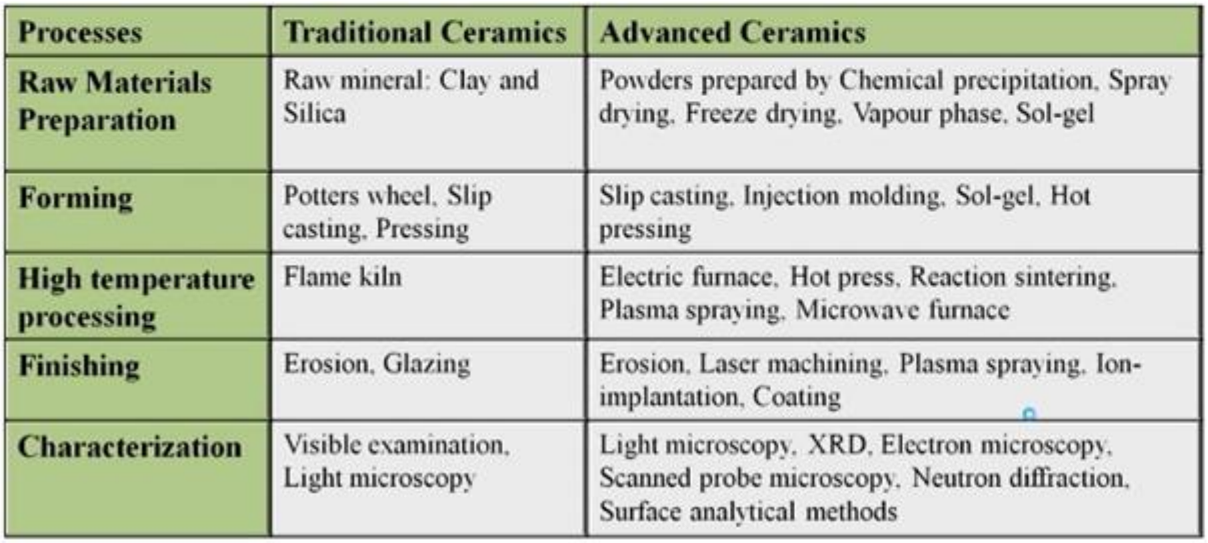


Figure 3.10: Classifications of the advanced ceramics based on applications

3.6 Preparations of traditional and advanced ceramics:

Now we will discuss about the preparations of advanced and the traditional ceramics. For traditional ceramics, first raw material is to be prepared by using the raw material as a clay and silica. In case of advanced ceramics, we use the powders, generally prepared by the chemical precipitation methods, spray drying, freeze drying, vapour phase, or may be by the sol-gel method. The forming process for the traditional ceramics is the use of potters wheel, slip casting, pressing. And for the advanced ceramics forming process are the slip casting, injection moldings, sol-gel method, hot pressing. In case of high temperature processing, generally for the traditional ceramics generally flame kiln is used. But for the advanced ceramics generally we are using the electric furnace, hot press, reaction sintering, plasma spraying and microwave furnace. Finishing products, generally for the traditional ceramics weare doing by it erosions or may be the glazing methods, advanced ceramics we are using the erosions, laser machining, plasma spraying, ion-implantation which is the latest technology or maybe the coating technology.

For the characterizations of the traditional ceramics, we do the visible examinations or maybe simple the light microscopy. For advanced ceramics we use light microscopy, XRD electron microscopy, scanning probe microscopy, neutron defractions, and surface analytical methods. By given figure 3.10 we you can easily understand the processes for conventional and advanced ceramics and advanced technology to characterize.



Processes	Traditional Ceramics	Advanced Ceramics
Raw Materials Preparation	Raw mineral: Clay and Silica	Powders prepared by Chemical precipitation, Spray drying, Freeze drying, Vapour phase, Sol-gel
Forming	Potters wheel, Slip casting, Pressing	Slip casting, Injection molding, Sol-gel, Hot pressing
High temperature processing	Flame kiln	Electric furnace, Hot press, Reaction sintering, Plasma spraying, Microwave furnace
Finishing	Erosion, Glazing	Erosion, Laser machining, Plasma spraying, Ion-implantation, Coating
Characterization	Visible examination, Light microscopy	Light microscopy, XRD, Electron microscopy, Scanned probe microscopy, Neutron diffraction, Surface analytical methods

Figure 3.11: preparations of advanced and the traditional ceramics

3.7 Properties of ceramics:

The properties of ceramics have been divided into two parts, one is called the physical properties, another one is known as the chemical properties. The physical properties are density, porosity, mechanical properties, thermal properties, magnetic properties and electrical properties. The other properties are the chemical properties as chemical resistance to weak acids and weak base.

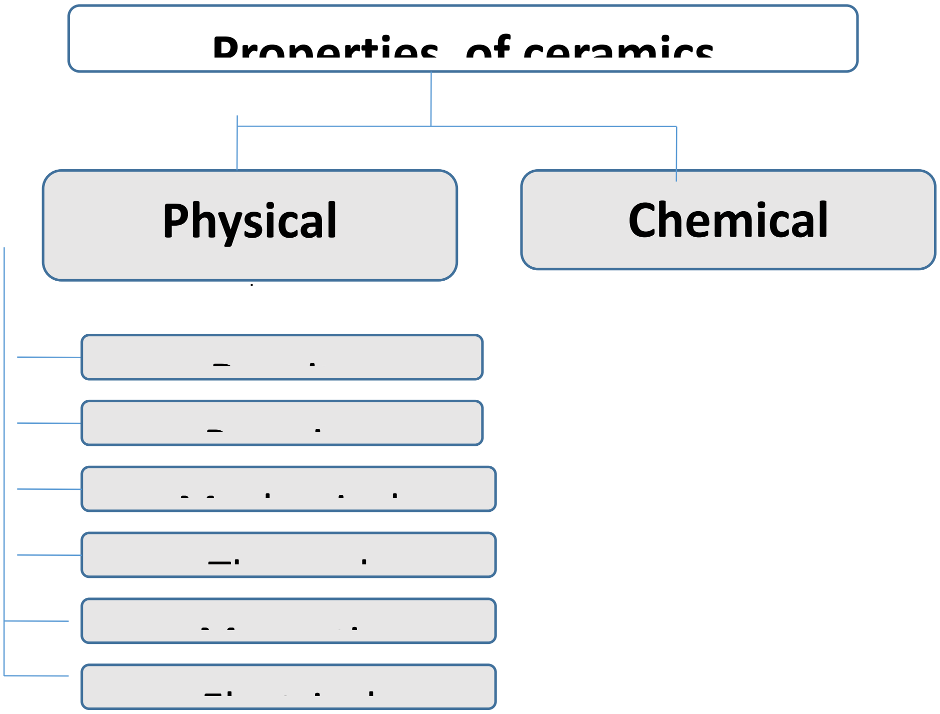


Figure 3.12: Properties of ceramics

3.8. Physical Properties of ceramics:

The main physical properties of ceramics are the density, density, porosity, mechanical properties, thermal properties, magnetic properties and electrical properties.

3.8.1 Density:

Most of ceramics are lighter than the steel and metals but heavier than the polymers. Generally the density of ceramics is 20 to 70% of density of the steel or metals. The density ranging from 2 to 6 g/c^3. This is the general idea about the density of ceramics but it maybe more for some advanced ceramics. As the strength of ceramics increases, thedensity becomes heavy and vise-versa. For example diamond has more strength due to the high density whereas foam has less strength due to its less density. From this particular image it can be observed that the density of the foam is lighter, so automatically its strength is also less. But in case of diamond, the density is too high and its strength is also too high.

The ceramics density ρ is calculated as

$$\rho = \frac{n'(\sum A_C + \sum A_A)}{V_C\, N_A}$$

where n' denotes number of formula units within the units cell, A_C are the sum of the atomic weight of all cations and A_A are the sum of the atomic weight of all anions. V_C is the unit cell volume, N_A is the Avogadro's number generally it is 6.023 x 10^{23}. The term percent theoretical density is define as

$$\%\ \text{Theoretical Density} = \frac{\text{Measered density}}{\text{Theoretical Density}} \times 100$$

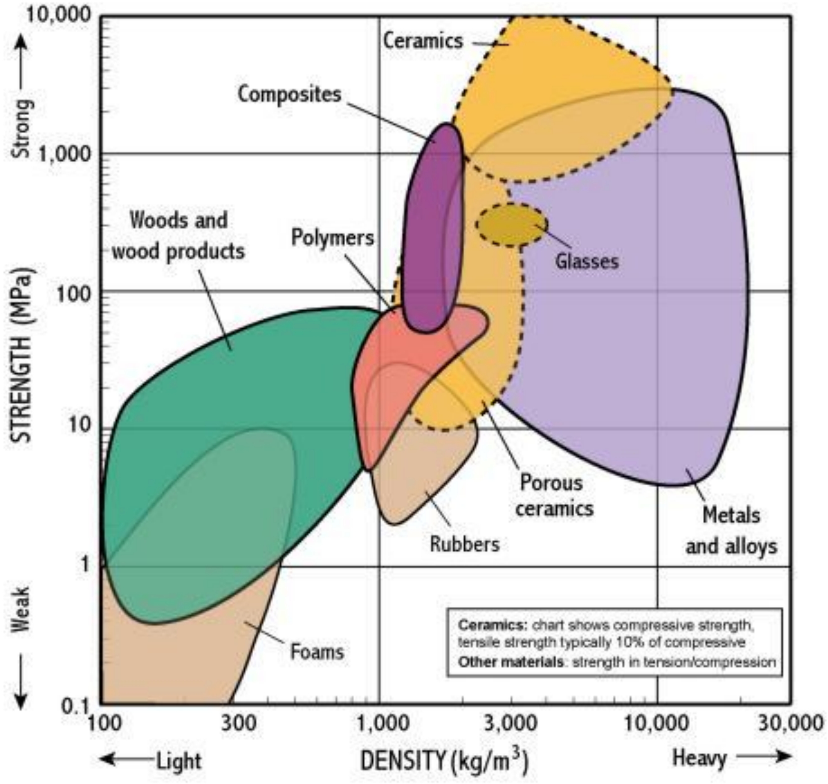


Figure 3.13: Density of ceramics

3.8.2 Porosity:

Porosity of the ceramics or white fractions is a measure of the void or empty spaces in a material. It is a fraction of volume of voids over the total volume. Generally ceramic materials have no open porosity. The size of porosity may be from nanometer to micrometer and can be generated through the appropriate selection of raw materials, themanufacturing process and the use of the additives. The generation of porosity is totally controllable. In some ceramic material the magnitude of the modulus of elasticity E and flexural strength σ_{FS} decreases with increase in volume fraction porosity.

$$E = E_0(1 - 1.9P - 0.9P^2)$$

$$\sigma_{FS} = \sigma_0 \exp(-\,nP)$$

where E_0 is the modulus of elasticity of the nonporous materials and σ_0 and n are the experimental constants.

Figure 3.14(a) shows that the modulus of elasticity is going to be decreased and the volume fraction porosity is going to be increased. The same thing is being happened for the flexural strength. The flexural strength is also going to be decreased and the volume fraction of porosity is going to be increased. The influence of porosity on the modulus of elasticity and flexural strength for concrete at room temperature is shown in the figure 3.14(b).

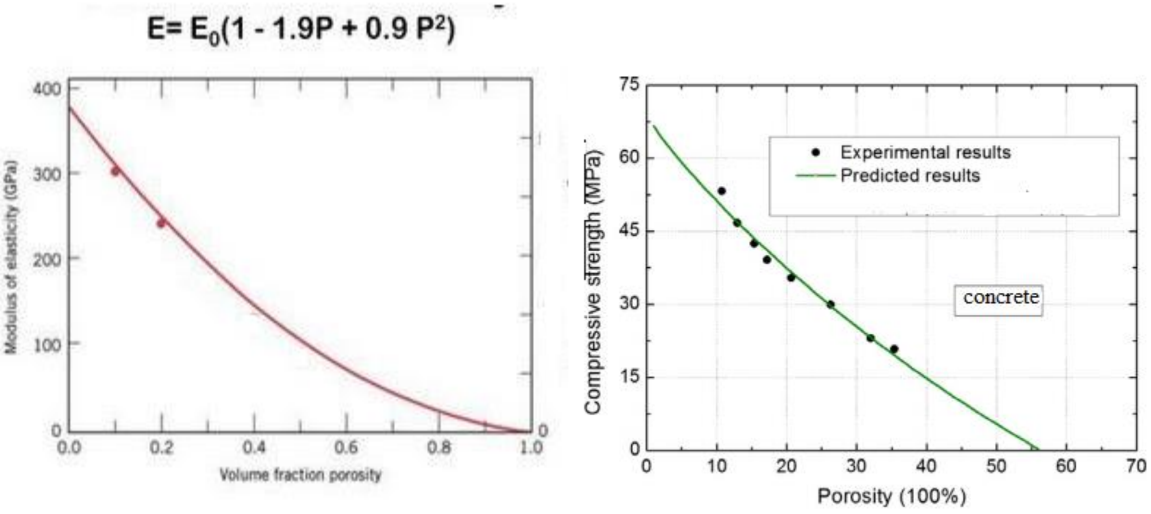


Figure 3.14: (a) modulus of elasticity and porosity (b) modulus of elasticity and flexural strength

3.8.3 Mechanical properties:

The usual mechanical properties of materials are tensile strength, elastic behavior, plastic deformation, fracture etc. In case of ceramics, the mechanical properties are limited as ceramics generally fracture before any plastic deformation. The brittle fracture process consists of the formation and propagation of cracks through the cross section of material in the direction perpendicular to applied load.

3.8.3.1 Flexural strength:

Stress strain behavior of the ceramics is not usually determined by a tensile test because it is difficult to prepare a test on ceramic specimens having required geometry. Further it is difficult to grip brittle materials without fracturing, because on giving the stress by the clip, material will break. And the ceramics break or failed after only about 0.1% of strain, so generally we are not going to do any kind of tensiletesting for ceramic materials. Therefore the stress at fracture is determined by using the flexure test is known as the flexural strength which can be considered as equivalent to the tensile strength of that particular ceramic material. Flexural strength, also known as modulus of rupture or bend strength or transverse rupture strength is a material property, defined as the stress in a material just before it yields in a flexure test. The transverse bending test is most frequently employed, in which a specimen having either a circular or rectangular cross-section is bent until fracture or yielding using a three-point flexural test technique. The flexural strength represents the highest stress experienced within the material at its moment of yield. It is measured in terms of stress and generally denoted by σ. For the calculation of stress- strain behavior using three point loading methods is used as shown in figure 3.15.

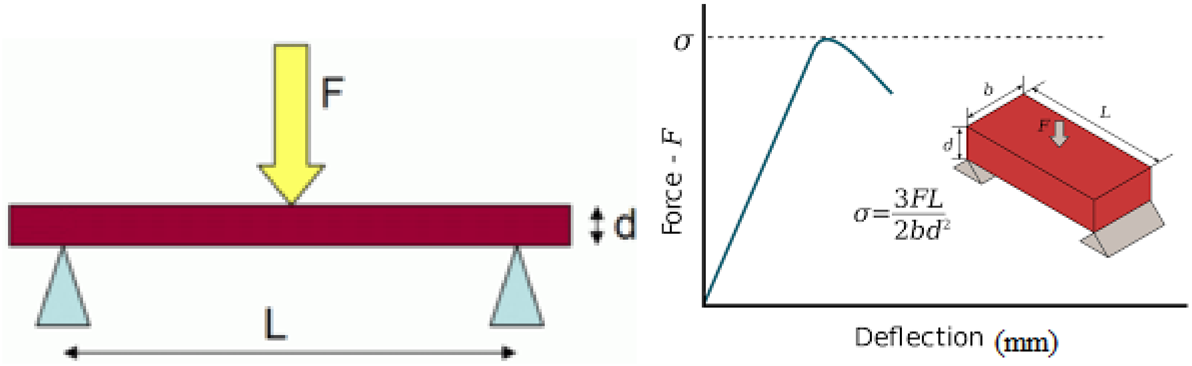


Figure 3.15: Three-point bending setup for flexural strength

The resulting stress for a rectangular sample under a load in a three-point bending setup (Fig. 3.15) Measuring flexural strength is given by the formula

$$\sigma = \frac{3FL}{2bd^2}$$

Where F= Axel load (force)

L= length of support span

b= width

d= depth or thickness of material

F is the load (force) at the fracture point

3.8.3.2 Elastic behavior of ceramic materials:

Elastic stress strain behavior for ceramic materials using flexural test is similar to the tensile test results for the metals. Elastic modulus slope of ceramics is usually higher thanfor metals, because ceramics are bonded either covalently or ionically and always it is much higher than the metallic bonds. The range of elastic modulus for ceramic is about 70 to 500 GPa. Figure 3.16 shows the stress stain behavior of aluminum oxide and glass. From this particular curve we can understand that the diamond generally it is coming around 900 GPa, but for aluminum oxide it is lesser.

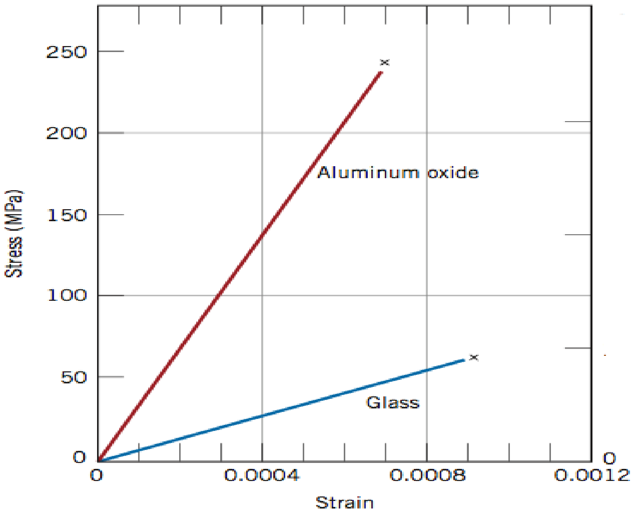


Figure 3.16: Elastic stress strain behavior for ceramic materials

3.8.3.3 Strength of ceramics:

Ceramics have compressive strengths about 10 times higher than their tensile strength. The tensile strength of ceramics is low because the existing flaws giving the stress concentrations of that particular materials. Ceramics are usually used in applications where load or compressive in nature, it depends on the material compositions, production conditions, manufacturing process, grain size of initial materials and their additives, so this is the common graphs generally we are showing that strength of the ceramics is automatically more or less than the metals.

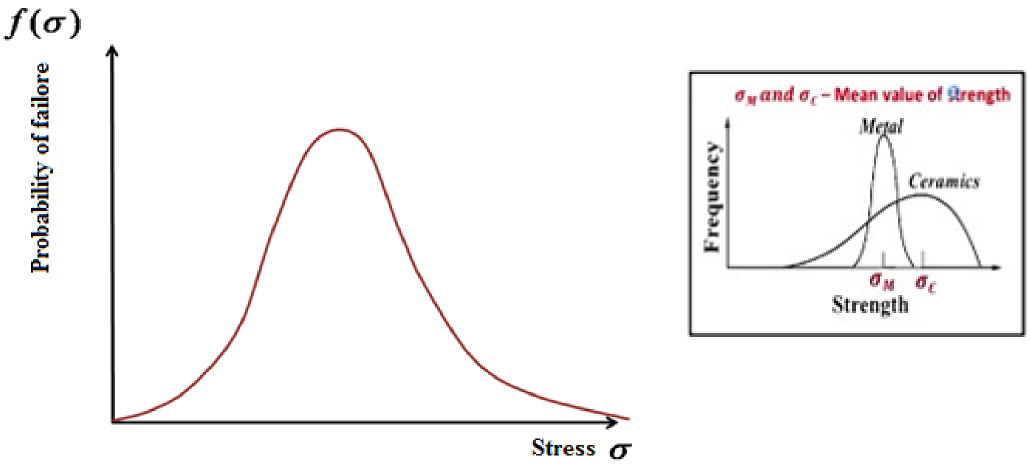


Figure 3.17: Strength of ceramics

3.8.3.4 Plastic deformations of ceramics:

Plastic deformation is the permanent distortion that occurs when a material is subjected to tensile, compressive, bending, or torsion stresses that exceed its yield strength and cause it to elongate, compress, buckle, bend, or twist. First we have to understand the mechanism of the plastic deformations. In crystalline ceramics plastic deformation occurs as in the metals by the motion of dislocations. The hardness and brittleness of crystalline ceramics materials are due to the difficulty of slip for covalent bonding. Covalent bonding or maybe the ionic bonding is very strong bonding and slip for bonding is not possible. In ceramics, covalent bonds are stronger therefore the ceramics are brittle in nature. Lack of plasticity is due to ionic and covalent bonding direction, which is in directional in nature. For the non-crystalline ceramics, plastic deformation does not occur by dislocation motion. For non-crystalline ceramics because there is no regular atomic structure, materials deformed by viscous flow that is the breaking and reforming of atomic bonds allowing ions and atoms to slide past each other like in liquid.

In this case viscosity of the non-crystalline ceramic η is given as

$$\eta = \frac{F/A}{dv/dy}$$

where F/A is the share force per unit area or share stress(τ) , A is the area, and v is the velocity, y is the distance and dv/dy is the change in velocity with distance in a direction perpendicular to the plate itself.

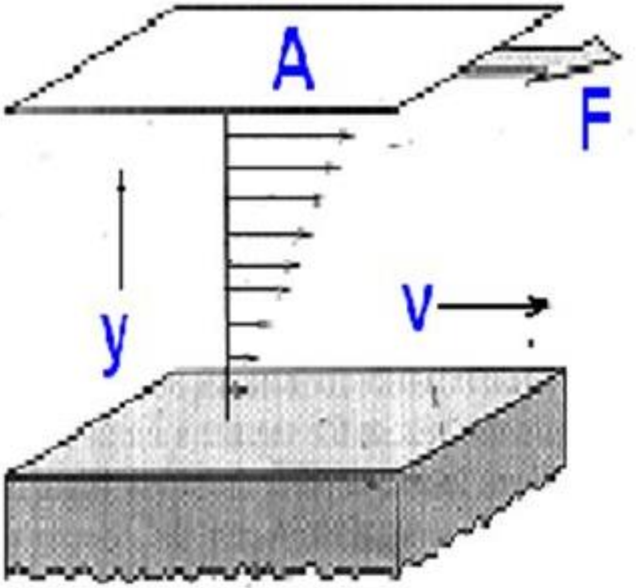


Figure 3.18: Representation of viscous flow of atoms in a glass ceramics as in fluid

3.8.3.5 Brittle fracture of ceramics:

At room temperature both crystalline and non-crystalline ceramics shows fracture before any plastic deformation in response to an applied tensile load. Brittle fracture processes consist of the formation and propagation of cracks through the cross section of material in direction perpendicular to the applied load. This is very important parameters and the crack formation is taking place for the ceramic materials. Crack growth in crystalline ceramics maybe either trans-granular through the grains or maybe the inter-granular along grain boundaries. Figure 3.19 shows the stress strain curve of a ceramic material and at the elastic limit, brittle fracture is occurred in a particular point as shown.

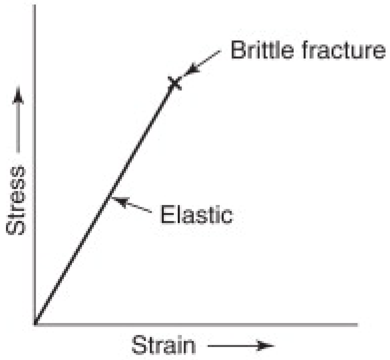
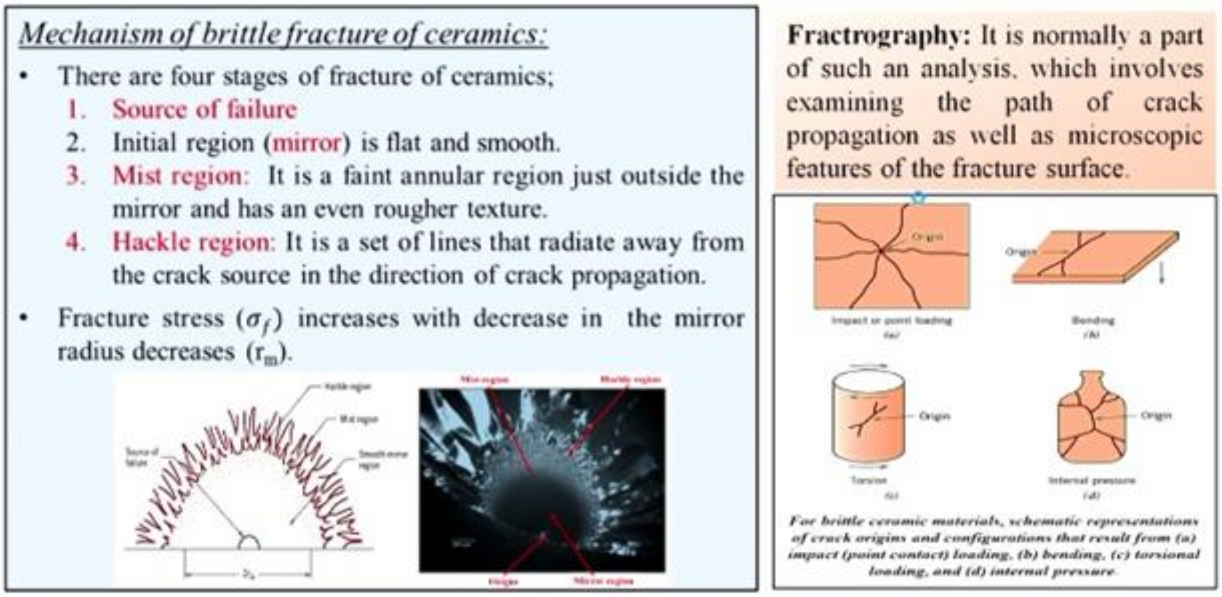


Figure 3.19: Brittle fracture of ceramics

Now we will understand the mechanism of brittle fracture in ceramics. There are four stages of fracture ceramics. For example consider breaking of a glass. For better understand of the fracture in glass ceramics materials, we can divide the mechanism in four steps. First one is source of failure, second is the initial region or mirror, next is called the mist region and last one is called the hackle region. First is source, this is nothing but glass, so this is source of failure. Second one is some initial area or maybe the initial region. The initial region is the zone of fracture actually.
Next, third is called the mist region, this zone is data side, it is faint annular region just outside the mirror and has an even rougher texture. Next forth is hackle region, it is a set of lines you can find that there is a cracks lines and called it, the radiate away from the crack source in the direction of crack propagations.



Mechanism of brittle fracture of ceramics:

- There are four stages of fracture of ceramics;
  1. Source of failure
  2. Initial region (mirror) is flat and smooth.
  3. Mist region: It is a faint annular region just outside the mirror and has an even rougher texture.
  4. Hackle region: It is a set of lines that radiate away from the crack source in the direction of crack propagation.
- Fracture stress (σ_f) increases with decrease in the mirror radius decreases (r_m).

Fractrography: It is normally a part of such an analysis, which involves examining the path of crack propagation as well as microscopic features of the fracture surface.

For brittle ceramic materials, schematic representations of crack origins and configurations that result from (a) impact (point contact) loading, (b) bending, (c) torsional loading, and (d) internal pressure.

Figure 3.20: Mechanism of brittle fracture of ceramics

Fractrography is a part of such an analysis which involves examining the part of a crack propagations as well as microscopic features of the fracture surface. So we can the origin and then after that the crack is propagating into different directions, so crack is propagating into the different directions. The bending of the crack originating is taking place and then crack is propagating into this all directions. Suppose we have a glass bottles or maybe some ceramic material bottle, and internally you have to give a high pressure, and the crack propagation is taking place in this particular ceramic materials.

3.8.3.6 Hardness:

One beneficial mechanical property of ceramics is their hardness which is often utilized when an abrasive or grinding action is required. Because when we are going to grind any material so we are going to choose that abrasive particles which is more harder than the walk piece material, so ceramics materials are consideredas the hardest material, so for ceramics hardness is defined at the resistance to elastic deformations of the surface, hardness is affected from porosity in the surface, the grain size ofthe microstructure and the effects of grain boundary phases.

The high hardness of technical ceramics results in favorable wear resistance, ceramics are thus good for tribological applications means for any kind of friction or maybe the wear mechanisms. Test procedures of determining the hardness of ceramic materials according to Knoop, Vickers, Rockwell as all shown in this particular table. So if you see that material class here left hand sideall are the different type of ceramic materials and we are going to give the example of the weakerhardness of those in the gigapascal, so for glasses it is 5 to 10, for zirconia aluminum nitrides its 10 to 14, for alumina silicon nitrides it is 15 to 20, silicon carbides and boron carbides is generally 20 to 30, cubic boron nitrides which is also one kind of hardest material which we are synthesizing in our laboratory, it’s known as 40 to 50 gigapascals, and for diamond it is 60 to 70 or more.

3.8.3.7 Toughness of ceramic materials:

The toughness of a material is measured by its resistance to fracturing. Typically, ceramics are characterized by hardness as well as a lack of toughness. Among Fine Ceramics (also known as "advanced ceramics"), zirconia possesses relatively high levels of toughness. Now we are going to discuss about the toughness of ceramic materials, so both ceramics and glasses at room temperature will undergo the first fracture, in a tensile test before any plastic deformations has occurred, they have a fracture toughness about 50 times lesser than the metals, even though their bonding forces are higher, yes, because as I already told they’re possessing the covalent or maybe the ionic bonding which is much harder than the metallic bonding. Using hot pressing reaction bonding to improve toughness, so this is the simple stress strain curve and we have already gone through these graphs into the metal parts so this is simply giving you the toughness of that particular ceramic material.

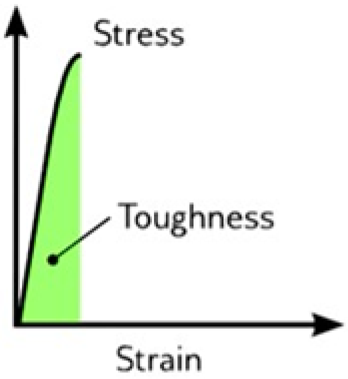


Figure 3.21: Toughness of ceramic materials

3.8.4 Thermal properties of ceramics:

Now we are going to discuss about the thermal properties of ceramics, when we talk about the thermal property, first we should know the thermal conductivity.

3.8.4.1 Thermal conductivity:

Thermal conductivity is the property of a material that indicates the ability to conduct the heat so that heat can easily flow from one point to another point. Ceramic have low thermal conductivity due to ionic covalent bonding which does not have free electron. On the other hand metals have good thermal conductivity because metals have large number of free electrons which are responsible for conduction. Thus the thermal conductivity of metals is much higher than the ceramic materials. If thermal heat energy is transmitted through a solid rod, then flux of thermal energy j_u can be give as

$$j_u = -K\frac{dT}{dx}$$

Where K is coefficient of thermal conductivity, $\frac{dT}{dx}$ is the temperature gradient at steady state flow. Thermal flux is nothing but energy transmitted per unit time across per unit volume. Ceramic materials are used for thermal insulations due to their low thermal conductivity except silicon carbide, aluminum nitride. These all are the exceptional ceramic materials. The applications of Aluminum nitride is used in IC packages so generally for the electronic purposes for semiconductors that emit high volume of heat. Zirconia blocks heat effectively and it’s coefficient of thermal conductivity is low, it is used for kiln walls which are exposed to high temperature. Generally zirconia blocks are used for the furnace or maybe oven, or may be the high temperature obligations.

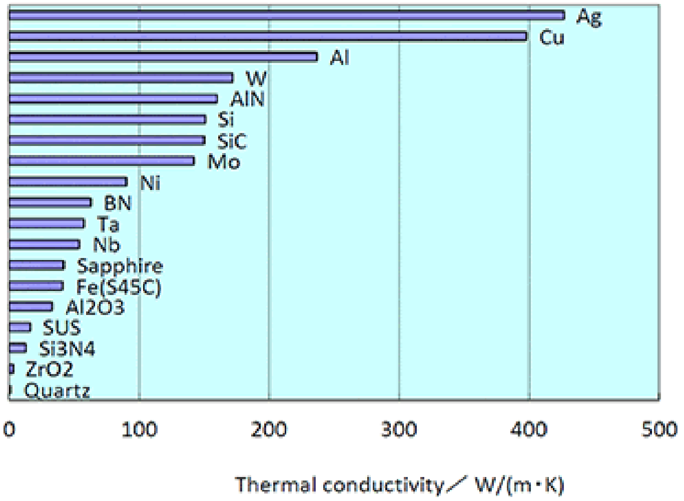


Figure 3.22: Thermal conductivity of different ceramic and metals

so in figure 3.22 the thermal conductivity of different materials are shown. when you are talking about the fine ceramics zirconia is only 3, but whereas aluminum nitride is 150. Same thing we can find for the metals like cemented carbide, tungsten carbide with cobalt it is having 85 and carbon steel it is having SC is 41, and alumina and silicon carbide and silicon nitride they are much lesser than the metals one. So high thermal conductivity like aluminum nitrides so if you give the temperature, the temperature will go from one point to another point that means the temperature will be homogeneously dispersed throughout the material. When we talk about the zirconia the temperature is not flowing smoothly to hold material.

3.8.4.2 Thermal expansion coefficient of ceramics:

The coefficient of thermal expansion indicates how much a material expands per unit raise in temperature. Thermal expansion of a solid is change in size of a solid due to change in temperature. If the lattice vibrations are perfectly harmonic then interatomic vibrations follow Hook’s law exactly, and there is no change in the dimension of solid on raising the temperature of solid. However, in actual, the vibrations are not perfectly harmonic and dimensional changes occurs during the change of temperature. Thermal expansion of solid is a consequence of displacement of ions or atoms of the material as temperature changes. The thermal expansion of solid is characterized by volume thermal expansion coefficient & which is defined as change in volume per unit volume per unit temperature rise as given below.

$$\alpha_V = \frac{1}{V}\frac{dV}{dT}$$

We can also define linear coefficient which is

$$\alpha_L = \frac{1}{L}\frac{dL}{dT}$$

Thermal expansion depends also on the bond strength between the atoms that make up the material. Thermal expansion of ceramic materials is generally lower than that of metals. Applications parts for high-precision measuring equipment generally we are using this kind of materials. Strong bonding, fine ceramics like diamonds, silicon carbides, silicon nitride and alumina have low thermal expansion coefficient. Weak bonding like stainless steel have higher thermal expansion in comparison.

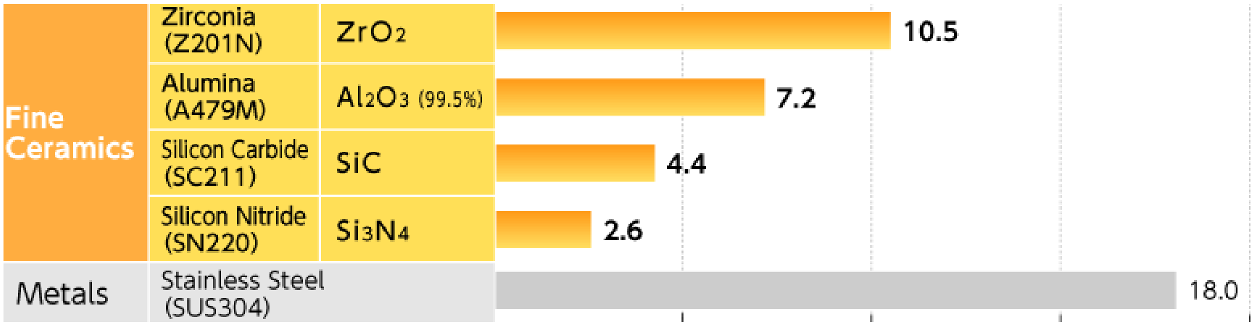


Figure 3.23: Thermal expansion coefficient of ceramics of different ceramic and metals (in $10^{-6}/^0C$)

Figure 3.32 is the data table you for Thermal expansion coefficient of ceramics and metals. In this table for silicon nitride it is $2.6 \times 10^{-6}/^0C$, but for the zirconia oxide it is about $10.5\times 10^{-6}/^0C$, but it is for stainless steel it is $18\times 10^{-6}/^0C$, and it is for cemented carbide it is generally $5.5\times 10^{-6}/^0C$. So for fine ceramics you can see that a very negligible amount of expansion has been taken place due to the temperature, and thus its value is only $7.1\times 10^{-6}/^0C$ for alumina but simultaneously when we are talking about the metals you can find for stainless steel it is $18.6 \times 10^{-6}/^0C$. So the thermal expansion here is much higher than the alumina itself.

3.8.4.3 Specific heat capacity:

The specific heat capacity or specific heat is amount of heat required to raise the material temperature by 1°C. The specific heat capacity or specific heat is the heat capacity of unit mass (one gram of the substance). Heat capacity or thermal capacity is a physical property of a material.

Specific heat of substance is defined as

$$c = \frac{dQ}{m.dT}$$

where symbols have usual meaning.

Specific heat capacity of ceramic materials is higher than that of metals.

3.8.4.4 Thermal shock resistance:

Thermal shock refers to the ability of material to withstand the sharp changes in temperature. It means if we are going to change the temperature the material, shape and size is not going to change so rapidly. For example silicon nitride, a particularly heat tolerant material displays superior resistance to thermal shock. When we are raising the temperature of that silicon nitride up to 550 degree centigrade and suddenly we are dipping that materials into the water, no material shape has been changed or maybe the material properties is not going to be changed. Some ceramic materials have very low coefficient of thermal expansion therefore their resistance to thermal shock is very high, despite of low ductility such as fused silica.

So there is certain formula to measure the thermal shock resistance R_S is given as

$$R_S = \left(\lambda \times \sigma_{fs}\right)/(a \times E)$$

Where is λ thermal conductivity of that particular materials, σ_{fs} is the flexural strength, a is the coefficient of the thermal expansion, and E is the modulus of elasticity.

3.8.5 Electrical properties of ceramics:

If we discuss about the electrical properties of ceramics, first property is electrical conductivity. Other electrical properties are superconductivity, piezoelectric effect, dielectrics properties etc.

3.8.5.1 Electrical conductivity:

Electrical conductivity is the ability of material to conduct the electric current. Most of ceramic materials are dielectric in nature. The materials having very low electrical conductivity but supporting the electrostatic field is called dielectric. Electrical conductivity of ceramics varies with the frequency of field applied on it and also with temperature. Thus is due to the fact that charge transport mechanisms are frequency dependent that is the important one. Ceramics have very low electrical conductivity due to ionic covalent bonding which does not form the free electrons. Here we are going to give an example of an thermistor, so thermistor its an electronic componentutilizing a property in which the electrical resistance decrease as temperature increases. actually here we are going to give the temperature, as the temperature is increasing so the resistance of this particular ceramic material is going to be decreased.

3.8.5.2 Super conductivity:

We have already studied about superconductivity in the course of condensed matter Physics. There is one interesting parameters which is known as super conductivity of ceramics. Super conductors can transport electric current without any resistance and thus without any losseswhatsoever. Despite of very low electrical conductivity of most of the ceramic materials there areceramics, possessing the super conductivity properties and show near to zero electric resistivity. Examples are lanthanum, yttrium, barium, copper oxide ceramic maybe super conducting at temperature as high as 138K. This critical temperature is much higher than superconductivity critical temperature of some other superconductors up to 30 K.

3.8.5.3 Piezoelectric effect:

Piezoelectric Effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. The word Piezoelectric is derived from the Greek piezein, which means to squeeze or press. Piezoelectric property of ceramic can be defined by piezoelectric effect. For generating piezoelectric effect, mechanical stress is applied between two surface of a solid dielectric which generates the voltage between the surfaces. A piezoelectric or piezo motor is an electric motor, which is based on the change of shape of piezoelectric materials when an electric field is applied. This change of shape, and combined with the stick-slip phenomenon produces mechanical displacements in the form of linear of rotary motion. Some ceramics lead, zirconate, titanate, barium titanate, bismuth titanate, lead magnesium niobate have piezoelectric properties. Piezoelectric ceramics are used for manufacturing various transducers, actuators and sensors like hydrophones, sonar, strain gauges, medical ultrasound equipment.

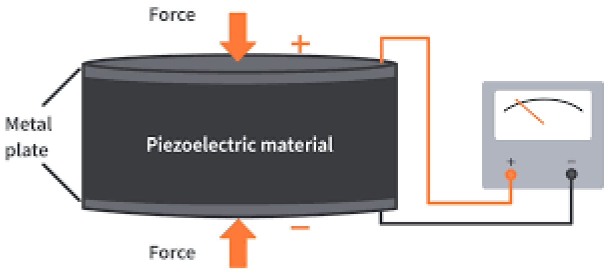


Figure 3.24: Piezoelectric effect

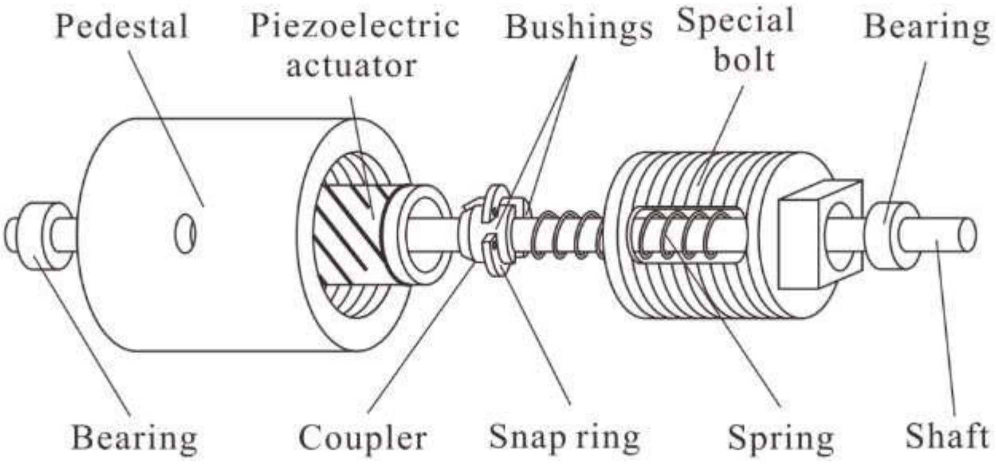


Figure 3.25: Piezoelectric or piezo motor

3.8.5.4 Dielectric property of ceramics:

Dielectrics are insulating or non-conducting ceramic materials. They exhibit the property of electrical polarization. A dielectric material is a material that supports charge without conducting it to a significant degree.

The dielectric constant (ε_r or denoted by K) of a material is defined as the ratio of the permittivity of the medium (□) to the permittivity of free space ($\square_o$). It can also have defined as the ratio of the capacitance with dielectric (C_d) and with air (C_A) between the plates.

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{C_d}{C_A}$$

In principle all insulators are dielectric, although the capacity to support charge varies greatly between different insulators. These materials do not conduct electrical current when an electric field is applied, they are not inert to the electric field. The field may cause a slight shift in the balance of charge within the material to form an electric dipole. They are used in many applications such as capacitors, memories, sensors, actuators etc. In high voltage insulator applications high electrical resistivity ohm meter and high dielectric strength kilovolt per meter is required. Dielectric strength is the ability of a material to prevent electrical conductivity at high voltage. Dielectric strength (DS) is defined as the maximum voltage required to produce a dielectric breakdown through the material and is expressed as volts per unit thickness.

$$DS = \left(\frac{dV}{dx}\right)_{max} = \frac{V_b}{d}$$

where V_b is breakdown voltage and d is thickness. The higher the dielectric strength of a material is better quality of an insulator. The is ceramic used as an insulator because it doesn't have any loose electrons and dielectric strength of ceramic is high as compared to metals.

3.8.6 Magnetic properties of ceramics:

Magnetic ceramics are prepared by sintering technology from iron oxide and barium strontium carbonate with small amounts of other metal oxides and these are called the ferrites. There are two types of magnetic ceramics, first one is known as the isotropic ceramics and second one is known as the anisotropicceramics. Isotropic ceramics is defined as the magnet with equal magnetic properties in all directions, and anisotropic ceramic is defined as the magnet with magnetic properties differs in different directions. Ferrite combines good magnetic properties means high magnetizations with very low electrical conductivity, low conductivity of ferrites allows reducing energy loss caused by eddy currents induced in the material when it works in high frequency magnetic fields.

The applications of ferrites or magnetic ceramics ferrite are antennas, speaker magnets, magnetic resonance imaging for the biomedical applications generally we are doing it for our bone cracks or maybe some other things, MRI, audio visual recording heads etc.

3.9 Chemical properties of ceramics:

Ceramics have good chemical resistance to weak acids and weak base. However, very strong acids or strong bases tends to produce ion exchange reactions and dissolve the structures. For example HF is commonly used to intentionally each ceramic surfaces composed of silicates. If – ion that causes the actual damage to that ceramic materials, this are soluble in certain strong acids and strong bases usually non-crystalline glassy phases dissolve first and capable of selective ion leaching and ion-exchange reactions. Aluminum Oxide (Al_20_3) and Silicon Carbide (SiC) ceramics are resistant to almost all chemicals and are used in applications that cause other materials to fail. Unlike metals, ceramics will rarely breakdown due to corrosion and they are resistant to acids and bases. However, some ceramics will perform better than others depending on specific corrosion resistance requirements.

3.10 Advantage of ceramics:

There are a large number of advantages of ceramics materials. First it is harder than the conventional structure metals, low coefficient of friction, extremely high melting point, corrosion resistance, low density, extreme hardness, inexpensive, easily available, glazed ceramic does not stain. There is certain disadvantages also, first is called the dimensional tolerances difficult to control during processing, weak in tension, poor shock resistance can crack when hit with heavy items because they are very brittle in nature.

The main characteristics of ceramics are low density, high melting point, high hardness, high elastic modulus, low toughness, high electrical resistivity, low thermal conductivity, high temperature wear resistance, high thermal shock resistance and the high corrosion resistance.

3.11 Applications of ceramics:

Ceramics have a large number of applications. Ceramics are used in electronics industry as dielectric, capacitor, circuits etc. Because of their lightweight, they are used in the space industry. They serve as cutting instruments, refractory substances, electrical insulators and thermal insulators. Photoelectrochemical devices or cells PEC are solar cells that produce electrical energy or hydrogen through a process similar to water electrolysis. The aluminum oxide which is also known as alumina, as chromium doped alumina is used for making the lasers. Aluminum nitride is used in many electronic applications such as in electrical circuits operating at high frequency. The diamond is used in industrial abrasives, cutting tools, abrasion resistant coatings etc. Lead zirconium titanate, widely used for the piezoelectric material. Silicon carbide is used as coating on other material for protection from extreme temperature because it can withstand the high temperature. Titanium boride, great toughness property and hence found application in armor productions, generally for the defense applications. Zirconia used in making oxygen gas sensors as additive in many electronic ceramics.

3.12 Summary:

1. Ceramic materials are inorganic nonmetallic compounds which are hard, brittle, heat-resistant and corrosion-resistant, hard, strong in compression, and weak in shearing and tension. They are non-metallic oxide, nitride, or carbide material

2. Common examples are brick, earthenware, porcelain, pottery objects (pots, vessels, or vases), figurines made from clay, either by itself or mixed with other materials like silica. Some advance examples are silicon carbide for the cutting disk, carbon ceramics for the disk brakes, semiconductors, electrical insulators, composites such as fiberglass and carbon fiber etc.

3. Generally ceramics can be classified in two categories as traditional ceramics and the advanced ceramics. Traditional ceramics are Whitewares, clay products, bricks, tiles, Abrasive, refectories, Cements, glasses.

4. On the basis of chemical composition advanced ceramics are classified as the silicon nitrate or maybe the aluminum nitrate,silicate ceramics like porcelain, magnesium silicate, mullite etcetera,

carbide ceramics like silicon carbide, boron carbide, tungsten carbide. This kind of carbides we are using for cutting tool materials, oxides ceramics like aluminum oxide, aluminum, titanate, magnesium oxide.

5. Based on applications, advanced ceramics can be Classified into two parts, one is known as the electro ceramics, another is known as the advanced structural ceramics. In case of electro ceramics, first is the coating ceramics, then conducting ceramics, magnetic ceramics, and the optical ceramics. In case of the advanced structural ceramics, first is the nuclear ceramics, bio ceramics, tribological ceramics and the automotive ceramics.

6. The main physical properties of ceramics are the density, density, porosity, mechanical properties, thermal properties, magnetic properties and electrical properties.

7. Most of ceramics are lighter than the steel and metals but heavier than the polymers. Generally the density of ceramics is 20 to 70% of density of the steel or metals. The density ranging from 2 to 6 g/c^3

The ceramics density ρ is calculated as

$$\rho = \frac{n'(\sum A_C + \sum A_A)}{V_C\, N_A}$$

8. Porosity of the ceramics or white fractions is a measure of the void or empty spaces in a material. It is a fraction of volume of voids over the total volume.

9. The usual mechanical properties of materials are tensile strength, elastic behavior, plastic deformation, fracture etc.

10. Flexural strength, also known as modulus of rupture or bend strength or transverse rupture strength is a material property, defined as the stress in a material just before it yields in a flexure test. Measuring flexural strength is given by the formula

$$\sigma = \frac{3FL}{2bd^2}$$

11. Elastic modulus slope of ceramics is usually higher than for metals, because ceramics are bonded either covalently or ionically and always it is much higher than the metallic bonds. The range of elastic modulus for ceramic is about 70 to 500 GPa.

12. Ceramics have compressive strengths about 10 times higher than their tensile strength. The tensile strength of ceramics is low because the existing flaws giving the stress concentrations of that particular materials.

13. Plastic deformation is the permanent distortion that occurs when a material is subjected to tensile, compressive, bending, or torsion stresses that exceed its yield strength and cause it to

elongate, compress, buckle, bend, or twist.

14. Brittle fracture processes consist of the formation and propagation of cracks through the cross section of material in direction perpendicular to the applied load. This is very important parameters and the crack formation is taking place for the ceramic materials.

15. For ceramics hardness is defined at the resistance to elastic deformations of the surface, hardness is affected from porosity in the surface, the grain size ofthe microstructure and the effects of grain boundary phases.

16. The toughness of a material is measured by its resistance to fracturing.

17. Ceramic have low thermal conductivity due to ionic covalent bonding which does not have free electron.

18. Thermal expansion of ceramic materials is generally lower than that of metals. Strong bonding, fine ceramics like diamonds, silicon carbides, silicon nitride and alumina have low thermal expansion coefficient. Weak bonding like stainless steel have higher thermal expansion in comparison.

19. Specific heat capacity of ceramic materials is higher than that of metals.

20. Thermal shock refers to the ability of material to withstand the sharp changes in temperature. Some ceramic materials have very low coefficient of thermal expansion therefore their resistance to thermal shock is veryhigh, despite of low ductility such as fused silica.

21. Electrical conductivity is the ability of material to conduct the electric current. Most of ceramic materials are dielectric in nature.

22. There is one interesting parameters which is known as super conductivity of ceramics. Super conductors can transport electric current without any resistance and thus without any losses. Despite of very low electrical conductivity of most of the ceramic materials there areceramics, possessing the super conductivity properties.

23. Piezoelectric Effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. Some ceramics lead, zirconate, titanate, barium titanate, bismuth titanate, lead magnesium niobate have piezoelectric properties.

24. Dielectrics are insulating or non-conducting ceramic materials. They exhibit the property of electrical polarization. A dielectric material is a material that supports charge without conducting it to a significant degree.

25. Magnetic ceramics are prepared by sintering technology from iron oxide and barium strontium carbonate with small amounts of other metal oxides and these are called the ferrites.

26. Ceramics have good chemical resistance to weak acids and weak base.

3.13 Glossary:

Ceramics – Inorganic nonmetallic compounds which are hard, brittle, heat-resistant and corrosion-resistant, hard, strong in compression, and weak in shearing and tension

Whitewares- ceramic products that is white to off- white in appearances

Abrasives - Abrasives are very hard substances used for grinding, shaping or polishing the other materials

Refractories- Refractories are materials that are resistant to high temperature, used predominantly as furnace linings

Cements- Cement is a ceramic binder used for construction that sets hardens and adheres to other materials binding them together, generally for the building construction applications.

Glasses – Glass is a solid material with amorphous structure which means that atoms are not organized according to a well-ordered.

Porosity - Porosity of the ceramics or white fractions is a measure of the void or empty spaces in a material.

Flexural strength- the stress in a material just before it yields in a flexure test.

Plastic deformations of ceramics Plastic deformation is the permanent distortion that occurs when a material is subjected to tensile, compressive, bending, or torsion stresses

Thermal shock- Thermal shock refers to the ability of material to withstand the sharp changes in temperature

Piezoelectric- Piezoelectric Effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress.

Tensile strength- the stress at the maximum on engineering stress strain curve.

Fracture- The separation of a material into two or more piecesby applying stress called the fracture

Fracture strength- stress is the breaking strength or the fracture strength.

Toughness- measure of the ability of a material to absorb energy up to fracture

Hardness- resistance of material to plastic deformations usually by the indentation.

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3.15 Suggested Reading:

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3.16 Terminal Questions:

1. What do you mean by ceramics? Give the classification of ceramics.
2. Give a classification of different type of ceramics.
3. What are physical properties of ceramics?
4. Why mechanical properties of ceramics are significant? Give some important mechanical properties of ceramics.
5. What are advanced ceramic materials? Based on the applications classify advanced ceramics.
6. Define the Porosity of the ceramics.
7. Define flexural strength and explain the flexure test for determining flexural strength.
8. Define Elastic stress strain behavior for ceramic materials. Draw the stress strain curve for a ceramics.
9 What is the meaning of strength of ceramics? With the help of stress and fracture probability curve explain the behavior of ceramics.
10. Explain the terms plastic deformation in ceramics.
11. Define brittle fracture in case of ceramics. With the help of stress and strain curve explain the brittle fracture behavior of ceramics.
12. Define hardness and toughness of ceramic materials.
13. Define thermal properties of ceramics.
14. Explain thermal conductivity of different ceramic and compare it with metals.
15. What is Thermal shock resistance different ceramic?
16. Explain Electrical conductivity of different ceramic.
17. Define Piezoelectric Effect and give the example of ceramics used for Piezoelectric.
18. What is Dielectrics? What are the ceramic materials used for Dielectrics.
19. Give the Advantage and disadvantage of ceramics materials.

UNIT 4 POLYMERS

Structure

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4.2 Objectives
4.3 Classification of polymers
4.4 Classification of polymers based on origin of source
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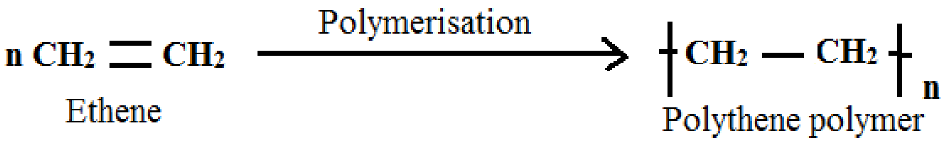
4.1 INTRODUCTION

In previous units we have discussed abut different material as metals, ceramics, polymer composites etc. In this unit we study the polymers. Most of the scientific terms are originate from the Greek during the period of Aristotle (384–322 BC). The term polymer is also a Greek word. The word polymer is made by two terms poly means many and mer means unit or parts. If a large number of monomer units are linked together to form a large macromolecule, it is called polymer. Generally it may contain 10^3 to 10^7 monomer or unit, and referred to as macromolecules. Monomers are linked to each other by the covalent bonds, so generally in polymer we can see the covalent bonds, a single polymer molecule may consist of hundreds to a million monomers and may have been linear, branched and the network structure. A simplest example polymer is transformations of the ethane to the polythene as given below.



$$n\,CH_2 = CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2 - CH_2 \right]_n$$

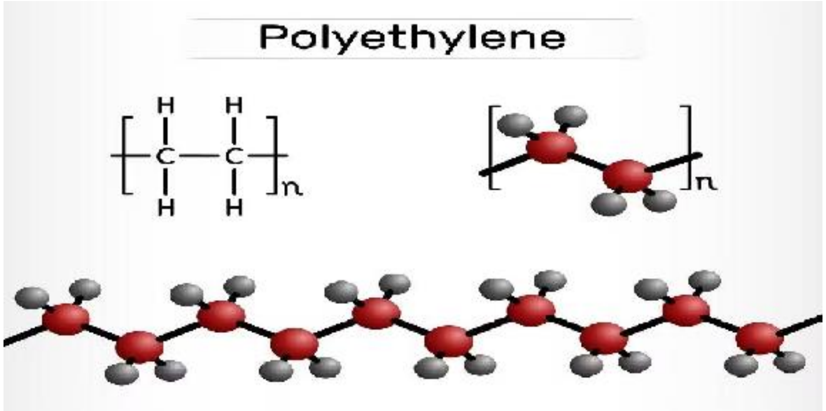


Figure 4.1: Polythene polymer

n represents the number of ethane monomers which converts in polythene polymer by using polymerization process. Thus same monomers is attaching ethane altogether and then after that they are making the polythene polymer.

4.2 Objectives:

After reading this unit we will able to understand:

1. Basic idea polymer
2. Classification of polymer
3. Classification of polymer

4. Preparation of some important polymers (Polythene, Polytetrafluoroethene or Teflon, preparation of some important polymers, polyacrylonitrile, Nylon 6 6, Polyester, Bakelite, Rubber
5. Properties of polymers
6. Applications of polymers

4.3 Classification of polymers:

Now we classify the polymer. Generally we can do the four broad classifications of the polymer. First one is that based on source, then based on structure of polymers, based on mode of polymerizations and based on molecular forces. So first based on source it is also divided into three parts, one is called the natural polymers, semi-synthetic polymers, and the synthetic polymers. Based on structure of polymers, it is also divided into three parts one is called the linear polymers, branched chain polymers, and the cross linking polymers.

On the based on mode of polymerizations, it is called the addition polymers and the condensation polymers, and then whenwe are talking about the molecular forces it is also divided into some parts that is elastomers, fibres, thermoplastic polymers, thermosetting polymers, and polymerization mechanism it is alsodivided into two parts that is addition or chain growth polymerizations and the condensation polymerization.

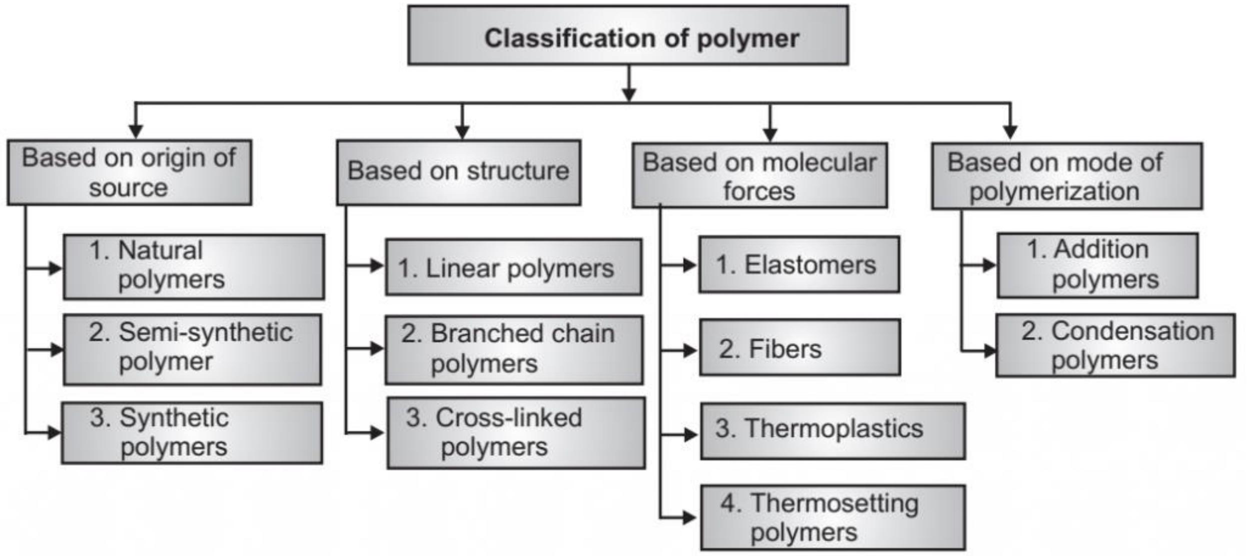


Figure 4.2: Classification of polymer

4.4 Classification of polymers based on origin of source:

There are **three types of polymer** under this category, namely, natural, semi-synthetic polymers and synthetic.

4.4.1 Natural polymers:

The natural polymers are those polymers which we are getting from the environment that means they are derived from the plants and animals. Example of natural polymers are wood, rubber, cotton, wool, proteins, starch, cellulose, enzymes, silk etc. so this all are we are directly getting from some plants or maybe some animals. They occur naturally and are generally found in plants and animals. These polymers are environment friendly and generally biodegradable and called biopolymers.

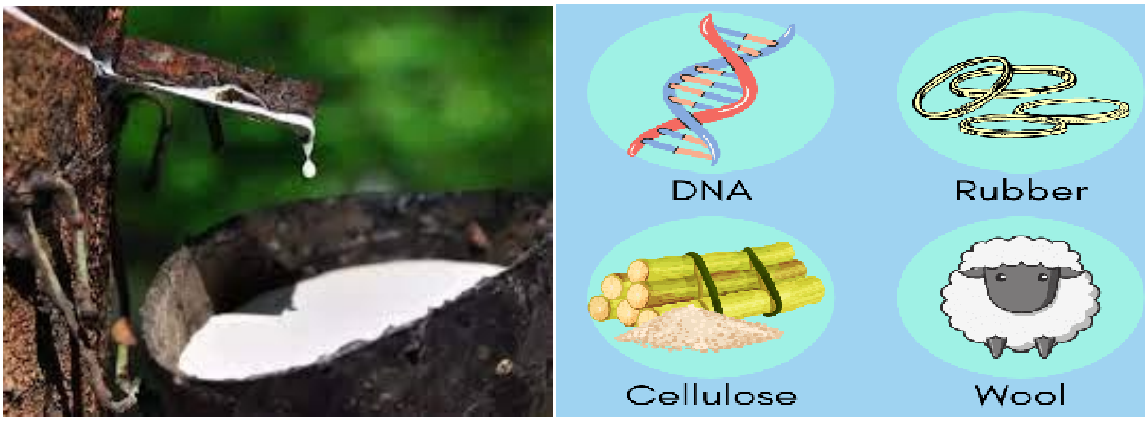


Figure 4.3: Natural polymers

4.4.1 Semi-synthetic polymers:

The semi-synthetic polymers are those polymers which are originally natural like cellulose and undergo further chemical modification. Derivatives such as cellulose acetate which is known as the rayon and the cellulose nitrate are semi-synthetic polymers.

Figure 4.4: Semi-synthetic polymers

4.4.2 Synthetic polymers:

The synthetic polymers are synthesized in industry or maybe in lab from the chemical substances. We prepare this kind of polymers as per our requirement. They are manmade polymers and now a day extensively used in daily life and industry. Examples are like plastic, polyethylene, or maybe polythene and synthetic rubbers like Buna-S and the synthetic fibres like the nylon etc.

Figure 4.5: Synthetic polymers

4.5 Classification of polymers based on structure:

This classification is based on structure of polymers and there are **three types of polymer** under this category, namely, linear chain, branch chain polymers and cross linked polymer.

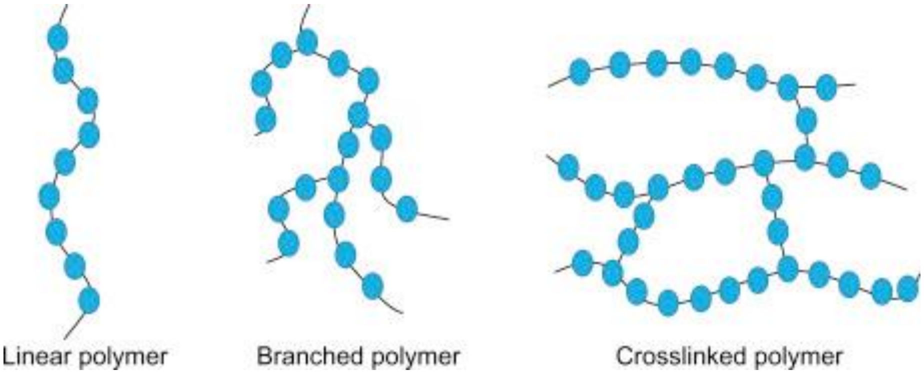


Figure 4.6: Types of polymer based on structures

4.5.1 Linear chain polymers:

The linear polymers consist of a long and straight chain like high density polythene, polyvinyl chloride. In figure 4.1 same monomers of ethane make linear chain together and they makes the polythene polymer. PVC (polyvinyl chloride) is also largely used for making pipes, and an electric cable is an example of a linear polymer. Figure 4.6a shows a long chain of large number or all units or mers.

Figure 4.7: PVC (polyvinyl chloride) polymer

4.5.2 Branch chain polymers:

Branch chain polymers contain linear chains having some branches. Figure 4.6b shows a long chain having some branches. Example is low density polythene and

4.5.3 Crossed Linked polymers:

In case of crosslinked or maybe the network polymers, they formed some kind of bi-functional or tri-functional monomers and contains strong covalent bonds between the various linear polymer chains. So these polymer chains make some linkage or maybe the cross linking among the chains. Figure 4.6c shows a linked chain. Examples are bakelite and the melamine.

Figure 4.8: Bakelite and Melamine polymer

4.6 Classification of polymers based on molecular force:

The classification based on molecular forces is basically depend on magnitude of the intermolecular forces present in polymer. It divided into four subgroups. First one is called the elastomers, second is fibres, third is the thermoplastic polymers and last is thermosetting.

4.6.1 Elastomer:

Elastomer are any rubbery material composed of long chainlike molecules, or polymers, that are capable of recovering their original shape after being stretched to great extents hence the name *elastomer*, from "elastic polymer." Elastomers are nothing but the rubber or rubber like solid with elastic properties. Polymer chains are held together by the weakest intermolecular forces, weak binding forces causes the polymer stretching. So we can stretch it up to certain limit. The examples are Neoprene, Bono-S, Bono-N. When we are using this kind of elastomers we are adding with some fillers or maybe some kind of additives, for example of the tire we are adding natural rubber with the styrene butadiene rubber. The process of adding filler is called bi-vulcanizations. Vulcanizations is cross linking process in which rubber molecules are converted into 3D network of interconnected polymer chains through chemical cross linking of sulfur. Here we have given only the sulfur generally we are doing the vulcanizations by the hydrogen peroxide also. So simply cross linking are to be made in between the polymer chains in this kind of materials.

Figure 4.9: Elastomer examples as rubber bands, seals and packing

4.6.2 Fibres:

Fibres is thread forming solids which possess high tensile strength and high modulus and have strong intermolecular forces like hydrogen bonding which leads to close packing of the chains. The examples are polyamides, nylon 6, 6, polyesters are maybe known as the terylene.

Figure 4.10: Polyamides, nylon yarn and polyesters fibres

4.6.3 Thermoplastics:

Thermoplastics are defined as polymers that can be melted and recast indefinitely. They are molten when heated and harden upon cooling. Thermoplastic polymers is something like, if we give a shape and then give it heat, it can again melt and again we can give it the heat, so it is not the permanent one. These have intermediate forces of attraction. Example is polyvinyl chloride.

Figure 4.11: Thermoplastics

4.6.4 Thermosetting:

Thermosetting plastics are made up from long chains of molecules that are cross-linked. They have a very rigid structure. Once heated, thermosetting plastics can be moulded and pressed into shapes. Once set they cannot be reheated since they are permanently set. In thermosetting polymers if we give a shape, particular shapes after that we cannot change it. So cross linked or branched polymer molecules which on heating undergo extensive cross linking in moulds and again become infusible, these cannot be reused that is the vital point for the thermosetting polymers. Examples are bakelite, urea-formaldehyde resins etc.

So generally if we see the whole order of strength of this kindof materials so first thermosetting, then after that fibres and then after that thermoplastics and last is the elastomers. These polymers greatly improve the material's mechanical properties. It provides enhanced chemical and heat resistance. Example is phenolics, epoxies and silicones.

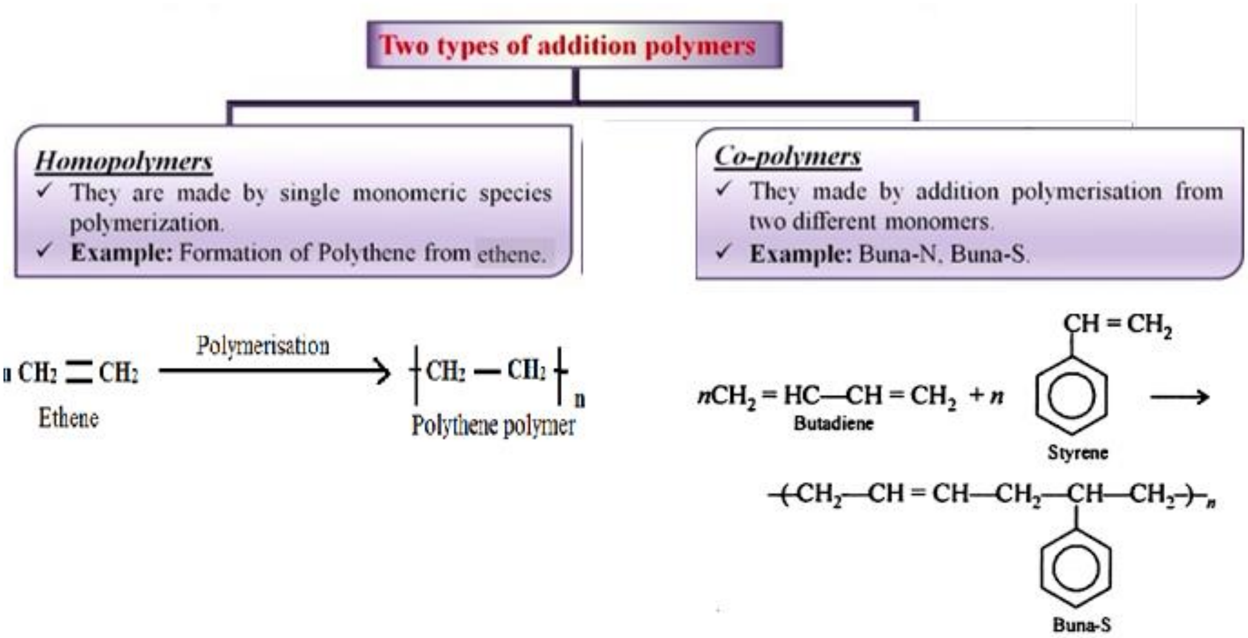
Figure 4.12: Thermosetting plastic

4.7 Classification of polymers based on mode of polymerization:

This is the classification based on growth of polymerizations which means mechanisms of polymerization. There are two types of polymerizations reactions generally taking place, first one is called the addition polymerizations and second one is condensation polymerizations.

4.7.1 Addition polymerizations:

It is also known as the chain growth polymerizations. In this case polymer is form from monomer without loss of any material. The product is exact multiple of original monomeric molecules proceeds by initial formation of some reactive species like free radicals or ions and by the addition of reactive species to othermolecule with regeneration of reactive features. Examples are poly ethane, Teflon, polyvinyl chloride (PVC) etc. Addition polymerization is of two types. First is homopolymers and second is copolymers. Homopolymers polymers are that in which it formed by repeated addition of monomer. The example is polythene as shown in figure. Second is copolymers that made by addition of two different monomers.



Two types of addition polymers

Homopolymers

- ✓ They are made by single monomeric species polymerization.
- ✓ **Example:** Formation of Polythene from ethene.

Co-polymers

- ✓ They made by addition polymerisation from two different monomers.
- ✓ **Example:** Buna-N, Buna-S.

Figure 4.13: Homopolymers and copolymers

4.7.2 Condensation polymerizations:

Condensation polymers, are formed by the repeated condensation reactions between two different bi-functional on with the tri-functional monomeric units. In this polymerization reaction, the eliminations of the small molecules such as water, or alcohol or hydrogen chloride etc takes place and are called byproducts. The examples of the condensation polymers are nylon 6, terylene nylon 6, 6, perylene, polyesters. In case of nylon 6, 6 we are adding adipic acid with the hexamethylene diamine and then make the nylon 6, 6 and the water is obtained as byproduct, and after removing this water and nylon 6, 6 is obtained.

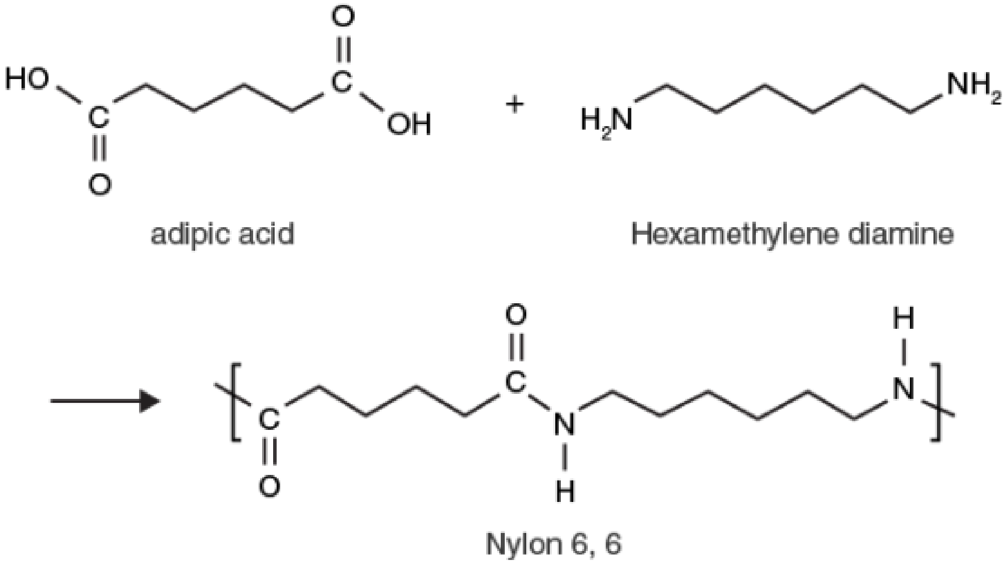


Figure 4.14: Condensation polymerizations

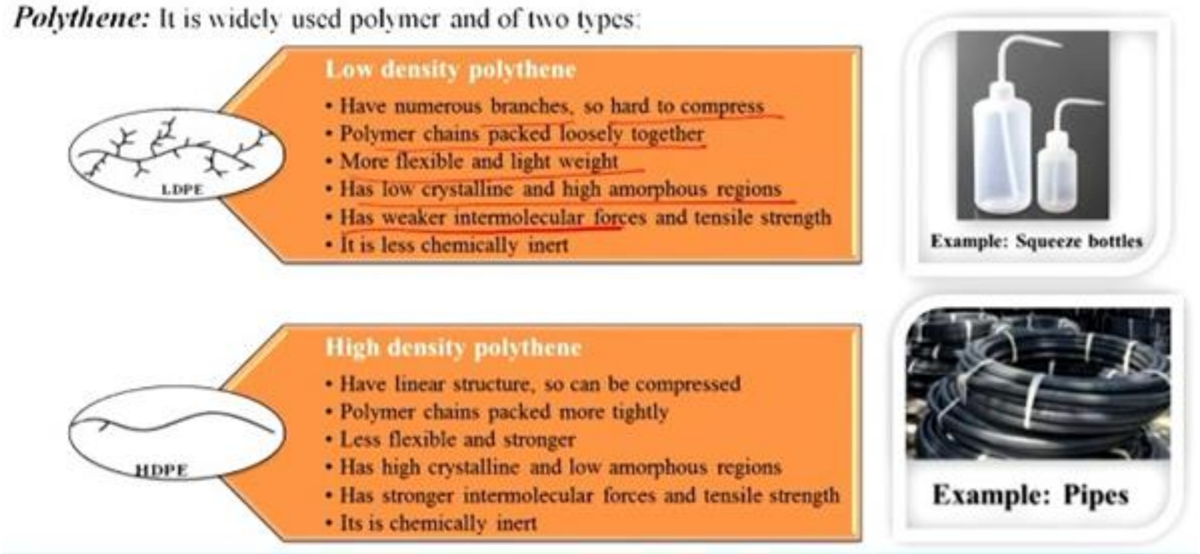
4.8 Preparation of some important polymers:

Now we discuss about the preparation of some important polymers.

4.8.1 Polythene:

Polythene is prepared by addition polymerizations. It is widely used polymer and of two types, one is called the low density polythene, another one is called the high density polythene. Low density polythene sometimes we are calling it as a LDPE. It has numerous branches so hard to compress. Polymer chains packed loosely together, more flexible and light weight. It has low crystalline and high amorphous regions, weaker intermolecular forces and tensile strength. It is less chemically inert. Example is as the squeeze bottles. Generally it is used for the chemical reactions, because it should not be very hard so that we can squeeze it and the water will come out.

When you talk about the high density polyethylene called HDPE, it has some linear structures so can be compressed, polymer chains packed more tightly so strength is more, less flexible and stronger. It has high crystalline and low amorphous regions, has stronger intermolecular forces and the tensile strength. It is chemically inert. The example is the pipes which are generally used for the wiring applications in our household.



Polythene: It is widely used polymer and of two types:

Low density polythene

- Have numerous branches, so hard to compress
- Polymer chains packed loosely together
- More flexible and light weight
- Has low crystalline and high amorphous regions
- Has weaker intermolecular forces and tensile strength
- It is less chemically inert

High density polythene

- Have linear structure, so can be compressed
- Polymer chains packed more tightly
- Less flexible and stronger
- Has high crystalline and low amorphous regions
- Has stronger intermolecular forces and tensile strength
- Its is chemically inert

Figure 4.15: Polythene

4.8.2 Polytetrafluoroethene or Teflon:

Polytetrafluoroethene is also known as the Teflon. It is manufactured by heating tetrafluoroethene with a free radical or maybe the persulphate catalyst at high pressures. The properties of Teflon are chemically inert, resistant to attack by the corrosive reagents. It is uses in making oil seals and gaskets, using for the nonstick surface coated utensils. So tetrafluoroethene in the presence of catalyst and high pressure we are making it the Teflon, we are using it for the nonstick pan.

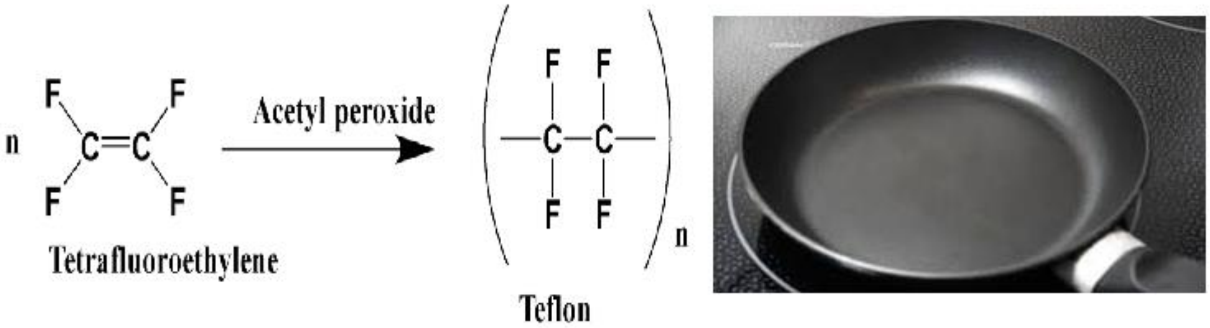


Figure 4.16: Teflon

4.8.3 Polyacrylonitrile:

Addition polymerizations of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile. It is uses as a substitute for the wool in making commercial fibres as orlon or maybe the acrilan. It is also called the synthetic wool.

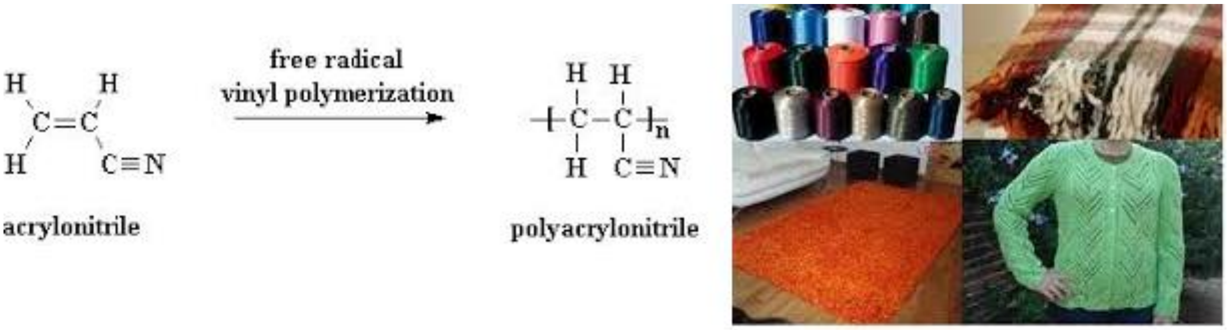


Figure 4.16: Polyacrylonitrile

4.8.4 Polyacrylonitrile:

Next we are going to discuss about the preparation of some important condensation polymers. One important example is the polyamides. It possesses the amide linkages and an important example of the synthetic fibres as nylons, product of condensation polymerizations of diamines with dicarboxylic acids and also of amino acids and their lactams. Nylon 6 6, is condensation polymerization of hexamethylene diamine with adipic acid under high pressure and the temperature is almost 553 kelvin and water is byproduct is also generated. Uses are making sheets, in bristles for brushes and in the textile industry. Another example is nylon 6. It is obtained by heating the caprolactum with water at high temperature, so caprolactum in the presence of water, at temperature varies from 533 to 543 kelvin. Generally in manufacture of tyres, cords, fabrics and the ropes we are using the nylon 6.

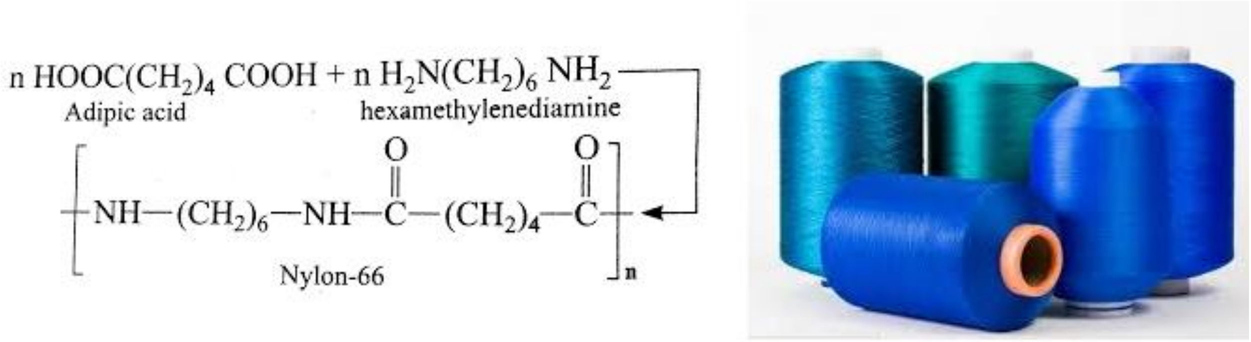


Figure 4.17: Nylon 6 6

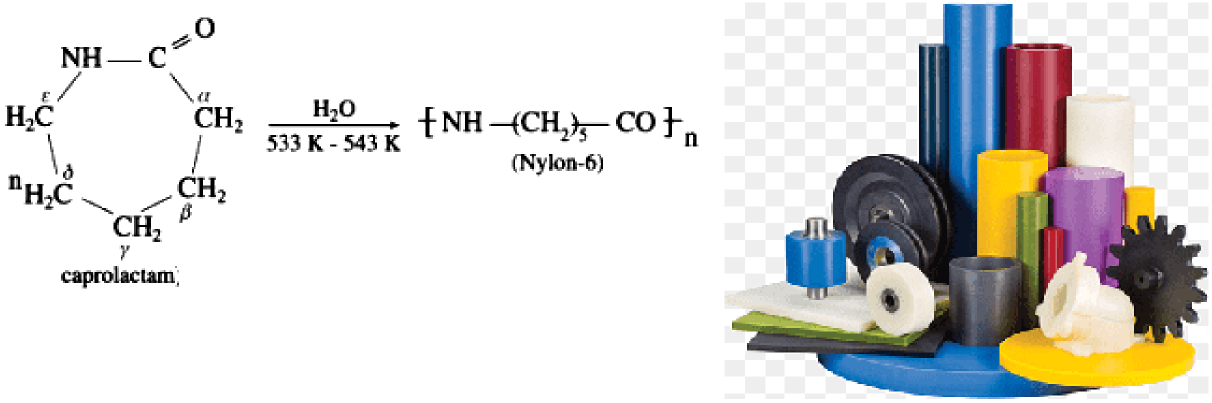


Figure 4.18: Nylon 6

4.8.5 Polyesters:

Polyester is a synthetic or man-made fiber material. Polyesters are condensation products of the dicarboxylic acids and the diols. It is manufactured by heating a mixture of ethylene glycol and the terephthalic acid at 420 to 460 kelvin in presence of zinc acetate antimony trioxide catalyst. The major industrial polyesters include polyethylene terephthalate, polycarbonate, degradable polyesters, alkyds, and unsaturated polyesters. The most commonly used polyester is polyethylene terephthalate (PET). Other example is Terylene, a synthetic polyester fibre. It is produced by polymerizing ethylene glycol and terephthalic acid. It is widely used in textile industries and a kind of materials generally used fordresses, suits or may be other dress materials. It is crease resistant material. This material is also used for helmets which nothing but terylene blendingwith cotton, wool fibres, and glass reinforcing materials.

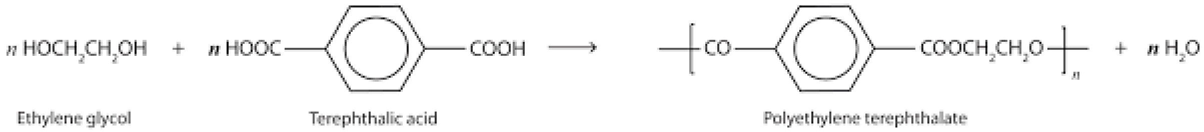


Figure 4.19: Polyethylene terephthalate (PET)

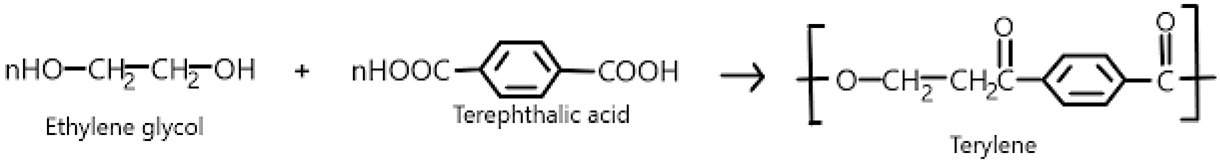


Figure 4.20: Terylene

4.8.6 Bakelite:

Bakelite is phenol formaldehyde polymers is condensation product of phenol with formaldehyde in presence of an acid or maybe the base catalyst. Novolac is the best example, which is nothing but a initial and linear product. Novolac is used in paints. On heating with formaldehyde undergoes cross linking to form an infusible solid mass called the Bakelite. Bakelite is used for making the combs, phonograph records, electrical switches and handles of the various utensils as cooker and frying pan. It is very hard and it is also the temperature resistant materials.

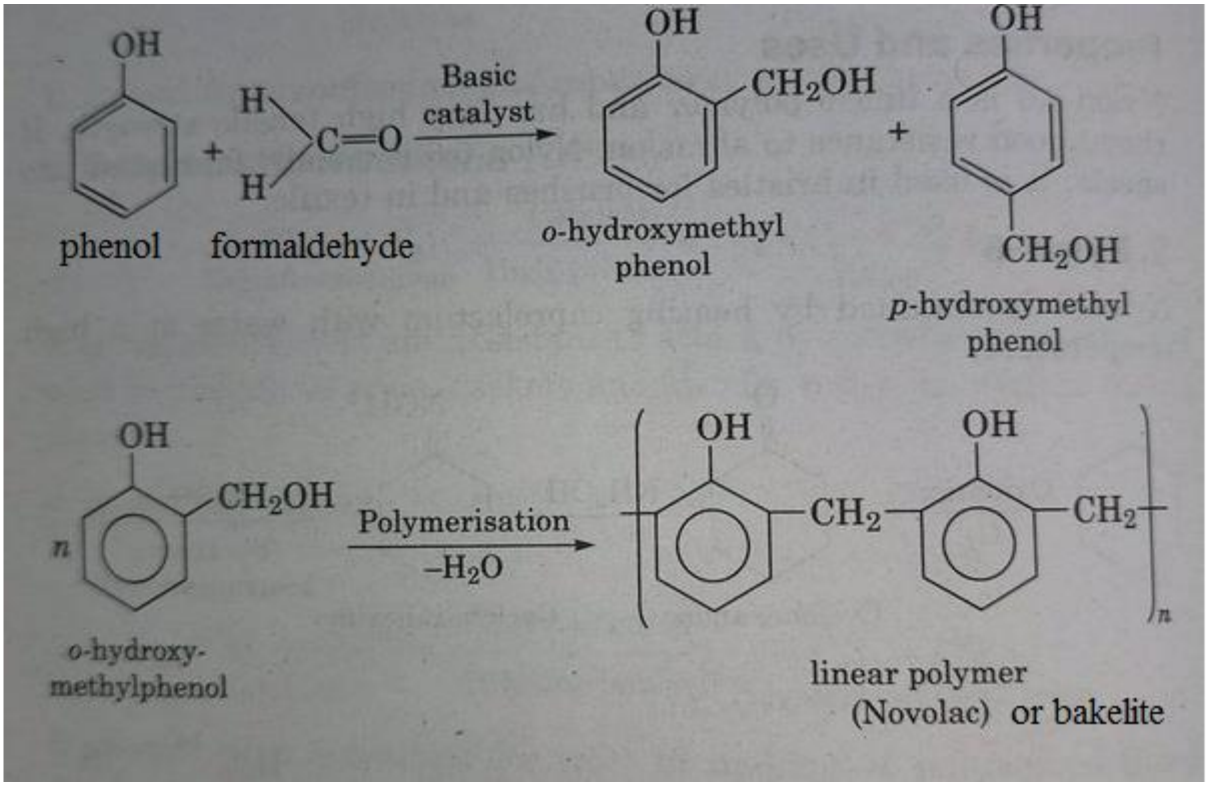


Figure 4.21: Bakelite

Bakelite is obtained when Novolac is allowed to undergo cross-linking in the presence of a cross-linking agent. Phenol taken in excess for the cross-linking agent in the formation of bakelite. So phenol formaldehyde can be made by the condensation methods for making the bakelite and water is coming as a byproduct materials. Figure 4.8 shows several examples of the bakelite products.

4.8.7: Copolymer:

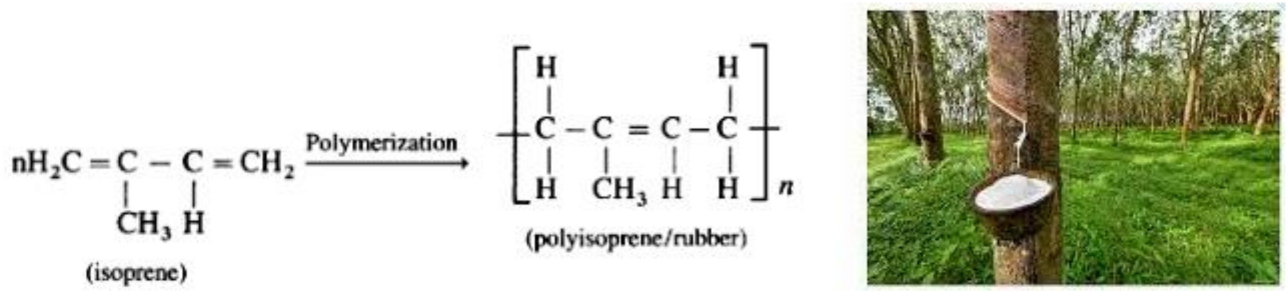
Polymerization reactions in which a mixture of more than one monomeric species is allowed to polymerize and to form a copolymer is called Co-polymerizations,. Copolymer can be made not only by chain growth polymerizations, but by step growth polymerizations also. It contains multiple units of each monomer used in the same polymeric chain. Examples are mixture of 1, 3 butadiene and styrene can form a copolymer, so 1, 3 butadiene with styrene with some conditions we are making the butadiene styrene copolymer, copolymers have properties quite different from the homopolymers. Butadiene styrene copolymer its quite tough, good substitute for the natural rubbers, sometimes used for manufacture for the auto tyres, floor tiles, and the cable insulations.

4.8.8: Rubber:

Rubber is a polymer that has the primary property to stretch and shrink. It is an elastomer that can come back to its original shape after being deformed. It is used in elastic rubber bands, erasers, tires of vehicles etc. Rubber is two types one is called the natural rubber, another one is called the synthetic rubber. Rubber is also called India rubber, latex, Amazonian rubber, caucho, or caoutchouc.

Natural rubber

Natural rubber is directly extracted from the bark of a rubber tree. It is basically polymers of the organic compound isoprene, with minor impurities of other organic ompounds. Thailand, Malaysia, and Indonesia are three of the leading rubber producers. Types of polyisoprene are used as natural rubbers. Currently, rubber is harvested mainly in the form of the latex from the rubber tree (*Hevea brasiliensis*) or others trees of this family. The latex is a sticky, milky and white colloid drawn off by making incisions in the bark and collecting the fluid in vessels in a process called tapping. The latex then is refined into the rubber that is ready for commercial processing. Natural rubber is used extensively in many applications and products, either alone or in combination with other materials. In most of its useful forms, it has a large stretch ratio and high resilience and also is water-proof. Generally natural rubber becomes soft at high temperature nearly 335 K and brittle at low temperatures generally less than 283 K. It is made by polymerization of isoprene (2 methyl-1, 3-butadiene).



$$nH_2C=\underset{CH_3}{C}-\underset{H}{C}=CH_2 \xrightarrow{\text{Polymerization}} \left[-\overset{H}{\underset{H}{C}}-\underset{CH_3}{C}=\underset{H}{C}-\overset{H}{\underset{H}{C}}- \right]_n$$

Figure 4.22: Natural Rubber

Synthetic rubber

A synthetic rubber is an artificial elastomer. They are polymers synthesized from petroleum byproducts. About 32-million metric tons of rubbers are produced annually in the United States, and of that amount two thirds are synthetic. Synthetic rubber, just like natural rubber, has many uses in the automotive industry for tires, door and window profiles, seals such as O-rings and gaskets, hoses, belts, matting, and flooring. Polyisoprene molecule consists of various chains held together by weak Van der Waals interactions. Because intermolecular forces are very weak over there, so vulcanizations of rubber is to be done which means adding two or more rubbers and then in between them some cross linking materials like hydrogen peroxide or maybe the sulfur are used. By using such cross linking material, one kind of polymeric chain takes place. vulcanization improves the physical properties as high water absorption capacity, soluble in nonpolar solvent, nonresistance to attack by the oxidizing agents. Examples are neoprene and buna-N.

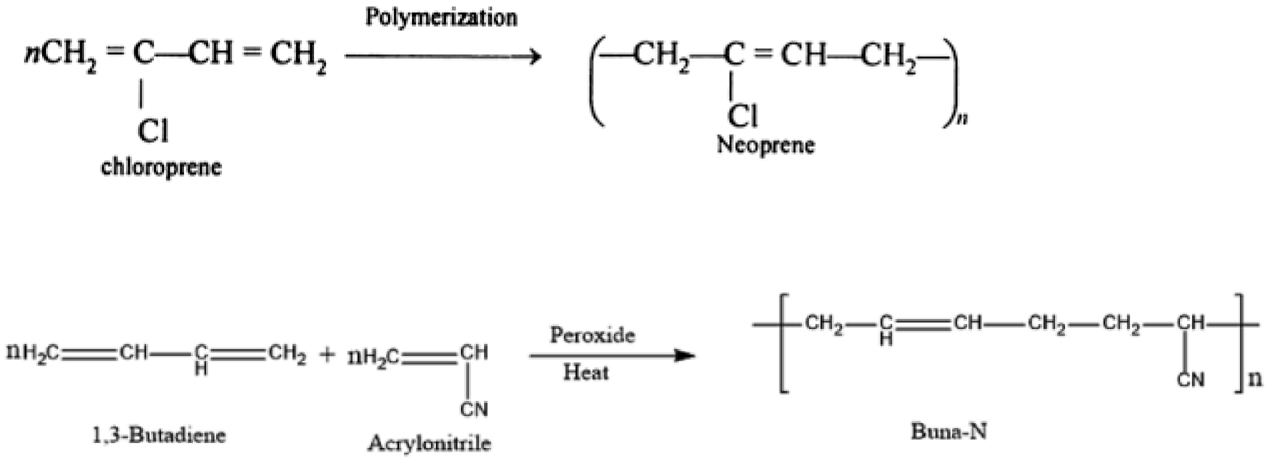


Figure 4.23: Synthetic Rubber Neoprene and Buna-N

So there are two types of techniques by which we can prepare this synthetic rubbers, first one is neoprene which is formed by the free radical polymerizations of the chloroprene. Generally we are using it for the conveyor belts, gaskets, and hoses. Buna-N generally obtained by copolymerizations of the 1, 3 butadiene, and acrylonitrile in presence of peroxide catalyst.
Buna N has resistance to the actions of petrol, lubricating oil, and the organic solvents. Therefore Buna-N is used for oil seals, tank lining and etc.

4.9: Properties of polymers:

The properties of polymers are divided in four groups as physical properties, thermal properties, mechanical properties and chemical properties as given in figure 4.24.

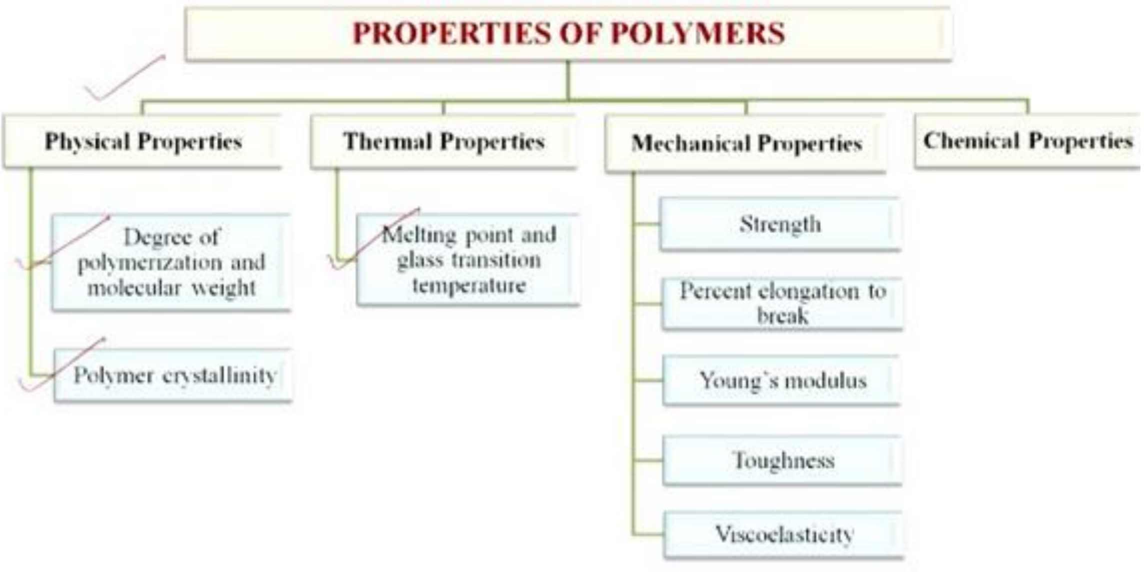


Figure 4.24: Properties of polymers

4.9.1: Physical Properties of polymers:

. The physical properties are again divided in are two subgroups, one is the degree of polymerizations and molecular weight, and another one is the polymer crystallinity. Physical properties give the idea about molecular weight, degree of polymerizations, crystallinity of polymer and the density of polymer. These all together is known as the physical properties of polymer.

4.9.1.1: Degree of polymerizations and the molecular weight:

Degree of polymerizations

The number of repeating units in the polymer chain is known as the degree of polymerizations. The degree of polymerization (DP) in a polymer molecule is simply the number n indicated in the repeated units in the polymer chain as shown below.

$$\left[CH_2 - CH_2 \right]_n$$

Polythene polymer

The molecular weight of the polymer molecule is the product of the degree of polymerizations (DP) and the molecular weight of the repeating unit. For example, molecule with DP=1000 will have a molecular weight of 28,000. Because polymeric materials do not consist of strictly identical molecules, but instead are a mixture of many species having different values of DP, thus we define the only an average value of DP of material. Hence, measured polymer molecular weights are only average values.

Molecular weight averages

A polymer's molecular weight is also defined as the sum of the atomic weights of individual atoms that comprise a molecule. It indicates the average length of the bulk resin's polymer chains. The polymer molecules are not identical but they are a mixture of many species with different degree of polymerizations that is with different molecular weights. There is a range or distribution of molecular weights.

Thus synthetic polymers have a distribution of molecular weights. Different methods of measuring the molecular weight yield different types of averages. Two of the most important are the number-average and the weight-average molecular weights. Suppose that you have a set of values $\{x_1, x_2, \ldots, x_n\}$ for which you calculate an average value. If the probability of each value occurring are given by $\{P_1, P_2, \ldots, P_n\}$ then the average is given by the sum below

$$\sum_{i=0}^{\infty} P_i x_i$$

Number average molecular weight

Suppose that you have a mixture of polymer molecules with different molecular weights in which the number of molecules having a particular *molecular weight*, M_i is given by N_i. The "number-average" probability of a given mass is

$$P_i = \frac{N_i}{\sum_{j=0}^{\infty} N_j}$$

and the number-average molecular weight is given by

$$\bar{M}_n = \sum_{j=0}^{\infty} \frac{N_i}{\sum_{j=0}^{\infty} N_j} M_i = \frac{\sum_{i=0}^{\infty} N_i M_i}{\sum_{j=0}^{\infty} N_i}$$

The number average is the simple arithmetic mean, representing the total weight of the molecules present divided by the total number of molecules. Most thermodynamic measurements are based on the number of molecules present and hence depend on the number-average molecular weight. Examples are the colligative properties, osmotic pressure and freezing point depression. End-group analysis also produces a value for $\bar{M}_n$.

Weight-Average Molecular Weight

The probability factor in a weight-average emphasizes the mass of the molecules so that the heavier molecules are more important.

$$P_i = \frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j}$$

The weight-average formula can be given as

$$\bar{M}_w = \sum_{j=0}^{\infty} \left(\frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j} \right) M_i = \frac{\sum_{i=0}^{\infty} N_i {M_i}^2}{\sum_{j=0}^{\infty} N_j M_j}$$

Molecular weight measurements that depend on the contributions of molecules according to their sizes give weight-average molecular weights. Light scattering and ultracentrifuge methods are examples of this type of technique.

The degree of polymerizations can be calculated using the number average molecular weight which is nothing but number average molecular weight by the molecular weight of the repeating unit.

4.9.1.2: Polymer crystallinity:

The crystallinity of a polymer refers to the degree as to which there are regions where the polymer chains are aligned with one another as in crystalline structure. The polymer crystallinity give the information about the crystalline and the amorphous nature of polymers. Polymer chains are very large and found in the polymer in two forms as the lamellar crystalline, another one is called the amorphous. In Lamellar crystalline the chains folds make lamellar structure arranged in the regular manner. In amorphous polymer the chains are in irregular manner, so lamellar are embedded in amorphous part and communicate with other lamellar via tie molecules. Polymers having high degree of crystallinity are rigid and have high melting point but their impact resistance is too low. Amorphous polymers are soft and have lower melting points.

The percentage crystallinity is given as

$$\%\, crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

where ρ_c is the density of the completely crystalline polymer, ρ_a is the density of the completely amorphous polymer and ρ_s is the density of the sample.

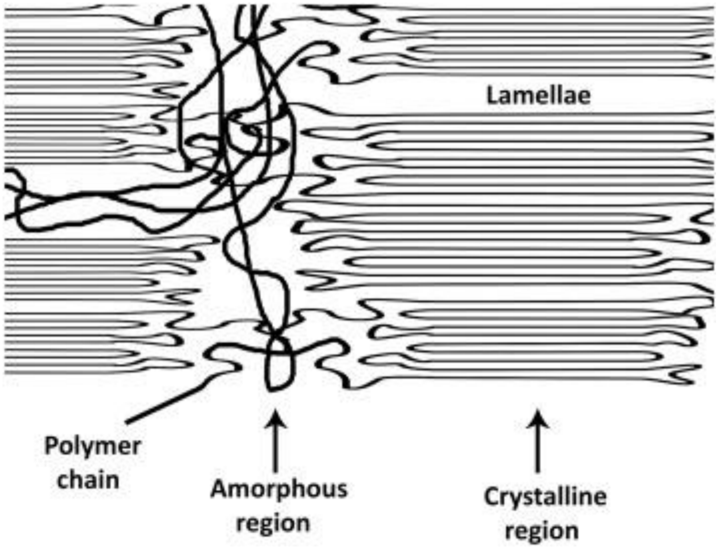


Figure 4.25: Crystalline and the amorphous nature of polymers

4.9.2 Thermal properties:

For the application of polymer material it is important to study the thermal properties of material. The thermal properties of the polymers are based on two important parameters. First one is the melting point T_m, and another one is glass transition temperature T_g. As the temperature of a polymer drops below T_g, it behaves as brittle material as glass. As the temperature rises above the T_g, the polymer becomes more rubber-like. In general T_g is much below the room temperature. Thus, knowledge of T_g is important in the selection of polymer materials for various applications. The transition temperature is unique properties of the polymers or any kind of elastomer materials. Glass transition temperature is the property of amorphous regions of polymer whereas the crystalline region is characterized by the melting point. Therefore for the rubber or maybe the elastomers find the glass transition temperature and for any kind of polymer find out the melting point. The glass transition temperature is the second order transitions whereas the melting point is the first order transitions. The value of glass transition temperature is not unique because the glassy state is not in equilibrium, so generally the glass transition temperature for natural rubber is -70^{0}C. The glass transition temperature value depends on several factors such as molecular weight, measurement methodson the rate of heating or cooling.

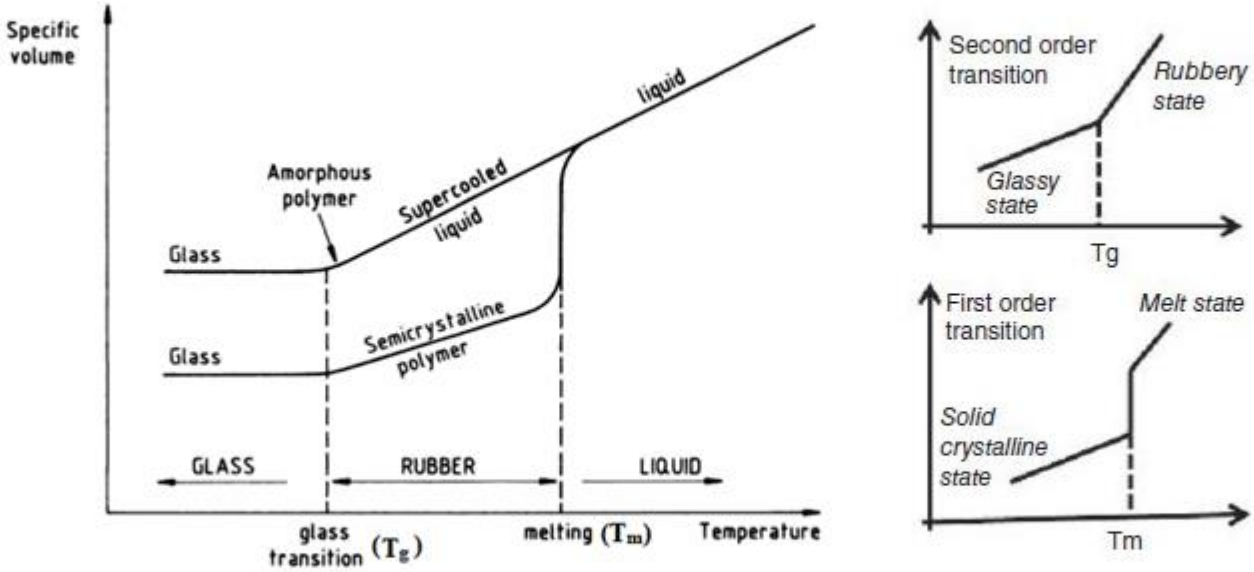
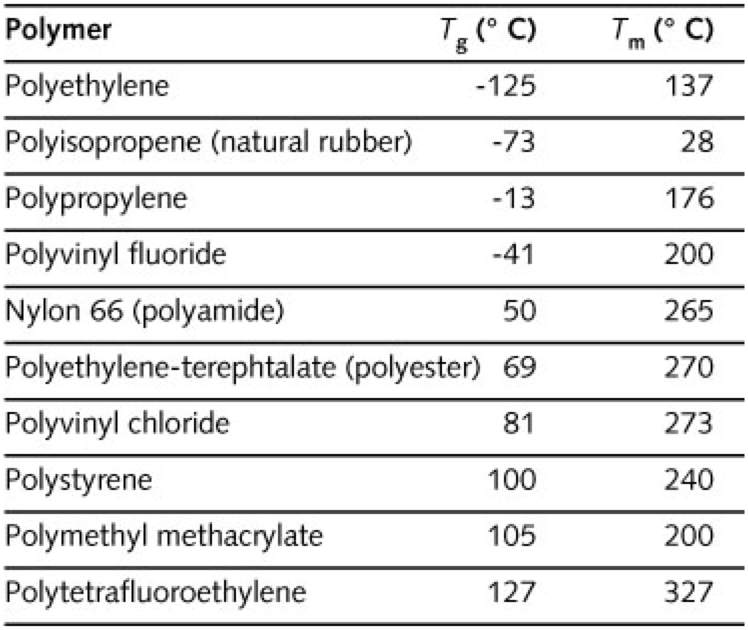


Figure 4.25: Glass transition temperature T_g and melting point T_m

Semi-crystalline polymers shows both the transitions correspondence to their crystalline and amorphous regions so have true melting temperatures at which the ordered phase turns to disordered phase. The amorphous regions soften over a temperature range known as the glass transaction temperature. Glass transition, glass for glass materials generally it varies up to the glass transition temperature then it is rapidly increasing the volume. In case of semi-crystalline it is quite less and for the crystalline solids its totally increasing in a rapid manner.

So amorphous polymers do not possess any melting temperature but all polymer possess that glass transition temperature. Generally the glass transition temperature of the polymer is around 10 to 15 degree, so the polymer melting temperature point TM is increased if the double bonds, aromatic groups, bulky, or maybe the large side groups are present in the polymer chains, because they restrict the flexibility of the chain itself.



Polymer	T_g (° C)	T_m (° C)
Polyethylene	-125	137
Polyisopropene (natural rubber)	-73	28
Polypropylene	-13	176
Polyvinyl fluoride	-41	200
Nylon 66 (polyamide)	50	265
Polyethylene-terephtalate (polyester)	69	270
Polyvinyl chloride	81	273
Polystyrene	100	240
Polymethyl methacrylate	105	200
Polytetrafluoroethylene	127	327

Figure 4.26: Glass transition temperature T_g and melting point T_m of some polymer

The cross links between the chains restricts the rotational motions and raise the glass transition temperature, hence higher cross linked molecule will show the higher glass transition temperature than that with lower cross linked molecules.

Factor affecting the glass transition temperature:

1. Strong intermolecular forces cause high glass transition temperature.
2. Presences of some stiff chains like amide, salfone, or carbonyl increase the glass transition temperature.
3. Presences of cross linkage in the chains restrict the motions and it increases the glass transition temperature.
4. The presence of pendant group can change the glass transition temperature. A pendant group (sometimes called pendent) or side group is a group of atoms attached to a backbone chain of a long molecule of a polymer.

5. Adding the plasticizers which are a low molecularweight and non-volatile material to polymer increase their chain flexibility and reduced the intermolecular cohesive force between the polymer chains. It decreases the glass transition temperature.
6. The glass transition temperature is also affected by the molecular weight of the polymer, T_g is increased with the molecular weight. The molecular weight generally is related to the glass transition temperature bythe Fox Flory equations as given below

$$T_g = T_{g,\infty} - \frac{K}{M_n}$$

where $T_{g,\infty}$ is the glass transition temperature at all molecular weight of infinity, K is the empirical parameter called the Fox-Flory parameter is related to the free volume inside the polymer, M_n molecular weight. It is observed that the glass transition temperature is increasedup to the molecular weight of approximately 20,000 and after this limit the glass transition temperature is not affected.

4.9.3 Mechanical properties:

The mechanical properties of the polymers it is divided into 5 parts, one is strength, percent elongation to break, Young's modulus,toughness, and another one is that viscoelasticity.

4.9.3.1 Mechanical strength:

Mechanical strength is the stress required to break a polymer. There are several types of mechanical strength as tensile, torsional, impact, flexural and compressional. The tensile strength is the strength on stretching of the polymer. Torsional is related to the twisting ofthe polymer. Torsional strength is the strength of bearing torsional force before breaking. Impact strength is strength to sustain the hammering. Flexural strength is related to bending of the polymer. The compressional means the compression of the polymer.

The strength of polymer depends on the nature of polymer chains. The network is the highest one, then cross linked, then the branched and linear is the lowest one.

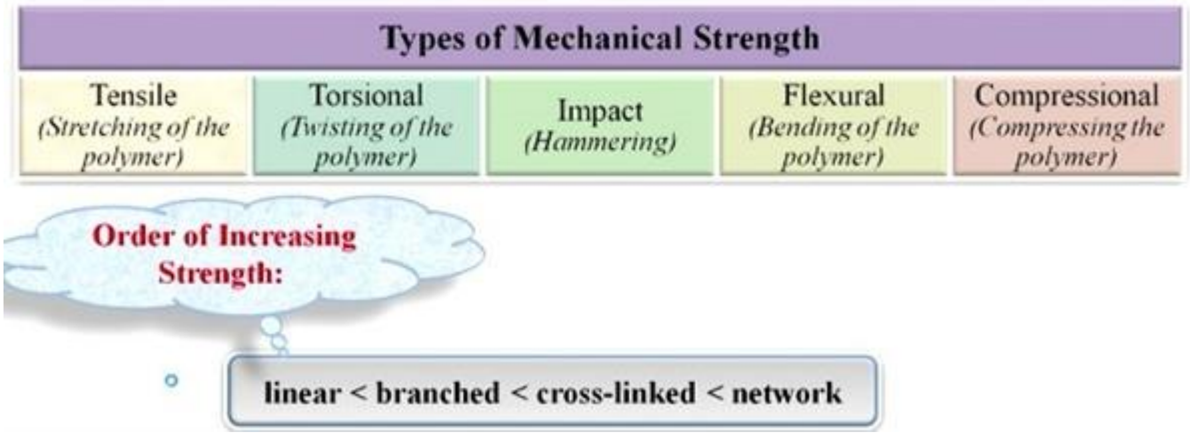


Figure 4.27: types of mechanical strength of polymer and dependence on polymer chains

Polymer stress-strain curves are produced by stretching a sample at a constant rate through the application of a tensile force. By using a constant rate of testing the strain-rate dependency of polymer behaviour is not allowed to dominate. The stress strain curve of some polymers are shown in figure 4.28.

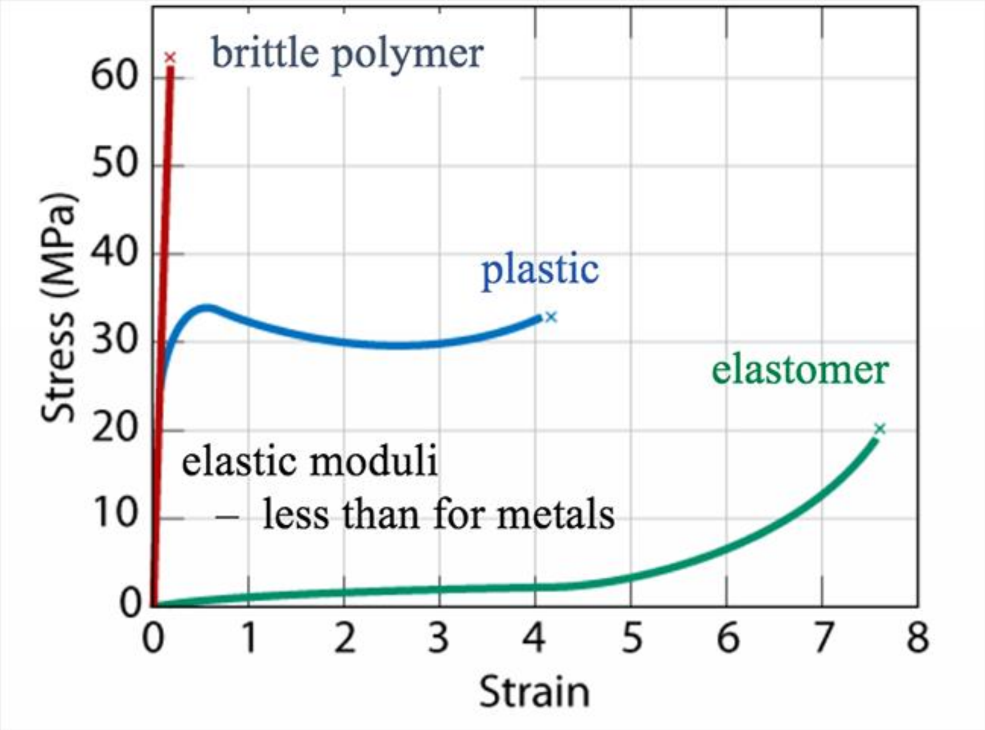


Figure 4.28: Stress strain curve of the polymers

Factor affecting the strength of polymers:

1. **Molecular weight:** First one is the molecular weight, where tensile strength plays a vital role. Tensile strength of polymer raises with increased in molecular weight and reaches at the saturation level at some value of the molecular weight. The relation of Tensile strength of polymer and molecular weight is given by following relation

$$\sigma = \sigma_\infty - \frac{A}{M}$$

where sigma infinity is the tensile strength of polymer with molecular weight of infinity, A is some constant, and capital M is molecular weight of that particular polymer.

Cross linking in polymer restricts motions of chain and increase the strength of the polymers. Similarly crystallinity increases the strength but because in crystalline phases intermolecular bonding is more significant, hence the polymer deformation can result in the higher strength leading to the oriented chains itself.

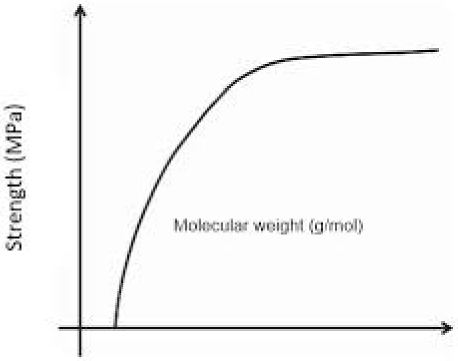


Figure 4.29: Tensile strength with molecular weight of the polymer

The variations of the tensile strength with molecular weight of a polymer is shown in figure 4.29. It can be seen that if we are increasing the molecular weight up to certain time the strength will increaseand then after that it will become constant.

2. **Percentage elongations of break:**

Percentage elongations of break is also known as the ultimate elongations is the strength in the material to its breakage. Suppose we are having one polymer and we are pulling it, then it will increase and after certain time it will fail. So it measures the percentage change in the length of material before fracture. It is a measure of the ductility, ceramics have very low less than 1%, metals have moderate, generally 1to 50%, thermoplastic is more than 100% and thermosets is also less than 5% value of elongationto break.

3. **Young's modulus:**

The modulus of elasticity or the tensile modulus is the ratio of stress to the strain in the linearly elastic region. Elastic modulus is a measure of the stiffness of the material, so generally it is denoted by capital E which is nothing but the ratio of tensile stress σ by the tensile strain ϵ.

$$E = \frac{\sigma}{\epsilon}$$

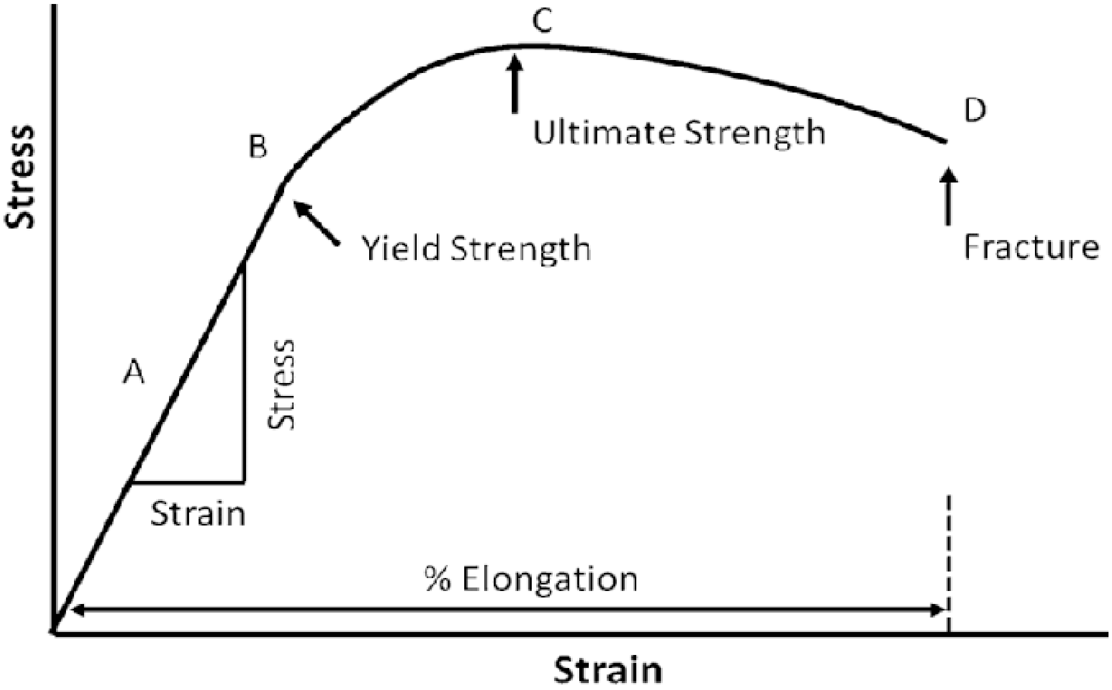


Figure 4.30: Percentage elongations of break and Young's modulus of polymer

4. **Toughness:**

Toughness of a material isgiven by the area under a stress strain curve. It measure the energy absorb by the material before it breaks. Generally it is given by

$$Toughness = \int_{0}^{\epsilon_f} \sigma d\epsilon$$

where ϵ_f is the true strain at fracture, so this is the whole toughness of a polymeric materials. So from the stress strain curve is shown which compares the stress strain behavior of different types of materials, from this you can see we have given the examples of thebrittle polymer. For examples of the ductile polymer, and we have given the high elastic. Rigid materials possessthe high Young's modulus such as brittle polymers and ductile polymers also possess the similar elastic modulus but with higher fracture toughness.

5. **Viscoelasticity**:

There are two types of deformations first one is known as the elastic deformations, and the second one is called the viscous deformations. Elastic deformations means the strain is generated at the moment the constant load or stress is applied and the strain is maintained until the stress is not released. Thus on removal of stress the material recovers its original dimensions completely. The deformation is reversible because it will come to again to its original positions. In this case

$$E = \frac{\sigma}{\epsilon}$$

where symbols have usual meaning.

But in case of viscous deformations, strain generated is not instantaneous and it is time dependent, when the load is removed material does not return to its original dimensions completely. There is little bit stress will be present in the material, so deformations is irreversible. In this case

$$\sigma = \gamma \frac{d\epsilon}{dt}$$

where γ (gamma) is the viscosity and $\frac{d\epsilon}{dt}$ is strain rate.

Low strain rate polymer should combine behavior of elastic and plastic deformation depending on temperature and strain rate. At low temperature and high strain rate elastic behavior is observed and at high temperatures the viscous behavior is also observed. So combine behavior of viscosity and elasticity is observed at intermediate temperature and the strain rate value. So generally we are having one elastic behavior materials, when we are adding with some viscous behavior materials we are getting the viscoelastic properties of that particular materials. This behavior is terms as the viscoelasticity and the polymer is termed as the viscoelastic polymer.

4.9.4 Chemical properties:

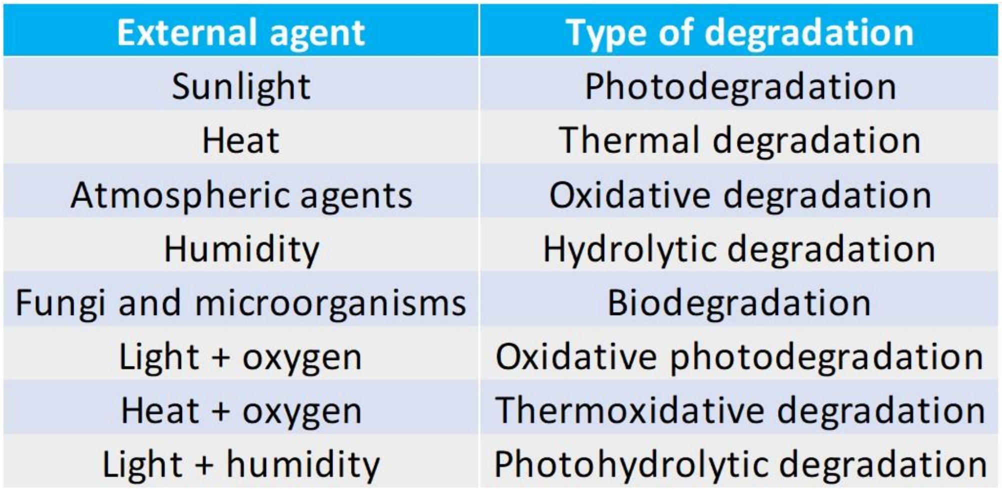
One of the significant factors for determining the chemical properties of polymers is bonding among the molecules. Different side groups on the polymers can link by ionic bonding or by hydrogen bonding. If polymers contain amide or carbonyl groups, they can form the hydrogen bonds between adjacent chains. Dipole bonding is not as strong as the hydrogen bonding.

For example, in polyesters there are dipole-dipole bonding between the oxygen atoms in C = O groups and the hydrogen atoms in C-H groups. Generally polymeric materials are noncorrosive in nature because upon exposure to liquid they may experience by the swelling or maybe the dissolution. Polymers may deteriorate by the swelling and the dissolution, it is also another properties of the polymers.

4.10 Polymer degradations:

It is change in the properties like strength, colour, shape, molecular weights, etc of polymer or polymer based products under the influence of one or more environmental factors such as heat, light, moisture or chemical. For example suppose we keep a polymer into the environment or maybe buried into the soil or maybe dipping it into the water for a longer time, the we can see the degradation of that particular polymer. In the process of degradation, covalent bonds of polymers are rupture as a result of the environmental factors. Due to chemical complexity of polymers their degradation mechanism are not well understood still research are going on.

There are different types of degradation of polymer. If polymer is degraded by exposure to high temperature, this is known as thermal degradation. If it is under shear action mechanical degradation will take place. Similarly, if it is under the action of oxygen, ozone and chemicals, the chemical degradation will takes place. If a polymer is exposed to electromagnetic, ultrasonic radiations, light induced degradation will takes place. If it is open to the moisture or maybe the liquid, hydrolysis or swelling or maybe the dissolution will takes place. Some types of degradation under the influence of different agents are shown in figure 4.31.



External agent	Type of degradation
Sunlight	Photodegradation
Heat	Thermal degradation
Atmospheric agents	Oxidative degradation
Humidity	Hydrolytic degradation
Fungi and microorganisms	Biodegradation
Light + oxygen	Oxidative photodegradation
Heat + oxygen	Thermoxidative degradation
Light + humidity	Photohydrolytic degradation

Figure 4.31: Polymer degradations

4.11 Comparisons of different properties of Polymer with metal and ceramics:

Now we are going to just give a brief idea about the different properties of ceramic, metal and polymer. If we talk about the hardness, ceramic is having very high, metal is low, and polymer is also low. If we talk aboutthe ductility, for ceramic materials it is very low, for metal it is high, and for polymer also itis high. If we are talking about the electrical conductivity, so generally for the ceramic materialsit has intermediate, for metal it is too high, but polymer it is low generally it acts as a one kind ofinsulator. If we talk about the thermal conductivity for ceramic it is intermediate, metal it is high,for polymer also it is very low as shown in figure 4.32.

Property	Ceramic	Metal	Polymer
High Temperature Strength	High	Medium	Low
Thermal Shock Resistance	Low / Medium	High	High
Wear Resistance	High	Medium	Low
Hardness	High	Medium	Low
Tensile Strength	Medium	Medium / High	Medium
Elastic Modulus	High	Medium	Low
Compressive Strength	High	Medium	Low
Density	Low / Medium	Medium / High	Low
Toughness	Low / Medium	High	Medium
Corrosion Resistance	High	Low / Medium	Low / Medium

Figure 4.32: different properties of Polymer with metal and ceramics

4.12 Characteristics of polymers:

Polymers have following characteristics

1. Low density
2. Low coefficient of friction
3. Good corrosion resistance
4. Good mould ability
5. Poor tensile strength
6. Low mechanical properties
7. Poor temperature resistance

4.13 Advantages and disadvantages of polymers:

Following are the advantages of polymers.

1. It resist to corrosions and the chemicals
2. Low electrical and thermal conductivity
3. Low density
4. High strength to weight ratio that is the prime considerations for choosing the polymer.

5. Wide choice of colours and the transparencies
6. Ease of manufacturing and complexity of the design possibilities
7. It is very cheap material.

Following are the disadvantages of polymers.

1. Comparatively low strength and low dimensional stability.
2. Have low heat resistance
3. High performance plastics have very high cost
4. They are softer than metals and are more susceptible to deformation under load
5. Brittle at low temperature
6. They are also flammable, it can burn easily.

4.14 Application of polymers:

Some common applications of the polymers are give below

1. For the sports we are using for some helmets, some balls
2. For medical application we are using some kind of tissue scaffolds, some bones, joints, nowadays we are using some kind of orthopedic implants.
3. For industry we are using some automobile parts, for using insulations, for packing materials.
4. For agriculture we are using it for the preventing soil erosions, reducing the irrigation facility
5. Solar cell, fuel cell, batteries
6. Electrode materials, super capacitor etc.
7. Clothing, floor coverings, garbage disposal bags, and packaging
8. Automobile parts, windshields for fighter planes, pipes, tanks, packing materials, insulation, wood substitutes, adhesives, matrix for composites, tires etc.
9. Elastomers are all polymer applications used in the industrial market.

4.14 Polymer recycling processes:

One of the problems in today’s society is the generation of waste. Thus, with the increase in the use of polymers, this agenda has become important. This is considering the methods of decomposition and collection of materials are not efficient. Biodegradable polymers in everyday life can be good solutions. Natural polymers are formed in nature during the growth cycles of all organisms. Natural biodegradable polymers are called biopolymers. Polysaccharides, as starch and cellulose, represent the most characteristic family of these natural polymers. It is excellent solution for alternatives that contribute positively to the health of the environment. This is only possible due to these compounds being non-polluting and not needing special disposal.

4.15 Summary:

1. The word polymer is made by two terms poly means many and mer means unit or parts. If a large number of monomer units are linked together to form a large macromolecule, it is called polymer. Generally it may contain 10^3 to 10^7 monomer or units. A simplest example polymer is transformations of the ethane to the polythene

2. Based on source of origin there are **three types of** namely, natural polymers, semi-synthetic polymers and synthetic polymers.
3. The natural polymers are those polymers which we are getting from the environment that means they are derived from the plants and animals. Examples of natural polymers are wood, rubber, cotton, wool, proteins, starch, cellulose, enzymes, silk etc.
4. The semi-synthetic polymers are those polymers which are originally natural like cellulose and undergo further chemical modification. Derivatives such as cellulose acetate which is known as the rayon and the cellulose nitrate are semi-synthetic polymers.
5. The synthetic polymers are synthesized in industry or maybe in lab from the chemical substances.

6. There are **three types of polymer** under the classification based on structure of polymers, namely, linear chain, branch chain polymers and cross linked polymer.

7. The linear polymers consist of a long and straight chain like high density polythene, polyvinyl chloride.

8. In case of crosslinked or maybe the network polymers, they formed some kind of bi-functional or tri-functional monomers and contain strong covalent bonds between the various linear polymer chains.

9. **Elastomer** are any rubbery material composed of long chainlike molecules, or polymers, that are capable of recovering their original shape after being stretched to great extents hence the name *elastomer*, from “elastic polymer.”

10. Fibres is thread forming solids which possess high tensile strength and high modulus and have strong intermolecular forces like hydrogen bonding which leads to close packing of the chains. The examples are polyamides, nylon 6, 6, polyesters are maybe known as the terylene.

11. Thermoplastics are defined as polymers that can be melted and recast indefinitely. They are molten when heated and harden upon cooling. Thermoplastic polymers is something like, if we give a shape and then give it heat, it can again melt and again we can give it the

heat, so it is not the permanent one. These have intermediate forces of attraction. Example is polyvinyl chloride.

12. Thermosetting plastics are made up from long chains of molecules that are cross-linked. They have a very rigid structure. Once heated, thermosetting plastics can be moulded, shaped and pressed into shapes.
13. Addition polymerizations or chain growth polymerizations is case when polymer is form from monomer without loss of any material and product is exact multiple of original monomeric molecules.
14. Condensation polymers, are formed by the repeated condensation reactions between two different bi-functional on with the tri-functional monomeric units. In this polymerization reaction, the eliminations of the small molecules such as water, or maybe alcohol or maybe hydrogen chloride etc takes place and are called byproducts.

4.16 Glossary:

Polymer – A large number of monomer units are linked together to form a large macromolecule, it is called Polymer

Natural polymers- polymers which we are getting from the environment that means they are derived from the plants and animals

Semi-synthetic- polymers which are originally natural like cellulose and undergo further chemical modification

Synthetic- polymers are synthesized in industry or maybe in lab from the chemical substances.

Crosslinked- strong covalent bonds between the various linear polymer chains.

Elastomer- rubber like solid with elastic properties

Fibres- In case of polymer, fibres is thread forming solids which possess high tensile strength and high modulus and have strong intermolecular forces like hydrogen bonding

Thermoplastics- polymers that are melted and recast indefinitely. They are molten when heated and harden upon cooling.

Thermosetting- Once heated, thermosetting plastics can be moulded and pressed into shapes. Once set they cannot be reheated since they are permanently set.

Condensation polymers- In this polymerization reaction, the eliminations of the small molecules such as water, or alcohol or hydrogen chloride etc takes place and are called byproducts.

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4.18 Suggested Reading:

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4.19 Terminal Questions:

1. What do you mean by polymers? Give the classification of polymers.
2. Give a classification of different type of polymers.
3. What are physical properties of polymers?
4. Why mechanical properties of polymers are significant? Give some important mechanical properties of polymers.
5. What are advantages and disadvantages of polymers materials?
6. Define the Degree of polymerizations of the ceramics.
7. Define Polymer crystallinity and explain the percentage Polymer crystallinity.
8. Define melting point T_m, and glass transition temperature T_g of Polymer. Give the Factor affecting the glass transition temperature.
9 What is the meaning of Mechanical strength of polymer? With the help of stress strain curve of some polymers explain the behavior of Polymer.
10. Explain the terms Percentage elongations of polymer.
11. Define Viscoelasticity of polumer.
12. Define hardness and toughness of polymer materials.
13. Define thermal properties of polymer.
14. Explain chemical properties of polymers.
15. What is polymer degradations and give the different types of degradations.
16. Give the comparisons of different properties of polymer with metal and ceramics.
17. Give the applications of polymers.

UNIT 5 NANOMATERIALS

Structure

5.1 INTRODUCTION

In the last few years, nanotechnology has emerged as a new branch that changes the concept of science and technology. Now it is the science and technology of the future. Nanoscience and nanotechnology are expected to transform our understanding of almost every natural phenomenon including quantum mechanics, material science astrophysics, biosciences, etc. The technology itself is in its nascent stage and needs a comprehensive understanding of the various aspects of objects to which it is applicable. Nanomaterials can be formed naturally and artificially. For example, nanoparticles are available in humic substances, which are chemically extracted fractions of total natural organic carbon, *volcanic ashes,* dust storms, biological **systems,** titanium dioxide, silver, Synthetic amorphous silica, iron oxide, pigments, **etc.** Further, nanotechnology is widely used in the steel and paint industries. It has the potential for revolutionizing how materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact.

Early contributions in this field came from James Clark Maxwell and Richard Adolf Zsigmondy. Zsigmondy investigated colloidal solutions including sols of gold as well as other nanomaterials. American physicist Richard Feynman is credited with the first modern systematic discussion and formal announcement of nanotechnology as an important field of scientific development. In 1959 Richard Feynman is quoted that "There's Plenty of Room at the Bottom" for nanomaterials. Though he did not coin the term 'nanotechnology', he emphasized the significance of manipulation of matter at a very small scale such that these studies will allow the understanding of processes occurring in complex situations.

The respective discoveries of scanning tunneling and atomic force microscopes in the 1980s are considered milestones for the development of nanotechnology as a field. These microscopes allowed atomic-level imaging of materials which is crucial for manipulating matter at atomic/molecular scales. The parallel advancements in computer technology facilitated large-scale simulations and analyses of materials by supercomputers, thereby providing significant insights into the structure as well as properties of the materials. The simultaneous modeling, visualizing, as well as manipulation activities, greatly stimulated research investigations in the twentieth century.

5.2 Objectives:

After reading this unit we will able to understand:

1. Basic idea about nanomaterials
2. Nanoscale and Nanoscale properties
3. Classification of nanomaterials
4. Quantum dots and Quantum confinement
5. Preparation of nanomaterials
6. Properties of nanomaterials

7. Applications of nanomaterials

5.3 Nanoscale and nanomaterials:

Conventionally, nano means nanometer scale ($1n = 10^{-9}m$). To understand the nanoscale, it can be compared with human hair which has a diameter 400000 nm, and the size of a bacteria is nearly 300 to 500 nm. In general, the human eye can see an object of size 10000 nm (0.01mm) as a dot point. So, the nanoscale is very small scale compared to our ability to see without any aid. Nanoscience is simply the study of materials or structures of size 1-100 nm. The minimum size is set to 1 nm; thus, a single atom or very small clusters of atoms cannot be considered nanoparticles. If a cluster of 10 hydrogen atoms (or other molecules) are lined up then its size becomes 1 nm. However, the necessary condition for denoting clusters of atoms as nanomaterials is the onset of a quantum phenomenon instead of the actual dimension at which the effect occurs.

In nanomaterials, the surface area effects include the size as well as the shape of the object. Therefore, nanoscience is not just the science of the small, but the science where materials with small dimensions demonstrate new physical phenomena, collectively described as quantum effects. Quantum effects are size-dependent and significantly differ from the properties of macro-scaled or bulk materials. The changed properties may be color, solubility, strength, electronic and thermal conductivities, magnetic behavior, mobility, chemical and biological activities, etc.

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, and electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging, and drug delivery. Engineered nanomaterials are resources designed at the molecular (nanometer) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts.

Nanomaterials are already in commercial use; some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints, and varnishes. Nano-coatings and nanocomposites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles, and automobiles. There are novel UV-blocking coatings on glass bottles that protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl-rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams, and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

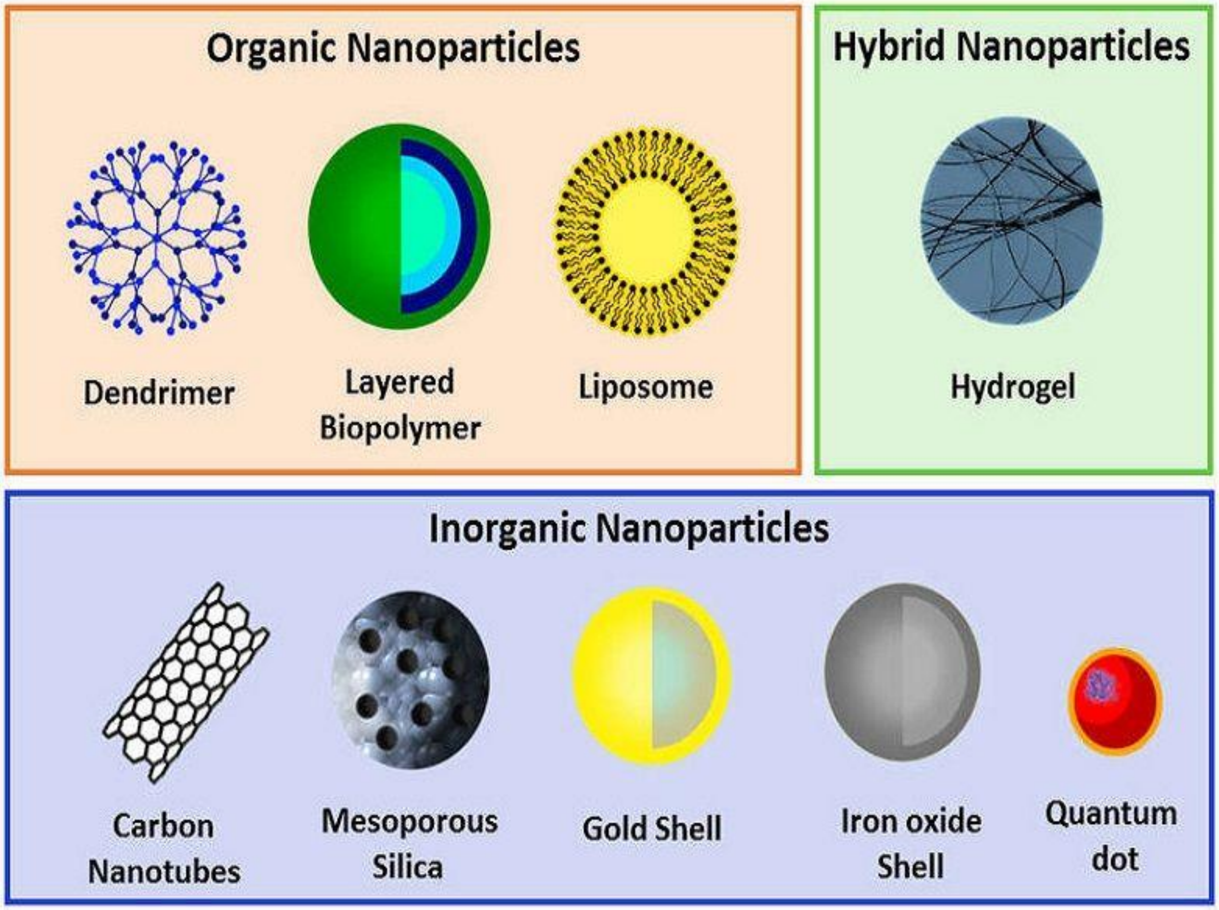


Figure 5.1: Examples of nanomaterials

5.4 Nanoscale properties:

As we have already discussed the nanoscale is unique and the properties of matter such as conductivity, hardness, toughness, electrical, magnetic properties, and other properties meet the properties of atomic and molecular scale which are nothing but wave-particle duality and quantum effect. Thus, the properties of nanomaterials are due to the influence of quantum effects.

The nanoscale properties of the material are not necessarily the properties of bulk material properties and these cannot be studied in conventional ways. For example, the nanowires or nanoscale circuit components do not follow the ohms law however it is a universal law for bulk conductors. This difference occurs due to the nanoscale arrangement of an atom of a conductor in which the few atoms of conducting material line up in a line and shows different properties. On the other hand, in bulk conductor material, there are a large number of free electrons. The two main reasons why materials at the nanoscale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area-to-volume ratio than their conventional forms, which can leadto greater chemical reactivity and affect their strength. Also at the nanoscale, quantum effects can become much more important in determining the material's properties and characteristics, leading to novel optical, electrical, and magnetic behaviors.

5.5 Classification of Nanomaterials:

Nanomaterials have an extremely small size and have at least one dimension of order 1-100 nm. Nanomaterials are classified as zero-dimensional (for example, nanoparticles), one-dimensional (for example, nanotubes & nanorods), two-dimensional (for example, nanosheets, graphene), and three-dimensional (for example, particles, nano prisms & nanoflowers). They can exist in single, fused, aggregated, or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots, and fullerenes. Nanomaterials display different physical and chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, and silica).

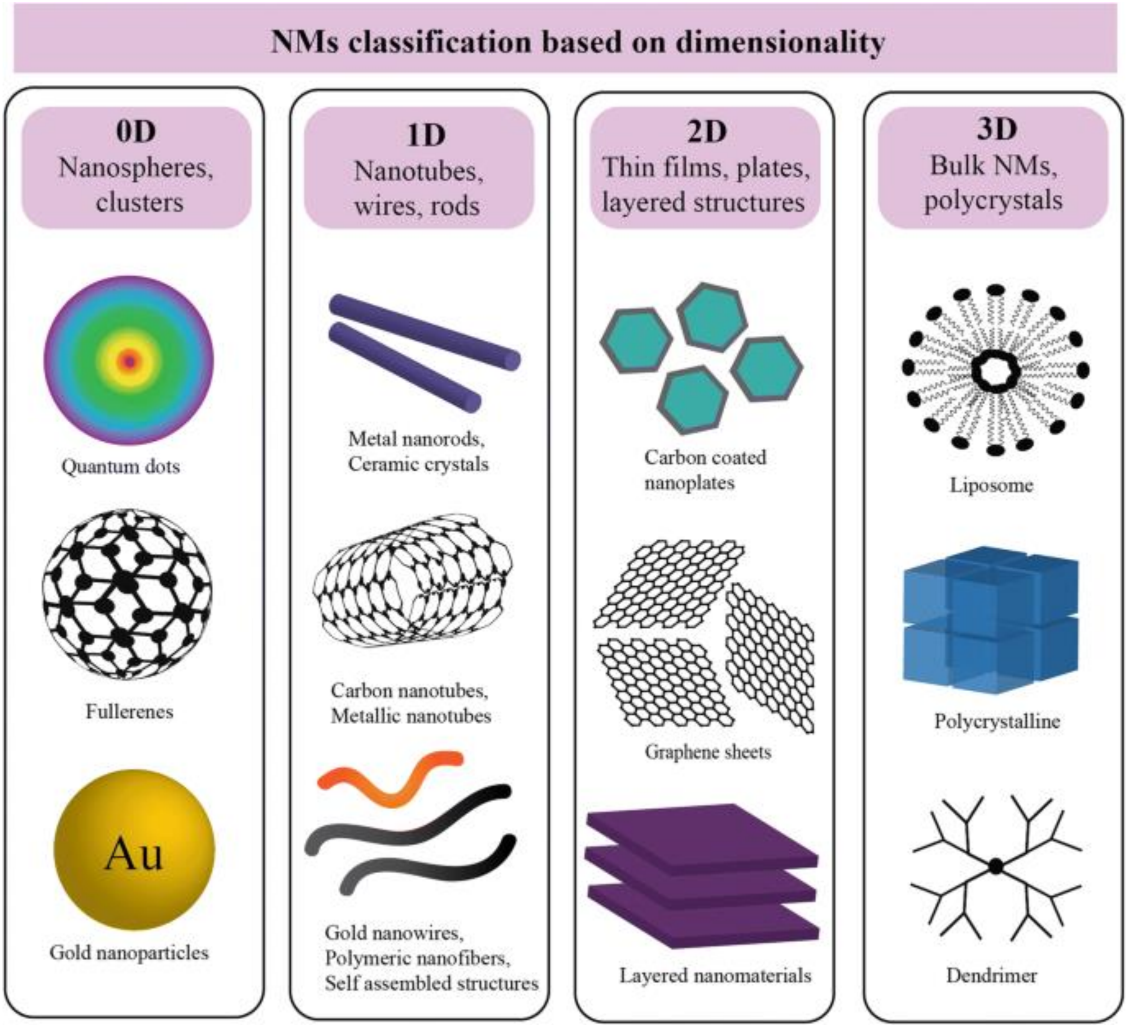


Figure 5.2: Classification of Nanomaterials

On the basis of material types, nanomaterials are two types.
1. Organic nanomaterials
2. Inorganic nanomaterials

5.5.1 Organic nanomaterials:

The *organic nanomaterials*, which consist of carbon-based components, are characterized by a highly versatile control of both chemical compositions. An increasing number of studies focus on the uses of nanomaterials with organic structure for the regeneration of bone, cartilage, skin, or dental tissues. Fullerene is an example of an *organic nanomaterial.*

Fullerene:

Buckminsterfullerene (C_{60}) simply fullerene or buckyball is the smallest member of the fullerene family. *The fullerene is allotropes of carbon which are graphene sheets rolled into tubes or spheres. The fullerene has carbon nanotubes which are important due to their electrical and mechanical properties. To produce fullerene, apply a large current is applied between two graphite electrodes in an inert atmosphere, and carbon plasma is produced between the electrodes and when it is cooled the residues may be fullerenes. The fullerene is a rounded symmetrical large molecule of 90 carbon atoms. It is also named Buckminsterfullerene* after American scientist R. Buckminster Fuller. Fuller designed a geodesic dome in which 90 carbon atoms are arranged symmetrically as shown in Figure 5.3. The atoms of C are arranged as a series of interlocking hexagons and pentagons for a structure similar to football. It consists of 12 pentagons and 20 hexagons. It was discovered in 1985 by Professor Harry Kroto and two other chemists Dr Richard E. Smalley and Dr. Robert F. Clark. They all were jointly awarded by Noble Prize in 1999.

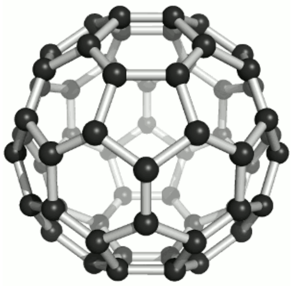


Figure 5.3: Fullerene nanomaterials

5.5.2. Inorganic nanomaterials:

Inorganic materials used for nanoparticle consists mainly of silica and metals such as gold, silver, iron oxide, etc. Nanoparticles within this class are commonly exploited for diagnostic and imaging purposes, although they may also be deployed as therapeutics given their capacity for drug loading and their unique physicochemical properties that facilitate approaches such as photothermal tumor ablation. Examples of in*organic nanomaterials are* Au, FePt, Ti, Ag, and SnO_2 nanomaterials. Some interesting inorganic nanomaterials are given below.

1. Nanophase ceramics are more ductile at elevated temperatures as compared to coarse-grained ceramics.

2. Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon- germanium such particles are called quantum dots and are used for infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

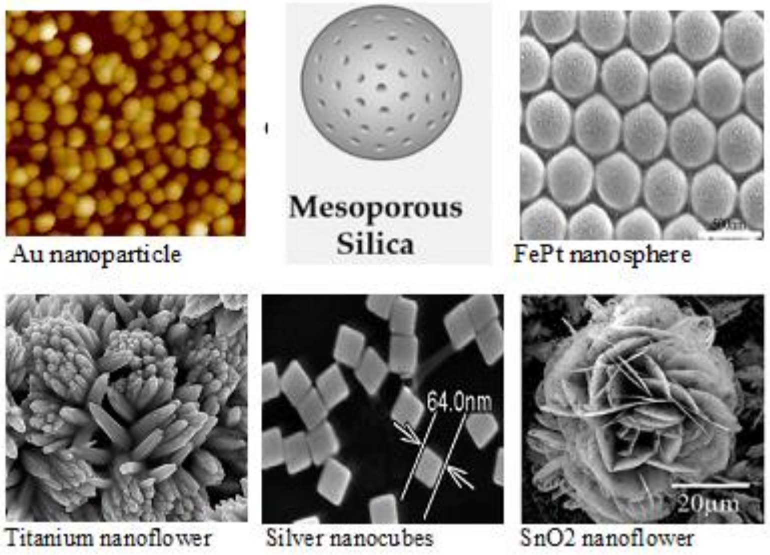
3. Nanosized metallic powders have been used for the production of gas-tight materials, dense parts, and porous coatings. Cold welding properties combined with ductility make them suitable for metal-metal bonding, especially in the electronic industry.

4. Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials, the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetic behavior. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high-density information storage, and magnetic refrigeration.

5. Nanostructured metal clusters and colloids of mono and polymetallic composition have a special impact on catalytic applications. They may serve as precursors for new types of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity, and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.

6. Nanostructured metal-oxide thin films are receiving growing attention for the realization of gas sensors (NO_2, CO, CO_2, CH_4, and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO_2) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cells and nano-structured titanium oxide porous films for their high transmission and significant surface area enhancement leading to strong absorption in dye-sensitized solar cells.

7. Polymer-based composites with a high content of inorganic particles that lead to a high dielectric constant are interesting materials for photonic band gap structure.



Au nanoparticle FePt nanosphere

Titanium nanoflower Silver nanocubes SnO2 nanoflower

Figure 5.4: Some nanomaterials

5.6 Quantum Dots and Quantum Confinement:

Quantum Dots (QD) are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers. QDs may contain 10-50 atoms of semiconducting materials. QDs are semiconductor particles having optical and electronic properties that differ from those of larger particles as a result of quantum mechanics. They are a central topic in nanotechnology and materials science. When the QDs are illuminated by UV light, an electron in the QD can be excited to a state of higher energy. In the case of a semiconducting QD, this process corresponds to the transition of an electron from the valence band to the conduction band. The excited electron can drop back into the valence band releasing its energy as light. This light emission (photoluminescence) is illustrated in Figure 5.5. The color of that light depends on the energy difference between the conduction band and the valence band, or the transition between discrete energy states when the band structure is no longer well-defined in QDs.

Quantum Confinement effects describe electrons in terms of energy levels, potential wells, valence bands, conduction bands, and electron energy band gaps. The Quantum Confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron. As Quantum Dots are created in semiconductor materials, the electrons in Quantum Dots have a range of energies. The concept of energy levels, band gap, conduction band, and valence can also be applied to the electrons in Quantum Dots. However, there is a difference in these properties in the bulk semiconductor material and Quantum Dots. The bulk dimension of crystals is much larger than the Bohr radius or separation between electrons and holes. If the size of a semiconductor crystal becomes small enough i.e., approaches to the size of exciton’s Bohr radius, then the electron energy levels can no longer be treated as continuous and becomes discrete. There is a small and finite separation between energy levels. This situation of the discrete energy levels is called Quantum Confinement and under this situation, the semiconductor material loses the bulk semiconductor properties and behaves as a Quantum Dot.

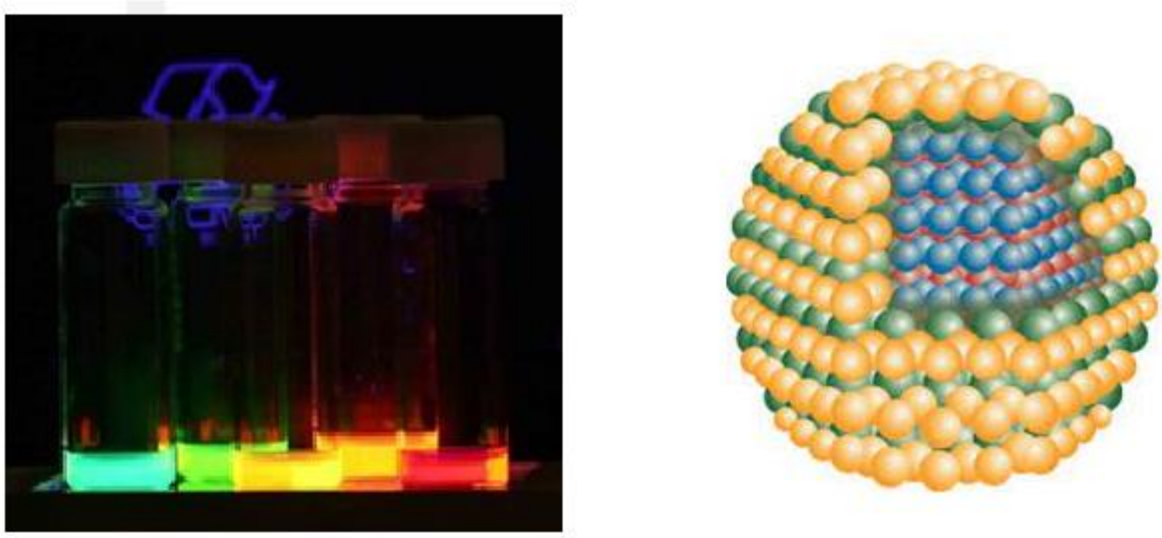


Figure 5.5: (a) Colloidal quantum dots irradiated with a UV light. (b) Different size QD.

5.7 Preparation of Nanomaterials:

There are many different ways to prepare nanostructured materials. Macromolecules, nanoparticles, buckyballs, nanotubes, etc., can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (also called bio-mimetic processes). Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application. The goal of any synthetic method for nanomaterials is to yield a material that exhibits properties that are a result of their characteristic length scale being in the nanometer range (1-100 nm). Accordingly, the synthetic method should exhibit control of size in this range so that one property or another can be attained. Often the methods are divided into two main types, "bottom-up" and "top-down".

Bottom-up methods

Bottom-up methods involve the assembly of atoms or molecules into nanostructured arrays. In these methods, the raw material sources can be in the form of gases, liquids, or solids. The latter requires some sort of disassembly prior to their incorporation onto a nanostructure. Bottom-up methods generally fall into two categories: chaotic and controlled.

Chaotic processes involve elevating the constituent atoms or molecules to a chaotic state and then suddenly changing the conditions so as to make that state unstable. Through the clever manipulation of any number of parameters, products form largely as a result of the insuring kinetics. The collapse from the chaotic state can be difficult or impossible to control and so ensemble statistics often govern the resulting size distribution and average size. Accordingly, nanoparticle formation is controlled through the manipulation of the end state of the products. Examples of chaotic processes are laser ablation exploding wire, arc, flame pyrolysis, combustion, and precipitation synthesis techniques.

Controlled processes involve the controlled delivery of the constituent atoms or molecules to the site(s) of nanoparticle formation such that the nanoparticle can grow to a prescribed size in a controlled manner. Generally, the state of the constituent atoms or molecules is never far from that needed for nanoparticle formation. Accordingly, nanoparticle formation is controlled through the control of the state of the reactants. Examples of controlled processes are self-limiting growth solution, self-limited chemical vapor deposition, shaped pulse femtosecond laser techniques, plant and microbial approach, and molecular beam epitaxy.

Top-down methods

Top-down methods adopt some 'force' (e. g. mechanical force, laser) to break bulk materials into nanoparticles. A popular method that involves mechanical breaking apart bulk materials into nanomaterials is 'ball milling'. Besides, nanoparticles can also be made by laser ablation which applies short pulse lasers (e. g. femtosecond laser) to ablate a target (solid).

5.7.1 Mechanical grinding:

Mechanical attrition is a typical example of the ‘top down’ method of synthesis of nanomaterials, where the material is prepared not by cluster assembly but by the structural decomposition of course-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity. The relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials. The major advantage often quoted is the possibility of easily scaling up to tonnage quantities of material for various applications. Similarly, the serious problems that are usually cited are;

1. Contamination from milling media and/or atmosphere, and
2. To consolidate the powder product without coarsening the nanocrystalline microstructure.

In fact, the contamination problem is often given as a reason to dismiss the method, at least for some materials. Here we will review the mechanisms presently believed responsible for the formation of nanocrystalline structures by mechanical attrition of single-phase powders, mechanical alloying of dissimilar powders, and mechanical crystallization of amorphous materials. The two important problems of contamination and powder consolidation will be briefly considered.

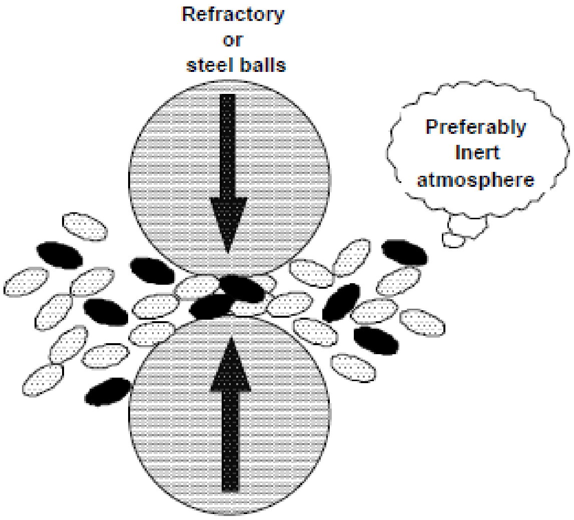


Figure 5.6: Schematic representation of the principle of mechanical milling

Mechanical milling is typically achieved using high-energy shakers, planetary balls, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling, and the milling atmosphere. Nanoparticles are produced by the shear action during grinding.

Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles be handled in an appropriate vacuum system or glove box. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed. Based on the energy of the milling process and the thermodynamic properties of the constituents, the alloy can be rendered amorphous by this processing.

5.7.2 Wet Chemical Synthesis of Nanomaterials:

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top-down method where single crystals are etched in an aqueous solution forproducing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom-up method consists of the sol-gel method, precipitation, etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

5.7.3 Sol-gel process:

The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursorssuch as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides $M(OR)_{\mathbf{z}}$ can be described as follows:

$MOR + H_2O \rightarrow MOH + ROH$ (hydrolysis) $MOH + ROM \rightarrow M\text{-}O\text{-}M + ROH$ (condensation)

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

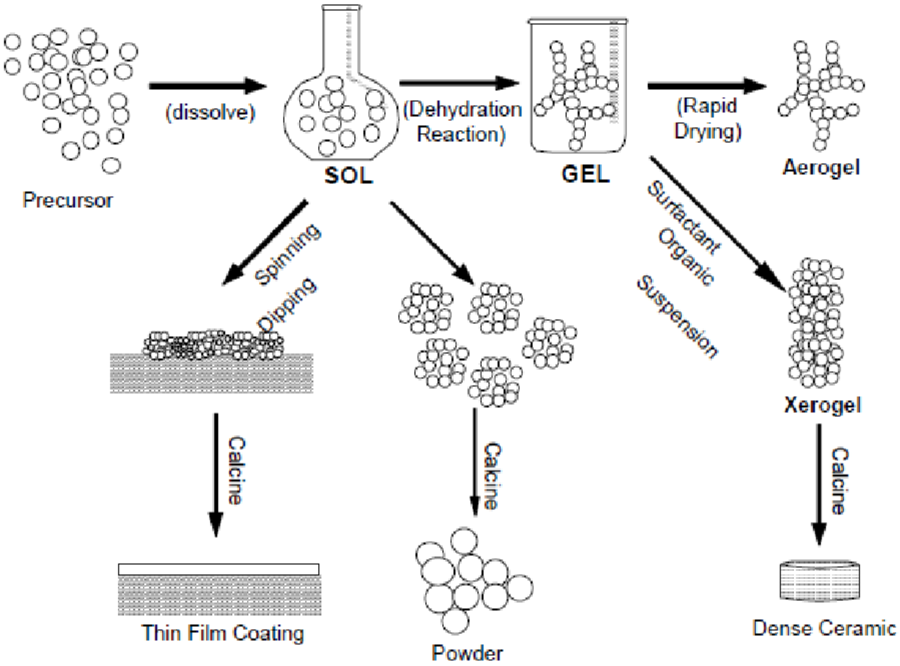


Figure 5.7: Schematic representation of the sol-gel process of synthesis of nanomaterials.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide or alcohol-bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscosity of the solution.
3. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
4. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rateperiod, (ii) the critical point, (iii) the falling rate period, and (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an *aerogel*.
5. Dehydration, during which surface-bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800^0C.
6. Densification and decomposition of the gels at high temperatures (T>800^0C). The pores of the gel network are collapsed, and the remaining organic species are volatilized.

The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics, or ceramic materials at very low temperatures compared to the high-temperature process required by melting glass or firing ceramics.

The major difficulties to overcome in developing a successful bottom-up approach are controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwantedreactant is left on the product and completely removing any growth aids that may have been used in the process. Also, production rates of nano powders are very low by this process. The mainadvantage is one can get mono-sized nano particles by any bottom-up approach.

5.7.4 Gas Phase Synthesis of Nanomaterials:

The gas-phase synthesis methods are of increasing interest because they allow elegant ways to control process parameters in order to be able to produce size, shape, and chemical composition-controlled nanostructures. Before we discuss a few selected pathways for the gas-phase formation of nanomaterials, some general aspects of gas-phase synthesis need to be discussed. In conventional chemical vapor deposition (CVD) synthesis, gaseous products either are allowedto react homogeneously or heterogeneously depending on a particular application.

1. In homogeneous CVD, particles form in the gas phase and diffuse towards a cold surface due to thermophoretic forces, and can either be scrapped off from the cold surface to givenano-powders, or deposited onto a substrate to yield what is called ***particulate films***.

2. In heterogeneous CVD, the solid is formed on the substrate surface, which catalyzes the reaction, and a dense film is formed.

In order to form nanomaterials several modified CVD methods have been developed. Gas phase processes have inherent advantages, some of which are noted here:
(a) An excellent control of size, shape, crystallinity, and chemical composition
(b) Highly purified materials can be obtained
(c) Multicomponent systems are relatively easy to form
(d) Easy control of the reaction mechanisms

Most of the synthesis routes are based on the production of small clusters that can aggregate to form nanoparticles (condensation). Condensation occurs only when the vapor is supersaturated and, in these processes, homogeneous nucleation in the gas phase is utilized to form particles. This can be achieved both by physical and chemical methods.

5.7.5 Furnace:

The simplest fashion to produce nanoparticles is by heating the desired material in a heat-resistant crucible containing the desired material. This method is appropriate only for materials that have a high vapor pressure at heated temperatures that can be as high as 2000°C. Energy is normally introduced into the precursor by arc heating, electron-beam heating, or Joule heating. The atoms are evaporated into an atmosphere, which is either inert (e.g.: He) or reactive (so as to form a compound). To carry out synthesis, materials with very low vapor pressure have to be fed into the furnace in the form of a suitable precursor such as organometallics, that decompose in the furnace to produce a condensable material. The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. In case a compound is being synthesized, these precursors react in the gas phase and form a compound with the materialthat is separately injected into the reaction chamber. The clusters would continue to grow if they remain in the supersaturated region. To control their size, they need to be rapidly removed from the supersaturated environment by a carrier gas. The cluster size and its distribution are controlled by only three parameters:

1) the rate of evaporation (energy input),
2) the rate of condensation (energy removal), and
3) the rate of gas flow (cluster removal).

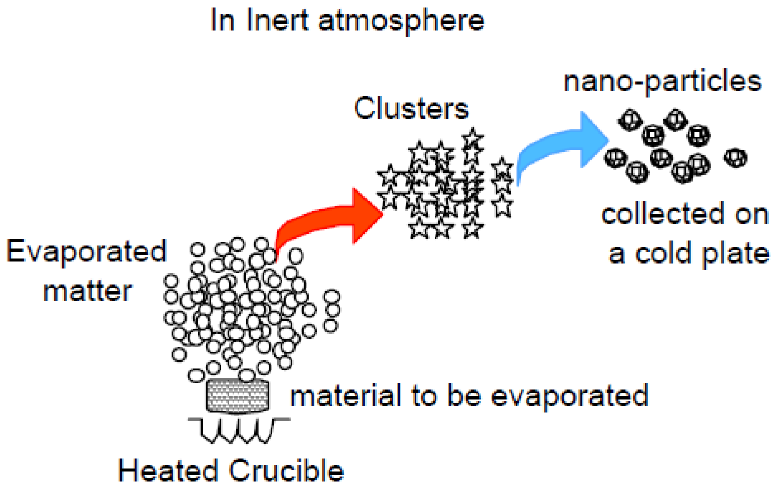


Figure 5.8: Schematic representation of gas phase process of synthesis of the nanomaterials from a heated crucible.

Because of its inherent simplicity, it is possible to scale up this process from the laboratory (mg/day) to industrial scales (tons/day).

5.7.6 Flame-assisted ultrasonic spray pyrolysis:

In this process, precursors are nebulized and then unwanted components are burnt in a flame to get the required material, e.g., ZrO_2 has been obtained by this method from a precursor of Zr $(CH_3 CH_2 CH_2O)_4$. Flame hydrolysis which is a variant of this process is used for the manufacture of fused silica. In the process, silicon tetrachloride is heated in an oxy-hydrogen flame to give highly dispersed silica. The resulting white amorphous powder consists of spherical particles with sizes in the range of 7-40 nm. The combustion flame synthesis, in which the burning of a gas mixture, e.g., acetylene and oxygen or hydrogen and oxygen, supplies the energy to initiate the pyrolysis of precursor compounds, is widely used for the industrial production of powders in large quantities, such as carbon black, fumed silica, and titanium dioxide. However, since the gas pressure during the reaction is high, highly agglomerated powders are produced which is disadvantageous for subsequent processing. The basic idea of low-pressure combustion flame synthesis is to extend the pressure range to the pressures used in gas phase synthesis and thus to reduce or avoid agglomeration. Low-pressure flames have been extensively used by aerosol scientists to study particle formation in the flame.

A key for the formation of nanoparticles with narrow size distributions is the exact control of the flame in order to obtain a flat flame front. Under these conditions, the thermal history, i.e., time and temperature, of each particle formed is identical and narrow distributions result. However, due to the oxidative atmosphere in the flame, this synthesis process is limited to the formation of oxides in the reactor zone.

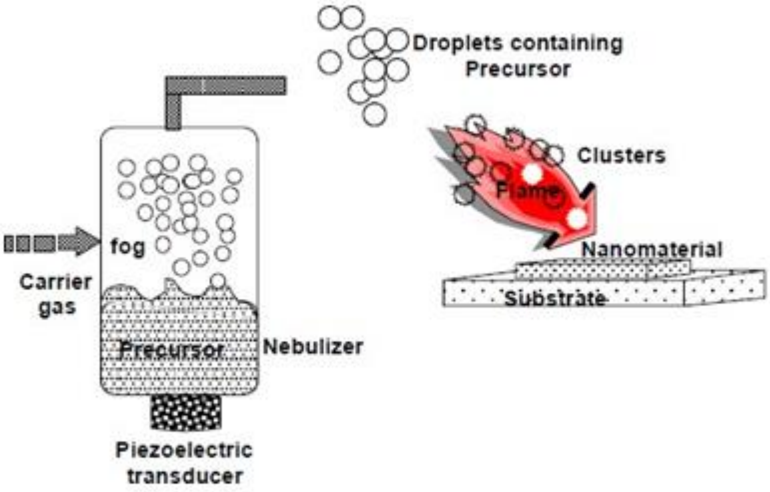


Figure 5.9: Flame assisted ultrasonic spray pyrolysis

5.7.7 Gas Condensation Processing (GPC):

In this technique, a metallic or inorganic material, e.g., a suboxide, is vaporized using thermal evaporation sources such as crucibles, electron beam evaporation devices, or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr). Cluster form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase. The cluster or particle size depends critically on the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar, or Kr, and on the evaporation rate/vapor pressure of the evaporating material. With increasing gas pressure, vapor pressure, and mass of the inert gas used the average particle size of the nanoparticles increases. Lognormal size distributions have been found experimentally and have been explained theoretically by the growth mechanisms of the particles. Even in more complex processes such as the low-pressure combustion flame synthesis where a number of chemical reactions are involved the size distributions are determined to be lognormal.

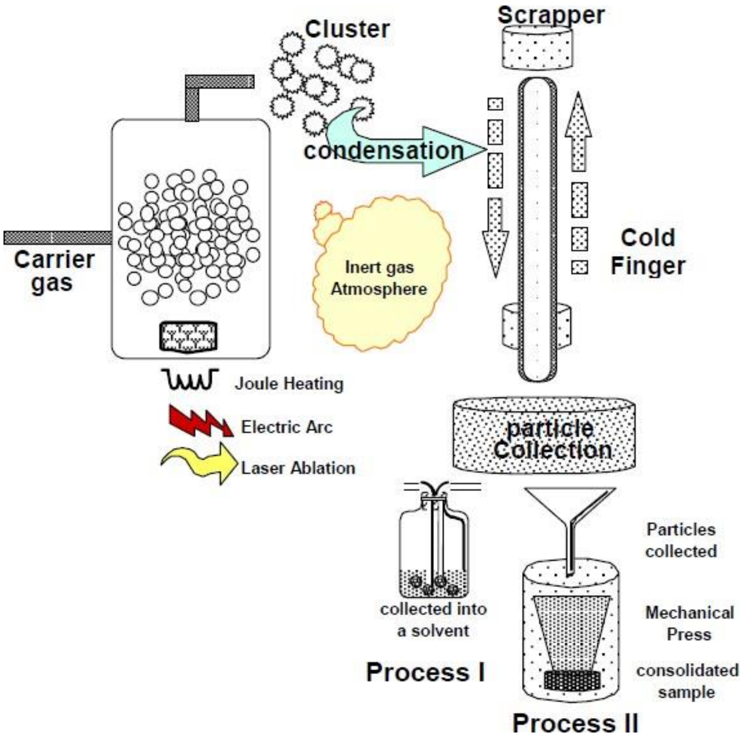


Figure 5.10: Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.

Originally, a rotating cylindrical device cooled with liquid nitrogen was employed for theparticle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no agglomeration. Subsequently, the nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate. In addition to this cold finger device, several techniques known from aerosol science have now been implemented for use in gas condensation systems such as corona discharge, etc. These methods allow for the continuous operation of the collection device and are better suited for the large-scale synthesis of nano-powders. However, these methods can only be used in a system designed for gas flow, i.e., a dynamic vacuum is generated by means of both continuous pumpingand gas inlet via a mass flow controller. A major advantage over conventional gas flow is the improved control of the particle sizes. It has been found that the particle size distributions in gas flow systems, which are also lognormal, are shifted towards smaller average values with an appreciable reduction of the standard deviation of the distribution. Depending on the flow rate of the He-gas, particle sizes are reduced by 80% and standard deviations by 18%.

The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta, or Mo). If metals with high melting points ormetals that react with the crucibles, are to be prepared, sputtering, i.e., for W and Zr, or laser orelectron beam evaporation has to be used. Synthesis of alloys or intermetallic compounds by thermal evaporation can only be done in exceptional cases where the vapor pressures of the elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed. Composite materials such as Cu/Bi or W/Ga have been synthesized by simultaneous evaporation from two separate crucibles onto a rotating collection device. It has been found that excellent intermixing on the scale of the particle size can be obtained.

However, control of the composition of the elements has been difficult and reproducibility is poor. Nanocrystalline oxide powders are formed by controlled post-oxidation of primary nanoparticles of a pure metal (e.g., Ti to TiO_2) or a suboxide (e.g., ZrO to ZrO_2). Although the gas condensation method including the variations has been widely employed to prepare a variety of metallic and ceramic materials, quantities have so far been limited to a laboratory scale. The quantities of metals are below 1 g/day, while quantities of oxides can be as high as 20 g/day for simple oxides such as CeO_2 or ZrO_2. These quantities are sufficient for materials testing but not for industrial production. However, it should be mentioned that the scale-up of the gas condensation method for industrial production of nanocrystalline oxides by a company called nanophase technologies has been successful.

5.7.8 Chemical Vapor Condensation (CVC):

As shown schematically in Figure 5.11, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapor Condensation or the CVC process. Depending on the processing parameters nucleation of nanoparticles is observed during chemical vapor deposition (CVC) of thin films and poses a major problem in obtaining good film qualities. The original idea of the novel CVC process which is schematically shown below where it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance the homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time, both particle and film formation can be obtained.

Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form, a metal-organic precursor is introduced into the hot zone of the reactor using a mass flow controller. Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesized. Additionally, more complex oxides such as $BaTiO_3$ or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature. The extension to the production of nanoparticles requires the determination of a modified parameter fieldin order to promote particle formation instead of film formation. In addition to the formation of single-phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of:

1. Mixtures of nanoparticles of two phases or doped nanoparticles by supplying twoprecursors at the front end of the reactor, and
2. Coated nanoparticles, i.e., n-ZrO_2 coated with n-Al_2O_3 or vice versa, by supplying a second precursor at a second stage of the reactor. In this case, nanoparticles that have been formed by homogeneous nucleation are coated by heterogeneous nucleation in thesecond stage of the reactor.

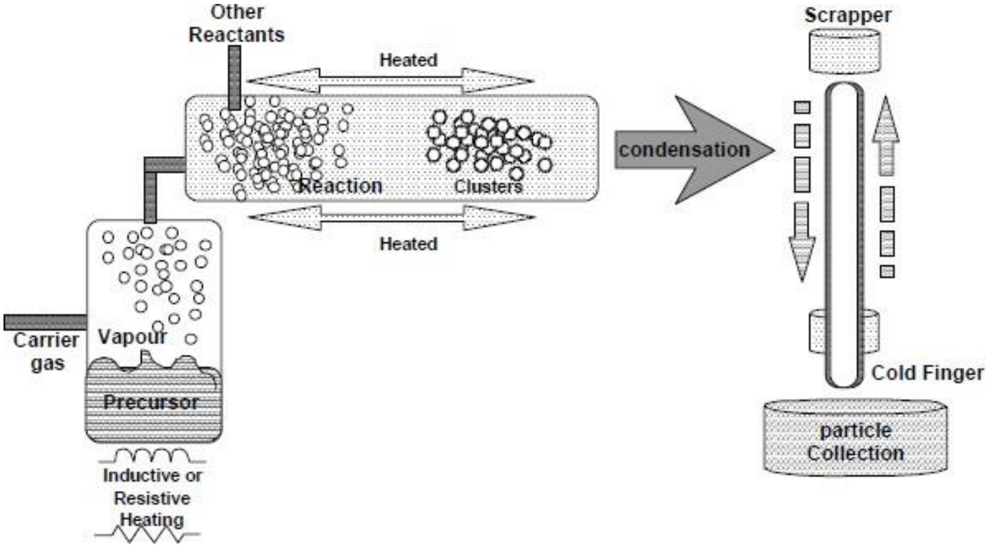


Figure 5.11: A schematic of a typical CVC reactor

Because CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small-scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

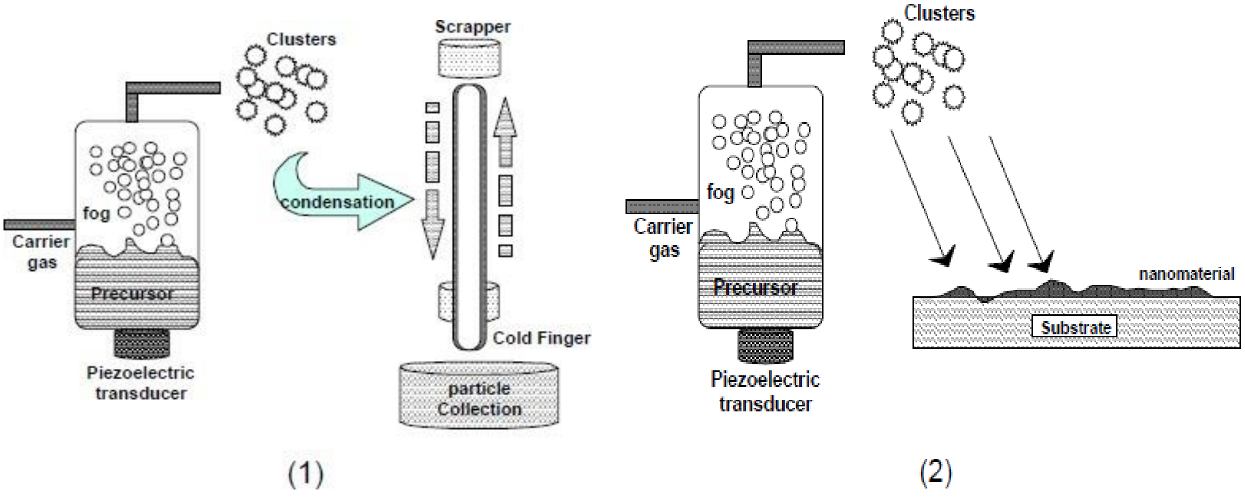
5.7.9 Sputtered Plasma Processing:

This method is yet again a variation of the gas-condensation method accepting the fact that the source material is a sputtering target and this target is sputtered using rare gases and theconstituents are allowed to agglomerate to produce nanomaterial. Both dc (direct current) and rf (radio-frequency) sputtering has been used to synthesize nanoparticles. Again, reactive sputtering or multitarget sputtering has been used to make alloys and/or oxides, carbides, and nitrides of materials. This method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal.

5.7.10 Microwave Plasma Processing:

This technique is similar to the previously discussed CVC method but employs plasma instead of high temperature for the decomposition of the metal-organic precursors. The method uses microwave plasma in a 50 mm diameter reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor such as a chloride compound is introduced into the front end of the reactor. Generally, the microwave cavity is designed as a single-mode cavity using the TE10 mode in a WR975 waveguide with a frequency of 0.915 GHz. The major advantage of plasma-assisted pyrolysis in contrast to thermal activation is the low-temperature reaction which reduces the tendency for agglomeration of the primary particles. Thisis also true in the case of plasma-CVD processes. Additionally, it has been shown that by introducing another precursor into a second reaction zone of the tubular reactor, e.g., by splitting the microwave guide tubes, the primary particles can be coated with a second phase. For example, it has been demonstrated that ZrO_2 nanoparticles can be coated by Al_2O_3. In this case, the inner ZrO_2 core is crystalline, while the Al_2O_3 coating is amorphous. The reaction sequence can be reversed with the result that an amorphous Al_2O_3 core is coated with crystalline ZrO_2. While the formation of the primary particles occurs by homogeneous nucleation, it can be easily estimated using gas reaction kinetics that the coating on the primary particles grows heterogeneously and that homogeneous nucleation of nanoparticles originating from the second compound has a very low probability. A schematic representation of the particle growth in plasma is given below:

Figure 5.12: Schematic representation of (1) nanoparticle (2) particulate film formation.



5.7.11 Particle precipitation aided CVD:

In another variation of this process, colloidal clusters of materials are used to prepare nanoparticles. The CVD reaction conditions are so set that particles form by condensation in the gas phase and collect onto a substrate, which is kept under a different condition that allows heterogeneous nucleation. By this method, both nanoparticles and particulate films can be prepared. An example of this method has been used to form nanomaterials e.g., SnO_2, by a method called pyrosol deposition process, where clusters of tin hydroxide are transformed into small aerosol droplets, following which they are reacted onto a heated glass substrate.

5.7.12 Laser ablation:

Laser ablation has been extensively used for the preparation of nanoparticles and particulate films. In this process, a laser beam is used as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications. The small dimensions of the particles and the possibility to form thick films make this method quite an efficient tool for the production of ceramic particles and coatings and also an ablation source for analytical applications such as the coupling to induced coupled plasma emission spectrometry, ICP, the formation of the nanoparticles has been explained following a liquefaction process which generates an aerosol, followed by the cooling/solidification of the droplets which results inthe formation of fog. The general dynamics of both the aerosol and the fog favors the aggregation process and micrometer-sized fractal-like particles are formed. The laser spark atomizer can be used to produce highly mesoporous thick films and the porosity can be modified by the carrier gas flow rate. ZrO_2 and SnO_2 nanoparticulate thick films were also synthesized successfully using this process with quite identical microstructure. Synthesis of other materials such as lithium manganate, silicon, and carbon has also been carried out by this technique.

5.8 Properties of Nanomaterials:

Nanomaterials have structural features in between those of atoms and the bulk materials. While most micro-structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer size of the materials which render them: (i) a large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have an extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effects on the materials, which bring quantum effects.

The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn, will modify the electronic and optical properties of the materials. For example, lasers and light-emitting diodes (LEDs) from both the quantum dots and quantum wires are very promising in future optoelectronics. High-density information storage using QD devices is also a fast-developing area. Reduced imperfections are also an important factor in the determination of the properties of the nanomaterials. Nanostructures and Nanomaterials favor a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased material perfectionaffects the properties of nanomaterials. For example, the chemical stability of certain nanomaterials may be enhanced, and the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known. Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties have also been proposed.

5.8.1 Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on the optical properties of nanomaterials include optical detectors, lasers, sensors, imaging, phosphor, display, solar cell, photocatalysis, photo-electrochemistry and biomedicine.

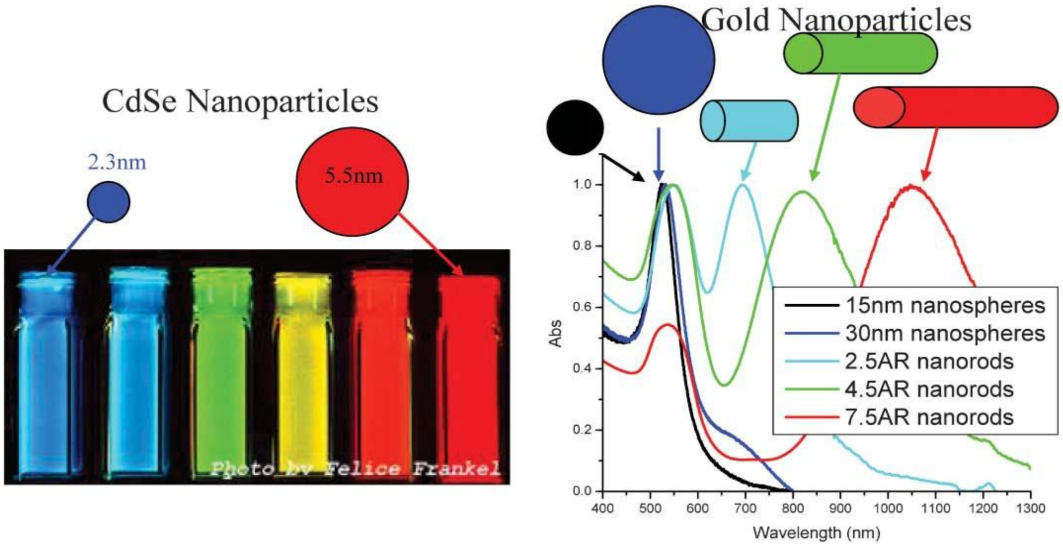


Figure 5.13: Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles (Chem. Soc. Rev., 2006, 35, 209–217).

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, the shape can have a dramatic influence on the optical properties of metal nanostructures. Fig. 5.13 exemplifies the difference in the optical properties of metal and semiconductor nanoparticles. With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres. However, when anisotropy is added to the nanoparticle, such as the growth of nanorods, the optical properties of the nanoparticles change dramatically.

5.8.2 Electrical Properties:

Electrical Properties of Nanoparticles" discuss the fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, and electrical conductivity of nanocomposites. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

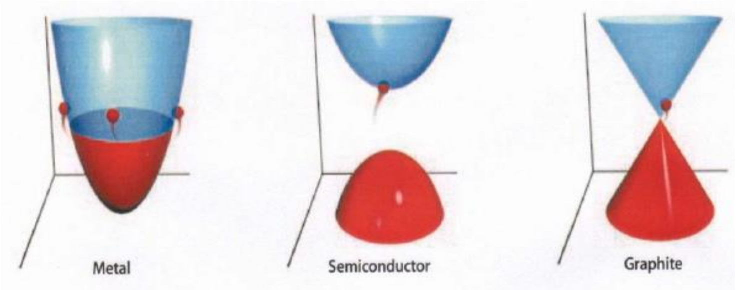


Figure 5.14: Electrical behavior of nanotubes (P. G. Collins and Ph. Avouris, *Scientific American*,62, 2000, 283).

In electrically conducting carbon nanotubes, only one electron wave mode is observed which transports the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance; and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface ofthe mercury droplet and contribute to the electrical current transport.

5.8.3 Mechanical Properties:

Mechanical Properties of Nanoparticles deals with bulk metallic and ceramic materials, the influence of porosity, the influence of grain size, super-plasticity, filled polymer composites, particle-filled polymers, polymer-based nanocomposites filled with platelets, carbon nanotube-based composites. The discussion of mechanical properties of nanomaterials is, to some extent, only of quite basic interest, the reason being that it is problematic to produce macroscopic bodies witha high density and a grain size in the range of less than 100 nm. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance.

These materials are polymers that contain nanoparticles or nanotubes to improve their mechanical behaviors, and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter is generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly definedgrain sizes and porosities. Therefore, model calculations and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a nanoparticulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles, or platelets, and on the degree of agglomeration. In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer the properties obtained. Although, potentially, the best composites are those filled with nanofibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand, by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture. Among the most exciting nanocomposites are polymer-ceramic nanocomposites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers of thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

5.8.4 Magnetic properties:

Bulk gold and Pt are non-magnetic, but at the nano size, they are magnetic. Surface atoms are not only different from bulk atoms but they can also be modified by interaction with other chemical species, that is, by capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be possible that non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in the nano range. One can obtain magnetic nanoparticles of Pd, Pt, and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, ferromagnetism arises from the structural changes associated with side effects.

However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior. The surface and the core of Au nanoparticles with 2 nm in diameter show ferromagnetic and paramagnetic character, respectively. The large spin-orbit coupling of these noble metals can yield a large anisotropy and therefore exhibit high ordering temperatures. More surprisingly, permanent magnetism was observed up to room temperature for thiol-capped Au nanoparticles. For nanoparticles with sizes below 2 nm, the localized carriers are in the d-band. Bulk Au has an extremely low density of states and becomes diamagnetic, as is also the case for bare Au nanoparticles. This observation suggested that modification of the d-band structure by chemical bonding can induce a ferromagnetic-like character in metallic clusters.

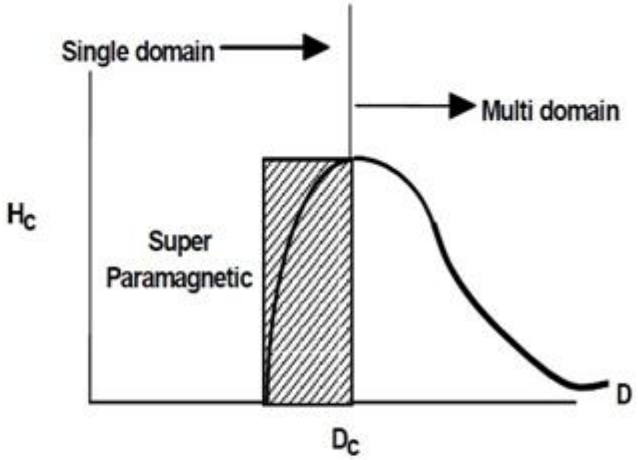


Figure 5.15: Magnetic properties of nanostructured materials.

5.9 Application of nanomaterials:

Nanomaterials can be used in a wide range of applications, some of those listed below. They have unique, beneficial physical, chemical, and mechanical properties.

1. Electronics and IT Applications

Nanotechnology has greatly contributed to major advances in computing and electronics, leading to faster, smaller, and more portable systems that can manage and store larger and larger amounts of information. These continuously evolving applications include:

(a) Transistors, the basic switches that enable all modern computing, have gotten smaller and smaller through nanotechnology. At the turn of the century, a typical transistor was 130 to 250 nanometers in size. In 2014, Intel created a 14-nanometer transistor, then IBM created the first seven-nanometer transistor in 2015. Smaller, faster, and better transistors may mean that soon the computer's entire memory may be stored on a single tiny chip.

(b) Using Magnetic Random-access memory (MRAM), computers will be able to "boot" almost instantly. MRAM is enabled by nanometer-scale magnetic tunnel junctions and can quickly and effectively save data during a system shutdown or enable resume-play features.

(c) Ultra high-definition displays and televisions are now being sold that use quantum dots to produce more vibrant colors while being more energy efficient.

(d) Flexible, bendable, foldable, rollable, and stretchable electronics are reaching various sectors and are being integrated into a variety of products, including wearables, medical applications, aerospace applications, and the Internet of Things. Flexible electronics have been developed using, for example, semiconductor nanomembranes for applications in smartphone and e-reader displays. Other nanomaterials like graphene and cellulosic nanomaterials are being used for various types of flexible electronics to enable wearable and “tattoo” sensors, photovoltaics that can be sewn onto clothing, and electronic paper that can be rolled up. Making flat, flexible, lightweight, non-brittle, highly efficient electronics opens the door to countless smart products.

(e) Other computing and electronic products include flash memory chips for smartphones and thumb drives; ultra-responsive hearing aids; antimicrobial/antibacterial coatings on keyboards and cell phone casings; conductive inks for printed electronics for RFID/smart cards/smart packaging; and flexible displays for e-book readers.

(f) Nanoparticle copper suspensions have been developed as a safer, cheaper, and more reliable alternative to lead-based solder and other hazardous materials commonly used to fuse electronics in the assembly process.

2. Medical and Healthcare Applications:

Nanotechnology is already broadening the medical tools, knowledge, and therapies currently available to clinicians. Nanomedicine, the application of nanotechnology in medicine, draws on the natural scale of biological phenomena to produce precise solutions for disease prevention, diagnosis, and treatment. Below are some examples of recent advances in this area:

(a) Commercial applications have adapted gold nanoparticles as probes for the detection of targeted sequences of nucleic acids, and gold nanoparticles are also being clinically investigated as potential treatments for cancer and other diseases.

(b) Better imaging and diagnostic tools enabled by nanotechnology are paving the way for earlier diagnosis, more individualized treatment options, and better therapeutic success rates.

(c) Nanotechnology is being studied for both the diagnosis and treatment of atherosclerosis or the buildup of plaque in arteries. In one technique, researchers created a nanoparticle that mimics the body’s “good” cholesterol, known as HDL (high-density lipoprotein), which helps to shrink plaque.

(d) The design and engineering of advanced solid-state nanopore materials could allow for the development of novel gene sequencing technologies that enable single-molecule detection at low cost and high speed with minimal sample preparation and instrumentation.

(e) Nanotechnology researchers are working on different therapeutics where a nanoparticle can encapsulate or otherwise help to deliver medication directly to cancer cells and minimize the risk of damage to healthy tissue. This has the potential to change the way doctors treat cancer and dramatically reduce the toxic effects of chemotherapy.

(f) Nanomedicine researchers are looking at ways that nanotechnology can improve vaccines, including vaccine delivery without the use of needles. Researchers also are working to create a universal vaccine scaffold for the annual flu vaccine that would cover more strains and require fewer resources to develop each year.

3. Energy Applications:

Nanotechnology is finding application in traditional energy sources and is greatly enhancing alternative energy approaches to help meet the world's increasing energy demands. Many scientists are looking into ways to develop clean, affordable, and renewable energy sources, along with means to reduce energy consumption and lessen toxicity burdens on the environment:

(a) Nanotechnology is improving the efficiency of fuel production from raw petroleum materials through better catalysis. It is also enabling reduced fuel consumption in vehicles and power plants through higher-efficiency combustion and decreased friction.

(b) Nanotechnology is also being applied to oil and gas extraction through, for example, the use of nanotechnology-enabled gas lift valves in offshore operations or the use of nanoparticles to detect microscopic down-well oil pipeline fractures.

(c) Researchers are investigating carbon nanotube "scrubbers" and membranes to separate carbon dioxide from power plant exhaust.

(d) Researchers are developing wires containing carbon nanotubes that will have much lower resistance than the high-tension wires currently used in the electric grid, thus reducing transmission power loss.

(e) Nanotechnology can be incorporated into solar panels to convert sunlight to electricity more efficiently, promising inexpensive solar power in the future. Nanostructured solar cells could be cheaper to manufacture and easier to install since they can use print-like manufacturing processes and can be made in flexible rolls rather than discrete panels. Newer research suggests that future solar converters might even be "paintable."

(f) Nanotechnology is already being used to develop many new kinds of batteries that are quicker charging, more efficient, lighter weight, have a higher power density, and hold electrical charge longer.

(g)In the area of energy harvesting, researchers are developing thin-film solar electric panels that can be fitted onto computer cases and flexible piezoelectric nanowires weaved into clothing to generate usable energy on the go from light, friction, and/or body heat to power mobile electronic devices. Similarly, various nanoscience-based options are being pursued to convert waste heat in computers, automobiles, homes, power plants, etc., to usable electrical power.

4. Environmental Remediation:

In addition to the ways that nanotechnology can help improve energy efficiency. There are also many ways that it can help detect and clean up environmental contaminants:

(a) Nanotechnology could help meet the need for affordable, clean drinking water through rapid, low-cost detection and treatment of impurities in water. Engineers have developed a thin film membrane with nanopores for energy-efficient desalination. This molybdenum disulfide (MoS_2) membrane filtered two to five times more water than current conventional filters.

(b) Nanoparticles are being developed to clean industrial water pollutants in groundwater through chemical reactions that render the pollutants harmless. This process would cost less than methods that require pumping the water out of the ground for treatment.

(c) Nanotechnology-enabled sensors and solutions are now able to detect and identify chemical or biological agents in the air and soil with much higher sensitivity than ever before.

5. Future Transportation Benefits:

Nanotechnology offers the promise of developing multifunctional materials that will contribute to building and maintaining lighter, safer, smarter, and more efficient vehicles, aircraft, spacecraft, and ships. In addition, nanotechnology offers various means to improve the transportation infrastructure:

(a) As discussed above, nano-engineered materials in automotive products include polymer nanocomposites structural parts; high-power rechargeable battery systems; thermoelectric materials for temperature control; lower rolling-resistance tires; high-efficiency/low-cost sensors and electronics; thin-film smart solar panels; and fuel additives and improved catalytic converters for cleaner exhaust and extended range. Nano-engineering of aluminum, steel, asphalt, concrete, and other cementitious materials, and their recycled forms offers great promise in terms of improving the performance, resiliency, and longevity of highway and transportation infrastructure components while reducing their life cycle cost. New systems may incorporate innovative capabilities into traditional infrastructure materials, such as self-repairing structures or the ability to generate or transmit energy.

(b) Nanoscale sensors and devices may provide cost-effective continuous monitoring of the structural integrity and performance of bridges, tunnels, rails, parking structures, and pavements over time. Nanoscale sensors, communications devices, and other innovations enabled by nanoelectronics can also support an enhanced transportation infrastructure that can communicate with vehicle-based systems to help drivers maintain lane position, avoid collisions, adjust travel routes to avoid congestion and improve drivers' interfaces to onboard electronics.

(c) The use of nanotechnology-enabled lightweight, high-strength materials would apply to almost any transportation vehicle. For example, it has been estimated that reducing the weight of a commercial jet aircraft by 20 percent could reduce its fuel consumption by as much as 15 percent.

6. Better Insulation Materials:

(a) Nanocrystalline materials manufactured by the sol-gel method give rise to foam-like structures known as “aerogels.” In spite of being extremely lightweight and porous, these aerogels can hold loads equal to 100 times their weight. Aerogels are made up of continuous 3D networks of particles with air (or any other fluid, such as a gas) trapped at their interstices.

(b)Since aerogels are porous and include air trapped at the interstices, they are used for insulation in homes, offices, etc. This considerably reduces the cooling and heating bills, thus saving power and decreasing the associated environmental pollution.

7. Phosphors for High-Definition TV:

(a) The resolution of a monitor or television is subject to the size of the pixel. These pixels are fundamentally composed of materials known as “phosphors,” which glow when struck by a stream of electrons within the cathode ray tube (CRT). The resolution enhances with a reduction in the pixel size or the phosphors.

(b) Nanocrystalline zinc selenide, cadmium sulfide, zinc sulfide, and lead telluride prepared through the sol-gel methods are potential materials for enhancing the resolution of monitors. The use of nano phosphors is intended to lower the cost of these displays to make personal computers and high-definition televisions (HDTVs) affordable for an average household in the United States.

8. Tougher and Harder Cutting Tools

(a) Cutting tools made of nanocrystalline materials like carbides of tantalum, tungsten, and titanium, are a lot harder, much more erosion-resistant and wear-resistant, and last longer than their traditional (large-grained) equivalents. They also allow the manufacturer to machine several materials much faster, thereby boosting productivity and largely minimizing manufacturing costs.

9. High-Power Magnets:

(a) A magnet’s strength is measured in terms of saturation magnetization and coercivity values. These values will increase when there is a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains) of the grains. It has been demonstrated that magnets made of nanocrystalline yttrium-samarium-cobalt grains have highly uncommon magnetic properties because of their extremely large surface area.

(b) Common applications for these high-power rare-earth magnets include ultra-sensitive analytical instruments, quieter submarines, land-based power generators, automobile alternators, motors for ships, and magnetic resonance imaging (MRI) in medical diagnostics.

5.10 Summary:

1. The word nano means nanometer scale ($1\text{n m} = 10^{-9}\text{m}$). Nanomaterials with small dimensions demonstrate new physical phenomena, collectively described as quantum effects. Quantum effects are size-dependent and significantly differ from the properties of macro-scaled or bulk materials. The changed properties may be color, solubility, strength, electronic and thermal conductivities, magnetic behavior, mobility, chemical and biological activities, etc.Thus, the properties of nanomaterials are due to the influence of quantum effects.

2. Nanomaterials are classified as zero-dimensional (for example, nanoparticles), one-dimensional (For example, nanotubes & nanorods), two-dimensional (for example, nanosheets, graphene), and three-dimensional (for example, particles, nano prisms & nanoflowers).
3. Buckminsterfullerene (C_{60}) simply fullerene or buckyball is the smallest member of the fullerenes family. *The fullerene is allotropes of carbon which are graphene sheets rolled into tubes or spheres. The fullerene has carbon nanotubes which are important due to their electrical and mechanical properties.*
4. Quantum dots (QD) are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers. Quantum Dots may contain 10-50 atoms of semiconducting material. Quantum dots are semiconductor particles having optical and electronic properties that differ from those of larger particles as a result of quantum mechanics.
5. Quantum confinement effects describe electrons in terms of energy levels, potential wells, valence bands, conduction bands, and electron energy band gaps. The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron.
6. There are many different ways to prepare nanostructure materials. Macromolecules or nanoparticles or buckyballs or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (sometimesalso called bio-mimetic processes).
7. Nanomaterials have structural features in between those of atoms and bulk materials. While most microstructure materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer

size of the materials. Due to their small dimensions, nanomaterials have an extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more "surface" dependent material properties.

4.11 Glossary:

Nano: nano means nanometer scale ($1\text{n m} = 10^{-9}\text{m}$).

Quantum effects Quantum effects are size-dependent and significantly differ from the properties of macro-scaled or bulk materials

Engineered nanomaterials: Resources designed at the molecular (nanometer) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts.

organic nanomaterials: which consist of carbon-based components

Fullerene*: The fullerene is a rounded symmetrical large molecule of 90 carbon atoms. also named Buckminsterfullerene* or Buckyball.

Inorganic materials: Inorganic materials used for nanoparticle consists mainly of silica and metals such as gold, silver, iron oxide, etc.

Quantum dots: Quantum dots (QD) are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers. Quantum Dots may contain 10-50 atoms of semiconducting material. The concept of energy levels, band gap, conduction band, and valence can also be applied to the electrons in Quantum dots. However, there is a difference in these properties in the bulk semiconductor material and quantum dots.

Ablation: Removal of particles from a bulk material by melting or evaporation.

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4.13 Suggested Reading:

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4.14 Terminal Questions:

1. What do you mean by nanomaterial? Give the classification of nanomaterial.
2. Give a classification of different types of nanomaterial. Explain it with examples.
3. What are quantum dots and quantum confinement?
4. Why properties of nanomaterial are significant? Give some important properties of nanomaterial.
5. Explain organic and inorganic nanomaterials and give some examples also.
6. What are zero-, one-, two-, and three-dimensional nanomaterials?
7. Explain the Mechanical grinding method for the preparation of nanostructure materials.
8. What is so special about nanotechnology?
9. Explain the wet chemical synthesis method for the preparation of nanostructure materials
10. What is graphene?
11. Give the different methods for synthesizes nanomaterials.
12. Explain the sol-gel process method for the preparation of nanostructure materials.
13. Give the applications of nanomaterials.
14. What is Bucky Ball?
15. How nanotechnology is useful in the field of Medical Science?

UNIT 6 BASIC TECHNIQUES OF SYNTHESIS

Structure

6.1 Introduction

Material science has many aspects; but there are three general regions: the study of structures of materials, the study of reactions of materials, and the synthesis of materials. Previously, it was generally thought that synthesis, compared with structure and reactions, was more empirical and devoid of rigid theory. As our understanding of structures and reactions has advanced, however, synthesis has also gradually become theoretically grounded and systematized. In this chapter, we shall glimpse of the state of the art of modern synthesis. This will help you to recognize the significant role of synthesis in modern material science.

6.2 Objective

After studying this unit you should be able to:

- To learn about the aspects of crystal growth.
- Gain knowledge about the basic elements of single crystal growth.
- Describe the zone refining.
- Know about the different doping techniques of elemental and compound semiconductors.

6.3 Introduction to crystal growth

Historical perspective: The most frequent form of solid material is the crystal because of its uniform atomic structure. Crystals were formed on the surface of Earth under severe conditions of high pressure, temperature, and other environmental variables. Each crystal, specifically, starts out small and develops when new atoms are added. Many grow from mineral-rich water, but others can also grow from melted rock or even vapour. Surprisingly diverse crystal structures are formed by the combination of atoms under the influence of various temperatures and pressures. The duration of the procedure ranges from a few days to perhaps a thousand years. This is how crystals commonly develop in the crust of the Earth. These crystals were created in the Earth's crust more than a million years ago. They happened as the Earth's liquid consolidated. The most frequent form of solid material is the crystal because of its uniform atomic structure. Crystals were formed on the surface of the earth through intense Crystals are not new to mankind, as they exist in the ancient period. Many cultures have made use of salt crystals for cooking and other things. Under direct sunlight, seawater was evaporated to produce these salt crystals.

The Ancient Egyptians used lapis lazuli, turquoise, carnelian, emerald, and clear quartz in their jewelry. They employed some crystals for beauty purposes, such as using malachite or galena as eye makeup, and some stones for protection and health. Crystals are not new to mankind, as they exist in the ancient period. Many cultures have made use of salt crystals for cooking and other things. Under direct sunlight, seawater was evaporated to produce these salt crystals. The Ancient Egyptians used lapis lazuli, turquoise, carnelian, emerald, and clear quartz in their jewelry. They employed some crystals for beauty purposes, such as using malachite or galena as eye makeup, and some stones for protection and health. Without the use of crystals, there is no modern technology that would be even remotely as effective. Without crystals, there would be no electronic industry, no photonic industry, and no fiber-optic communications, which depend on materials/crystals in the field of semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid-state lasers, non-linear optics, piezoelectric, electro-optic, acoustic-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries.

In recent years, Crystal growth has drawn more attention because of the rising need for materials for technological applications. Quartz crystals are widely used in gadgets like cell phones, television receivers, and, of course, watches and clocks. Sandpaper is manufactured from garnet crystals. For grinding wheels and strong sandpaper, corundum crystals are utilized. Drill bits and saw blades used to cut through rock contain diamond crystals. Calcite crystals are ground up and used to make Tums and heated to make cement. Plaster is made by heating gypsum crystals. Halite (salt) crystals are employed in a variety of industrial chemical processes and on food. Iron ore is composed of magnetite and hematite crystals. Ruby crystals were used in the earliest red lasers. Even in this modern civilized world, decorations such as rings, necklaces, bracelets, and other cosmetic jewellery made of Diamond, Sapphire, and Ruby are coveted and cherished possessions. The tiny twist is that these crystals can now be created and grown in laboratories.

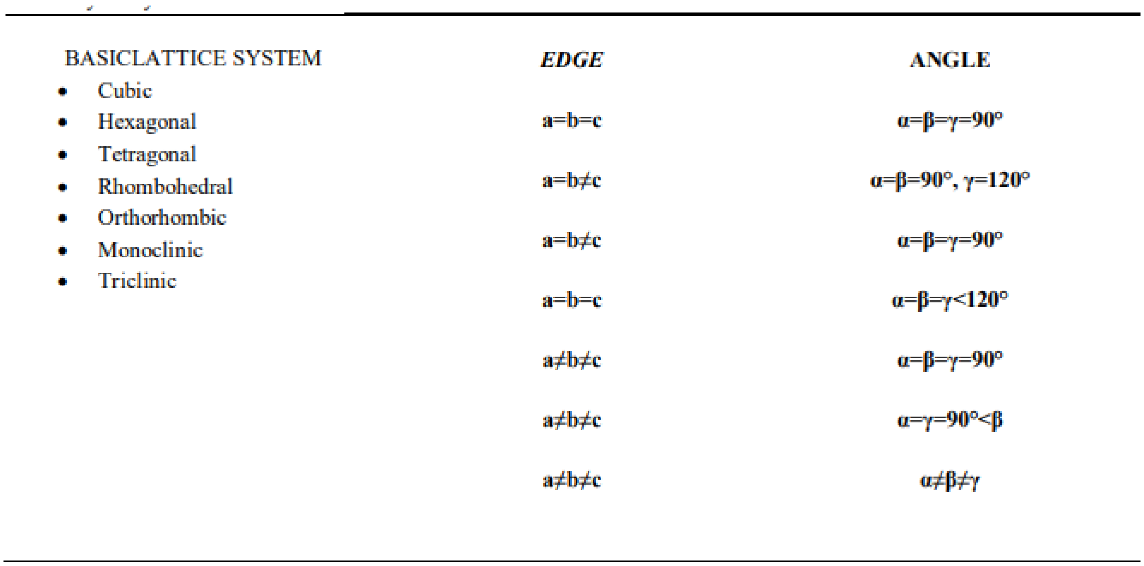
Crystal structure

A crystalline solid is created by repeating its building blocks (unit cells) in a three-dimensional periodic pattern on a regular basis. A unit cell is a building block of the crystal structure that explains the full crystal structure and symmetry with atom locations and major axes in detail. Lattice constants or lattice parameters are the length, edges of major axes, and angle between unit cells. The crystal systems are formed by these characteristics. A Crystal System is one of the many different types of crystals, space groups, and lattices. Crystals and space groups are classified into seven crystal systems based on their point groups.

The Seven Crystal Systems approach to classification is based on lattice and atomic structure. The atomic lattice is a collection of atoms arranged in a symmetrical arrangement. The lattice can be used to determine the appearance and physical qualities of the stone.

The seven crystal systems are as shown in Table 6.1:

Table 6.1: The seven crystal systems.



BASICLATTICE SYSTEM	***EDGE***	**ANGLE**
Cubic	**a=b=c**	**α=β=γ=90°**
Hexagonal	**a=b≠c**	**α=β=90°, γ=120°**
Tetragonal	**a=b≠c**	**α=β=γ=90°**
Rhombohedral	**a=b=c**	**α=β=γ<120°**
Orthorhombic	**a≠b≠c**	**α=β=γ=90°**
Monoclinic	**a≠b≠c**	**α=γ=90°<β**
Triclinic	**a≠b≠c**	**α≠β≠γ**

The crystal system is critical for distinguishing different minerals such as graphite and diamond. Both are crystals of carbon molecules, but we can tell them apart by how the components are packed together and the orientation of the unit cells and lattice plane.

Properties of crystals

Since crystals have highly ordered arrangements of atoms and molecules. They have -

1) Firm structure.

2) Hold a definite and fixed shape.

3) Rigid and incompressible.

4) Have geometric shapes and flat faces.

5) They have definite heat of fusion.

6) When cutting with a sharp edge, the two new halves will have smooth surfaces (Cleavage Property).

7. Due to strong intermolecular interactions, the gaps between the atoms are relatively small. As a result, crystals with high melting and boiling points are formed.

8) The intermolecular force is also consistent across the structure. Crystals exhibit long-range order, which indicates that the atom arrangement is repeated over a long distance. A crystal has the same structure, orientation, and lattice characteristics along its entire length.

9) Nature is anisotropic. The magnitude of physical qualities (such as refractive index, electrical conductivity, thermal conductivity, and so on) varies with crystal orientation.

Types of solid materials**:** Solids are generally distinguished as (Figure 6.1).

- Single crystalline
- Polycrystalline
- Amorphous

The length scale across which the atoms are associated to one another by translational symmetry, i.e. periodicity or long-range order, is the basic difference between single crystal, polycrystalline, and amorphous materials. Polycrystals have local periodicity, while single crystals have unlimited periodicity. Amorphous materials have no long-range order.

An perfect single crystal has an atomic structure that repeats itself on a regular basis throughout its whole volume. Translational symmetry connects each atom in the structure to every other equivalent atom even at infinite length scales.

A polycrystalline solid is made up of numerous different grains or crystallites. Each grain can be viewed as a single crystal having long-range order in its atomic structure. There is no link between neighbouring grains in an isotropic polycrystalline material. As a result, there is no periodicity across a polycrystalline sample on a large enough length scale.

Because amorphous materials, such as window glass, lack long-range organisation, they lack translational symmetry. The spacing between atoms in the structure are determined at random.

Only crystals have long-range order, whereas liquids and amorphous materials have short-range order that fixes the distances between atoms.

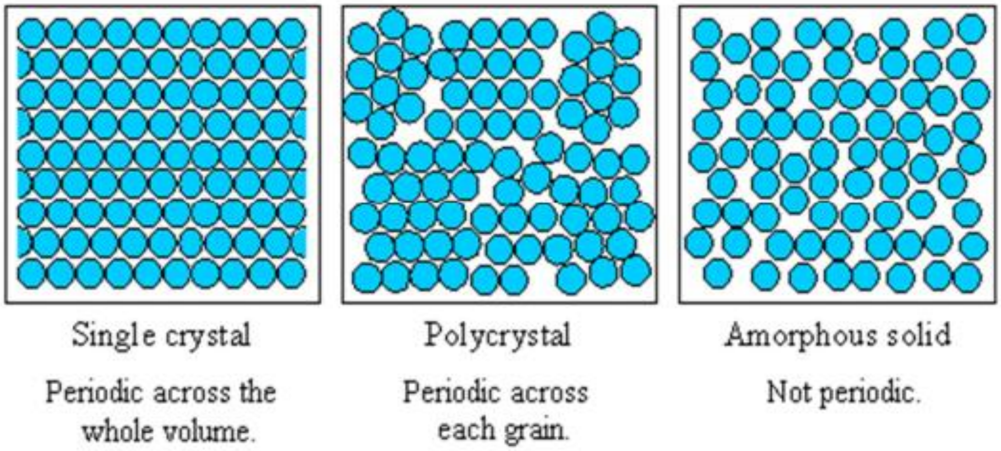


Figure 6.1: Types of solid materials.

A. ***Single Crystalline***

A single crystal frequently has distinct flat faces as well as some symmetry. The actual shape of the crystal is determined by parameters such as temperature, pressure, material properties, and others. The angles between the faces will be material-specific and will define an optimal shape. Depending on the nature of the material and how it was created, the properties of crystalline samples might be fully isotropic or significantly anisotropic.

B. ***Poly Crystalline***

Polycrystalline materials are solids made up of several tiny crystals known as grains. Grain boundaries separate the grains, which have arbitrary crystallographic orientations. The lattice arrangement of atoms within each grain is nearly same, but the atom orientation varies for each adjoining grain. The grain border is the surface that separates neighbouring grains.

C. ***Amorphous***

Amorphous solids, which lack the three-dimensional long-range order of crystalline materials, have a more random arrangement of molecules, short-range order across a few molecular dimensions, and physical properties that differ greatly from those of their crystalline counterparts. Amorphous solids, like liquids, lack an orderly arrangement of atoms or ions in a three-dimensional structure. These materials do not have a distinct melting point, and the solid-to-liquid change takes place across a wide temperature range. Amorphous solids' physical properties are generally isotropic, meaning they do not rely on the direction of measurement and have the same magnitude in different directions.

6.4 Single crystals

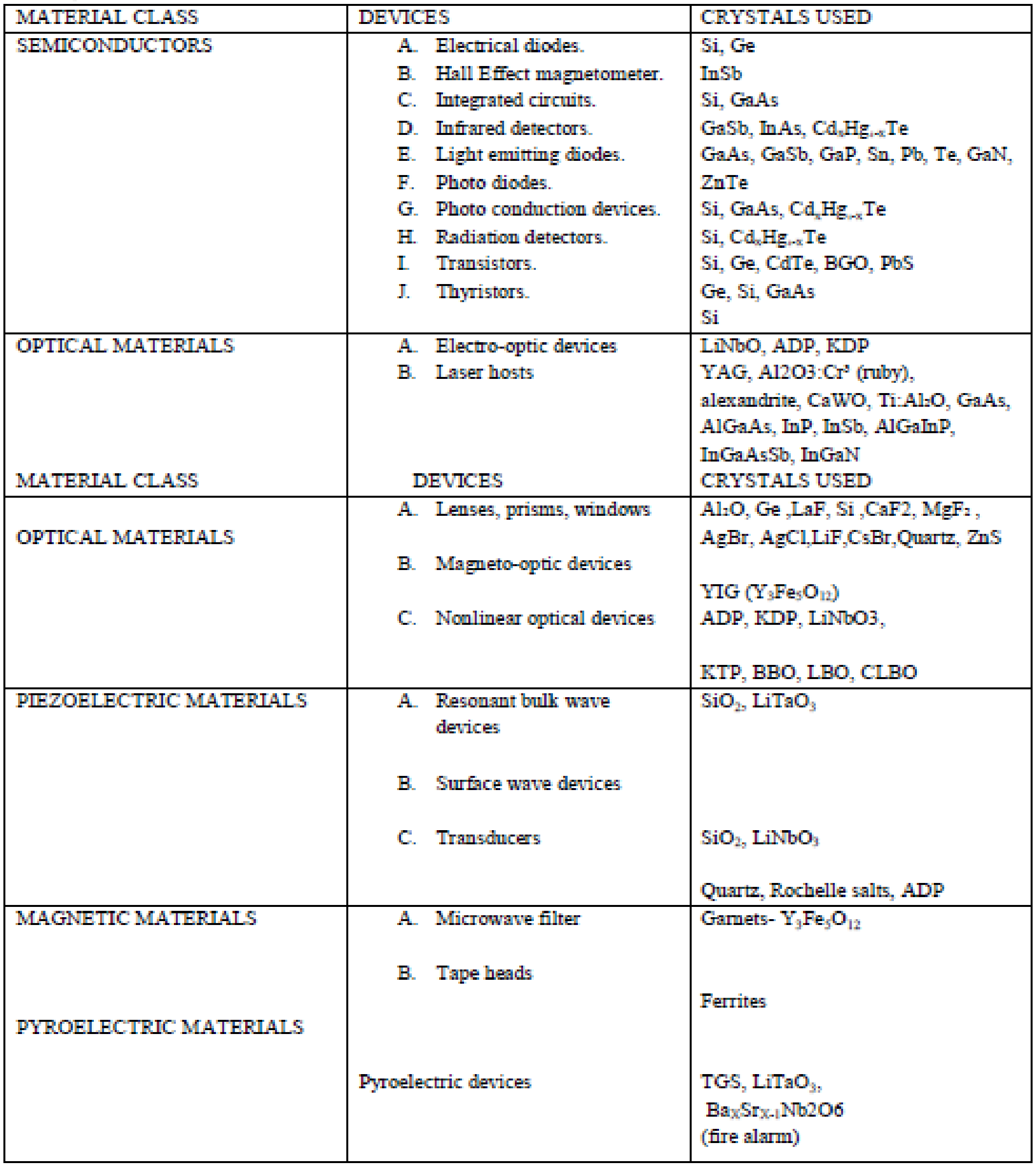
A single crystal is a mixture of components that can be produced into an item that is essentially a single enormous "grain," i.e., one continuous crystal. The crystal structure of a single crystalline material is nearly flawless, and the arrangement of the atoms or molecules is strictly ordered. The crystal lattice is continuous across the sample, with no grain boundaries. The absence of defects associated with grain boundaries can provide crystals with unique properties, including mechanical, optical, and electrical capabilities that can also be anisotropic depending on the type of crystallographic structure. Single crystals are useful in research and development. Single crystals, according to some researchers and scientists, are real solids since they have few to no defects. As a result, knowledge of the physics and chemistry of solid-state single crystals is required. For many research, polycrystalline samples can be used instead of single crystals, but single crystals are often preferable. Poly crystals, as we know, have grain boundaries. The effect of grain boundaries will be included in the analysis of a material's bulk property if measured on a polycrystalline specimen. Electrical conductivity, which is extremely impurity sensitive, is one such example where single crystals are crucial. Impurities tend to segregate at grain boundaries, blocking current flow. As a result, single crystals are usually always required to determine any conductivity measurement. Light scattering is another typical impact of grain boundaries and accompanying voids, hence single crystals are necessary in optical research as well (Table 6.2). Many properties of crystals are affected by the crystallographic direction in which they are measured, because the spatial arrangement of the constituent atoms is not uniform in all directions. As a result, determining a directionally dependent property in a polycrystalline specimen with randomly oriented crystallites yields merely an average value of the property, masking the directional dependency. Single crystals have numerous technological applications. In quartz oscillators, for example, single-crystal quartz has substantially superior frequency stability than polycrystalline samples. Oriented single crystals are generally used in nonlinear optical conversion techniques.

There are two primary reasons for the deliberate use of single crystal.

1) The effects of grain boundaries conceal or complicate many physical properties of solids.

2) Only if the whole internal symmetry of the crystal structure is preserved throughout the sample can the full spectrum of tensor interactions between applied physical cause and observed effect be obtained.

Table 6.2: Different types of material class.



MATERIAL CLASS	DEVICES	CRYSTALS USED
SEMICONDUCTORS	A. Electrical diodes. B. Hall Effect magnetometer. C. Integrated circuits. D. Infrared detectors. E. Light emitting diodes. F. Photo diodes. G. Photo conduction devices. H. Radiation detectors. I. Transistors. J. Thyristors.	Si, Ge InSb Si, GaAs GaSb, InAs, $Cd_xHg_{1-x}Te$ GaAs, GaSb, GaP, Sn, Pb, Te, GaN, ZnTe Si, GaAs, $Cd_xHg_{1-x}Te$ Si, $Cd_xHg_{1-x}Te$ Si, Ge, CdTe, BGO, PbS Ge, Si, GaAs Si
OPTICAL MATERIALS	A. Electro-optic devices B. Laser hosts	LiNbO, ADP, KDP YAG, Al2O3:Cr^{3} (ruby), alexandrite, CaWO, Ti:Al_2O, GaAs, AlGaAs, InP, InSb, AlGaInP, InGaAsSb, InGaN
MATERIAL CLASS	DEVICES	CRYSTALS USED
OPTICAL MATERIALS	A. Lenses, prisms, windows B. Magneto-optic devices C. Nonlinear optical devices	Al_2O, Ge ,LaF, Si ,CaF2, MgF_2 , AgBr, AgCl,LiF,CsBr,Quartz, ZnS YIG ($Y_3Fe_5O_{12}$) ADP, KDP, LiNbO3, KTP, BBO, LBO, CLBO
PIEZOELECTRIC MATERIALS	A. Resonant bulk wave devices B. Surface wave devices C. Transducers	SiO_2, $LiTaO_3$ SiO_2, $LiNbO_3$ Quartz, Rochelle salts, ADP
MAGNETIC MATERIALS PYROELECTRIC MATERIALS	A. Microwave filter B. Tape heads Pyroelectric devices	Garnets- $Y_3Fe_5O_{12}$ Ferrites TGS, $LiTaO_3$, Ba_XSr_{X-1}Nb2O6 (fire alarm)

6.5 Why crystals should be grown artificially

Natural crystals are not as pure as lab-made or artificially generated crystals. We could change the composition of crystals by growing them in labs and other artificial means to suit our needs. The orientation of atoms and molecules influences crystals' physical, optical, and chemical properties. Crystals created in the lab can have their orientation, lattice characteristics, and elemental makeup changed, whereas naturally occurring crystals cannot.

Organic crystals are generally polycrystalline, making them unsuitable for semiconductor and other technological applications; this is where artificially lab-grown crystals make a significant contribution. Depending on the requirements, lab-grown crystals might be single or polycrystalline. The crystal growing industry is worth billions of dollars. With the advancement of technology and customer demand for computing gadgets, the crystal growth business will continue to increase.

6.6 Single crystal

Single crystals are one of the most important groups of materials due to their continuous, uniform, and highly-ordered structure which enables them to possess unique properties. In many aspects, single crystal materials can be found to be advantageous over polycrystalline materials, and many properties which are found in single crystals cannot be replicated in polycrystals. Currently, even with the technological developments of advanced polycrystalline materials which are designed for specific applications, the electrical, optical, thermal, mechanical, and other properties of single crystals still remain superior. For these reasons, it is not surprising that single crystals, and the methods for their fabrication, are a topic of interest among many researchers.

Single crystals have found extensive use in optical, electronic, optoelectronic, and other applications. Specifically, single crystal semiconductors are one of the most widely researched and used materials. These materials have been applied for various electronic and optoelectronic devices and components, such as light-emitting diodes (LEDs), photodetectors, wide-bandgap devices, high-power lasers, consumer electronics, and more. For example, current computer chip production is not possible without high-quality single crystal silicon (Si) wafers. Due to their outstanding optical and electronic properties, single crystals of III–V semiconductors, such as GaAs, GaN, InP, InAs, and others, are an integral part of devices for application in fiber-optic communication, wireless and satellite communication, solid-state lighting, and more. The importance of single crystal alumina, also known as sapphire, as well as yttrium aluminum garnet (YAG), for laser materials has also been demonstrated through numerous applications. Sapphire has been used in the electronics industry both as a passive substrate material and active device (e.g. silicon-on-sapphire); likewise, it is used for rocket domes, optical data storage, radiation detection, LED devices, optical windows, and other applications. On the other hand, YAG single crystals, and especially Nd^{3+}-doped YAG, are known for their important application in solid-state laser devices, such as waveguide lasers and single crystal fibers for high-power lasers, as well as scintillation crystals, and others. Piezoelectric single crystal materials, which were initially developed and utilized as transducers for sonar devices and medical ultrasonic diagnostic devices, have also been applied in sensors, actuators, medical transducers, energy harvesters, and more. As it can be seen, single crystal materials are capable of covering a wide variety of applications, which range from scientific- and research-related to daily life.

Another important use of single crystal materials is as substrates for films of different materials; this enables a whole new collection of applications. Single crystals can be used not only as a mechanical support or a surface at which layer or layers of materials are being deposited but can also act as a single crystal seed during epitaxial growth, when the deposited film takes on orientation of the substrate, and sometimes even a lattice structure. Likewise, the fabrication of single crystal epitaxial films on various substrates, which are a vital part of a wide range of devices for electronic, optoelectronic, magneto-optic, and many other applications, although very challenging, is an important goal in the thin film industry due to the numerous advantages of single crystal films.

As technological development increases, the need for high-quality single crystal materials, both in bulk and in thin films, grows simultaneously. The availability of various single crystal materials has enabled the development of a new generation of electronic, optical, optoelectronic, and other devices. However, growth of high-quality single crystals, with stable and reproducible quality, low defect density, with various chemical compositions and sometimes even extreme thermodynamic properties is still one of the greatest challenges today. Furthermore, techniques which are currently used for growing single crystals experience many processing-related difficulties despite the technological advancements made throughout the years. Therefore, a high demand for various single crystal materials has imposed a need for improving the growth techniques that are currently used as well as developing new, alternative single crystal growth techniques.

6.7 Single crystal growth theory and techniques

6.7.1 GIBBS Surface Energy Theory

Gibbs developed the first quantitative theory of crystal formation based on thermodynamic principles. According to surface theory, the growing crystal takes on a shape with the lowest surface energy, i.e. the total free energy of a crystal in equilibrium with its surroundings under constant temperature and pressure is the lowest for a given volume. Taking the amount of free energy per unit volume throughout the crystal as constant, the condition becomes. Where σ_i is the surface free energy per unit area of the i^{th} face of area F_i, on a crystal bounded by n faces. Thus, only those faces will develop that lead to a minimum total surface free energy for a given volume.

6.7.2 Phase Transition

With a small change in temperature, one or more physical properties change. A change in a thermodynamic parameter, such as temperature, pressure, volume, or magnetic field, causes a phase transition. The most common cause of a phase transition is a change in temperature. There are six phase transitions between matter's three states. Endothermic reactions, such as melting, vaporisation, and sublimation, require heat to overcome intermolecular interactions. Ice melting and water boiling are common instances of phase transitions, as is the change of graphite into diamond at high pressures.

6.7.3 Nucleation

Nucleation is a critical phenomenon in crystal formation since it is the prior to crystal growth and the entire crystallisation process. Nucleation is simply defined as a change in free energy that occurs during the creation of a cluster in a new phase when a few atoms or molecules link together. Nuclei are clusters of such atoms or molecules that have the ability to permanently develop into bigger sized crystals. The formation of a new phase is a highly localised phenomena caused by system fluctuations that bring together a sufficient number of atoms or molecules to form a stable size. Many natural phenomena occur as a result of nucleation, the most common of which being the creation of raindrops. A nucleation event is the starting point for all natural and artificial crystallisation processes. Nucleation often happens at nucleation sites on surfaces that come into touch with the liquid or vapour. Nucleation sites can also be found in suspended particles or minute bubbles. This is referred to as heterogeneous nucleation. Homogeneous nucleation refers to nucleation without favoured nucleation locations. Process of nucleation is shown in Figure 6.2.

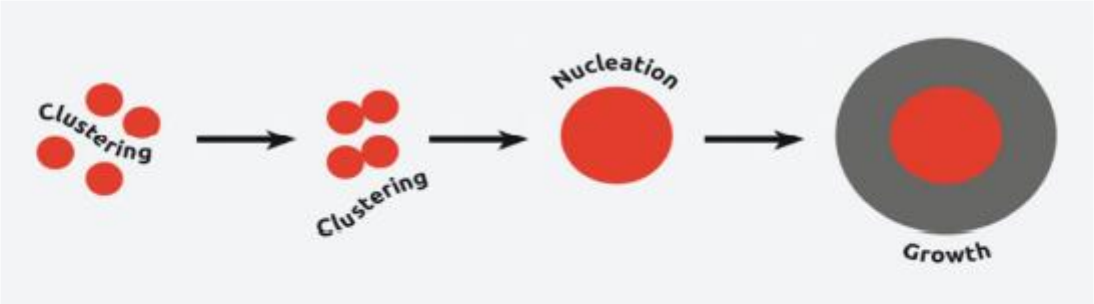


Figure 6.2: Process of nucleation.

6.7.4 Super Saturation

A supersaturated solution has more dissolved solute than a saturated solution and can be made by boiling a saturated solution, adding extra solute, and then slowly chilling it.

The super saturation of the gas or liquid phase with respect to the component requiring growth is the driving factor for crystallisation. A low saturation level will result in an excessively slow growth rate. At the other end of the supersaturation range, the rate of condensation surpasses the rate at which atoms or molecules can be incorporated onto the crystal lattice, causing the single crystal interface to fail and non-uniform cell growth to begin (Figure 6.3).

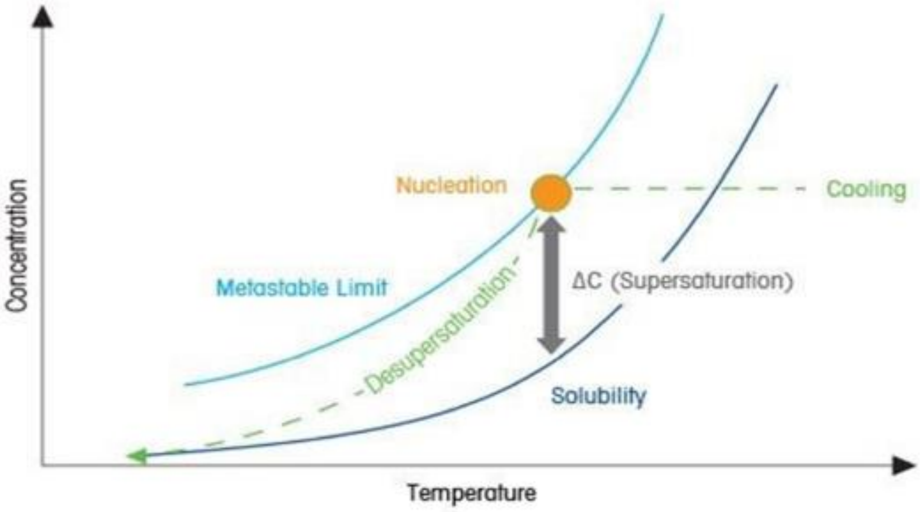


Figure 6.3: Process of supersaturation.

6.8 Single crystals growth

Crystal growth is a multidisciplinary field that includes physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, and other disciplines. There has been an increase in interest in crystal growth procedures over the last few decades, notably with the increasing demand for materials for technological applications. Crystal growth techniques range from simple and inexpensive to complex and costly, while crystallisation times range from minutes to hours, days, and months. Single crystals can be formed by transporting crystal elements in the solid, liquid, or vapour phases.

Crystal growth requirements:

Crystal growth from liquid and gaseous solutions, pure liquids, and pure gases can only occur if the system first achieves some degree of super saturation or super cooling. The supersaturated state is required for any crystallisation operation, and the degree of super saturation or divergence from the equilibrium saturated condition is the primary governing factor of the deposition process. Crystal growth can be used to compress these phases.

1. Attaining super saturation or super cooling.

2. The formation of a tiny crystal nucleus.

3. Crystal development in stages to produce distinct faces.

On the basis of this, crystal growth may be classified into three categories as follows,

Crystal growth techniques:

1) Growth from the solid phase.

2) Growth from the melts.

3) Growth from the liquid solution.

4) Growth from the vapour phase.

6.8.1 Growth from the solid phase

Solid-state single crystal growth (SSCG) is a process for growing crystals from a polycrystalline matrix. The single-crystal seeds started the growth of single crystals, which continued as the surrounding polycrystalline matrix was transformed into a single crystal. External pressure was shown to be useful during the procedure for lowering the porosity of the generated single crystal. Some grains grow larger than others during solid-phase growth.

6.8.2 Growth from the melts

Melting and resolidification are used to grow single crystals in melt growth. When a liquid is cooled below its freezing point, crystalization occurs. Apart from possible contamination from crucible materials and the surrounding atmosphere, no contaminants are introduced into the development process with this technique, and the rate of growth is typically significantly higher than in other procedures. Melt growth is the most common commercial method of crystal development.

The growth from melt can further be sub-grouped into various techniques –

- Czochralski method.
- Brigmann method.
- Vernuil method.
- Zone melting method.
- Skull melting

Czochralski Process

Jan Czochralski, a Polish physicist, created this procedure in 1915. The Czochralski method involves extracting a crystal from the melt against gravitational forces. The Czochralski method is well-known for producing large-scale single crystals of semiconductors, metals, salts, and gemstones. The most important application of this technology is the creation of semiconductors, notably single crystalline silicon, which cannot be grown easily using other methods. Silicon is a particularly essential material because of its many desired features; it is abundant and inexpensive, dependable, and has good semiconducting capabilities. Czochralski crystal growth process is shown in the Figure 6.4. The shape of the crystal in the Czochralski technique is not constrained by the shape of the crucible. The charge is melted and kept at a temperature just over its melting point in this procedure. The pulling rod is lowered until it touches the melt. Because the rod is cooler than the melt, crystallisation occurs at the pointed tip of the pulling rod. The crystal is slowly drawn. The pace of pulling is affected by elements such as thermal conductivity, charge latent heat of fusion, and the rate of cooling of the pulling rod. To maintain the formed crystal consistent and cylindrical, the seed is rotated.

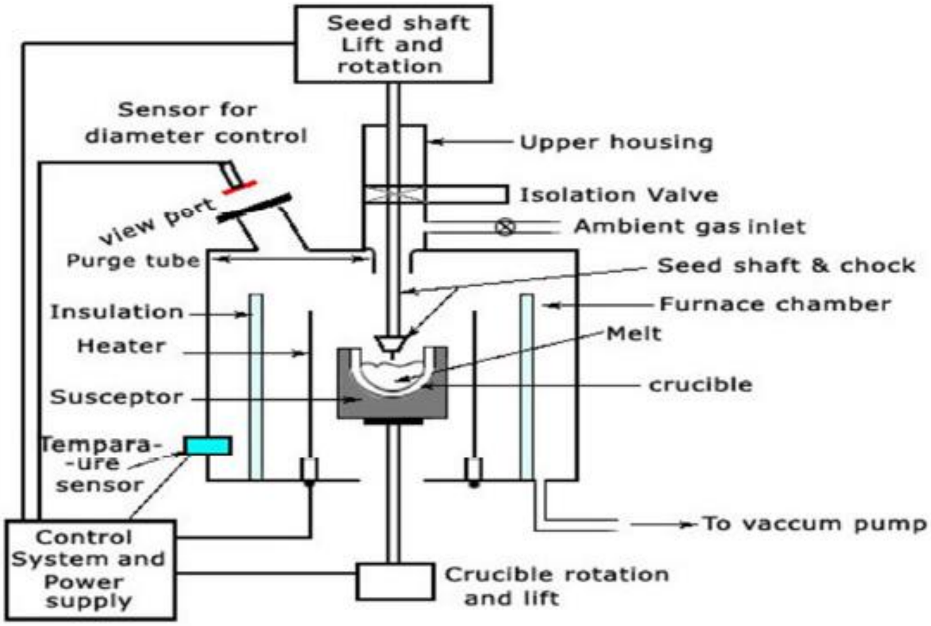


Figure 6.4: Czochralski crystal growth process.

a) Advantage: This technique is utilised to create big grain single crystals. As a result, it is widely employed in the semiconductor sector. Because there is no direct contact between the crucible walls and the crystal, a stress-free single crystal is produced.

b) Disadvantage: This approach is not suitable for incongruently melting compounds in general. The requirement for a seed crystal of the same composition limits its usage as an exploratory scientific research instrument.

Bridgman Method: This technique was named after its inventor Bridgeman in 1925, Stockbarger in1938. The Bridgman approach produces nucleation on a single solid-liquid interface by crystallizing in a temperature gradient environment (Figure 6.5). The crystallizing material is typically enclosed in a cylindrical crucible that is lowered via a temperature gradient in a vertical furnace. In other circumstances, the crucible is kept stationary in a furnace with a temperature profile that provides a linear gradient, and the furnace is subsequently pushed upward. In either case, an isotherm normal to the crucible's axis is gently moved through the crucible, causing the melt-solid contact to follow it. The entire material in the crucible is first melted and homogenized. If the crucible has a flat bottom, the first nucleation will be numerous crystallites at the bottom of the crucible when solidification begins. However, by appropriately altering the geometry of the crucible bottom, one of these crystallites can be made to dominate the solid-liquid interface. The stated shape is the most widely used and simplest crucible shape, with the bottom of the crucible having a conical tip, so that the melt first solidifies only in a small volume. As a result, only one or a few nuclei are created.

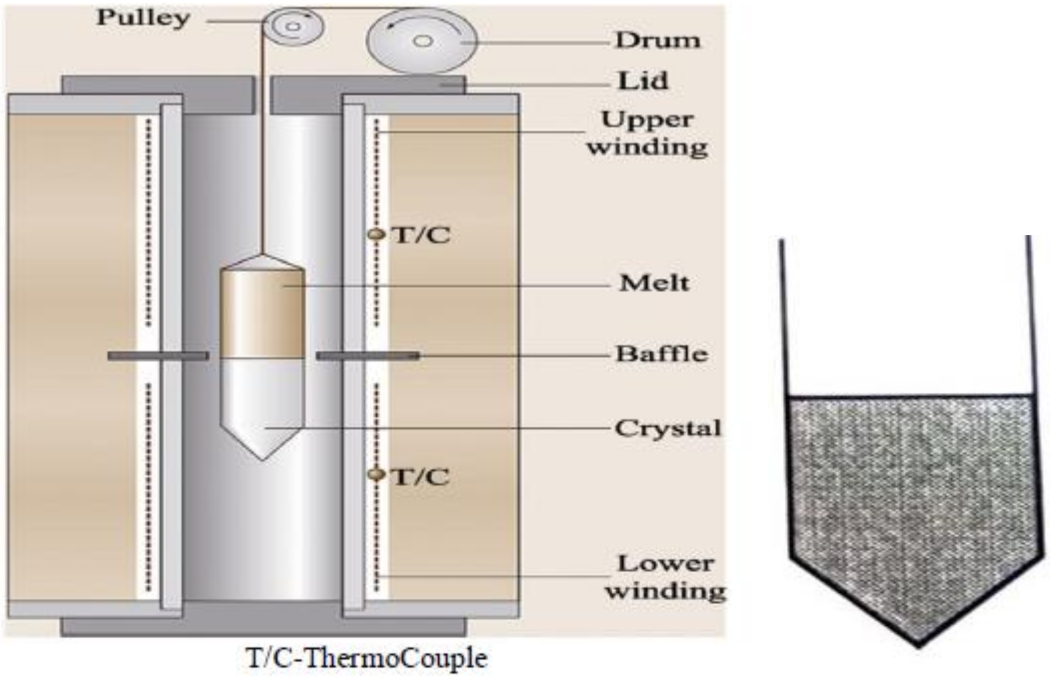


Figure 6.5: Bridgman Method crystal growth process.

Advantage:

- The Bridgman method's key advantage is its simplicity and ease of application.
- This approach provides for high growth rates and the formation of dislocation-free crystals.
- Choosing the right container can result in a crystal with a predetermined diameter.
- The Bridgman method can be altered to meet the material needs.

Disadvantage:

The compression of the solid during cooling by the contracting container can result in the formation of stresses strong enough to nucleate dislocations in the material.

Vernuil method:

The following is the basis of Vernuils method. Chemically pure fine powder which emerges through an Oxygen-hydrogen flame and falls onto the fused end of an oriented single crystal seed fixed to a lowering mechanism. A sophisticated tapping mechanism feeds the powder charge from bankeei. Coordination of the charge, hydrogen, and oxygen consumption with the rate of fall of the seed ensures crystallisation at a predetermined level of the device.

Advantage:

- The lack of a container avoids the problem of physical-chemical interaction between the melt and the container material.
- It is technically straightforward, and crystal formation can be observed.
- This procedure can be used to create a single crystal of ruby, sapphire, or other gemstone. This process can generate single crystals in a variety of shapes such as plates, discs, hemispheres, and cones.

Zone Melting Method: In this technique a liquid zone is created by melting a small amount of materials in a relatively large or long solid charge. Zone melting techniques basically enable one to manipulate distribution of soluble impurities or phases through a solid.

Advantage:

1. Zone melting technique is that impurities tend to be concentrated in the melted portion of the sample.
2. The process sweeps them out of the sample and concentrates them at the end of the Crystal bowl, which is then cut off and discarded.
3. Thus this method is sometimes used to purify semiconductor crystals.

Skull Melting Process:

The skull melting method is used to create high melting point materials. A radio-frequency "Skull crucible" system, a specialised melt technique, is used to create cubic zirconium. This is a super-hot melt method used to create the most generally acknowledged diamond substitute: cubic zirconia (cz). The major component of cubic zirconias, zirconium oxide, has an extraordinarily high melting point (4980'F). Conventional (low) melt crucibles are ineligible. As a result, a crucible-free process is unavoidable. Zirconia up to 10 cm long is produced using the Skull melting technique.

3) Growth from the vapour phase

a) ***Chemical Vapour Deposition:*** Chemical vapour deposition is the deposition of a solid on a heated surface as a result of a vapor-phase chemical reaction. It is an atomistic vapor-transfer process, which implies the deposition species are atoms, molecules, or a combination of these.

b) ***Physical Vapour Deposition (PVD):*** PVD is primarily a vaporisation coating process that involves the transfer of material onto the substrate. The technique is similar to chemical vapour deposition in that the raw materials/precursors, i.e. the material to be deposited, begin in solid form, whereas in CVD, the precursors are delivered to the reaction chamber in gaseous form.

c) Applications

- Metallurgical coating industries.
- Semiconductor and microelectronic industries.
- Telecommunications optical fibres.
- Wear-resistant coatings, corrosion-resistant coatings, heat-resistant coatings. High-temperature material preparation.

c) Applications

- Reactive gases are hazardous and must be handled with care.
- The uniformity of the deposition is difficult to control.
- Deposition occurs on both the substrate and the container walls. This makes cleaning harder.

6.8.4 Growth from the liquid solution

In this method, Crystals are grown from aqueous solution. This method is also widely practiced for producing bulk crystals. The four major types are

A. Low temperature solution growth.

B. High temperature solution growth.

C. Hydro Thermal growth.

D. Gel Growth.

6.9 Zone refining

Zone refining is a very useful method to get metals with high purity such as silicon and germanium. It is also referred to as zone melting, floating zone process, and travelling melting zone.

What is zone refining?

Zone refining is a modern technique to get the purest form of crystals from the impure elements specifically for the metals by using melting and crystallization processes. In this method, a narrow region of the crystal is first heated so that all the impurities get melted and forms a layer of the molten zone which moves along the areas of the crystal.

Zone refining is normally referred to as the method of purifying a crystal where there is a thin region of the crystal that undergoes a melting process. The molten zone formed is now moved across the crystal.

The impurities present in the metal are melted at the forward edge in the molten zone process and moved through the block of metal. The solidified pure element is left as residues behind in the process.

As they move through the block of metal, the impurities in the metal are concentrated in the melt and are transported to one end of the metal block (Figure 6.6).

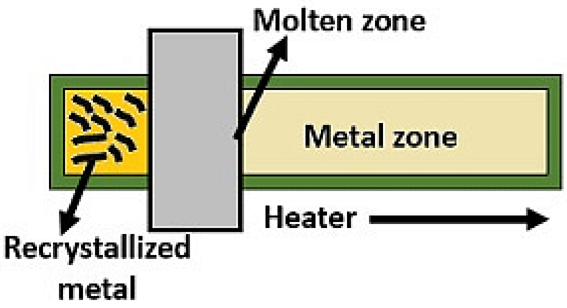


Figure 6.6: Zone Refining.

6.9.1 Principle of Zone refining

The principle of zone refining is that the impurities in an ingot or ore of metal are more soluble in the melt state when compared to the corresponding solid-state of the impurities.

In the zone refining process, the impurities are concentrated at one end of the block of metal so that the rest of the block is purified. It can be noted that the segregation coefficient (which is defined as the ratio of impurity in the solid-state to the impurity in the liquid or melt state) is generally less than 1.

This implies that when the conditions are set at the solid-liquid boundary, the atoms of the impurity tend to diffuse into the liquid region.

6.9.2 Process of Zone refining

In the zone refining process, a circular mobile heater is attached at one end of the impure metal rod (Figure 6.7). The circular mobile heater is now slowly pushed across the metal rod.

The metallic impurities melt in this heater's transient position. The impurity-containing melt advances along with the heater through the whole length of the metal rod. As the heater advances along the rod, the pure metal is allowed to solidify.

As the heater moves forward, the concentration of the impurities in the melt increases. This is because the impurities are more soluble in their corresponding melt state. Finally, the impurities are accumulated at one end of the metal rod.

The technique mentioned above is performed numerous times in the same direction. The end of the rod where the impurities have now gathered is cut off, leaving only the pure metal. As a result, the metal in its pure form is obtained. This method is particularly effective in removing impurities from semiconducting elements such as germanium, gallium, and silicon. This method is also employed in the refining of high-purity metals.

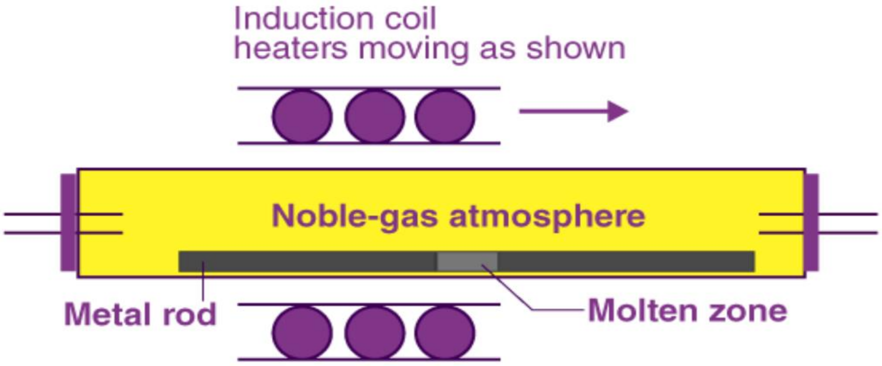


Figure 6.7: Process of Zone refining.

Applications of Zone Refining Process

- The zone refining process is normally used to get the purest form of elements. (Specifically the metals such as Germanium and Silicon)
- It is a commonly very effective process in the removal of impurities from semiconductors such as Ge (Germanium), Ga (Gallium), and Si (Silicon).
- Float zone refining or the Zone refining process is used in making the solar cells.
- The process is also used to make a single layer of crystal.
- The process is used for finding the organic and inorganic compounds as well.
- It is highly useful in preparing organic chemical standards for HPLC, absorbance, or fluorescence spectroscopy.
- The process is very useful for all those analytical methods that require the highest purity for standardizing or calibrating instrumentation.
- It is used for the process of crystallization to concentrate an enzyme, peptide, antibiotic, or any other thermally unstable substance.
- The process is used in the concentration of the heat-labile biological materials in preparation of the aqueous solution.

Limitations of Zone Refining Process

There are some limitations zone refining. Some of the limitations are shown below.

- Zone refining is a very costly process.

- Its applications are restricted to research facility reagents and important synthetics.
- Zone refining process is not carried out effectively when strong-fluid equilibrium isn't good for the impurities.
- It is required to combine zone refining with other techniques to get a high form of purity.

6.9 Doping

A semiconductor is a substance, usually a solid chemical element or compound that can conduct electricity under some conditions but not others, making it a good medium for the control of electrical current. It has almost filled valence band, empty conduction band and very narrow energy gape of the order of 1 eV. Energy gap of Silicon (Si) and Germanium (Ge) are 1.0 and 0.7 eVrespectively. Consequently Si and Ge are semiconductors. Effect of temperature on conductivity of semiconductors: At 0 K, all semiconductors are insulators. At finite temperature, the electrical conductivity of a semiconductor material increases with increasing temperature. With increase in temperature, outermost electrons acquire energy and hence by acquiring energy, the outermost electrons leave the shell of the atom. Hence with increase in temperature, number of carriers in the semiconductor material increases and which leads to increase in conductivity of the material.

Elemental and Compound Semiconductor:

***Elemental Semiconductor*:**

Semiconductors which are contributed by a single species of atoms are called elemental semiconductors. e.g. Silicon, germanium, calcium

***Compound Semiconductor*:**

Semiconductors which are contributed by two or more different species of atom is called compound semiconductors. e.g. Galium Arsenide (GaAs), Aluminium Arsenide (AlAs)

Compound semiconductors again classified in two types:

1. Binary Compound Semiconductor:

These types of semiconductors consists of two species of atom.

Galium Arsenide (GaAs)

Indium phosphide (InP)

2. Ternary Compound Semiconductors:

These types of semiconductors consists of three species of atom.

Galium Arsenide phosphide (GaAsP)
Aluminum Arsenide phosphide (AlGaP)

Preparation of Semiconductors: For preparing semiconducting devices, the basic materials such as Si and Ge must at least 99.99 % pure. Consequently extreme precautions have to be taken during the preparation of these elemental semiconductor materials. Various steps followed during the preparation of highly pure materials are as follows:

Preparation of pure Ge/Si: This is carried by using the following methods:

1. Distillation: It is based on the separation of materials due to difference in boiling points. The starting raw materials employed are germanium tetrachloride and trichloro silane for the preparation of pure Ge and Si respectively.

For example $GeCl_4$ (b.p.83.10C) is taken in a series of distillation stills and a layer of HCl placed over the charge, which facilitates in the removal of as (usually present as an impurity). Chlorine gas is then passed through the charge, which is heated electrically. The vapours passing through the fractionating column finally distils over in a receiver, kept in an ice bath. Pure $GeCl_4$ so obtained is then treated with extra pure water to get germanium oxide which is subsequently reduced (in an atmosphere of hydrogen) to get elemental Ge, which is subjected to further purification. Similarly, distilled trichloro silane ($SiHCl_3$) is employed to get silicon of high purity.

2. Zone refining:

The zone refining technique involves melting a narrow zone of long ingot of the material to be processed. This molten zone is then slowly moved by moving the heater gradually along the length of the ingot in one direction. This process is repeated multiple times till the required purity level is reached. In this process difference between solubility of impurities in the molten and solid phases is used to concentrate impurities at the end section of the ingots.

This method is particularly used when metals are required in high degree of purity. It is based on the principle that when an impure metal in a molten state is allowed to cool, only the metal crystallizes while the impurities remain present in the molten state (mass) or melt.

The impure metal converted into a rod which is heated at one end with a circular heater. A narrow zone of metal is melted. The heater is slowly moved along the rod. The pure metal recrystallizes out of melt while the impurities remain in the melt which moves along with the melted zone of the rod with the movement of heater. The process is repeated several times. The end of rod where impurities have collected is cut off. This method is employed for the purification of germanium, silicon, gallium etc., which are used in semi –conductors.

3. Czochralski Crystal pulling Technique:

Ge or Si obtained by zone refining method is polycrystalline, i.e., there is no regularity in their crystal structure and contain crystals of different sizes. But fabrication of most of the semiconductor devices requires single crystal of semi conducting materials. Consequently, theyare grown in the form of single crystals. This method involves growing the crystal on a single crystal seed; there by the atoms reproduce identical atomic arrangement as that of the seed crystal. In this process, solid polycrystalline semiconducting material is taken in a quartz chamber and heated by using RF power source, till it melts (Figure 6.8). Then the temperature is lowered to just above the melting point of Ge. At this stage, properly oriented single crystal of Ge, attached to a puller rod is carefully lowered into the melt, till it is in contact with the surface of the charge. Then the crystal is rotated slowly and then gradually pulled out so that the melt in contact with the seed crystal starts solidifying producing the orientation identical as that of the seed crystal. After this, the pull rate is kept at about 1.5 to 5 cm/minute and the rotation speed is maintained at about 100 rpm. Finally, an intrinsic crystal of Ge of 5cm diameter and 25 cm length is obtained. This crystal is tested for its conductivity and cut into wafers with the help of a diamond-tipped saw.

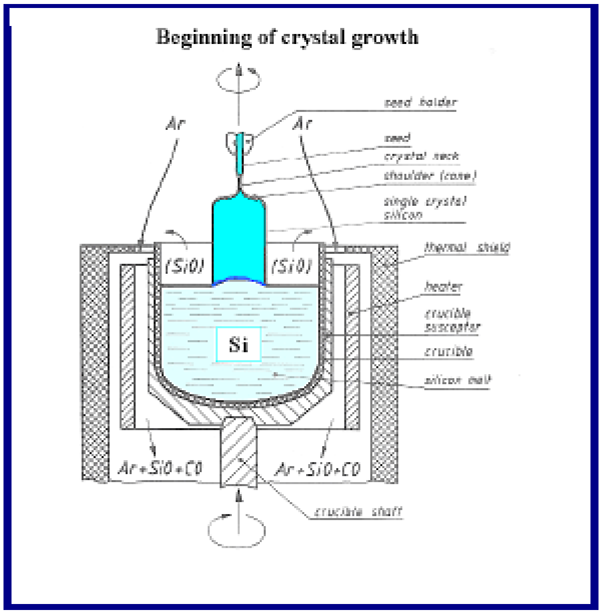


Figure 6.8: Czochralski Crystal pulling Technique.

Doping of Semiconductors

The addition of a small percentage of foreign atoms in the regular crystal lattice of silicon or germanium produces dramatic changes in their electrical properties, producing **n-type** and **p-type semiconductors**.

Pentavalent impurities

(5 valence electrons) produce n-type semiconductors by contributing extra electrons.

Trivalent impurities

(3 valence electrons) produce p-type semiconductors by producing a "hole" or electron deficiency.

6.11 Doping Techniques

For getting a doped material, calculated quantity of dopant (Boron or Phosphorus) is added to the melt before crystal pulling stage. Usually dopant atoms added are of the orderof one atom of B or P per 108 atoms of Ge or Si. Other methods of doping are:

6.11.1 Epitaxy

Involves in unified crystal growth or deposition of a thin crystal on another substrate, often with added dopants. The material in the epitaxial layer must have a little spacing and structure closed to that of the substrate. ex. Si on Ge or Ge on Si. The Si or Ge wafer (kept in graphite boat) is placed in a long cylindrical quartz tube reactor, which is then heated (by RF induction coil). Then gases containing compounds of Ge or Si mixed with calculated/appropriate quantities of dopant over the wafer results. The doped wafer so obtained is ready for the fabrication of semiconductor devices. It may be pointed out that for getting Si epitaxial film, $SiCl_4H_2$ and N_2 mixture is used. For carrying out n-type doping, this mixture is mixed with a calculated amount of phosphine (PH_3) and for p-type doping;Diborane (B_2H_6) is employed.

6.11.2 Diffusion technique

Involves in conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atom into the crystal lattice of the semiconductor material without any melting and it consists of heating a P-type dopant (Phosphorus or Stilbium). This causes some of the impurity atoms to condense on the surface of water and diffuse thereby resulting in a P-type semiconductor material.

By this technique, the extent of impurity atoms penetration can be controlled even less than a few millions of a centimetre by controlling the concentration of dopant atoms and temperature. This technique is especially employed for preparing n or p type semiconductors, used in very high frequency devices. This doping technique can also be used to prepare n-p-n type transistor with a base width of even 5 microns.

6.11.3 Ion implantation technique

Involves in bombarding the semiconductor material with an electrically controlled beam of high energy ions of B or P of 10000ev. This causes the implantation of some dopant atoms into the crystal lattice of semiconductor.

Main advantages of this technique are:

1. Implantation at low temperature
2. Extremely precise control of the dopant amount on desired specific semiconducting material
3. Obtaining deep or shallow regions of very precise and required penetration depths having high or low concentration of dopant. This technique is especially employed for the fabrication of high frequency devices.

Cutting into chips: the wafers obtained by above methods are then cut into chips by using methods such as chemical etching, ultrasonic vibrations, laser beams etc.

6.13 Summary

In this unit, you have studied about synthesis and preparation of nanomaterials. To present the clear understanding of topics, you have learn about the aspects of crystal growth. You have studied about the single crystal. We have discussed the importance of crystals grown artificially. You have also studied about the single crystal growth theory and techniques. In the unit, you have seen the various techniques of single crystals growth. You have also studied the detailed about the zone refining, principle and applications of zone refining. We have discussed different doping techniques of elemental and compound semiconductors. Many solved examples are given in the unit to make the concepts clear. To check your progress, self assessment questions (SAQs) are given place to place.

6.13 Glossary

Synthesis	Synthesis is the act of combining elements to form something new.
Zone Refining	Zone refining refers to the method of purifying a crystal wherein a thin region of the crystal undergoes melting.
Crystal Growth	Crystal growth is a major stage of a crystallization process, and consists of the addition of new atoms, ions, or polymer strings into the characteristic arrangement of the crystalline lattice.
Single crystalline	In a single crystalline solid, the regular order extends over the entire crystal.
Poly crystalline	The regular order only exists over a small region of the crystal, ranging from a few hundred angstroms to a few centimeters.
Nucleation	Nucleation is the process by which atoms or molecules come together to form a new phase or structure.
semiconductors	Materials which have a conductivity between conductors (generally metals) and non-conductors or insulators (such as most ceramics).
Impurities	The fact that a substance is dirty or lower in quality because it is mixed with another substance.
Doping	The addition of a small percentage of foreign atoms in the regular crystal lattice of silicon or germanium that produces dramatic changes in their electrical properties.

6.14 References

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2. Introduction to Crystal Growth and Characterization- Klaus-Werner Benz and Wolfgang Neumann.
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5. Theories and Techniques of Crystal Structure Determination -Uri Shmuel.
6. https://epgp.inflibnet.ac.in

6.15 Terminal Questions

Q 1: What is the basic principle of zone refining of metals?

Q 2**:** What is the basic applications of zone refining?

Q 3. How semiconductors are prepared by different techniques? Describe in detail.

Q 4**:** How single crystals are grown? Explain in detail.

Q 5. What do you mean by doping? Write down the different procedures of doing in semiconductors.

Q 6. What do you mean by Crystal Growth?

Q 7. Why single crystal is so important.

Objective Questions

1. Why is crystal growth important?

a) Increase the value of the product

b) Increase the size of the compound

c) Information about the structure of compounds

d) Information regarding the quality of product

2. What causes crystal growth?

a) Vapor

b) Solute

c) Melt

d) Vapour, Solution and melt

3. Which crystal grows the fastest?

a) Table Salt

b) Epsom salt

c) Ferro sulphate salt

d) Sea salt

4. Zone refining is based on the principle that:

a) Impurities of low boiling metals can be separated by distillation

b) Impurities are more soluble in molten metal than in solid metal

c) Different components of a mixture are differently adsorbed on an adsorbent

d) Vapours of volatile compound can be decomposed in pure metal

5. The method of zone refining of metals is based on the principle of:

a) Greater mobility of the pure metal than that of the impurity

b) Higher melting point of the impurity than that of the pure metal

c) Higher melting point of the solid metal than that of the impurity

d) Greater solubility of the impurity in the molten state than in the solid state

6. Which of the following is not refined by zone refining method?

a) Germanium

b) Silicon

c) Gallium

d) Gold

7). Why is zone refining carried out in an inert atmosphere?

a) To prevent reduction of metal

b) To prevent oxidation of metal

c) To reduce the external pressure

d) To reduce the external temperature

8) Zone refining process is used for the:

a) Concentration of an ore

b) Reduction of metal oxide

c) Purification of metal

d) Purification of an ore

Answer: 1: c), 2: d), 3: b), 4: b), 5: b), 6: d), 7: b), 8: c)

UNIT –7 THIN FILM PREPARATION METHOD

Structure

7.9 References
7.10 Suggested readings
7.11 Terminal questions

7.1 Introduction

Thin film is a layer of material ranging from fractions of manometer to several micrometre in thickness. A familiar application of thin films is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. Thin films of various materials have been the focus of much research owing to their vast applications in electronic and optoelectronic devices. These applications stem from the ability to deposit stable thin films of controlled morphology and thickness. The traditional procedures to produce thin films involving casting and spin coating do not meet the requirements of advanced device technologies. With advanced industrial requirements, uniform and stable nanometer thick films are needed. Additionally, many functional materials are not soluble in the common solvents. In such cases, vapor deposition techniques can be promising candidates to fabricate advanced functional devices. In this Chapter, we will study different methods for nanomaterial synthesis.

7.2 Objectives

After studying this unit you should be able to:

- Understand the various methods of fabricating thin films
- Understand the principle and working of Vacuum deposition technique
- Advantages and limitations of various thin film deposition techniques
- Understand the principle of Sputtering
- Learn to apply the knowledge of these techniques

7.3 Methods of Fabricating Thin Films

Thin films of various functional materials employed in such devices are increasingly chosen over traditional bulk components as electronic devices in our daily lives continue to miniaturise. Several gas-phase processes have been discovered to be capable of depositing high-quality thin films and are widely used in the coatings industry. They are, however, connected with ultrahigh vacuum systems and complex and costly instrumentation, and may entail poisonous or caustic chemical precursors. Alternative production processes, including as electrospray deposition, sol-gel, and molecular precursor, have been developed and are active study fields.

The manufacturing procedures for thin films can be split into two categories: (1) gas phase fabrication methods and (2) liquid phase fabrication methods. In this context, gas phase fabrication methods involve the deposition of materials in vapour form from small particles of bulk solid materials or chemical precursors, whereas liquid phase fabrication methods involve a reaction between a substrate and a chemical precursor in a liquid state.

7.3.1 Gas phase fabrication methods

7.3.1.1 Magnetron sputtering

This is one of the most well-established techniques that is widely used in the industries to fabricate coatings of many different materials, including metals, semiconductors, and alloys. Thin films fabricated via magnetron sputtering prove to be of superior quality in comparison to those fabricated using other gas phase methods. The schematic representation of the magnetron sputtering set-up is shown in Figure 7.1. Before deposition, the chamber is evacuated to ca. 10^{-4} kPa and then refilled with Ar gas which is used as the sputter gas. Using strong electrical and magnetic field, magnetron sputtering employs the bombardment of the selected target's surface by Ar+ ions which are formed as a result of the collision between Ar gas atoms and electrons trapped within the magnetic field. The Ar+ ions are attracted toward the negatively charged target (cathode) and the bombardment leads to the ejection of the targets particles which are then redeposited as a thin film on the substrate placed on the anode, opposite to the target. Depending on the type of power source utilized, magnetron sputtering can be divided into two types namely, (1) direct current (dc) magnetron sputtering and (2) radio frequency (rf) sputtering. While dc magnetron sputtering is relatively cheaper in comparison to rf, only electrically conductive targets like metals or doped semiconductors are used. Additionally, reactive gases such as oxygen or nitrogen gas are used to react with the sputtered materials, in the fabrication of thin films for metal oxides or nitrides, respectively. The technique is referred to as "reactive magnetron sputtering".

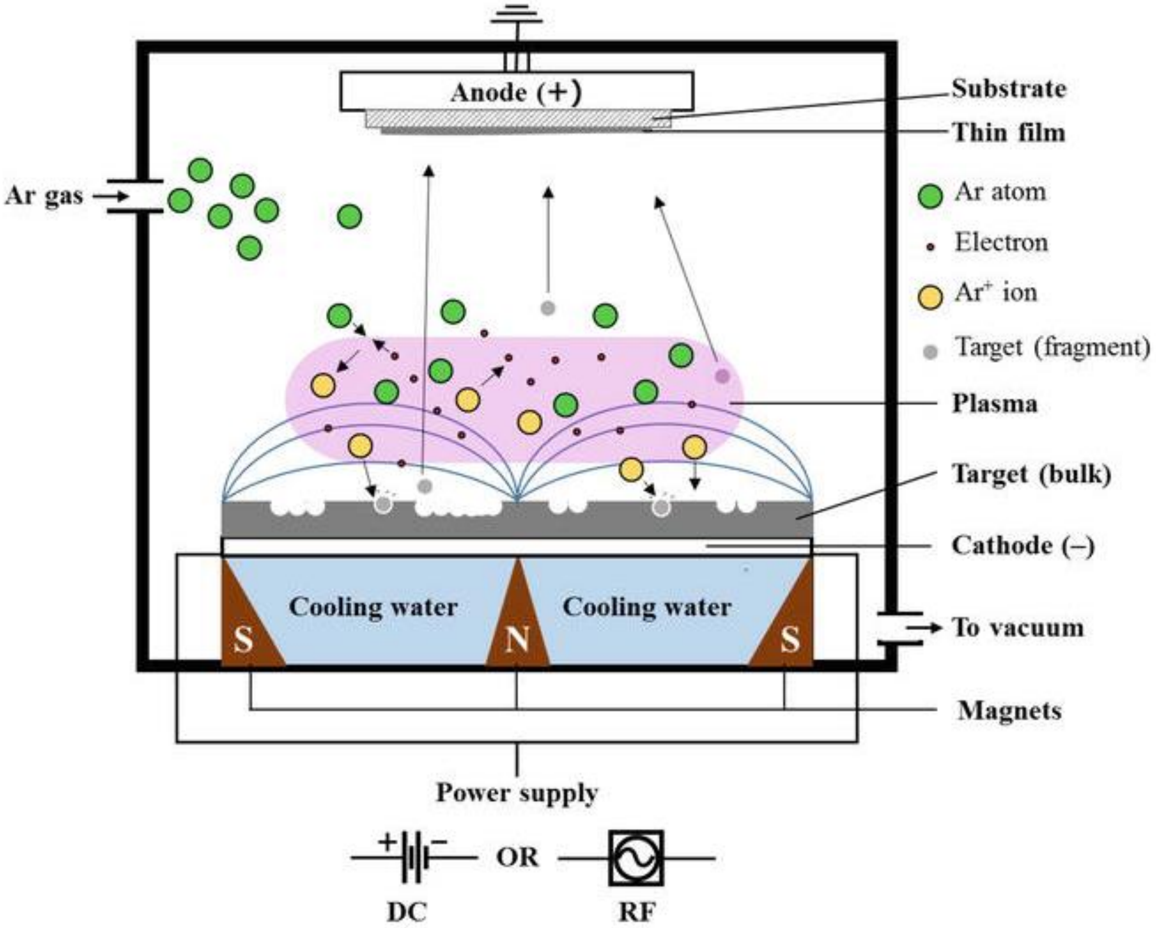

Figure 7.1: Schematic of magnetron sputtering apparatus and the deposition process.

7.3.1.2 Pulsed laser deposition (PLD)

The PLD setup is shown in Figure 7.2. The PLD technique employs the ablation of a target material with a strong, pulsed laser beam to produce a plume of vaporized materials which is then recondensed and deposited onto a substrate, placed opposite the target, under a reduced pressure atmosphere of ca. 10^{-1} –10^{-5} kPa. Depending on the target material, its morphology, and the laser pulse wavelength and duration, there is a specific threshold power density that is required to cause ablation. Therefore, a good understanding of the various parameters is required for a successful plume generation and subsequent thin film deposition. The stoichiometric transfer of materials from the target to the substrate earned PLD a reputation as fabrication of choice for thin films with complicated stoichiometry or sandwich structures, in comparison to other gas phase techniques. Although the fabrication of thin films with identical stoichiometry as the target materials is one of the superior characteristics of PLD, the stoichiometry can be compromised when multi-component materials with volatile constituents are used. As a remedy, a background gas such as oxygen or nitrogen is introduced in the reaction chamber to compensate for the lack of stoichiometry, during the fabrication of metal oxides or nitrides' thin films, respectively

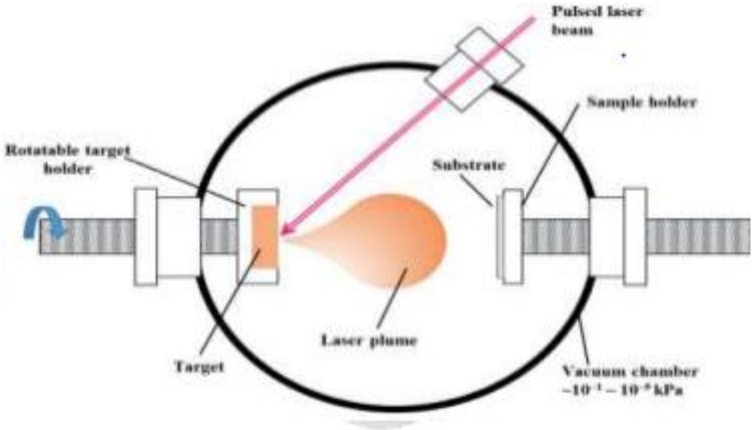

Figure 7.2. Schematic representation of PLD setup.

7.3.1.3 Atomic layer deposition (ALD)

The ALD technique is based on sequential and self-limiting reactions of a chemical precursor in vapor form, with an activated or functionalized surface of the substrate. The self-limiting property of this technique is realized in a sense that, if all functional sites on the substrate have reacted, no further reaction between the chemical precursor and the substrate will take place. Figure 7.3 illustrates the concept of ALD in the fabrication of a TiO_2 thin film. The steps are defined as follows: (a) precursor exposure, (b) purge, (c) reactant exposure, and (d) purge. By repetition of step (a)–(d), layers of TiO_2 can be easily formed and the thickness can be controlled at the atomic level. Under a vacuum pressure of ca. 10 kPa or less, the chemical precursors are maintained in a vapor phase by adjusting a specific temperature referred to as the "ALD temperature window", to achieve optimum reaction kinetics and avoiding condensation or thermal decomposition of the precursor. The superiority of ALD over other gas phase processes for the deposition of thin films is realized through its exceptional conformity, the ability to control thickness at the atomic level and tunable film composition. Through this route, the deposition of thin films on substrates with highly-structured geometries can be easily achieved, and ALD has been considered as the ideal method for fabricating highly conformal seed layers. This is also of great importance for applications in the concept of integrated batteries that aims at maintaining the storage capacity of miniaturized LIBs. Although the fabrication of metallic copper thin films has been achieved, the deposition of metallic thin films is generally limited due to the lack of precursors suitable for ALD processes. The vaporization of chemical precursors, difficulty in controlling their thermal decomposition and lack of efficient self-limited reactivity with surfaces are some of the challenging aspects in ALD. In addition, during the designing stages of certain chemical precursors, the by-products associated with the proposed chemical reaction need to be carefully considered as toxic or corrosive chemicals are likely to be those by-products.

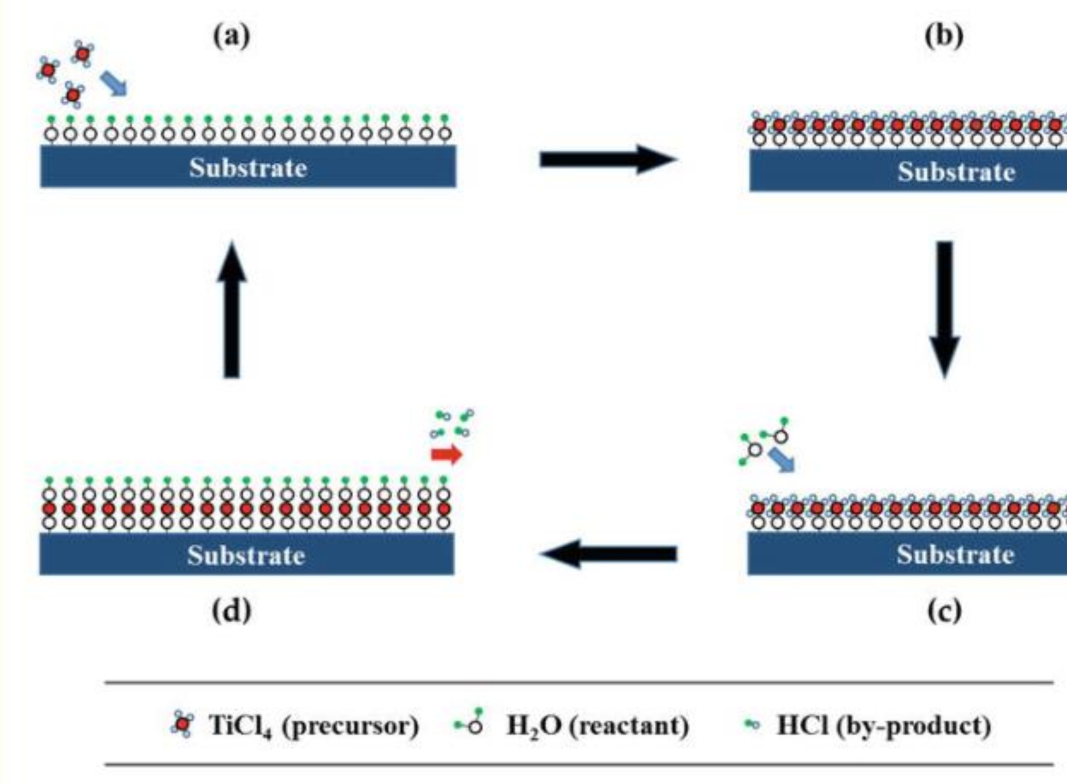

Figure 7.3. Schematic representation of 1 cycle of an ALD process for the deposition of a TiO_2 thin film from titanium tetrachloride and water.

7.3.1.4 Chemical vapor deposition (CVD)

Defined as the deposition of solids onto heated substrates from chemical reactions in vapor phase, CVD represents a versatile deposition technique of thin films for a wide range of materials, under vacuumed atmospheres and temperatures over 600°C, and it is an established technique for the deposition of thin film for microelectronics, ohmic and Schottky diode contacts, diffusion barriers, wear-resistant coatings, etc. The schematic representation of a CVD setup is shown in Figure 7.4. In a typical CVD experiment, a combination of chemical precursors showing stable vaporization behavior is carefully selected. Using an inert carrier gas, usually Ar or N_2 gas, the vaporized precursors are carried into an evacuated furnace (reaction chamber) and mixed with an additional reactive gas or two. In the fabrication of metal oxide thin films, oxygen gas is used as the additional carrier/precursor gas. On the other hand, if the desired thin film is metallic, such as Cu, a reducing atmosphere is created by using H_2 gas.

The CVD technique benefits from the fact that it does not require ultrahigh vacuum systems like in the magnetron sputtering and PLD techniques. In addition, CVD is a kinetically driven process, associated with minimized agglomeration and also benefiting from faster deposition rates, in comparison to ALD. Because different precursors have different evaporation rates, it is generally difficult to deposit multicomponent thin films by CVD. Other drawbacks of CVD include possible chemical and safety hazards of toxic, corrosive and flammable precursors or exhaust gases, and poor thin film adhesion-strength.

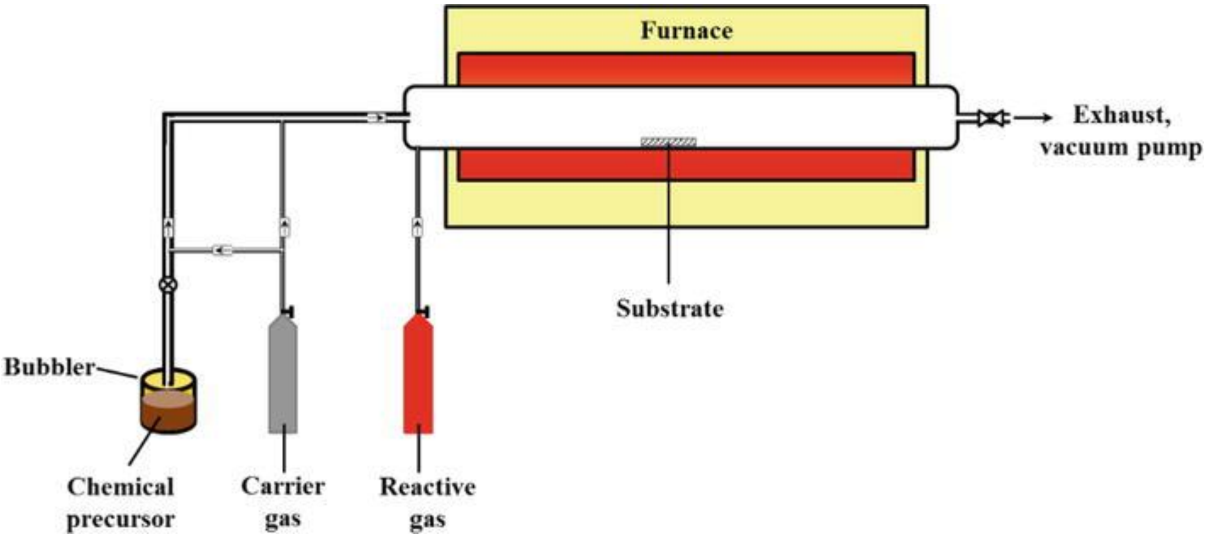

Figure 7.4. Schematic representation of a CVD setup.

7.3.2 Liquid phase processes

7.3.2.1 Electrospray deposition (ESD)

ESD involves the deposition of charged particles formed as a result of liquid atomization by an electrical force. The atomization of the liquid by electrical force allows for the generation of small particles, of narrow size distribution which can be uniformly dispersed over the substrate and, ESD has been considered as a promising technique for the formation of high-quality layers and films. If the ESD process is carried out at elevated temperatures, thin film formation is achieved through the thermal decomposition of the precursor solution during deposition and the process is referred called "electrospray pyrolysis (ESP)." The schematic representation of the ESD setup is shown in Figure 7.5. The ESD method is based on supplying a precursor solution through a metallic capillary which is maintained at high electrical potential. Ideally, the solution forms a Taylor cone at the tip of the capillary and emitted as a solution jet composed of many highly charged droplets that are homogeneously dispersed in the space between the nozzle and the counter metallic plate (substrate holder) by Coulomb repulsion forces. The quality of the resultant thin films can be easily controlled by adjusting variables such as the applied voltage, distance between the atomizing nozzle and, the flow rate, concentration and amount of the precursor solution.

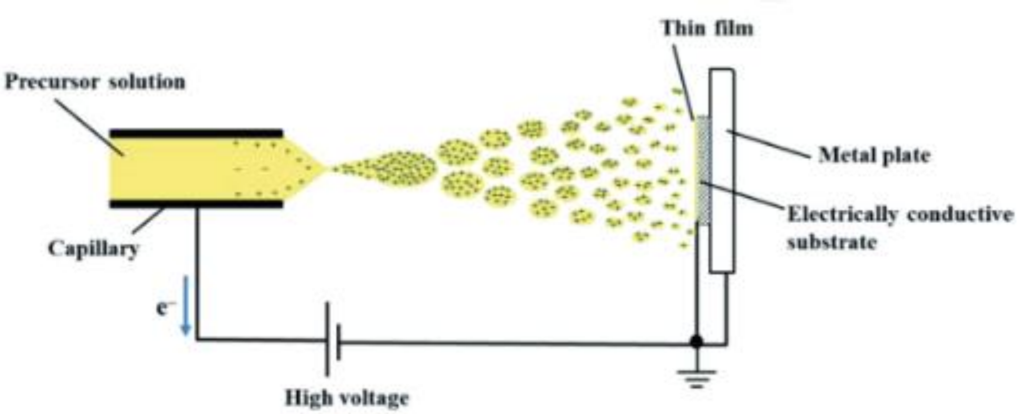

Figure 7.5.Schematic representation of an ESD setup.

7.3.2.2 Electrochemical deposition (ECD)

Considered as one of the cheapest methods for the deposition of thin films, ECD represents a major technology for mass production of large area metallic protective coatings in the industry. The deposition technique employs a combination of reduction and oxidation reactions of chemical precursors in electrolytes of aqueous solutions, organic solutions or fused salts. In addition to cost, other advantages of the ECD include low fabrication temperature, high purity and, the ease of controlling thin film thickness, uniformity and rate of deposition by adjusting the deposition parameters. The electro chemical technique can be divided into two groups, namely, (1) electrolysis plating which uses external power source to drive the electrochemical reaction that leads to the deposition of a thin film onto an electrically conductive substrate and, (2) electro-less plating which does not require external power supply but requires the use of catalysts to activate the surface of the specimen. The schematic representations of the electrochemical techniques for the fabrication of metallic copper thin films are given in Figure 7.6. During electrolysis deposition, the external power source causes the dissolution of the metal from the anode (usually a copper rod or plate). The dissolved Cu^{2+} ions are then reduced and redeposited on the surface of the electrically conductive substrate (Cathode). An electrolytic solution involving a salt of copper such as $CuSO_4$ is used for the electrochemical bath to maintain the balance of Cu2+ ions. In electroless plating, the electrolytic solution is also the source of the Cu^{2+} ions and a reducing agent such as formaldehyde (HCOH) is added to the plating bath. The introduction of a substrate with an activated surface (by $PdCl_2$ or $SnCl_2$) initiates the reduction of Cu^{2+} to metallic copper, subsequently forming a film on the surface of the substrate. In both the electrolytic and electroless plating, various alkaline or acidic electrolytic solutions are used and are important for maintaining the pH and stabilities of the plating baths.

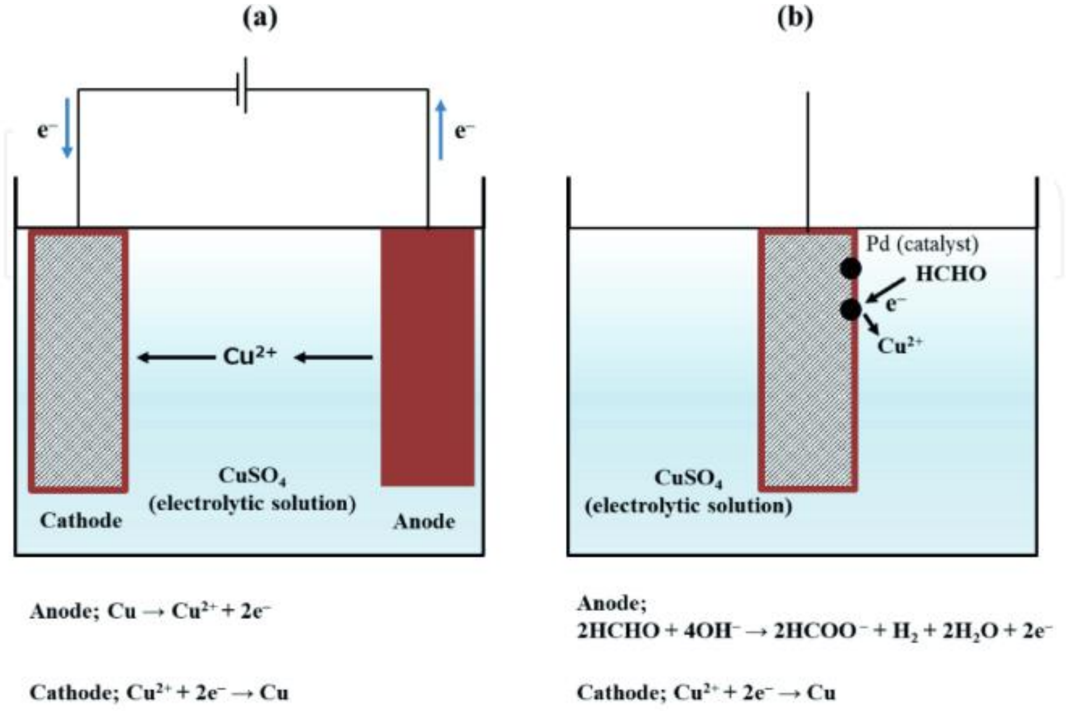

Figure 7.6. Schematic representation of the electrochemical deposition techniques. (a) Electroplating. (b) Electroless plating

7.3.2.3 Sol-gel method

The sol-gel method has emerged as a method of choice for the fabrication of ceramics and glasses and, it is considered as a cost-effective alternative to the well-established gas phase processes. The sol-gel method is a two-chemical processes technique based on the hydrolysis and condensation of molecular precursor's and has since been considered to be capable of offering new routes for the low temperature fabrication of oxide materials. Because all gel products may contain nanoparticles or are nanocomposites, the sol-gel method has been deemed as typical nanotechnology and the fabrication of thin films can be easily achieved after its integration with spin-coating or dip-coating.

In a typical sol-gel process, metal precursors (of the desired metal oxide) derived from metal salts in aqueous solutions, metal alkoxides in organic solvents, or a combination of the two are used. During the hydrolysis step, metal-hydroxide groups are formed by changing the pH of the aqueous solution or adding water to the metal alkoxides. The subsequent condensation reaction results in the formation of metal-oxygen-metal bonds, with different polymerization and poly condensation processes leading to the gradual formation of the solid phase network. Although a network of metal-oxygen-metal bonds of the desired metal oxide is obtained from the poly condensation step, additional drying and annealing steps are required for the removal of organic materials and improvement of the crystallinity of the resultant thin film. A typical sol-gel process for the formation of SiO_2 from silicone alkoxides is given in Figure 7.7. Although the sol-gel method has become an indispensable technique in the fabrication of thin films for metal oxides, principally, the fabrication of metallic thin films is not viable. In addition, a good understanding is required for the selection of appropriate precursors and the sophisticated chemical processes leading to the hydrolysis and condensation. The stabilization of the transition metals against hydrolysis, condensation, and other nucleophilic attacks is generally challenging. It is also important to make sure that the transition metal is sufficiently saturated in solution, to avoid different reaction mechanism. Finally, proper control of the moisture and hydrolysis conditions is required to avoid precipitation of the transition metal alkoxides. Therefore, all these aspects make the preparation of suitable coating precursors for the sol-gel method quite complicated.

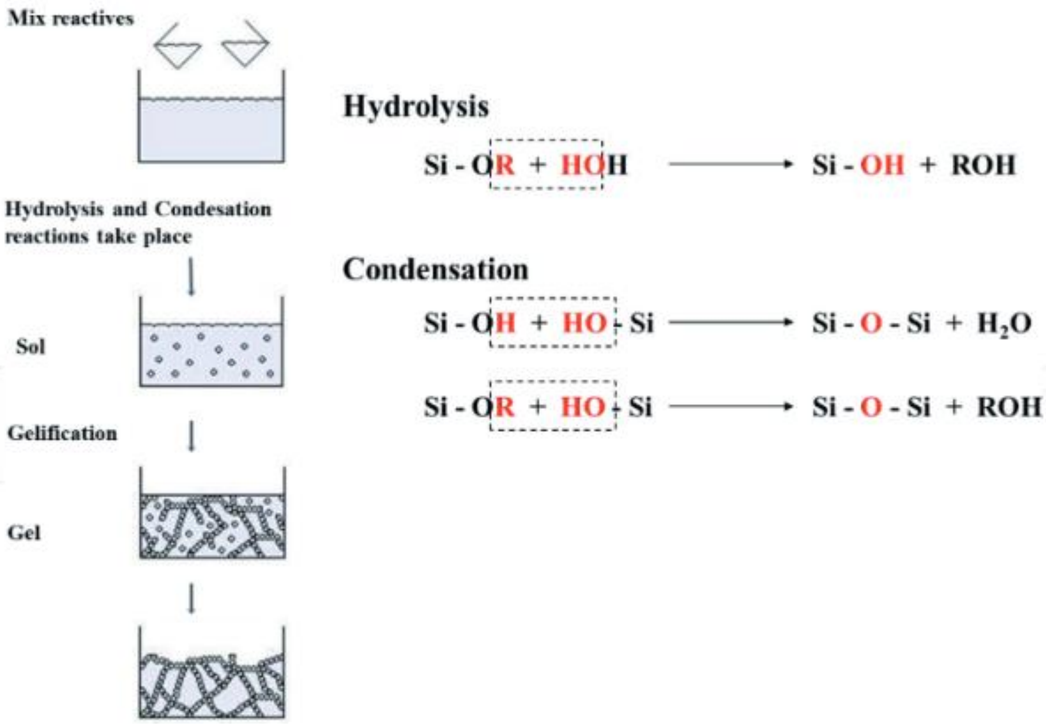

Figure 7.7. Typical sol-gel process for SiO_2 formation from silicon alkoxides.

7.3.2.4 Molecular precursor method (MPM)

The molecular precursor method is an effective, wet chemical process that was developed by the current authors, for fabricating nanocrystalline thin films of metals and, various metal oxides and phosphates. In the fabrication of these thin films by the MPM, metal complexes are dissolved in ethanol by combining them with appropriate alkylamines and this yields good coating solutions, with many practical advantages and are ideal for various coating procedures such as spin-coating, dip-coating, and flow-coating. Additionally, the development of aqueous precursor solutions have been successfully achieved and, these solutions can be easily applied for the fabrication of thin films via spray-coating at ambient conditions. To date, over 40 different kinds of thin films for metal oxides or phosphates have been easily fabricated by using the MPM. The procedure employed by the MPM is represented by the example of fabricating the titanium dioxide thin film illustrated in Figure 7.8.

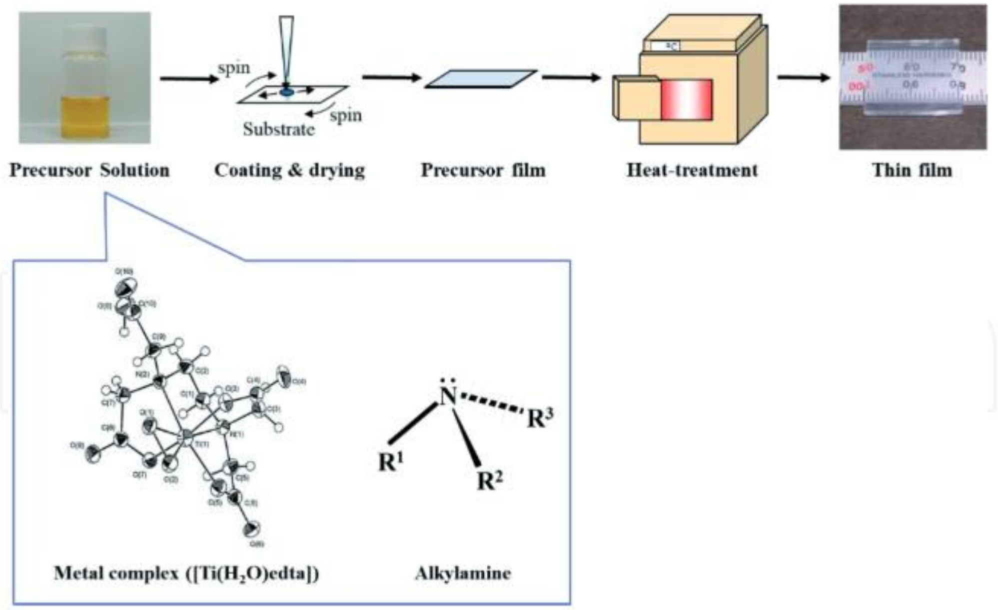

Figure 7.8. Procedure for fabricating a titania thin film via the MPM.

7. 4 Synthesis of Nanomaterials

The key component of nanoscience and nanotechnology is the synthesis of nanomaterials and nanostructures. Only when nanostructured materials are made accessible with appropriate size, shape, morphology, crystal structure, and chemical composition are new physical attributes and uses of nanoparticles conceivable. These notes offer a succinct and clear overview of the Top-down and Bottom-up methods to nanomaterial production. The unique optical, magnetic, electrical, mechanical, and chemical characteristics of nanostructures relative to bulk materials have increased interest in their production.

Synthesis techniques for nanomaterials:

Nanostructure materials have drawn a lot of attention since their shape and size-dependent physical, chemical, electrical, and magnetic characteristics differ dramatically from those of their higher dimensional equivalents.

- The performance of materials is dependent on their qualities, and several approaches have been developed to synthesise and produce nanostructure materials with controlled shape, size, dimensionality, and structure.

- The atomic structure, composition, microstructure, flaws, and interfaces in tern all depend on the synthesis's kinetics and thermodynamics, which in turn affect these factors.

Classification of Techniques for synthesis of Nanomaterials

Two typical methods for the fabrication of nanomaterials are shown in Figure:

a) Top- down approach

b) Bottom–up approach.

7. 4.1 Top-down approach

In a top-down approach, the bulk material is broken down into nanoscale structures or particles.

Top-down synthesis methods are an extension of those that have been utilised to create particles with a diameter of less than a micron (Figure 7.9).

Top-down strategies rely on either the removal or division of bulk material or the miniaturisation of bulk manufacturing methods to create the required structure with the right attributes. They are intrinsically simpler.

The top-down strategy's main drawback is the surface structure's flaws.

For instance, lithographically produced nanowires have a rough surface and may have several impurities and structural flaws. High-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, etc. are a few examples of such methods.

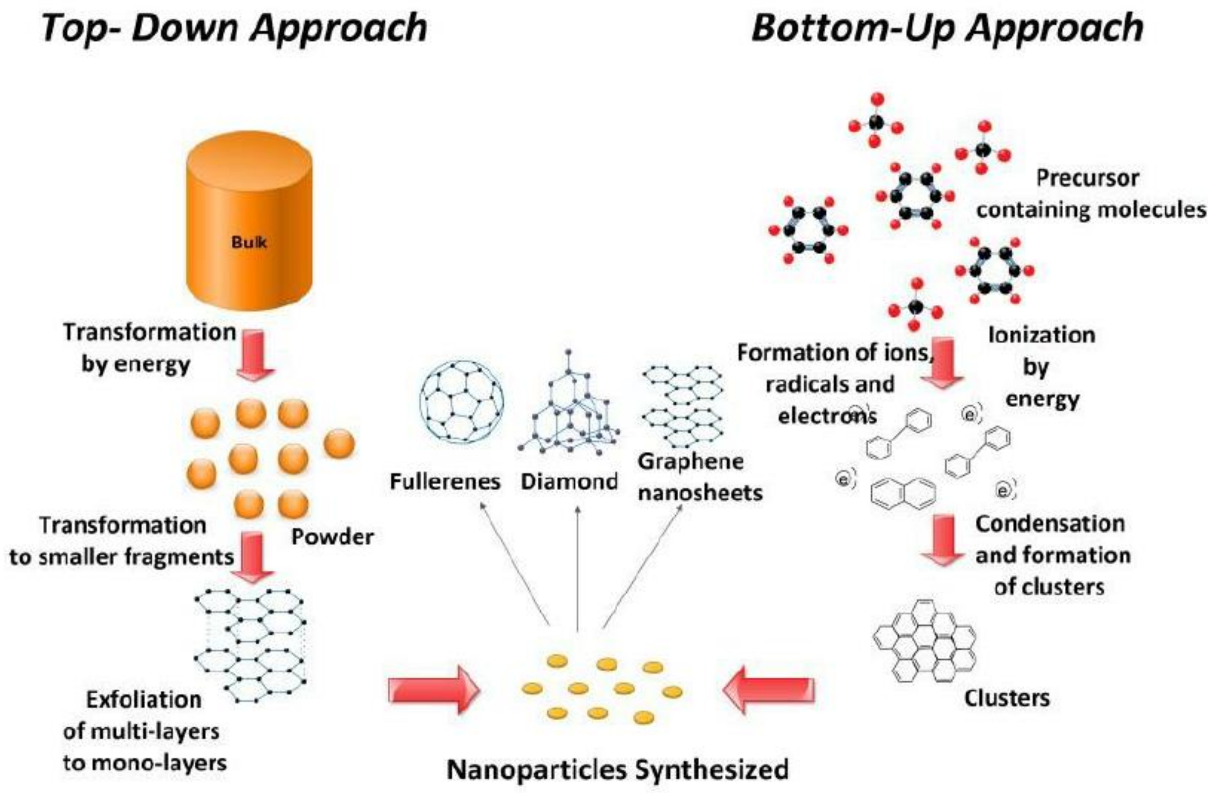

Figure 7.9: Schematic representation of ‘top-down’ and 'bottom-up’ approaches for synthesis of nanoscale materials.

7.4.2 Bottom-up approach

The term "bottom-up approach" refers to the building up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster (Figure 7.9).

- This alternative strategy has the potential to produce less waste and is therefore potentially more affordable.
- Many of these methods are still in development or are only now starting to be applied in the manufacture of nanopowders for commercial purposes.
- Some of the well-known bottom-up methods reported for producing luminescent nanoparticles include the oraganometallic chemical route, revere-micelle route, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, template assisted sol-gel, electrodeposition, etc.

7.5 Vacuum Deposition Technique

A range of several deposition processes known as vacuum deposition that are used to deposit thin films or layers of a material onto a substrate one atom at a time or one molecule at a time. Processing is done at pressures that are lower than the surrounding pressure (i.e., vacuum). The deposited films range in thickness from atomically thin to a few millimetres. The creation of a material's free-standing films is another application for this method. In light of this, alternate layers of various materials can also be deposited using this method (Figure 7.10). For instance, this method can be used to create optical coatings that have layers of various materials layered on top of one another.

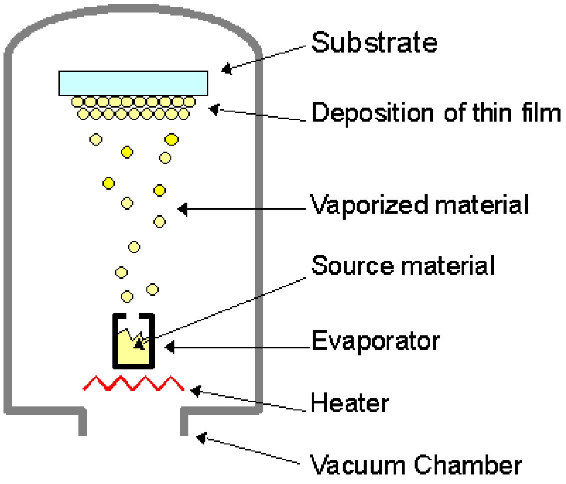

Figure 7.10: Concept of vacuum deposition.

The following reasons are given for film deposition in vacuum:

- The considerably lower particle density, therefore, the mean free path during collisions is long.
- Reduced contamination
- It is simple to regulate the gas and vapor's composition
-The vapours' flow can also be managed.
- Low pressure plasma conditions

Condensing or depositing vapors can be produced by:

- Thermal evaporation
- Sputtering
- Arc vaporization, etc.

The following reactions may occur during reactive deposition (where specific chemical reactions take place during the deposition process):

- The depositing species may react with a component of the gases present in the reactor (e.g., Ti +N→TiN)
- The depositing species and a co-depositing species may interact (Ti +C→TiC).

In a plasma environment, gases are activated ($N_2 \rightarrow 2N$) and precursor vapours are broken down ($SiH_4 \rightarrow Si + 4H$). Other applications for plasma include:

- Sputtering allows for the vaporisation of precursors
- Cleaning of the substrate
- Densification of the structure, and control of characteristics (ion plating)

According to the kind of vapour source used for film deposition, these methods may be divided into the following two groups:

Applications: Applications for vacuum deposition methods include:

- Electrical, semiconducting, and insulating coatings.
- Optical coatings
- Reflective coatings
- Lubricants for film
- Smart film coatings and low emissivity glass coatings
- Coatings that prevent diffusion, etc.

7.5.1 Physical Vapour Deposition Method

The term "physical vapour deposition" (PVD) refers to a class of vacuum deposition methods used to create coatings and thin films. In PVD, the material transitions from a precursor condensed phase to a vapour phase and back to a condensed phase (deposited as thin films). Sputtering, laser surface alloying, ion plating, and ion implantation are examples of commonly used PVD processes. It is commonly used to make thin films for mechanical, optical, chemical, or electrical purposes, including semiconductor devices like thin film solar panels, aluminized PET film for food packaging and balloons, and coated cutting tools for metalworking, among other things. The coatings made using this method most frequently are titanium, zirconium, chromium, and titanium aluminium nitride.

In PVD, the film is deposited over the entire exposed area of the object. Essentially, it is a vaporisation coating technique that transports the substance to be coated at the atomic level. The essential layer is produced by the gas phase precursor condensing onto the substrate. Throughout the deposition process, no chemical reactions take place. The steps of the process is carried out under vacuum, and comprises the following steps:

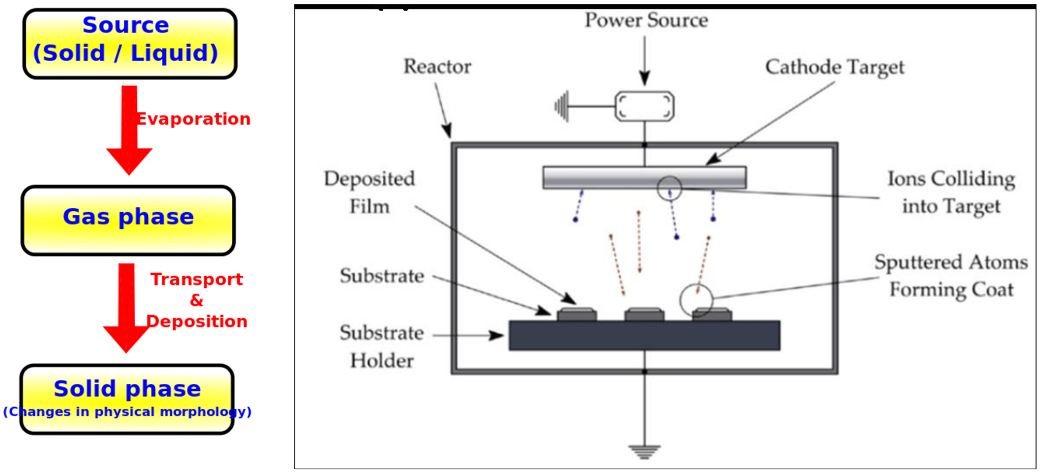

Figure 7.11 a) Flowchart for the PVD process and b) An illustration of the PVD setup

Evaporation

The target (material to be coated/deposited) is incident with high energy source like an electron/ion beam. The atoms from target surface are removed, therefore vaporising them.

Transport

Atomic vapours are transported from the target surface to the substrate's surface that needs coating.

Reaction

If compounds containing target metal atoms, such as metal oxides, nitrides, carbides, and similar materials, are to be deposited, this step is introduced. During the transport phase, when the metal atoms of the target evaporate, they react with the gas (specifically provided to react with the target metal) and deposit products of these metal atoms.

Deposition

It involves coating buildup on the substrate's surface. Depending on the technique used, certain interactions between the target material and reactive gases on the substrate's surface may occur simultaneously with the deposition process**.**

The experimental setup for the PVD method is shown in Figure 7.11. In either a quartz or alumina (ceramic) tube, the experiment is conducted. The tube can be mounted either horizontally or vertically depending on the application. Reaction chamber is evacuated at a pressure between 10^{-}

^{4} and 10^{-7} Torr prior to experimentation. The heating element is then activated, and carrier gas is then delivered into the chamber at a consistent flow rate. As carrier gases are introduced, the pressure inside the chamber rises to 200–500 Torr. Because the morphology of the created nanostructure is highly dependent on the pressure of the chamber and the flow rate of the carrier gas, the flow rate of the carrier gas is determined by the structure of the needed nanomaterial. After attaining the required conditions inside the chamber, the gas flow and temperature of the chamber are kept constant for the duration of the deposition. Precursor materials are vaporised at high temperatures and low pressure. Inert gases then transport these vapours to a lower temperature zone, where they gradually supersaturate. When they reach the substrate surface, they nucleate and develop the required nanostructures. Turning off the heat will stop the growth. By passing inert gas through the reaction setup, it is cooled to the surroundings.

7.5.1.1 Ion Plating (Through Plasma)

Metals including titanium, aluminum, gold, copper, and palladium are deposited on the surface of a feature via plasma based ion plating. The deposited layers range in thickness from 0.008 to 0.025 nm. This approach has the benefits of strong adhesion, surface polish, in-situ substrate washing prior to coating, and good control over the film shape. However, its drawbacks include strict control of process parameters, plasma contamination, and the possibility of blasted gas species contaminating the substrate and deposited layer. It is commonly found in X-ray tubes, pipe threads, turbine blades in aviation engines, steel drilling bits, and other applications

7.5.1.2 Implantation of ions

Instead of producing an entirely new layer, it produces alloys with the substrate surface, changing the surface's chemical makeup. Nitrogen, for instance, is used to improve the wear resistance of metals. Prior to the deposition procedure, substrate cleanliness is crucial in this approach. It is extremely vulnerable to issues caused by contamination since it only operates on species that are present on the substrate's surface. The procedure is carried out at room temperature, and the amount of time needed for deposition depends on the chosen coating material and the substrate's resilience to temperature changes. The amount of elements that can be vaporised and ionised inside of a vacuum chamber is the only restriction on ion implantation chemistry. Reproducibility, lack of posttreatment, and little waste are benefits. High temperatures will prevent the coating from producing a satisfactory finish. Limitations include difficulties with quality control and a lack of expertise and equipment. Anti-wear coatings for high-value components in biomedical equipment, tools, and gears and balls in the aerospace sector are typical uses. Additionally, it is employed in the semiconductor sector to deposit materials like as ceramics, silicon, gallium arsenide, gold, etc. onto a range of substrates.

7.5.1.3 Sputtering

Sputtering uses an etching method to change any surface's physical characteristics. Between the cathode, which contains the material to be deposited, and the anode, which serves as the substrate on which deposition is required, a gas plasma is produced. The thickness of typical depositions ranges from 0.00005 to 0.01 mm for thin films. Chromium, titanium, aluminium, copper, molybdenum, tungsten, gold, and silver are common depositions.

Applications include jewellery, watchbands, and eyewear with ornamental coatings. Sputtering is a procedure that is economical and cost-effective compared to other deposition processes, and as a result, it is widely employed in a variety of sectors. In the electronics sector, it is frequently employed to create coatings and films that have been severely sputtered. On chips, recording heads, magnetic and magneto-optical recording media, etc., these coatings may incorporate the deposition of thin film wires. Sputtering is used in the automotive sector to make ornamental films for plastic. It is used to make reflective films for big pieces of architectural glass in structures. Sputtering is used in the food packaging business to create thin plastic sheets for packaging.

7.5.1.4 Surface alloying

Laser surface alloying (modification) makes it easier for alloys to form by adding the chosen material to the melt pool. This method creates surfaces with increased wear and corrosion resistance, improved mechanical behaviours, excellent looks, and good performance at high temperatures.

The most typical method of surface alloying is laser cladding. For selective deposition over a certain region, laser cladding is utilised. Using a combination of pressure and heat, a thin metal layer is mixed with some base metal in this method. Although a thorough sample preparation procedure is not necessary, it can be necessary to roughen the surface before coating. Typically, following deposition, grinding and/or polishing are carried out. However, deposition of easily oxidised compounds needs inert gas streams. The deposition rates are influenced by the laser's power, frequency, and speed. The deposited layer ranges in thickness from a few hundred micrometres to millimetres. Delamination may occur as a result of film breaking in extremely thick deposited layers. Additionally, this method only deposits in the direct line of sight.

7.5.2 Chemical Vapour Deposition Method (CVD)

The most popular method for creating high-quality, exceptionally effective solid materials is CVD. Although making thin-film coatings for surfaces is one of its most well-liked uses, it may also be utilised to create superior powders and bulk materials. The infiltration process may also be used to create composite materials. Nearly every element on the periodic table is also deposited via CVD, sometimes in their purest forms and more frequently as mixed compounds.

Traditionally, a precursor gas (or gases) are delivered into the chamber that contains the substrates that need to be coated after being preheated. On and around these heated substrates, chemical reactions occur, causing thin films of the desired substance to deposit on the substrate's surface. Along with the deposition, byproducts are produced, which must be evacuated from the reaction chamber with the unused precursor gases. A typical CVD experimental setup and the process schematics are shown in Figure 7.12.

The procedures are summarised as follows:

1. Delivery of the reactants in gas phase to the reaction area (often with a carrier gas).
2. Convection across the boundary layer or diffusion
3. Precursors adhering to the substrate
4. Precursor surface diffusion to growth sites. Diffusion-less reaction might result in surface development that is harsh.
5. Surface chemical reaction, solid film production, and byproduct generation.
6. Desorption of waste materials
7. Extraction of gaseous waste products from the reactor.

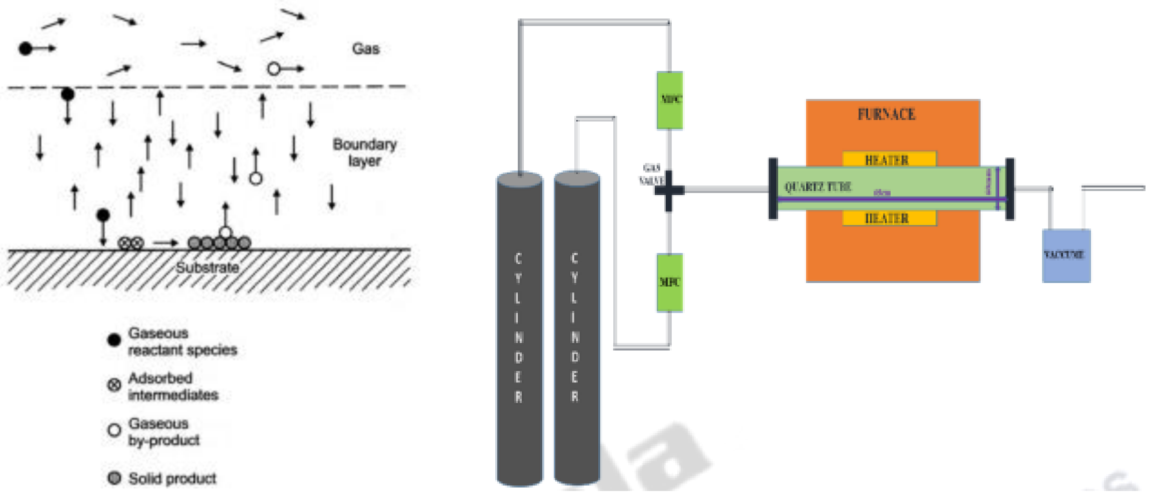

Figure 7.12: Schematics of (a) the CVD process, and (b) a conventional CVD setup.

The variety of deposited materials and the broad range of applications have led to the development of various different forms of CVD, as is to be expected. It can be done in reactors with hot or cold walls, extremely low to high pressures, carrier gases present or absent, and average operating temperatures ranging from 200 to 1600 °C. Some improved CVD techniques employ plasma, lasers, photons, hot filaments, ions, or combustion reactions to increase deposition speeds and lower deposition temperatures. Sputtering, ion plating, plasma-enhanced CVD, low-pressure CVD, laser-enhanced CVD, active reactive evaporation, ion beam, laser evaporation, etc. are a few of the techniques used in this technology. Their working pressure range allows you to differentiate each one of them based on how the chemical reactions are started, as follows:

- Typical ultrahigh vacuum pressures are less than 10^{-6} Pa (10^{-8} Torr).
- Low pressure. These methods benefit from less gas-phase interactions at low pressures, which increases the film's homogeneity.
- The atmosphere's pressure

  Vapour honing (to increase film adherence) and mechanical and/or chemical cleaning are also used as pretreatments for the substrate. The reaction chamber also has to be dry, leak-proof, and free of dust and moisture. CVD is used to increase the materials' resistance to corrosion and wear. Nickel, tungsten, chromium, and titanium carbide are common depositions. CVD offers many advantages. The main benefit is that this approach produces conformal films, meaning that the thickness of the film on an object's side walls is comparable to that on its top. As a result, extremely bent parts are evenly covered with films. The ability of CVD to deposit exceptionally high purity films in addition to a large variety of materials is another benefit. This is because using distillation procedures, contaminants from the gaseous precursors may be removed very easily. Fast deposition rates and the fact that it doesn't require as low of a pressure as the PVD technique are additional benefits.

7. 6 Sputtering

W. R. Groove, an English physicist, discovered the sputtering process (also known as cathodic sputtering) in 1852. Irving Langmuir refined it as a thin film deposition technique in 1920. Sputtering technique, a high-energy manufacturing process, is used to create stoichiometric thin films, i.e. without altering the composition of the original material from the target material. Sputtering works well to create non-porous compact films. This method is a useful tool for depositing multilayer films for mirrors or magnetic films for spintronics applications (devices that use the spin of electrons and holes in addition to their charge).

Through the mechanism of momentum exchange inside the plasma, high energy ions typically coming from some inert gas ambient like argon eject or sputter atoms from a solid target source. A thin film is formed by depositing (condensing) the ejected particles on a substrate's surface. Plasma is an ionised gas that is believed to constitute a separate phase of matter. The word plasma is derived from the Greek word "plassein," which means "to mould" or "to spread." Plasma is electrically conductive and have a significant impact by electric and magnetic fields. Ionisation in plasma results in a huge number of ions and free electrons. DC or AC voltages are used to create plasma, and a bias voltage is used to encourage ion acceleration on the target.

Sputtering mechanism

At a very high energy, inert gas ions like Ar+ bombarded the target surface. Depending on the energy of the ions and the ratio of ion mass to that of the target atoms, the ion-target interaction can be a complicated process (i.e., the kinetic energy of the impinging particle significantly influences what event would take place). The energy of the colliding ions affects how they interact with the target substance. When the incident ions' energy is relatively low (less than 5 eV), they may be reflected back, but when their energy is larger than 10 keV, the impact is almost head-on, and they get implanted in the target material (the foundation of ion implantation). A variety of interaction mechanisms are possible depending on the kinetic energy level, i.e., if it is between the two extremes, collision cascades can be created in the target atoms, vacancies can be created displace some of the atoms in the target, interstitials and other defby displacing ects, adsorbates are desorbed, photons are created while losing energy to the target atoms, and some target atoms/molecules, clusters, ions and secondary electrons.

A schematic illustration of numerous options is shown in below Figure 7.13.

The sputtering yield, which is defined as the number of species ejected per incident ion and rises with the energy and mass of the bombarding ions, is of interest for the deposition of materials.

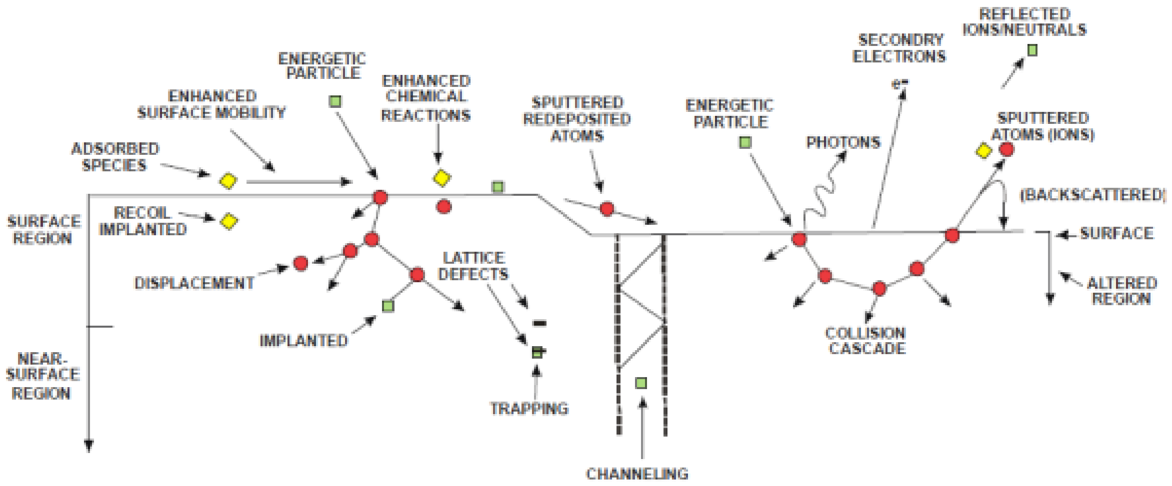

Figure 7.13: Interaction of an ion with target.

Sputter yield varies generally for various elements when the same incident ion with the same energy is used. As a result, when a target contains more than two distinct elements, the one with the highest sputter yield is added in greater quantity than the other components. However, the material with a high sputter yield also depletes more quickly, so that other components contribute a greater overall contribution. The deposited film now achieves the necessary stoichiometry. The sputtering yield, which is defined as the number of species ejected per incident ion and rises with the energy and mass of the bombarding ions, is of interest for the deposition of materials. Sputter yield varies generally for various elements when the same incident ion with the same energy is used. As a result, when a target contains more than two distinct elements, the one with the highest sputter yield is added in greater quantity than the other components. However, the material with a high sputter yield also depletes more quickly, so that other components contribute a greater overall contribution. The deposited film now achieves the required stoichiometry.

Three common methods used to create thin films utilising the sputtering process are Direct Current (DC), Alternating Current (AC), Radio Frequency (RF), and Magnetron sputtering.

For the highest sputter yield, a following set of conditions are valid:

(i) Process gas should be of high atomic weight.

(ii) Cathode material should be of low atomic weight.

(iii) Amount of reactive gas species should be low in the vessel.

In the sputter deposition procedures, "Argon" is the process gas that is most frequently used since it has a high sputter yield for most metals, is chemically inert and non-toxic, and is comparatively cheap when compared to the other noble gases (Krypton (Kr) and Xenon (Xe)). On the other hand, it is well known that oxygen gas rapidly forms metal oxides when reacting chemically with metals. Thus, in the current study, metal and metal oxide thin films are respectively deposited using argon and oxygen gases.

7. 6.1 RF sputtering

The fundamental concept of an RF sputtering system is shown in Figure 7.14 below. In RF sputtering, an alternating radio frequency potential is applied to the target, causing electrons to move back and forth and collide with gas atoms near the target surface, which is then used to periodically neutralise surface charges with plasma electrons, which have a higher mobility than positive ions. To couple the cathode through a matching network, a 13.56 MHz power source with 1 kW to 3 kW power and roughly 2 kV peak-to-peak voltage is often employed. This bias potential accelerates positive ions from the plasma towards the target's surface, and as a result, atoms sputter out as the energy from the accelerating ions is transferred to the target atoms. The considerably heavier ions in the plasma cannot keep up with the changing electric field at this high frequency alternating field. Thus, while the target acts as a cathode, only a positive charge might build up on its surface throughout the half cycle. Due to the great mobility of electrons, the plasma's electron current is stronger than the ion current, causing a fixed negative bias on the target relative to the plasma. The peak-to-peak RF voltage on the target surface is about half the magnitude of this bias potential. The positive ions in the plasma speed towards the target and strike the target surface when there is a negative bias on the electrode, which causes the atoms to sputter out.

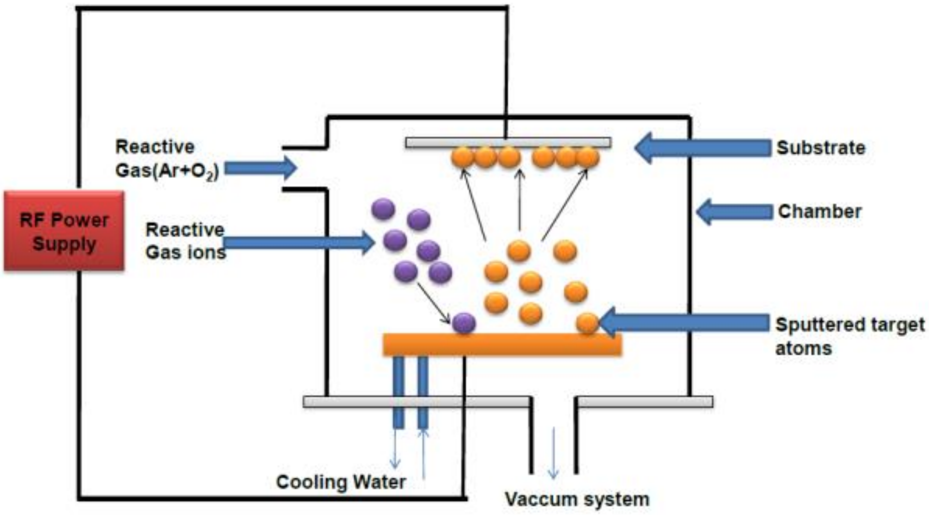

Figure 7.14: RF sputtering set up with matching network.

7.6.2 Magnetron sputtering

Using a magnetic field can increase the pace of DC/rf sputtering. One of the common techniques for improving the ionisation efficiency of electrons is magnetron sputtering (Figure 7.15). By adding parallel and perpendicular magnetic fields to the direction of the electric field, it extends the travel length of the sputtering particles, improving the efficiency of sputtering (sputter rate). The lower working pressure, for instance, allows for high sputtering rates to be produced at pressures as low as 0.5 torr of Ar. The magnetron sputtering system's typical schematic is seen in Figure 7.15. One of the common techniques for improving the ionisation efficiency of electrons is magnetron sputtering (Figure 7.16). By adding parallel and perpendicular magnetic fields to the direction of the electric field, it extends the travel length of the sputtering particles, improving the efficiency of sputtering (sputter rate). The lower working pressure is another significant benefit; for instance, high sputtering rates may be produced at pressures as low as 0.5 torr of Ar. The magnetron sputtering system's typical schematic is shown in Figure 7.15.

During magnetron sputtering magnets are positioned beneath the target electrodes. Here, magnets are employed to raise the proportion of electrons that participate in ionisation events, improve the likelihood that electrons will strike Ar+, and lengthen electron paths, all of which have a large positive impact on the ionisation efficiency. The secondary electrons that are released from the cathode surface during magnetron sputtering travel along helical trajectories that circumnavigate the magnetic field lines and experience more ionising collisions with gas neutrals close to the target surface. The magnetic field lengthens the time that electrons spend in the plasma, which enhances the likelihood that they will collide with other ions (Figure 7.16). Therefore, due to the magnetic field, the plasma may be sustained at lower gas pressure and provides a greater rate of deposition. In addition, because the ionisation is constrained close to the target, the substrate is not heated as much.

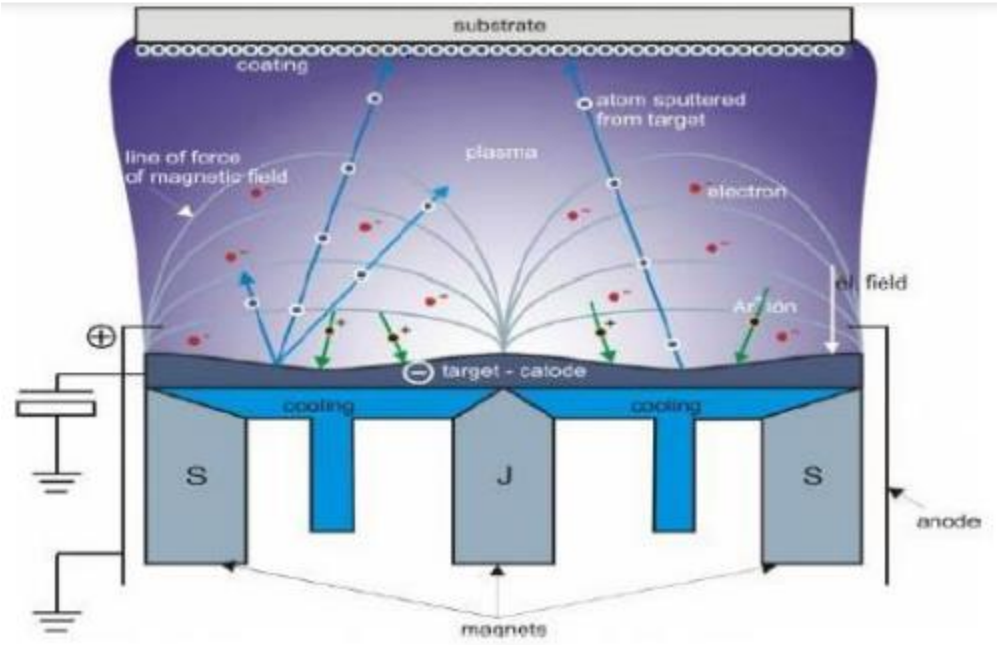

Figure 7.15: Schematic layout of a typical magnetron sputtering unit.

Figure depicts the 1" and 2" diameter magnetron electrode guns used in the RF Magnetron sputtering system. The sputtering system is equipped with three electrode guns, a substrate holding assembly, an integrated heater, and AC/DC motors that may be used for multilayer, confocal, and Glancing Angle Deposition (GLAD) thin film deposition. The multilayer configuration may be used to deposit two or more materials in a multilayered thin film, while the confocal configuration can be used to dope more than two materials. GLAD can be used to develop thin films with nanostructures or columns. The distance between the target and substrate may be adjusted from 2 cm to 7 cm in order to generate consistent thin film substrates in a range of sizes (1 cm to 2.54 cm in diameter). A heater that is PID-controlled is installed in the substrate holder (or assembly) in order to achieve substrate temperatures of up to 850° C. A water-cooled RF power supply (Comdel model: CX1250S/A) can deliver up to 100 W of RF power to the magnetron electrode. A matching device, which can work in either an automatic or manual mode, is attached between the target electrode and the RF power source to match the impedances and maintain the reflected power at zero. The sputtering system can also be utilised with a dc supply (Huttinger manufacture, Truplasma DC 4001). The water cooling system (Make: Warner Finley Pvt. Ltd.) has chilled water circulating at a temperature of 10o C to disperse the heat created during the sputtering process, and is coupled to the magnetron electrode and RF power supply.

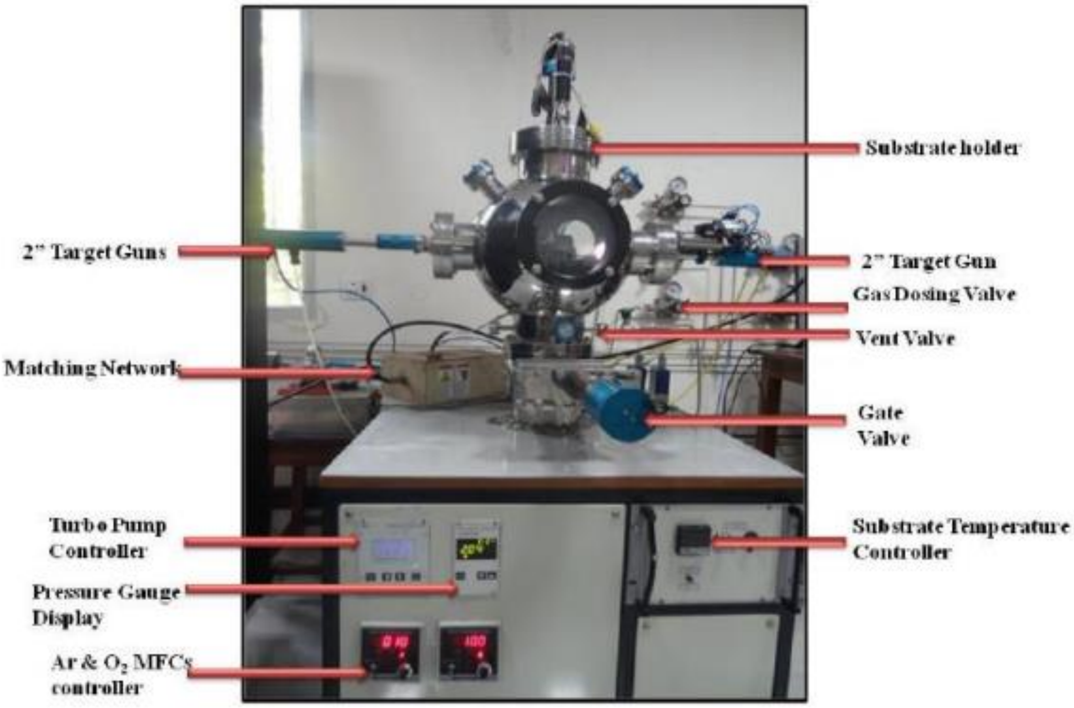

Figure 7.16: RF Magnetron sputtering system.

7.7 Summary

In this unit, you have studied about the different methods of thin film preparations and their applications. To present the clear understanding of thin film preparation, some commonly used methods of fabricating thin films have been discussed. The gas phase fabrication methods and liquid phase processes have been deliberated in detail. You have also studied the synthesis of nanomaterials. For synthesis of nanomaterials, Top-down approach and Bottom-up approach have been discussed in detail. The concept of different vacuum deposition technique have been elaborated. Basically, physical vapour deposition method and chemical vapour deposition method (CVD) have been explained. Among the available sputtering techniques we have discussed RF sputtering and Magnetron sputtering in detail. For understanding of different terminology of synthesis and preparation methods glossary have been discussed. To make the concepts clear many questions are given at the end of the unit.

7. 8 Glossary

Thin film	A layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness.
Nano materials	Materials with at least one external dimension that measures 100 nanometres or less or with internal structures measuring 100 nm or less.
Top-down approach	In a top-down approach, the bulk material is broken down into nanoscale structures or particles.
Fabrication	*construction of items from different parts using at least one of a range of processes and material*
Preparation	something prepared, manufactured, or compounded
Deposition	The settling of particles or sediment onto a surface.
Sputtering	Deposit (metal) on a surface by using fast ions to eject particles of it from a target.
Magnetron	*a two-element vacuum tube in which the flow of electrons is under the influence of an external magnetic field, used to generate extremely short radio waves*.

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7.11 Terminal Questions

1. What is PVD coating?
2. What is CVD coating?
3. Distinguish between PVD and CVD methods.
4. To produce a uniform film during physical vapour deposition:

   a. rotate substrate during evaporation

   b. use deep narrow crucibles to increase the directionality of evaporation beam

   c. increase the distance between source and substrate

   d. place extended source and substrate on surface of an imaginary sphere
5. The CVD (Chemical Vapor Deposition) process cannot be used to deposit which of the following materials?
   a. Cu
   b. Al_2O_3
   c. Poly-silicon
   d. Cork

   e. SiO_2
   f. Si_3N_4

4. What primary factors influence the nucleation process?
5. Why inert gas is used in sputtering?
6. Why is argon used in magnetron sputtering?
7. Explain working principle of magnetron sputtering system for the thin films deposition.
8. What are the disadvantages of sputtering?

Objective Questions:

1. Advantage(s) of sputtering is (are):

A) Good coating and step coverage

B) Good adhesion

C) Targets wear out uniformly

D) Preserves stoichiometry of multicomponent compounds

2. In physical vapor deposition, a more uniform film will be achieved

A) by rotating substrate during evaporation

B) by using deep narrow crucibles to increase the directionality of evaporation beam

C) by increasing the distance between source and substrate

D) by placing both extended source and substrate on surface of an imaginary sphere

3. Which of the following materials cannot be deposited by CVD (Chemical Vapor Deposition) method?

A) Si_3N_4

B) Poly-Silicon

C) Al_2O_3

D) Cu

E) Cork

F) SiO_2

4. What are the main parameters affecting the nucleation process

A) Charge of the substrate

B) Surface temperature

C) Roughness of the substrate

D) Deposition rate

5. Which deposition technique(s) should you use to get uniform thickness over an uneven substrate with trenches?

A) Chemical Vapor Deposition (CVD)

B) Sputtering

C) Physical Vapor Deposition (PVD) by evaporation

D) Atomic Layer Deposition

6. A simple evaporation-type thin-film deposition system has a shutter. Is it needed?

A) Thin films can be deposited even without shutter

B) It is virtually impossible to deposit thin films without shutter

C) The thin film thickness cannot be measured without first adjusting and stabilizing the deposition rate and then opening the shutter

D) Thin film can have some contaminations in the beginning of deposition process if the shutter is not used

E) It is needed for periodical termination of the deposition for better uniformity of the thin film.

UNIT –8 STRUCTURE ANALYSIS TOOLS

Structure

8.1 INTRODUCTION

Structural characterization of materials is essential to the systematic development of new materials and understanding how they behave in practical applications. In the present unit we will focus on the principal methods required to characterize broad range of materials such as metal, alloys, semiconductors, insulators, polymers, ceramics, nanostructures etc. for their applications based on mechanical, electrical, optical, magnetic, thermal properties of materials. This chapter will cover the basic principles and techniques of X-ray diffraction (XRD), Neutron diffraction, Low-energy electron diffraction, Thermal analysis: DTA, Thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) along with demonstrations of the instrument details.

8.2 OBJECTIVE

After studying this Unit, you shall be able to:

- Learn about the defects in crystal systems
- Learn about the necessity of X-rays as a characterization tools
- Bragg's Law of diffraction
- Application of Powder XRD
- Strengths and Limitations of X-ray Powder Diffraction
- Apply the concept of thermal analysis, thermogravimetric analysis, differential scanning calorimetry to different materials
- Learn to apply the knowledge of XRD, thermal analysis, thermogravimetric analysis, differential scanning calorimetry for research.

8.3 Defects in crystals

The atoms that make up an ideal crystal are expected to be organized in a periodic way. However, one can find some regions in actual crystals where the atoms' normal periodic arrangement is broken. These areas are referred to as faults, defects, or imperfections. The characteristics of crystals are impacted by their flaws. It is mainly because crystals display the majority of structure-sensitive characteristics. Defects in them affect the qualities of the structure that are sensitive, whether they be mechanical, optical, electrical, or any other.

8.3.1 Classification of Defects

Depending on the type of defects they are classified as point defects, line defects, plane defects, three-dimensional defects, electronic imperfections. Let us describe these defects in a slightly more detail. Defects are referred to as point defects if they are contained inside an extremely narrow region containing no more than a few lattice constants. Nearly a Zero-dimensional defect is a point defect. These kinds of defects fall under this category of defects, among others:

i. Simple vacancy or Schottky defect

ii. Frenkel defect

iii. Anti-Schottky defect

iv. Substitutional impurity atom

A Schottky defect is just a plain simple vacancy. There are no corresponding interstitial atoms or ions exist. An atom or ion that is absent from its usual place in the lattice, as seen in Figure 8.1, is referred to as a defect. These defects may be found to some degree in practically all crystals.

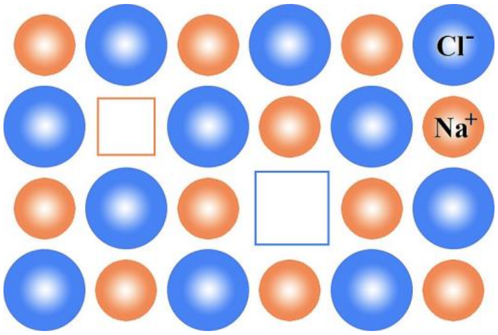

Figure 8.1: Simple vacancy or Schottky defect.

If an atom or ion is not at its normal site but is found to occupy a position somewhere in the interstice, it is called a Frenkel defect as shown in the Figure 8.2. It, therefore, involves creation of two imperfections – an interstitial atoms or ion and a vacancy.

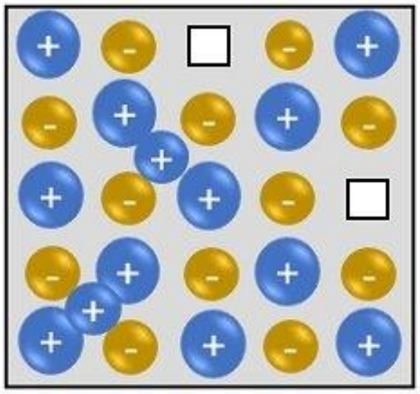

Figure 8.2: Frenkel defect formed by taking cation away from its lattice site and adjusting it into one of the nearby interstitial sites.

The third kind of defect, the anti-Schottky defect is just a single interstitial atom or ion, without there being any vacancy. When an atom is wedged into a hole, which is generally too small for it, between the atoms which occupy their normal lattice positions creates a defect known as "interstitials" (Figure 8.3). However if an atom of the crystal is replaced by some foreign atom, the defect thus created is called "impurity" (Figure 8.4).

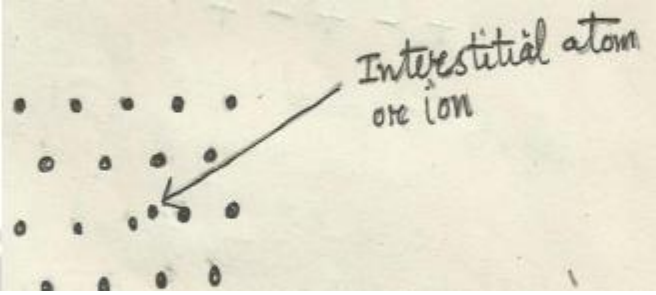

Figure 8.3: An interstitial atom or ion.

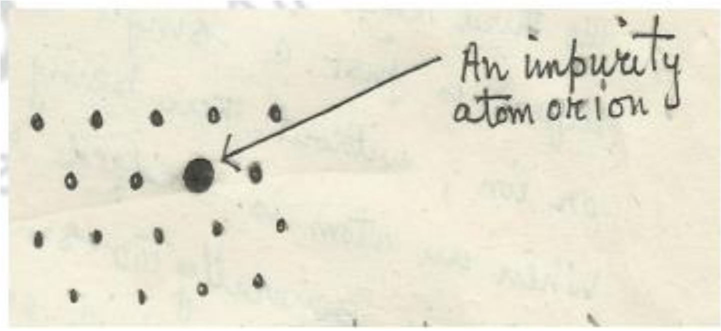

Figure 8.4: An impurity atom or ion.

Another type of defect occurs in ionic crystals when a multivalent impurity ion such as Cd^{++} is substituted for a lattice ion. Divalent cations such as Sr^{++}, Ca^{++} and Cd^{++} etc. are reported to enter the lattice together with positive ion vacancies, thereby neutralizing the extra charge of the impurity. The vacancy may be either free in the crystal or associated with the cation to form a complex. Some of each type of these defects will generally be present in a real crystal. At any temperature above absolute zero there will be some equilibrium number of these defects. At any given temperature there will be a possibility of an equilibrium condition set up within a solid when the number of defects of any particular type which are created per second is the same as the number of defects of that type which disappear each second.

8.4 X-RAY DIFFRACTION AND STRUCTURAL ANALYSIS

X-ray powder diffraction is a quick analytical method that may offer information on unit cell dimensions and is mostly used for phase identification of crystalline materials. The studied material is finely powdered, homogenised, and average bulk composition is determined.

8.4.1 Fundamental Principles of X-ray Powder Diffraction (XRD)

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample**.** In 1885, Wilhelm Conrad Rontgen, a German physicist, discovered X-rays. These are electromagnetic radiations with a wavelength ranging from 0.01 to 100 Å, which corresponds to the frequency in the range of 30 PHz - 300 EHz.

For the diffraction one can use radiation sources other than X-Rays such as neutrons or electrons can also be used in crystal diffraction experiments (Figure 8.5).

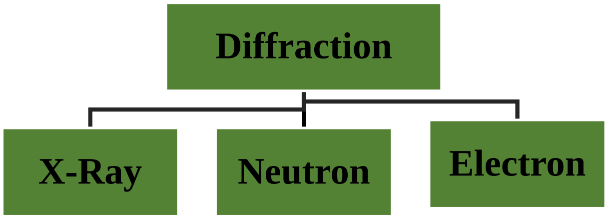

Figure 8.5: Types of diffraction.

The physical basis for the diffraction of electrons or neutrons is the same as that for the diffraction of X-Rays. The only difference is in the mechanism of scattering. The X-rays interact with electrons, neutrons interact with nuclei and electrons interact with electrons. The wavelength of X-rays is longer than gamma rays but shorter than ultraviolet rays. These rays are widely used for diagnostic radiography and crystallography, covering an extremely wide area.

Generation of X-rays:

In general, X-rays are generated either by X-ray tube or by synchrotron radiation. The X-ray tube is the primary X-ray source used in laboratories, whereas the synchrotron radiation needs a large-scale accelerator for obtaining high-energy radiation.

Figure 8.6 shown below demonstrates the X-rays induced by colliding high-energy thermal electrons with a metallic target (water cooled) such as copper, molybdenum, etc., which can emit strong X-rays of 1.541 Å, 0.71 Å, respectively. The emission of different X-rays from the copper metal is also shown schematically in Figure 8.7.

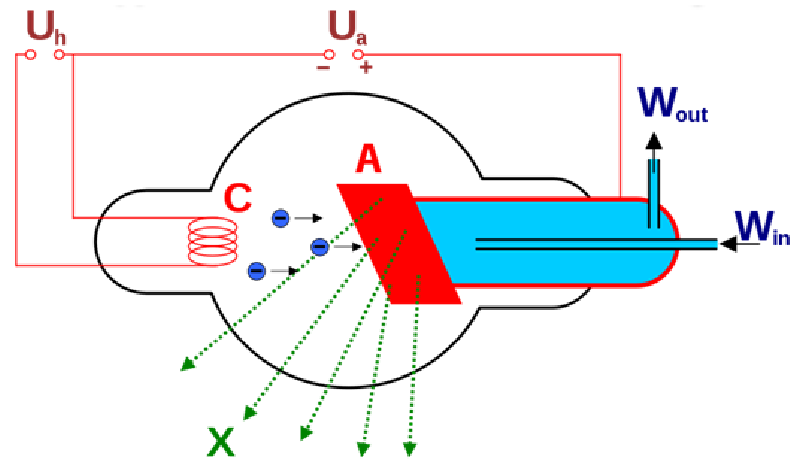

Figure 8.6: Schematic diagram of a water cooled X-ray tube.

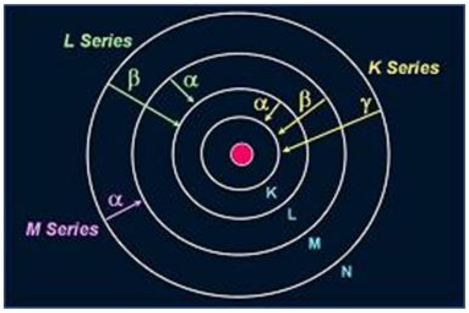

Figure 8.7: The characteristic X-rays are generated when the electron in the shells is flipped by high energy thermal electrons emitted from a filament.

These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$).

Sir William Henry Bragg and Son Sir William Lawrence Bragg proposed that Bragg's diffraction occurs when electromagnetic radiation or subatomic particle wave with a wavelength comparable to atomic spacing is incident upon a crystalline sample and scattered in a specular fashion by the atoms in the system and undergoes a constructive interference.

For a crystalline solid, the waves are scattered from lattice planes separated by the inter-planar distance d. When the scattered waves interfere constructively, they remain in phase (demonstrated later) since the path length of each wave is equal to an integer multiple of the wavelength.

The path difference between the two waves undergoing constructive interference is given by $2d \sin\theta$, where θ is the scattering angle. This leads to Bragg's law, which describes the condition for constructive interference from successive crystallographic planes (*hkl*) of the crystalline lattice.

Bragg's Law

$$n\lambda=2d \sin \theta$$

In a crystalline sample, this law connects the wavelength of electromagnetic radiation to the diffraction angle and lattice spacing. After that, the diffracted X-rays are detected, processed, and tallied. Due to the random orientation of the powdered material, scanning the sample across a range of 2 angles should provide all potential lattice diffraction directions. Because each mineral has its own set of d-spacings, converting the diffraction peaks to d-spacings enables for mineral identification. This is usually accomplished by comparing d-spacings to established reference patterns.

The production of X-rays in an X-ray tube is the basis for all diffraction procedures. The diffracted rays are collected once the X-rays are aimed towards the sample. The angle between the incident and diffracted rays is an important factor in all diffraction.

8.4.2 X-ray Powder Diffraction (XRD) Instrumentation and Working

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector (Figure 8.8). X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons (Figure 8.8). When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha1}$and $K_{\alpha2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.54 Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded.

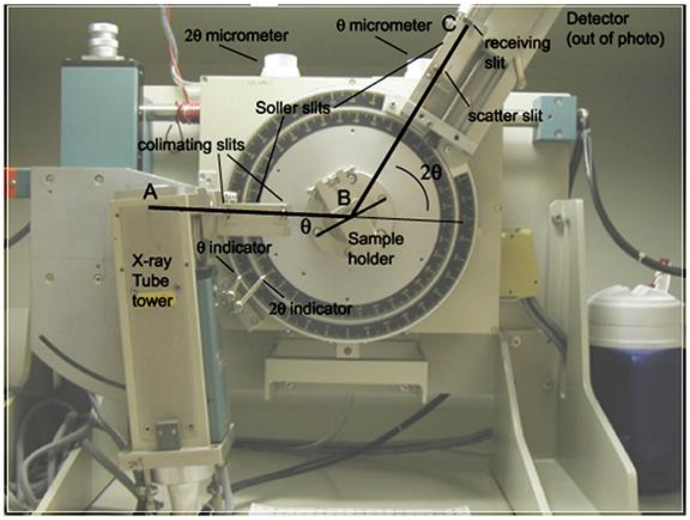

Figure 8.8: Image of a Modern Automated X-ray Diffractometer.

When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

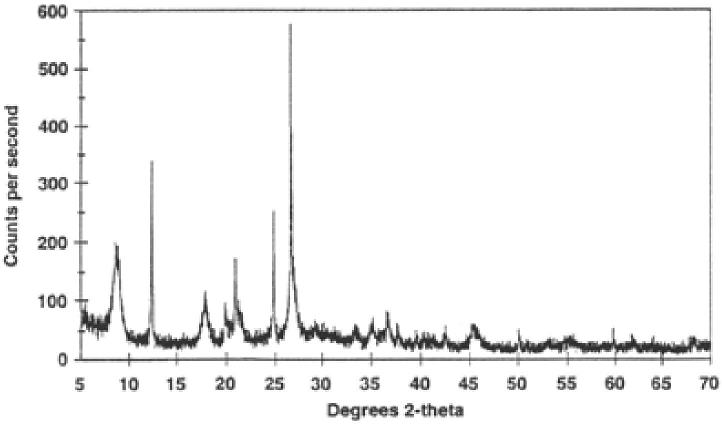

Figure 8.9: X-ray powder diffractogram. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this patter can be used to 'fingerprint' the mineral.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ (Figure 8.9). The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

The typical set up of X-ray diffractometer geometry and its components are shown in Figure 8.10**.**

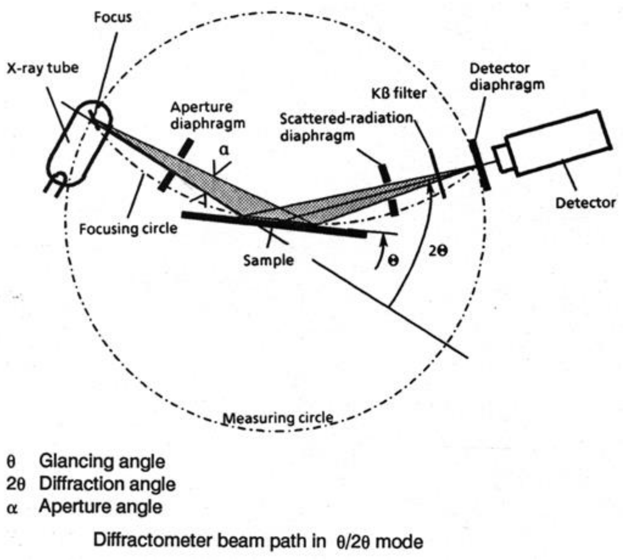

Figure 8.10: Diffractometer components and geometry.

8.4.3 Advantages and disadvantages of X-ray Powder Diffraction

Advantages

1. A powerful and quick (less than 20 minutes) procedure for identifying an unknown mineral.
2. In most situations, it yields a clear mineral identification.
3. There is very little sample preparation required.
4. XRD equipment is commonly accessible.
5. The interpretation of data is quite simple.

Disadvantages

1. The optimum material for identifying an unknown is homogeneous and single phase.
2. Access to a standard reference file of inorganic chemicals is required (d-spacings, hkls)

3. It takes tenths of a gram of material to make a powder.
4. The detection limit for combined materials is 2% of the sample.
5. Indexing patterns for non-isometric crystal systems is difficult for unit cell measurements.
6. Peak overlay is possible, and it gets worse for high angle ‘reflections’.

8.4.4 Application of XRD

There are a number of XRD analysis applications. Some of them are listed below:

1. XRD analysis is used to measure the average spacing between layers or rows of atoms
2. It determines the orientation of a single crystal or grain
3. Find the crystal structure of an unknown material
4. Measure the size, shape and internal stress of small crystalline regions
5. XRD is a non-destructive technique
6. It identify crystalline phases and orientation
7. XRD used to determine structural properties such as Lattice parameters (10-4Å), strain, grain size, expitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion.
8. To determine atomic arrangement.
9. Detection limits: ~3% in a two phase mixture; can be ~0.1% with synchrotron radiation
10. Measurement of sample purity.

With specialized techniques, XRD can be used to:

11. determine crystal structures using Rietveld refinement
12. determine of modal amounts of minerals (quantitative analysis)
13. characterize thin films samples by:
    a. Determining lattice mismatch between film and substrate and to inferring stress and strain.
    b. Determining dislocation density and quality of the film by rocking curve measurements
    c. Measuring superlattices in multi-layered epitaxial structures.

   d. Determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements.

14. make textural measurements, such as the orientation of grains, in a polycrystalline sample

SAS (Q 1). What are the basic conditions required for diffraction? Does the condition vary with the sources?

SAS (Q2). What is the typical range of X-ray wavelength?

SAS (Q3). Is X-ray with higher wavelength or lower wavelength good for materials characterization? Why?

8.5 Neutron diffraction

Neutron diffraction technique is a type of diffraction technique, which is used to determine the atomic and/or magnetic structure of a material. This technique is similar to X-ray diffraction but due to their different scattering properties, neutrons and X-rays provide complementary information. Neutron scattering is the technique of choice for condensed matter investigations in general, because thermal/cold neutrons are a non-invasive probe that do not deposit energy into the researched sample. The reason for selecting neutrons for diffraction is:

- It has no charge
- Neutron has no electric dipole moment and spin half.
- Neutrons interact through nuclear interactions. X-rays interact with matter through electromagnetic interactions with the electron cloud of atoms. For this, neutrons have high penetration (low absorption) for most elements making neutron scattering a bulk probe.
- Since neutron detection is through nuclear reactions the detection signal-to-noise ratio is high.
- Neutrons have the right momentum transfer and right energy transfer for investigations of both structures and dynamics in condensed matter.

- The utilisation of cold sources can provide a wide range of wavelengths. The size range of the probed ranges from near Angstrom to near micron

It's a crucial technique for studying magnetic ordering in some materials. In a neutron pattern, light atoms (such as H) are better resolved. They do not, however, make a major contribution to an X-Ray diffraction pattern. A sample to be studied is placed in a beam of thermal or cold neutrons to obtain a diffraction pattern. The obtained patterns provide information of structure of the material.

Advantages of Neutron Diffraction:

Neutron diffraction is a crucial technique for studying magnetic ordering in some materials. In a neutron pattern, light atoms are better resolved. They do not, however, make a major contribution to an X-Ray diffraction pattern.

Neutrons do not interact with electrons in the crystal since they are neutral. Unlike X-Rays, which are totally scattered by electrons, neutrons are entirely dispersed by nuclei. Neutrons have an innate magnetic moment despite being uncharged, therefore they will interact strongly with atoms and ions in the crystal that have a magnetic moment as well. For determining the crystal structures of solids containing light elements, neutrons are more useful than X-rays. Because the world's neutron sources are restricted, neutron diffraction is a unique and expensive technology. Neutrons are very penetrating, they do not heat up or destroy the sample, deuterium labelling is unique. They have the right wavelengths (Angstroms) and kinetic energies (μeV to meV) to probe structures and dynamics of materials.

Disadvantages of Neutron Diffraction:

A few disadvantages of neutron scattering follow:

- They are weakly scattered
- They have very low intensity (10^4 neutrons/mm^2.s)
- Neutron sources are very expensive to build and to maintain.
- Neutron sources are characterized by relatively low fluxes compared to x-ray sources (synchrotrons) and have limited use in investigations of rapid time dependent processes.
- Relatively large amounts of samples are needed: typically 1 mm-thickness and 1 cm

diameter samples are needed. So it is very difficult to work with the expensive samples or precious (hard to make) specimens.

8.5.1 Types of neutron scattering

There are basically four main types of neutron scattering:

1. The most basic method involves measuring the sample transmission. A monochromatic beam (or the time-of-flight approach), some collimation, and a basic neutron detector are required for this test (end-window counter). The sample content and relative proportions of the individual components are contained in transmission measurements. The relative ratio of carbon to hydrogen in crude oils, for example (the so-called cracking ratio), might be precisely quantified.

2. Elastic neutron scattering involves determining the scattered intensity as the scattering angle changes. This is a method of resolving the scattering variable $Q = (4\pi/\lambda) \sin(\theta/2)$ where and are the neutron wavelength and scattering angle, respectively. Step-scanning or a position-sensitive detector are used to accomplish this. Diffractometers (for single-crystal, powder diffraction or diffuse scattering from amorphous materials), reflectometers, and SANS devices are the most common types of elastic scattering equipment. Reflectometers and SANS instruments cover the low-Q range (Q< 0.5 Å-1) whereas diffractometers investigate the high-Q region (Q > 0.5 Å-1). They're all looking at sample formations, whether crystalline or amorphous.

3. Monochromation, collimation, scattering from a material, measurement of the neutron energy, and detection are the steps in quasielastic/inelastic neutron scattering. The extra step resolves the energy transfer during scattering using a crystal analyzer (or the time-of-flight approach). Inelastic scattering leads to limited energy transfers, whereas quasielastic scattering corresponds to energy transfers near zero. The triple axis, time-of-flight, and backscattering spectrometers are the most common types of quasielastic/inelastic spectrometers. The energy range covered by these sensors is eV to meV. They look at sample structure and dynamics. Phonon, optic, and other sorts of normal modes are studied using inelastic equipment. Diffusive modes are usually investigated with quasielastic instruments.

4. Another sort of quasielastic spectrometer is the spin-echo device. It was chosen because it evaluates correlations in the time (rather than the energy) domain. It employs polarised neutrons that precess in the pre-sample flight route, are quasielastically scattered from the sample, and then precess in the post-sample flight path in the opposite direction. The number of spin precessions is counted using a neutron spin analyzer. The number of spin precessions before and after the sample is proportional to the change in neutron velocity during scattering, and hence to the energy transfer. Scanned Q ranges are in the nanoseconds range, while probed times are in the nanoseconds range. This tool may be used to study diffusive movements in soft materials.

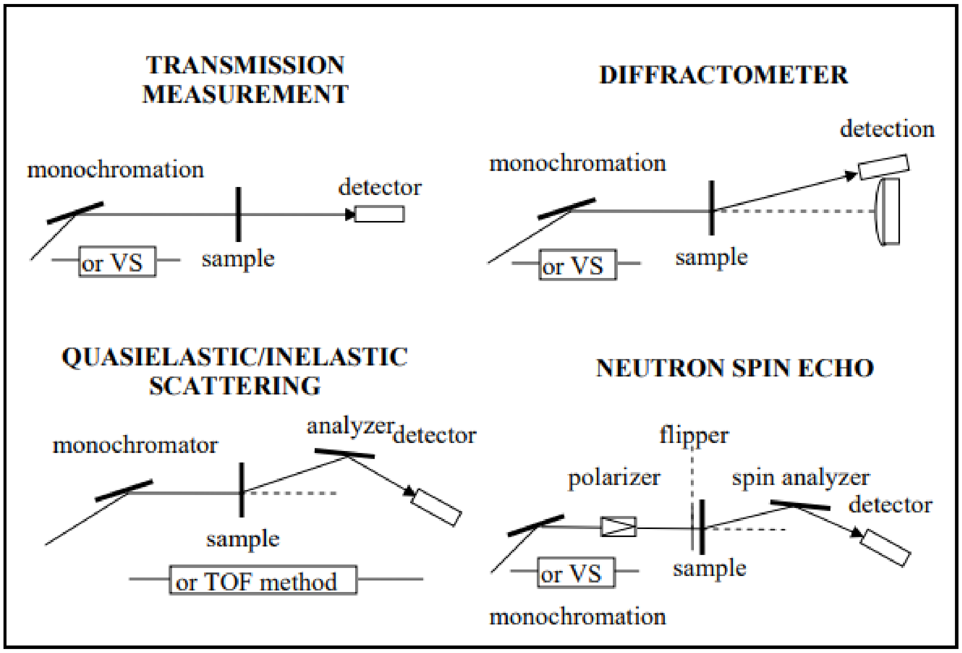

Figure 8.11: Schematic representation of the four types of neutron scattering methods.

SAS

1. What are the advantages of neutron scattering?

2. Neutrons interact with what part of the atom?

3. Name a couple of disadvantages of neutron scattering.

4. Name the four types of neutron scattering instruments.

8.6 LOW ENERGY ELECTRON DIFFRACTION

Low energy electron diffraction (LEED) is a very powerful technique that allows for the characterization of the surface of materials. Its high surface sensitivity is due to the use of electrons with energies between 20-200 eV, which have wavelengths equal to 2.7 – 0.87 Å (comparable to the atomic spacing). Therefore, the electrons can be elastically scattered easily by the atoms in the first few layers of the sample. In order to create a back-scattered electron diffraction pattern, the sample itself must be a single crystal with a well-ordered surface structure. LEED is an excellent approach for determining surface structure and characterisation. It can be used in one of two ways:

(i) **Qualitatively:** where the diffraction pattern is recorded and analysis of the spot positions yields information on the size, symmetry, and rotational alignment of the adsorbate unit cell with respect to the substrate unit.

(ii) **Quantitatively:** where the intensities of the various diffracted beams are recorded as a function of the incident electron beam energy to generate so-called I-V curves that, when compared to theoretical.

Experimental Details:

1. Figure 8.12 depicts a typical experimental setup for a LEED experiment. An electron beam of variable energy is produced by an electron gun, and is incident on the sample. The electrons are then backscattered from the sample surface onto a system of grids surrounding the electron gun. There are two types of backscattered electrons: elastically scattered electrons that form a series of diffracted beams that generate the LEED pattern, and inelastically scattered (low energy secondary) electrons that may account for 99 percent of the total flux but are not necessary. The elastically dispersed electrons are driven towards the fluorescent screen, S, which has a high positive potential, after passing through the first grid, G1 (which is earthed) (of the order of 5 kV). This provides enough energy for electrons in diffracted beams to stimulate fluorescence in the screen, resulting in a pattern of bright LEED spots. The grids G2 and G3 are set to a negative potential and are used to reject the bulk of the electron flow, which is composed of inelastically scattered electrons

and contributes to a bright, diffuse background throughout the whole LEED screen. The LEED pattern's potential is changed on these grids to reduce the hazy backdrop. A picture or video camera set on a chamber window directly opposite the LEED screen can record the LEED pattern that is noticed. What we see is a depiction in reciprocal space, not actual space, of the LEED pattern. To examine LEED patterns, a basic grasp of lattice representation in reciprocal space is required.

2. **Application:**

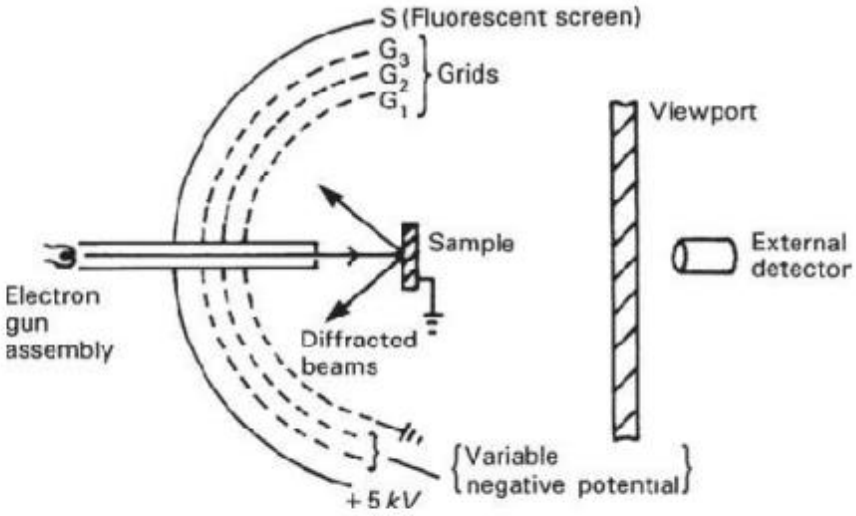

Figure 8.12: Schematic diagram of conventional LEED optics.

LEED Applications

Now, we will discuss the most common applications of LEED and the information that one can obtain with this technique.

1. ***Study of Adsorbents on the Surface and Disorder Layers:*** study of adsorbates on catalysts, due to its high surface sensitivity is the main applications of LEED.
2. ***Determination of Structure***: LEED–IV curves may provide precise information on the atoms' positions in a crystal. These charts show how the intensity of diffracted electrons

(spots) varies with the energy of the electron beam. The measurement of the intensity spectra, the computations for alternative models of atomic locations, and the search for the best-fit structure, which is defined by an R-factor, are the three key aspects of the structure determination procedure by this technology.

8. 7 THERMAL ANALYSIS

When a substance is heated, it undergoes changes in structural and chemical composition such as fusion, melting, crystallization, oxidation, decomposition, transition, expansion etc. Using thermal analysis such changes can be monitored in atmosphere of interest. The obtained information is useful in processing control and hence, the material properties of the system. Thermal Analysis (TA) is a group of techniques that study the properties of materials as they change with temperature. In practice thermal analysis gives properties like; enthalpy, thermal capacity, mass changes and the coefficient of heat expansion. Solid state chemistry uses thermal analysis for studying reactions in the solid state, thermal degradation reactions, phase transitions and phase diagrams.

There are several methods used commonly and are distinguished from each other by the property which is measured.

- Differential thermal analysis (DTA) - Measurement of difference in temperature between a sample and inert reference material
- Differential scanning calorimetry (DSC) -Measurement of heat flow to or from a sample wrt a reference material
- Thermogravimetric analysis (TGA) - Measurement of weight of a sample as a function of temperature
- Dielectric thermal analysis (DEA): dielectric permittivity and loss factor
- Dilatometry (DIL): Change in volume
- Dynamic mechanical analysis (DMA): Measurement of change in dimension of a material as function of temperature by application of an oscillating load

• Evolved gas analysis (EGA): gaseous decomposition products

• Laser flash analysis (LFA): thermal diffusivity and thermal conductivity

• Thermomechanical analysis (TMA): Measurement of change in dimension of a material as function of temperature by application of a static non oscillating load

• Thermo-optical analysis (TOA): optical properties

Now we will discuss some of the main thermal analysis in detail.

8.7.1 Differential thermal analysis (DTA)

DTA is the measurement of change in temperature of a material due to physical or chemical processes occurring in the material.

DTA is useful for studying:

- **Phase Transformations**
- **Melting temperatures**
- **Glass transitions**
- **Crystallization**

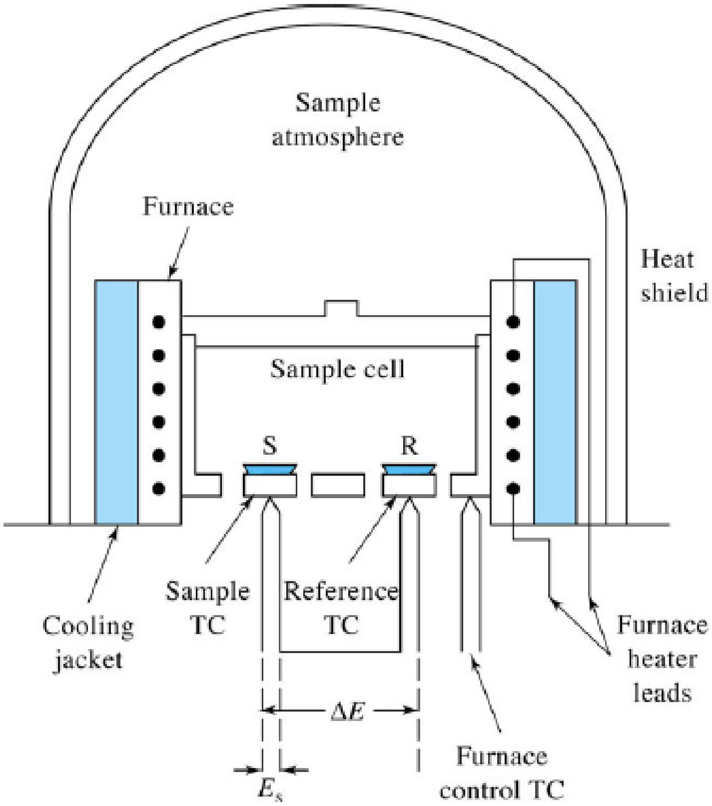

Figure 8.13: Instrument for DTA Analysis

Figure 8.13 shows the typical block diagram of DTA. The sample and inert reference (usually α - Alumina) are symmetrically placed in a furnace, which is typically controlled under a temperature. The sample and the reference are subjected to identical thermal cycles, such as a steady increase or drop in temperature or a series of temperature measurements. A differential thermocouple is used to record any temperature change between the sample and the reference during this process. The thermocouple on the sample side also detects the sample temperature.

Transitions observed as two different features in the DTA curve (Figure 8.14):

Step : Due to change in heat capacity, eg. In glass transition

Peak : Due to a phase transformation occurring in the material, eg. Melting, structural transition

- Peak may be endothermic or exothermic, observed on either side of the baseline. Peak may be endothermic or exothermic, observed on either side of the baseline

Transition temperature is given by the onset temperature, characteristic of the material, and independent of the operating conditions. Shape of peak and peak maximum are affected by the operating conditions

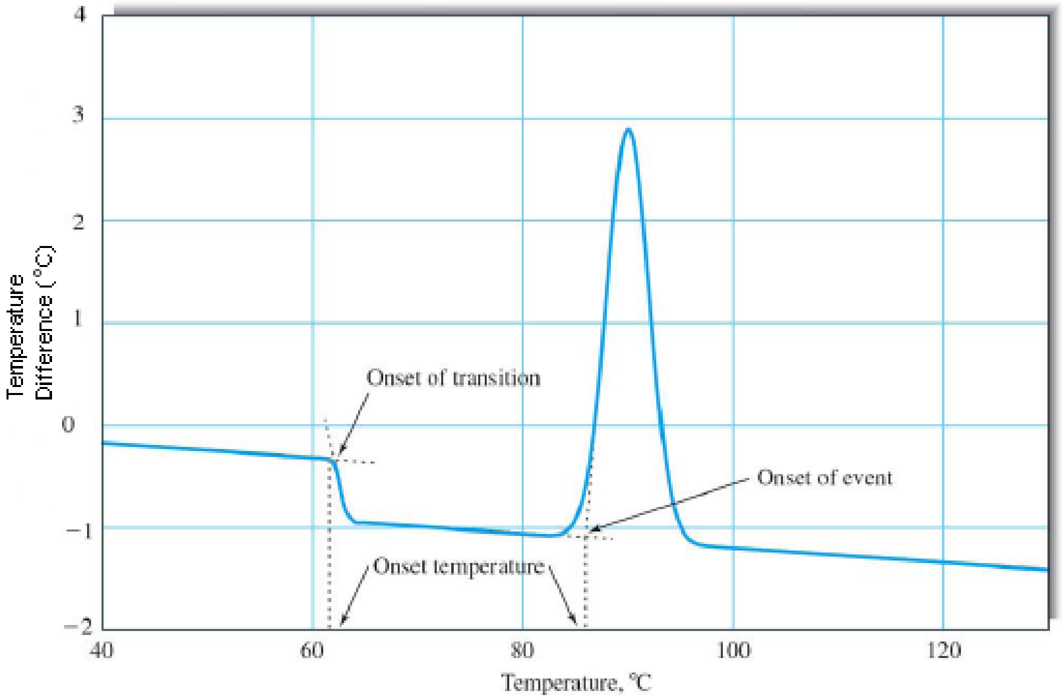

Figure 8.14: Transitions in DTA

Applications of DTA:

1. To construct phase diagrams.

2. To find an enthalpy (ΔH)

3. Phase Transformations

- Melting temperatures
- Glass transitions
- Crystallization

8.7.2 Thermogravimetric analysis

Thermogravimetric measures changes in weight in relation to changes in temperature. It is also known as thermal gravimetric analysis. It is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). Changes in the mass of a sample due to various thermal events (desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition) are studied while the sample is subjected to a program of change in temperature. Therefore, it is used in the analysis of volatile products, gaseous products lost during the reaction in thermoplastics, thermosets, elastomers, composites, films, fibers, coatings, paints, etc.

The measured weight loss curve gives information on:

- Changes in sample composition
- Thermal stability
- Kinetic parameters for chemical reactions in the sample

There are different types of TGA available:

1. ***Isothermal or Static TGA***: In this case, sample is maintained at a constant temperature for a period of time during which change in weight is recorded.

2. ***Quasi-static TGA***: In this technique, the sample is heated to a constant weight at each of a series of increasing temperature.

3. ***Dynamic TGA***: In this type of analysis, the sample is subjected to condition of a continuous increase in temperature at a constant heating rate, i.e., usually linear with time.

The instrument used for TGA analysis is a programmed precision balance for a rise in temperature (called as Thermobalance, see Figure 8.15). Thermobalance consists of an electronic microbalance (important component), a furnace, a temperature programmer and a recorder.

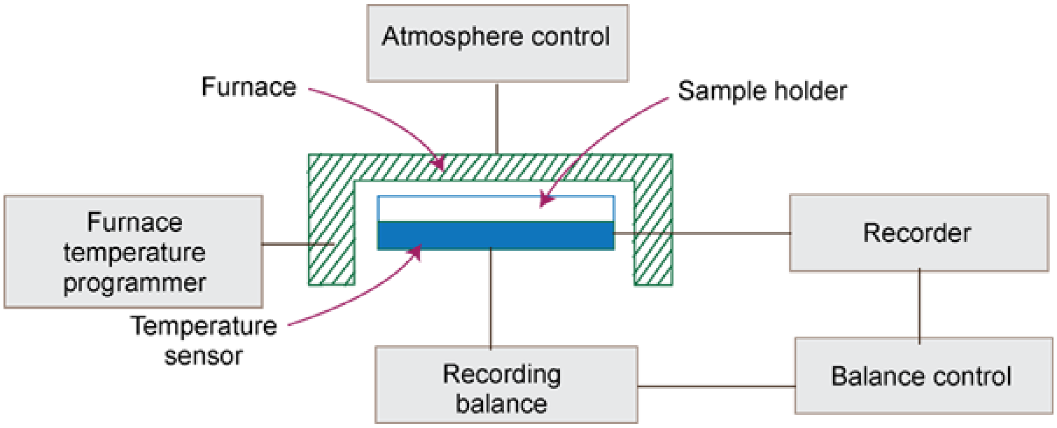

Figure 8.15: Block Diagram of a Thermo balance.

In the experiment, sample is placed in a crucible. The crucible is chosen such that the sample does not react with the crucible. Normally platinum or alumina crucibles are commonly used. The temperature range of interest is chosen. Then an appropriate heating rate is set (Typically 10^0C/minute). An appropriate atmosphere is also chosen, depending on the nature of the experiment

The weight loss ΔW is material dependant, but independent of the operating conditions

The temperature range over which the weight loss occurs, is dependent on the experimental conditions

The plot of mass/weight change in percentage versus temperature or time (known as TGA curves) is the typical result of TGA analysis as shown in Figure 8.16.

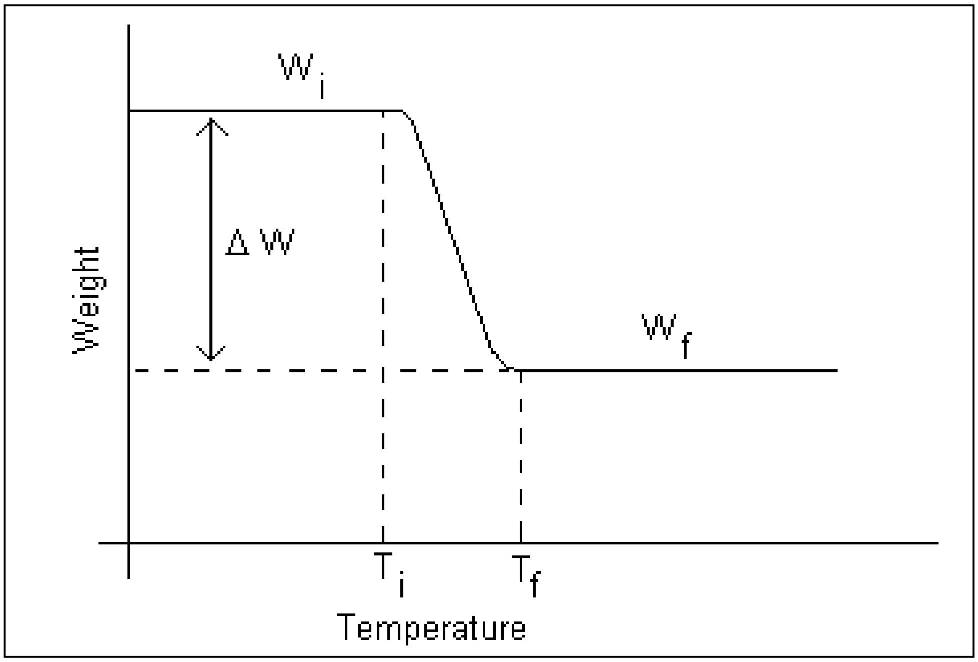

Figure 8.16: The plot of weight change with temperature.

There are two temperatures in the reaction: T_i (starting of decomposition temperature) and T_f (final temperature) representing the lowest temperature at which the onset of a mass change is seen and the lowest temperature at which the process has been completed, respectively. The reaction temperature and interval (T_f - T_i) strongly depend on the conditions of the experiments. Hence, they cannot have any fixed values.

Interpretation of TGA Curves:

TGA curves are typically classified into seven types according to their shapes. Figure 8.17 shows schematic of various types of TGA curves.

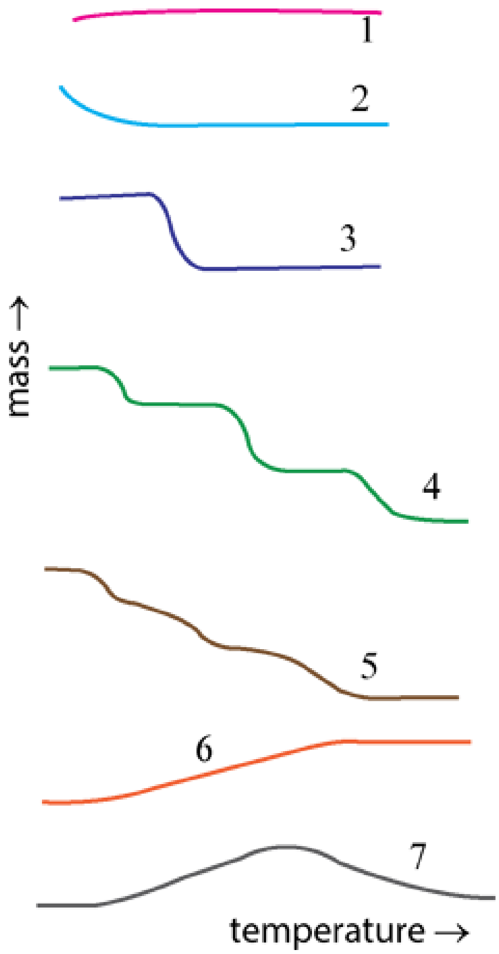

Figure 8.17: Schematic of various types of TGA curves.

- Curve 1: No change: This curve depicts no mass change over the entire range of temperature, indicating that the decomposition temperature is greater than the temperature range of the instrument.
- Curve 2: Desorption / drying: This curve shows that the mass loss is large followed by mass plateau. This is formed when evaporation of volatile product(s) during desorption, drying or polymerization takes place. If a non-interacting atmosphere is present in the chamber, then curve 2 becomes curve 1.
- Curve 3: Single stage decomposition: This curve is typical of single-stage decomposition temperatures having T_i and T_f.
- Curve 4: Multistage decomposition: This curve reveals the multi-stage decomposition processes as a result various reactions.

• Curve 5: Similar to 4, but either due to fast heating rate or due to no intermediates.
• Curve 6: Atmospheric reaction: This curve shows the increase in mass. This may be due to the reactions such as surface oxidation reactions in the presence of an interacting atmosphere.

• Curve 7: Similar to curve 6, but product decomposes at high temperatures. For example, the reaction of surface oxidation followed by decomposition of reaction product(s).

Applications of TGA:

1. Thermal stability of the related materials can be compared at elevated temperatures under the required atmosphere. TGA curve helps to explicate decomposition mechanisms.

2. Materials Characterization: TGA curves can be used to fingerprint materials for identification or quality control.

3. Compositional analysis: By a careful choice of temperature programming and gaseous environment, many complex materials/ mixtures can be analyzed by decomposing or removing their components. For example: filler content in polymers; carbon black in oils; ash and carbon in coals, and the moisture content of many substances.

4. Kinetic studies: A variety of methods can be used to analyze the kinetic features of weight loss or gain through controlling the chemistry or predictive studies.

5. Corrosion studies: TGA provides a means of studying oxidation or some reactions with other reactive gases or vapors

6. It is also used to check the material purity.

Examples of TGA curves:

Decomposition of calcium oxalate monohydrate (Figure 8.18, Figure 8.19)

- Calcium oxalate monohydrate, a standard material often used to demonstrate TGA performance.
- Exhibits three weight losses with temperature in an inert atmosphere (e.g. N_2).

- Experimental Conditions :
  - Temperature Range : RT to 1000°C
  - Ramp Rate : 10 °C/minute
  - Atmosphere : Air – 100 ml/min
- Calcium oxalate decomposes in three steps :

$$CaC_2O_4.H_2O \longrightarrow CaC_2O_4 + H_2O$$

$$CaC_2O_4 \longrightarrow CaCO_3 + CO$$

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2$$

$$\mathbf{CaCO_3 \longrightarrow CaO + CO_2}$$

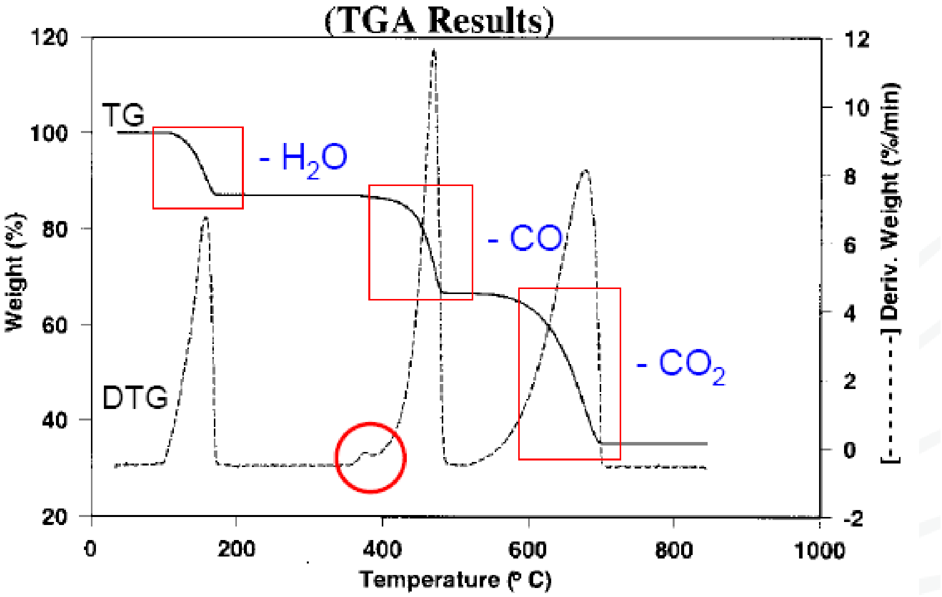

Figure 8.18: Decomposition of calcium oxalate monohydrate.

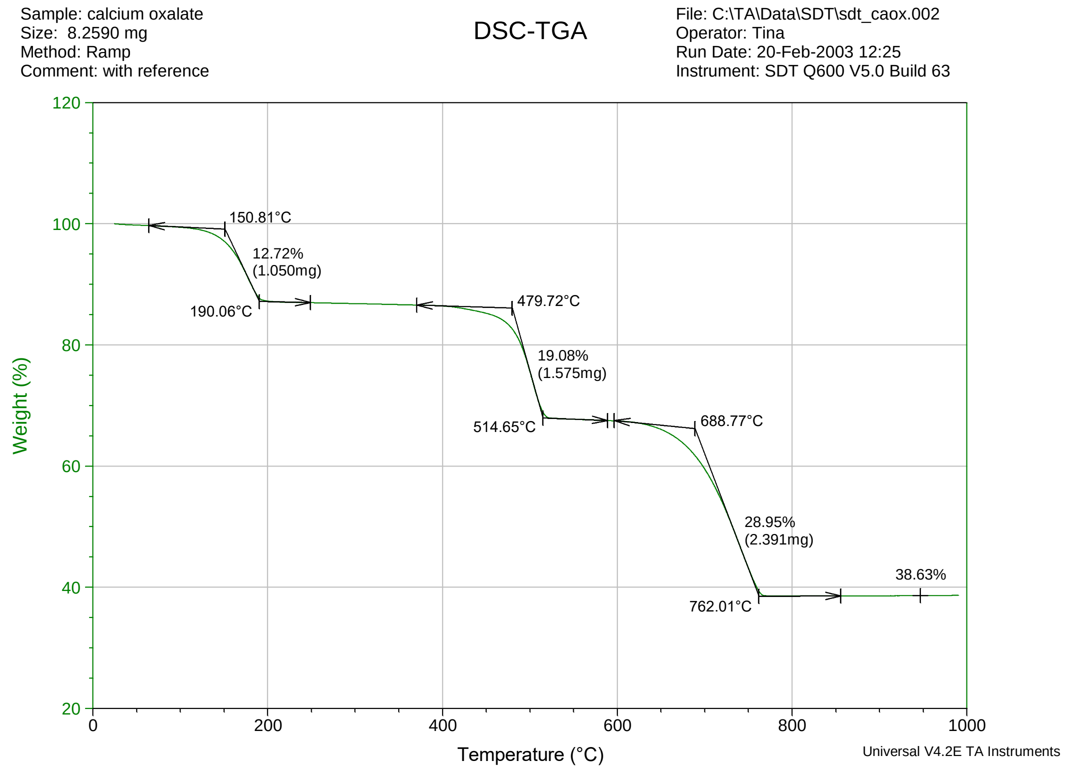

Figure 8.19: DSC-TGA curve of calcium oxalate monohydrate.

SAS1: What are the different types of TGA? Which is commonly used in research labs?

SAS2: Describe different types of TGA curves?

SAS3: What are the processes, which cause weight loss in TG curves?

SAS4: Describe few applications of TGA?

8.7.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) technique was developed by E.S. Watson and M. J. O'Neill in 1962 and commercial introduction was done at 1963 in Pittsburgh conference. It is a thermo-analytical technique which measures the change in heat flow to or from a material due to a physical or chemical process occurring at the material. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned and analyzed. In general, the temperature program of the DSC is designed to increase the sample holder temperature linearly as a function of time.

The main application of DSC is in studying phase transitions such as melting point, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

Description of DSC:

There are two types of DSC commercially available: Heat Flux (HF) Type and Power Compensation (PC) Type. Figure 8.20 shows the block diagram of HF and PC types.

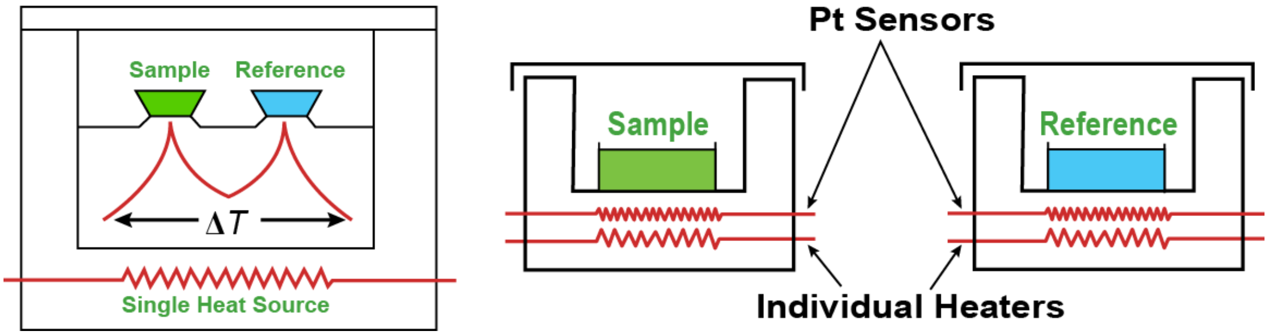

Figure 8.20: Schematic diagram of HF and PC types DSC.

In HF type DSC:

- Both sample and reference pans are heated by a single furnace through heat sink and heat resistor. Heat flow is proportional to the heat difference of heat sink and holders. The temperature versus time profile through a phase transition in a heat flux instrument is not linear.
- At a phase transition, there is a large change in the heat capacity of the sample, which leads to a difference in temperatures between the sample and reference pan.

- A set of mathematical equations convert the signal into heat flow information. By calibrating the standard material, the unknown sample quantitative measurement is achievable.

In PC type DSC:

Both sample and reference pans are heated by a different furnaces. When an event occurs in the sample, sensitive Platinum Resistance Thermometer (PRT) detects the changes in the sample, and power (energy) is applied to or removed from the sample furnace to compensate for the change in heat flow to or from the sample. As a result, the system is maintained at a “thermal null” state at all times. The amount of power required to maintain system equilibrium is directly proportional to the energy changes occurring in the sample. No complex heat flux equations are necessary with a power compensation DSC because the system directly measures energy flow to and from the sample.

In addition, PC type DSC has enhanced modulated temperature DSC (StepScan) technique and fast scan DSC (HyperDSC) for dramatic improvements in productivity, as well as greater sensitivity.

Furthermore, the heating and cooling rate of PC types DSC can be as high as 500°C/min.

Detection of phase transitions:

The underlying principle is that when the sample undergoes a physical transformation (phase transitions, etc), more or less heat will be needed to flow to it as compared to the reference to maintain both of them at the same temperature. This certainly depends on whether the process is exothermic or endothermic.

For example:

When a solid sample melts into a liquid, then it requires more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Similarly, when the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature.

By observing the difference in heat flows between the sample and reference, DSC is able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions.

Information about the DSC curves:

In general, the result of a DSC experiment is a curve of heat flux versus temperature or versus time. This curve can be used to calculate enthalpies of transitions, i.e., $\Delta H = kA$ (where, H is the enthalpy of transition, k is the calorimetric constant, and A is the area under the curve), which is done by integrating the peak corresponding to a given transition.

The value of k is typically given by the manufacturer for an instrument or can generally be determined by analyzing a well-characterized sample with known enthalpies of transition.

Applications of DSC:

DSC technique can be used to obtain glass transition, melting points, crystallization times and temperatures, heats of melting and crystallization, percentage of crystallinity, oxidative stabilities, heat capacity, completeness of cure, purities, thermal stabilities, polymorphism, recyclates or regrinds

***Evaluation and interpretation of DSC curves*:**

Figure 8.21 shows the typical DSC curve for a sample exhibiting endotherm of melting at a particular heating rate.

The onset of melting (122.8°C) and peak temperature of melting (123.66°C) can be determined by extrapolation technique and peak values, respectively.

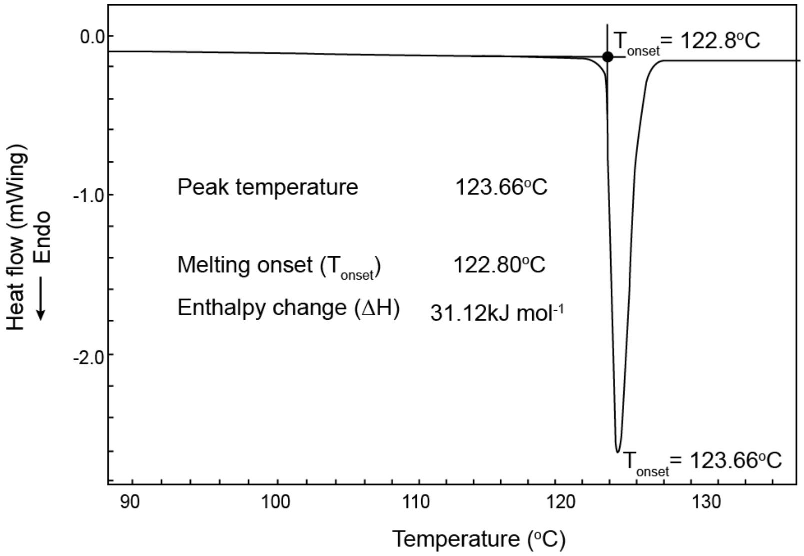

Figure 8.21: Typical DSC curve of a sample.

The enthalpy change can be calculated by integrating the area under the curve. The unit can be either J/g or J/mole depending on the nature of the sample.

Effect of heating rate:

Heating rate affects the melting point and enthalpy of melting. Figure 8.22 shows the typical DSC curves taken at different heating rate.

With increasing heating rate, the onset of the melting does not change significantly, but the peak point of melting shifts slowly to higher temperature.

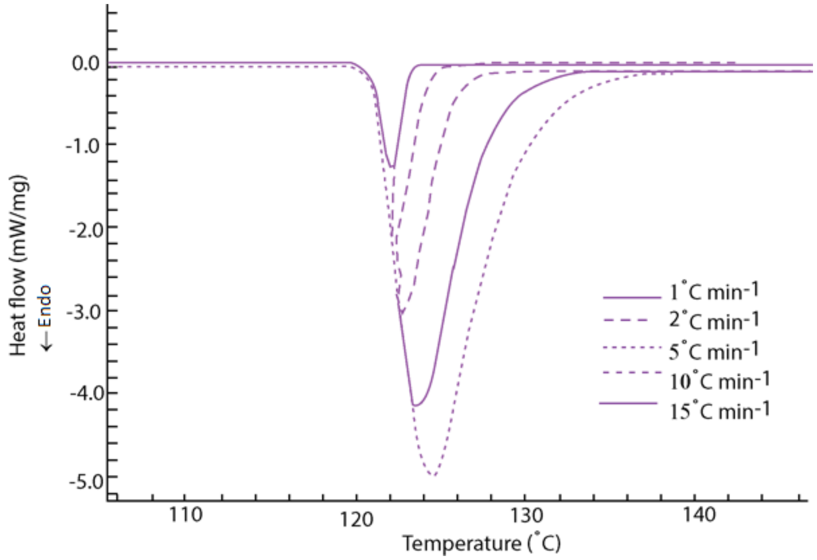

Figure 8.22: Typical DSC curves taken at different heating rates.

Effect of sample weight:

The sample weight also affects the thermal properties significantly. Figure 8.23 shows the typical DSC curves taken at a constant heating rate for different mass of the samples.

It could be clearly seen that the onset of melting, peak point of melting and enthalpy undergo small variations when the sample mass is changed.

Applications of DSC

DSC is useful for:

1. Determining enthalpies of reaction, or transformation
2. Determining the extent of crystallinity of a material
3. Studying glass transitions in glasses and polymers

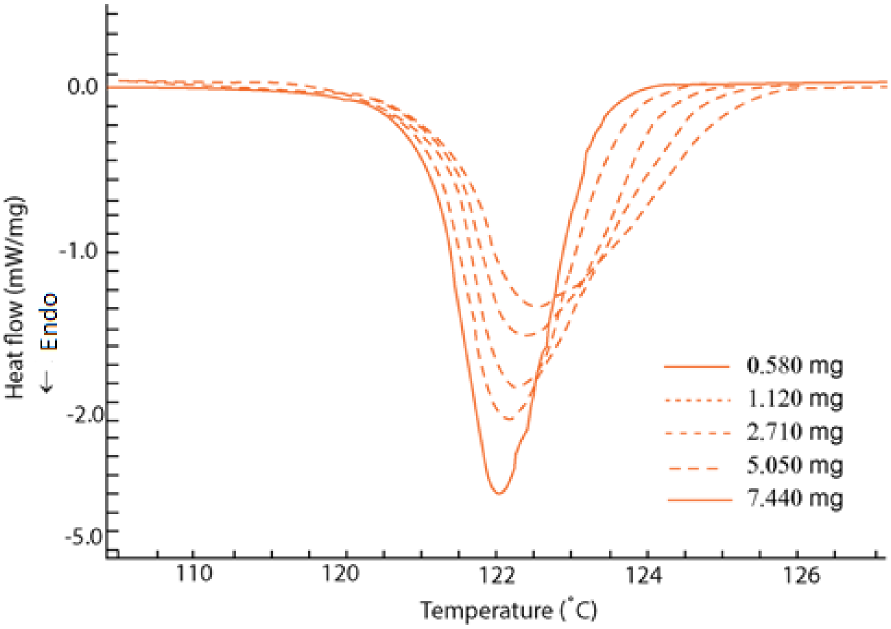

Figure 8.23: Typical DSC curves taken for different weighed samples.

Q22.1) What is differential scanning calorimetry? How it differs from DTA?

(Q22.2) What are the different types of DSC?

(Q22.3) What are the information can be extracted from DSC curves?

(Q22.4) Why do the DSC characteristics affected by the heat rate and sample weight?

(Q22.5) Are there any other parameters affect the DSC characteristics?

8.8 SUMMARY

Throughout the present chapter we have considered different types of structure analysis tools. We have considered first the defects and classification of defects in the crystals. After that we have dealt with principle, instrumentation and working of XRD, neutron and LEED and X-Ray powder diffraction. Application of these structure analysis also discussed. Then we have extended our discussion to different thermal analysis and their applications. Various examples are given in the unit to make the concepts clear. To check your progress, self-assessment questions (SAQs) are given place to place.

8. 9 GLOSSARY

Crystal defect	Imperfection in the regular geometrical arrangement of the atoms in a crystalline solid.
Diffraction	Diffraction is a change in the direction of a sound wave or a light wave caused by the presence of an obstacle in its path.
Thermal analysis	Technique used to analyze the time and temperature at which physical changes occur when a substance is heated or cooled.
X-rays	a form of electromagnetic radiation, similar to visible light.
Interstitial	an atom or ion situated in the interstices of a crystal lattice
Calorimetry	measurement of the quantity of heat
Crystallization	the process in which crystals are formed either from something that has been melted or from a solution.
Oxidation	a process in which a chemical substance changes because of the addition of oxygen.
Transition	the process in which something changes from one state to another.

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8.11 SUGGESTED READING

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2. Waseda, Yoshio, Eiichiro Matsubara, and Kozo Shinoda. X-ray diffraction crystallography: introduction, examples and solved problems. Springer Science & Business Media, 2011.
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8.12 SUGGESTED READING

Question 1. What kind of reference materials is used in DTA?

Question 2. What's the difference between DSC and DTA?

Question 3. What is the principle behind X-ray crystallography?

Question 4. What is XRD used for?

Question 5. What is Bragg's law?

Question 6. Why are X-rays used as the source beam?

Question 7. What information does the XRD pattern of a crystal provide?

Question 8. Explain an experimental procedure for finding the XRD pattern.

Multiple choice based question?

1. Thermal analysis is defined as ___________

a) Measurement of concentration of materials as a function of temperature

b) Measurement of solubility of materials as a function of temperature

c) Measurement of physical properties as a function of temperature

d) Measurement of line positions of crystals as a function of temperature

2. Which of the following statements given below is false?

a) TGA, DTA and DSC are measured using same instrument

b) TGA and DTA can be carried out simultaneously.

c) TGA, DTA and DSC are measured using different instruments.

d) TMA is a recent name of Dilatometry.

3. During DTA (Differential thermal analysis) what kind of reference material is used?

a) Chemically active

b) Physically active

c) Inert

d) Having catalytic property

4. In DTA, the ___________________ of sample and reference should be______________ until any thermal event take place. Fill up the appropriate options for the two blanks given from the choices given below.

a) Concentration, different

b) Concentration, same

c) Temperature, different

d) Temperature, same

5. What is the factor that limits the application of this differential thermal analysis method?

a) Huge apparatus

b) Insensitivity

c) Highly reactive

d) Low growth rate

6. In DTA method, the sample temperature was recorded on __________

a) Heating

b) Cooling

c) Gaseous

d) Liquid

7. In the normal DTA instruments, what is the size of the sample size to be used?

a) Very large

b) Moderate

c) Small

d) Very small

Answer: 1: c), 2: c), 3: c), 4: d), 5: b), 6: b), 7: c)

UNIT–9 MICROSCOPY TECHNIQUES

Structure

9.1 Introduction

A microscope is a device that enlarges an image of a small object to expose details that the naked eye cannot perceive. The optical microscope, which employs visible light focused through lenses, is the most used type of microscope. Resolution and magnification both are crucial, if you want to get a clear picture of anything very tiny. A microscope with great magnification but low resolution, for instance, will only produce a blown-up version of a hazy image. Different types of microscopes differ in their magnification and resolution. In the present chapter, we will discuss history, need and various types of microscope in detail. The chapter will also cover the concept of heat treatment, radiation damage and their applications.

9.2 Objectives

After studying this unit you should be able to:

- Understand the basis on microscope, and different types of microscopes.
- Understand the concept of electron microscope and its different types.
- Know the basics of heat treatment, methods and the applications of heat treatments.
- Understand the concept of radiation damage.

9.3 Introduction to microscopes

Microscopes are the instruments designed to produce magnified visual or photographic images of too small objects that cannot be seen with the naked eye. With the help of naked eye one cannot view the objects down to 1 mm. To overcome this difficulty lenses are used to magnify the minute objects. However, the lenses can magnify objects up to the limited extent, so many lenses were combined together to for an instrument known as microscope. These are very important because they possess the characteristics of magnitude and resolving. Light and electron microscopes are used to study the objects in the range 1 mm - 300 nm and 300 nm - 0.2 nm, respectively. A microscope is an instrument that can be used to observe small objects, even cells because they possess the characteristics of magnification and resolving power.

Resolving power of the microscope:

The ability of the microscope to resolve or to distinguish between the objects lying close together. The resolving power is the inverse of the distance between two objects that can be just resolved. This is given by the famous Abbe's criterion given by Ernst Abbe in 1873 as:

$$\Delta d = \frac{\lambda}{2nsin\theta}$$

Resolving power =

$$\frac{1}{\Delta d} = \frac{2nsin\theta}{\lambda}$$

Here n is the refractive index of the medium separating object and aperture. Note that to achieve high-resolution n sin θ must be large. This is known as the Numerical aperture.

For good resolution:

1. sin θ must be large. For this, the objective lens is kept as close to the specimen as possible.
2. A higher refractive index (n) medium must be used.
3. Decreasing the wavelength by using X-rays and gamma rays.

9.4 History of Microscopes

The first microscope was developed in 1590 by Dutch lens grinders Hans and Zacharias Jansen. In 1667, Robert Hooke described the microscopic appearance of cork (Figure 9.1). It was very simple and able to study the structure of tissue.

Compound microscope was developed at the beginning of 1660's by Janssen brothers and Galileo. This microscope consisted of two tudes that slid within one another, and had a lens at each end. The microscope was focused by sliding the tubes. The lens in the eyepiece was bi-convex (bulging outwards on both sides), and the lens of the far end (the objective lens) was plano-convex (flat on one side and bulging outwards on the other side). This advanced microscope had a 3 to 9 times power of magnification. Zacharias Janssen's father Hans may have helped him build the microscope.

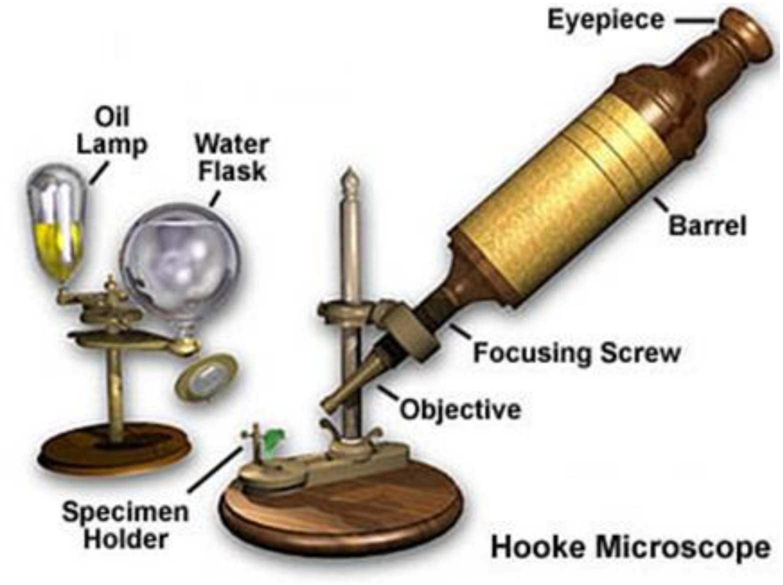

Figure 9.1: Zacharias Janessen and Hooke microscope.

Modern Microscopes: In 1900's, iron based structures were used to develop a microscope (Figure 9.2) due to its cheaper cost; Only one eyepiece (monocular); Outside light source; reflected onto mirror; Very functional; Still used today.

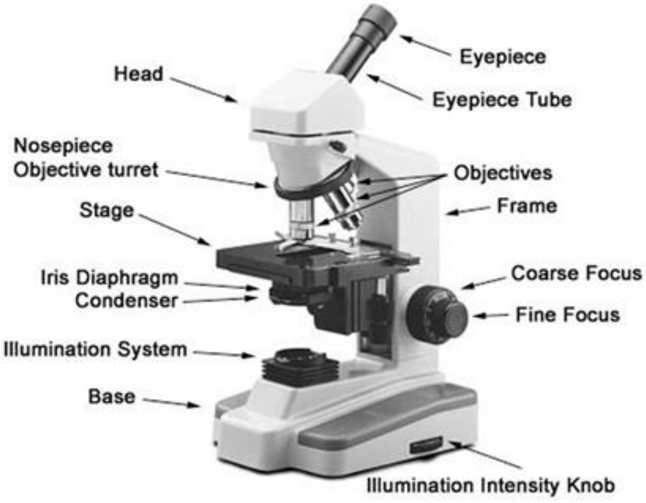

Figure 9.2: Photoview of single eye-piece microscopes.

After that fancy type microscopes were developed in 1998's show in Figure 9.3. This have many benefits such as they provided

- Easier to use

- Better images
- Large magnification
- Better lighting

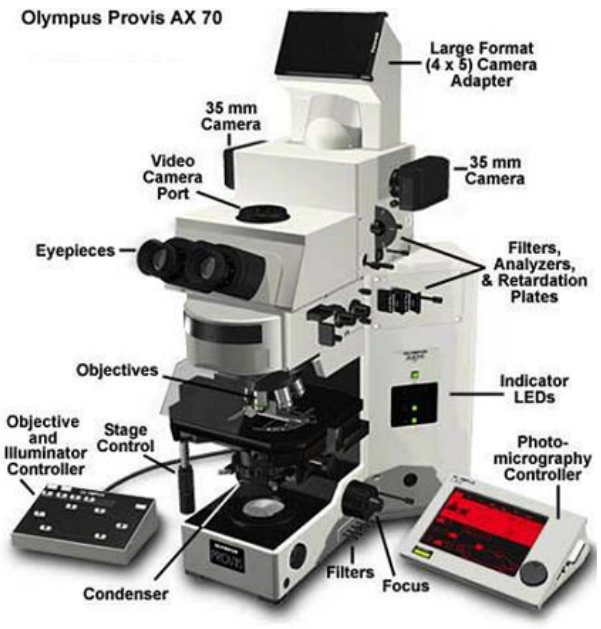

Figure 9.3: Photoview of single eye-piece microscope.

9.5 Need of microscopes

1. In research, process development, and reliability and failure analysis activities, several degrees of structural information are of interest.
2. It's more vital to investigate surface topography and morphology, such as grain size and shape, grain boundaries, element distribution in materials, compound presence, micro-cracking, textured surface development, and so on, in order to optimize the fabrication process.
3. Furthermore, cross-sectional views of multilayer structures are very important from an industrial standpoint, particularly in microelectronic device fabrication and optical coating technology, where interfacial nature, substrate interactions, and geometry and perfection of electronic devices with associated conducting and insulating layers are very important.

4. Microscopes are so critical for deciphering information at the atomic level and optimising the production process and consequent qualities in order to commercialize materials for products.

9.6 Types of Microscopes

There are different types of microscopes and each of these has different purposes of use. Some are suitable for biological applications, while others are used in educational institutions. Some microscope are also find application in metallurgy and studying three-dimensional samples.

Now we will discuss working principle and applications of some important type of microscopes:

- Simple microscope
- Compound microscope
- Electron microscope
- Stereomicroscope
- Scanning probe microscope

9.6.1 Simple Microscope

A simple microscope is defined as the type of microscope that uses a single lens for the magnification of the sample (Figure 9.4**)**. A simple microscope is a convex lens with a small focal length. Simple microscope has the following parts:

i) Foot, stand, ii) vertical limb, iii) folded arm, iv) a simple convex lens, v) glass stage, vi) reflecting mirror, vii) clips and adjustment screw (Figure 9.4**)**. Foot is known as supporting stand and used to bear the weight of the microscope. The vertical limb on the stand is fitted with the adjustment screw for the focusing. A simple convex lens is mounted on a vertical limb. Glass stage is the platform used for placing the slides with samples and stage clips are used to hold the slides in the proper place. The reflecting mirror is used for getting the light. The magnification of the simple microscope ranges 4 to 40 times depending upon the magnification of the lens.

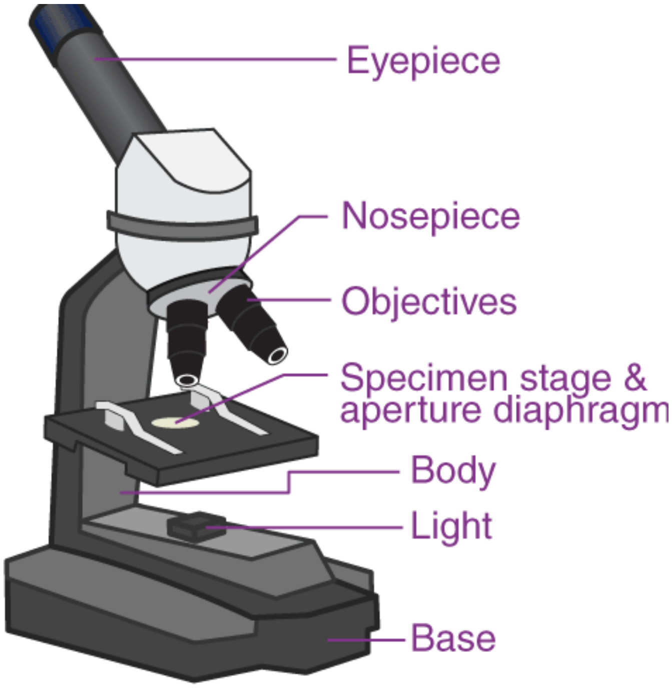

Figure 9.4: Photoview of Simple Microscope.

Principle of Simple Microscope

The working principle of a simple microscope is that when a sample is placed within the focus of the microscope, a virtual, erect and magnified image is obtained at the least distance of distinct vision from the eye that is held at the lens.

Application of Simple Microscope

- It is common among the watchmakers as they can view a magnified image of the smallest parts.
- It is also used by the jewellers for obtaining a magnified image of the fine parts of the jewellery.
- Most educational institutions such as schools and colleges use a simple microscope in their laboratories.
- Dermatologists (skin specialists) use simple microscopes to identify different skin diseases.

9.6.2 Compound Microscope

A compound microscope is defined as the type of microscope that has more than one lens (Figure 9.5). It has a combination of lenses and two optical parts known as an objective lens and eyepiece or ocular lens. It consists of three types of the lens systems which are as follows: i) Condenser lens system ii) Objective lens system iii) Eye –piece lens system or ocular lens system.

Condenser lens system: It occurs beneath the specimen and its function is the collection and focusing of light rays on the object or specimen which is placed on the stage of the microscope.

Objective lens system: It remains near and above the specimen. It produces and magnifies the image of the specimen.

Eye–piece lens system or ocular lens system: It remains near the eyes of the observer and magnifies and forms the image (secondary) of the (primary) image previously produced by the objective.

Compound microscope has the following parts: i) foot ii) mirror iii) stage iv) body tube v) nose-piece vi) arm vii) condenser viii) coarse adjustment ix) fine adjustment x) eye-piece xi) objectives (Figure 9.5).

Foot gives the support to the microscope and bears its weight. It comprises two parts the tripod foot and horse shoe-shaped foot. Mirror is fitted below the stage having concave and plane surfaces. It reflect light upward through the diaphragm and the hole in the stage. The stage is a rectangular platform with the sides attached to the arms. The body tube is normally 160 mm long and carries the objectives at the lower end and the eye-piece at the upper end. In the nose piece low power and high power lenses are fitted. Arm supports the body tube and coarse adjustment. Condenser is placed between the mirror and stage and used for the focusing light and adjusting the intensity of illumination. Coarse adjustment is attached to the body tube and very important for the rapid and precise focusing of the object. Coarse adjustment has a large head, by turning the head in the clockwise direction, the body tube moves downward, while by turning it in anticlockwise direction, the body tube moves upwards. Fine adjustment is very essential for the perfect image of the object. It moves the body tube up and down like the course adjustment. A slight revolution of fine adjustment is required for the exact and sharp focusing of the object. Eye piece lies at the top of the body tube. Eye piece may be replaced with another of lower or higher magnification. The objective are attached with the nose piece.

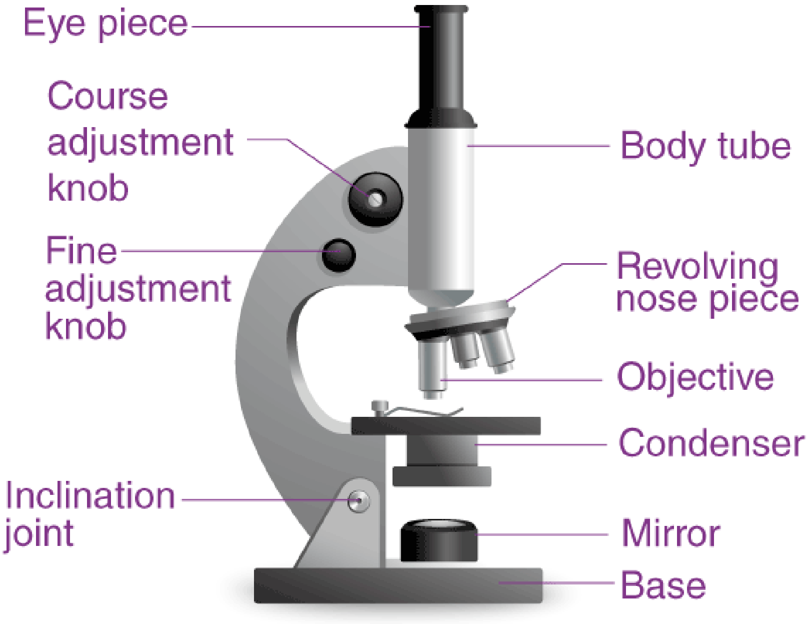

Figure 9.5: Photoview of Compound Microscope.

Principle of Compound Microscope

The working principle of the compound microscope is that the combination of lenses enhances the magnification of the sample. The sample is first viewed as a primary image in the tube and viewed again in the eyepiece.

Applications of Compound Microscope

- The study of bacteria and viruses is possible with the help of a compound microscope.
- A compound microscope finds application in forensic laboratories.
- It is also used in metallurgy.

9.6.3 Optical microscopes

Optical or light microscopy as shown in the Figure 9.6 involves passing visible light transmitted through or reflected from the sample through a single or multiple lenses to allow a magnified view of the sample.

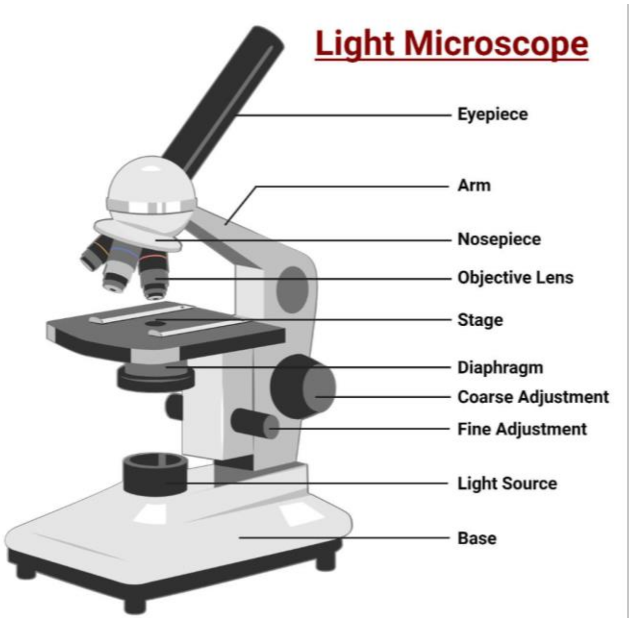

Figure 9.6: Schematic of light microscope.

The resulting image can be detected directly by the eye and/or imaged on a photographic plate or captured digitally.

The single lens with its attachments, or the system of lenses and imaging equipment, along with the appropriate lighting equipment, sample stage and support, makes up the basic light microscope.

***Types Light Microscope*:**

There are many types of light microscopes for imaging purposes:

- **Bright-field microscope:** Compound Light Microscope is another name for the Brightfield Microscope. It is an optical microscope that creates a dark picture against a brilliant background using light rays. It is the typical microscope that is employed in biological, cellular biology, and laboratory investigations on microorganisms.

- **Dark-field microscope:** The Dark-field microscope is an ordinary microscope with a special condenser. Dark-field microscopy is ideally used to illuminate unstained samples causing them to appear brightly lit against a dark background. Using basic stains, which provide contrast between the image and the image backdrop, this microscope is used to observe fixed and living specimens. It is specifically made with lenses, which are magnifying glasses, which change the specimen to create a picture seen via the eyepiece. In order to provide contrast between the image and the image backdrop, this microscope is used to study fixed and living specimens that have been stained with basic stains. The specimen is modified by magnifying glasses called as lenses, which are part of its unique design, to create an image that can be seen via the eyepiece.

- **Phase-contrast microscope:** Phase-contrast microscopy is an optical microscopy method that transforms brightness variations in the picture from phase shifts in light flowing through a transparent material. While phase shifts are imperceptible in and of themselves, brightness differences make them noticeable. The principle of phase contrast was discovered by Zernike (1955).

Phase contrast microscopy is used to visualize transparent specimens, when high-resolution is not required, including: Living cells (usually in culture), Microorganisms, Thin tissue slices, Fibers, Subcellular particles, including organelles.

- **Fluorescence microscope:** The Fluorescence microscope is based on the phenomenon of fluorescence. When a certain chemical compound are illuminated by ultraviolet rays they become excited at molecular level and start to emit light of visible rage. This phenomenon is known as fluorescence. The source in the Fluorescence microscope is ultraviolet rays of higher wave-length (3500 to 4000 Å). Scientists frequently employ fluorescence microscopy to detect the localization of molecules within cells and of cells within tissues because it is very sensitive, specific, and trustworthy. In order to provide contrast between the image and the image backdrop, this microscope is used to study fixed and living specimens that have been stained with basic stains. The specimen is modified by magnifying glasses called as lenses, which are part of its unique design, to create an image that can be seen via the eyepiece.

9.6.4 Electron Microscope

An electron microscope is defined as the type of microscope in which the source of illumination is the beam of accelerated electrons. It is a special type of microscope with a high resolution of images as the images can be magnified in nanometers.

Principle of Electron Microscope

The metal used in an electron microscope is tungsten. A high voltage current is applied which results in the excitation of the electrons in the form of a continuous stream that is used as a beam of light. The lenses used in the electron microscope are magnetic coils. These magnetic coils are capable of focusing the electron beam on the sample such that the sample gets illuminated. As the flow of current increases, the strength of the magnetic lens increases. The electron beam flow is designed such that it cannot pass through the glass lens.

Application of Electron Microscope

- Quality control and failure analysis in industries are done with the help of an electron microscope.
- The images obtained in an electron microscope can be captured as electron micrographs with the help of specialized cameras.
- The study of metals and crystals became easy with the introduction of an electron microscope.

There are two types of electron microscopes:

- The transmission electron microscope (TEM)
- The scanning electron microscope (SEM)

9.6.4.1 Transmission electron microscope (TEM)

TEM is a powerful electron microscope that focuses an electron beam on a specimen to create an incredibly detailed and highly magnified picture of the object. The magnification power is over 2 million times greater than that of a light microscope, generating a picture of the specimen that makes it simple to characterise the image's morphological characteristics, compositions, and crystallisation information. Louis de Broglie's discovery of cathode rays, which are similar to electrons, in the early 1920s cleared the door for the creation of the electron microscope, which employed an electron beam to produce wave motion.

The electrons were focused using magnetic fields as lenses. Following these findings, Ernst Ruska and Max Knolls created the first electron microscope in 1931. In 1933, Ernst Ruska and the Sieman's firm upgraded it to become a transmission electron microscope (TEM). When compared to a light microscope, this TEM microscope offers a number of benefits, and it also has a very high efficiency. The most potent microscopes used in labs are TEMs, which include both light and electron microscopes. They have a resolution limit of 0.2um since they can magnify tiny particles as small as 2nm.

Principle of Transmission Electron Microscope (TEM):

The Transmission Electron Microscope (TEM) operates on a similar concept to the light microscope. The main distinction is that whereas TEM utilizes an electron beam to concentrate on the specimen and create a picture, light microscopes employ light rays to focus and do the same.

Compared to light, which has a long wavelength, electrons have a shorter wavelength. In a light microscope, the resolution power rises as the wavelength of the light drops, whereas in a transmission electron microscope (TEM), when an electron lights the specimen, the resolution power grows as the wavelength of the electron transmission increases. Since the wavelength of electrons is around 0.005 nm, that is 100,000 times shorter than the wavelength of light, TEM offers about 1000 times greater resolution than a light microscope. It is true that the TEM can be used to examine the interior details of the tiniest particles, such as a virion particle.

Parts of Transmission Electron Microscope (TEM):

Their working mechanism is enabled by the high-resolution power they produce which allows it to be used in a wide variety of fields. It has three working parts which include:

1. Electron gun
2. Image producing system
3. Image recording system

***Electron gun*:** The Transmission Electron Microscope's component that generates electron beams is this. A cathode, which is a V-shaped filament of tungsten that is often heated, generates electrons (Figure 9.7). A control grid, also known as a Wehnelt cylinder, with a centre hole that is columnar to the tube, covers the tungsten filament. The cylindrical column hole of the cathode is above or below it. The anode's disk-shaped end, which also contains an axial hole, is negatively charged, as is the cathode and the control grid. The columnar aperture (hole), through which electrons are transferred from the cathode to the anode at high voltage and consistent energy, effectively focuses the specimen to create a sharply defined picture. Additionally, it features a condenser lens system, which uses the electron gun's column hole and energy intensity to concentrate the electron beam on the specimen. To focus the electron beam on the specimen, the TEM utilises two condenser lenses. The two condenser lenses each work to create an image; for example, the first lens, which has a high magnification, creates a smaller image of the specimen, which is then directed to the objectives by the second condenser lens.

***Image- Producing system*:** The columnar aperture (hole), through which electrons are transferred from the cathode to the anode at high voltage and consistent energy, effectively focuses the specimen to create a sharply defined picture (Figure 9.7). Additionally, it features a condenser lens system, which uses the electron gun's column hole and energy intensity to concentrate the electron beam on the specimen. To focus the electron beam on the specimen, the TEM utilises two condenser lenses. The two condenser lenses each work to create an image; for example, the first lens, which has a high magnification, creates a smaller image of the specimen, which is then directed to the objectives by the second condenser lens.

***Image-Recording System*:** The fluorescent screen that is utilised to observe and focus on the picture is what makes up this object. Additionally, they feature a digital camera that captures photographs that are then permanently stored (Figure 9.7). They have a vacuum mechanism in place to stop electrons from hitting air molecules or colliding with them, which would impair their mobility and ability to concentrate. Straight electron travel to the picture is made easier by a vacuuming system. An electric power source, a pump, a gauge, and valves make up the vacuuming system. The resulting grayscale or black and white image is referred to as a monochromatic image. Because the picture must be visible to the naked eye, electrons are permitted to pass through a fluorescent screen that is mounted to the bottom of the microscope. The image can also be taken digitally, viewed on a computer, and saved in the JPEG or TIFF file format. Depending on the recording device used, such as pixel cameras, the picture can be changed from its monochromatic form to a colourful image during storage. Pictures that are coloured make visualisation, recognition, and characterisation of the images simple.

Working of Transmission Electron Microscope (TEM):

The functioning mechanism of the equipment presented is a sequential procedure of the TEM's parts in order to signify:

- Electrons are generated by a heated tungsten filament in the electron cannon and are focused on the object by condenser lenses.
- The specimen's electron beam is focused using magnetic lenses. The vacuum enables electrons to form a clean image without colliding with any air molecules that would deflect them, thanks to the aid provided by the column tube of the condenser lens into the vacuum.
- When the electrons arrive at the sample, the sample scatters them, concentrating them on the magnetic lenses to create a huge, clear image. If the sample travels via a fluorescent screen, it creates a polychromatic image.
- The more electrons are dispersed by a thick specimen, the darker the picture will be since fewer electrons will reach the screen to be seen, whereas thinner, more transparent specimens would seem brighter.

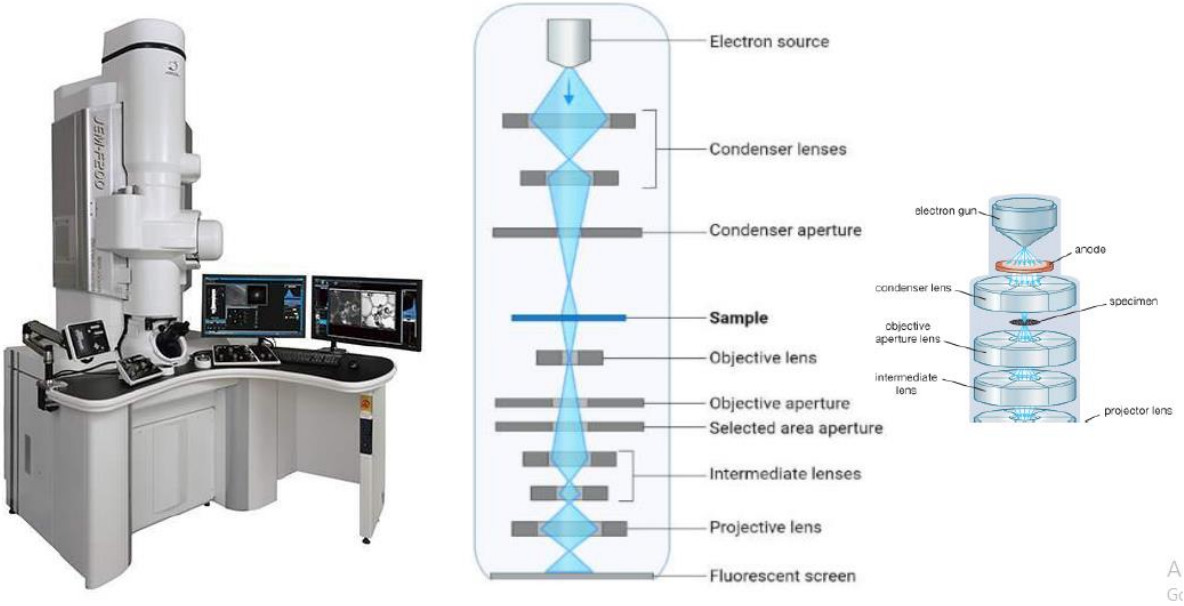

Figure 9.7: Transmission Electron Microscope (TEM).

Applications of Transmission Electron Microscope (TEM)

A vast range of disciplines, including biology, microbiology, nanotechnology, forensic research, etc., employ TEM. These applications include, among others:

1. to view and research the cell structures of fungus, viruses, and bacteria
2. to view the plasmids and flagella of bacteria
3. to observe the dimensions of the organelles seen in microbial cells
4. To research and distinguish between animal and plant cells.
5. Additionally, it is utilised in nanotechnology to research nanoparticles like ZnO nanoparticles.
6. It is used to find and classify broken or damaged microparticles, which furthers the ability of the particles' healing processes.

Advantages of Transmission Electron Microscope (TEM)

1. To see and research the cell structures of fungus, viruses, and bacteria
2. To see the plasmids and flagella of bacteria

3. To observe the dimensions of the organelles seen in microbial cells
4. To research and distinguish between animal and plant cells.
5. Additionally, it is utilised in nanotechnology to research nanoparticles like ZnO nanoparticles.
6. It is used to find and classify broken or damaged microparticles, which furthers the ability of the particles' healing processes.

Limitations of Transmission Electron Microscope (TEM)

1. TEMs are often highly expensive to buy.
2. They are fairly heavy to move about.
3. It takes a lot of work to prepare specimens for TEM viewing.
4. Artifact hazards can result from the application of chemical fixations, dehydrators, and embedments.
5. They require a lot of maintenance.
6. To function, it needs a steady influx of voltage.
7. They are employed in secluded locations where they are not exposed because of how sensitive they are to vibrations and electro-magnetic motions.
8. Unless they employ a fluorescent screen at the conclusion of viewing, it generates monochromatic visuals.

9.6.4.2 Scanning electron microscope (SEM)

Scanning Electron Microscope (SEM) is a type of electron microscope that scans surfaces of microorganisms that uses a beam of electrons moving at low energy to focus and scan specimens (Figure 9.8). The inefficiency of the wavelength of light microscopes led to the invention of electron microscopes. Compared to a light microscope, an electron microscope's relatively short wavelengths allow for superior resolution. Mafred von Ardenne created the first scanning electron microscope in 1937 with the intention of outperforming the transmission electron microscope. He focussed a beam of electrons on a tiny raster and utilised high-resolution power to scan it.

Principle of Scanning Electron Microscope (SEM)

The scanning electron microscope employs emitted electrons as opposed to transmitted electrons, which are used by the transmission electron microscope. According to the scanning electron microscope's operating theory, kinetic energy is used to generate signals from electron interactions. These electrons, which are utilised to observe crystalline elements and photons, are secondary electrons, backscattered electrons, and diffracted backscattered electrons. An image is created using backscattered and secondary electrons. While the backscattered electrons reveal contrast in the composition of the specimen's components, the secondary electrons that are released by the specimen serve as the principal means of identifying the morphology and topography of the specimen.

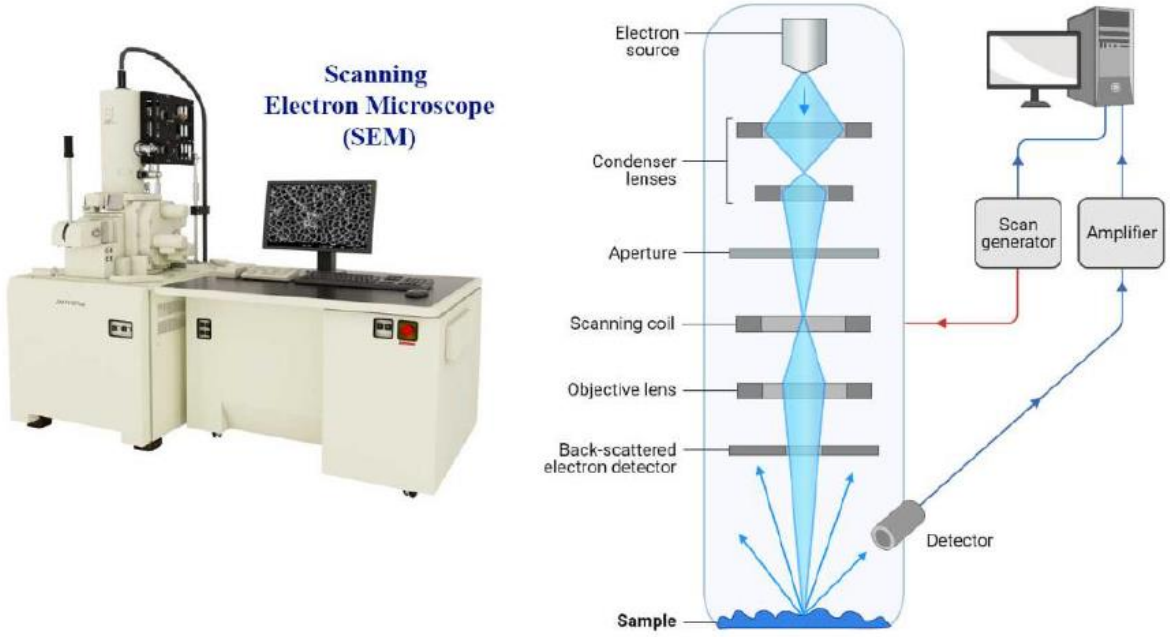

Figure 9.8: Scanning Electron Microscope (SEM)

Working of Scanning Electron Microscope (SEM)

- The tungsten filament lamps at the top of the column, which are similar to those used in transmission electron microscopes, are the source of the electrons and the electromagnetic lenses.
- After thermal energy is provided to the electron source, the electrons are released and permitted to flow quickly to the anode, which is charged positively.
- Primary dispersed (Primary) electrons with high energy levels and secondary electrons with low energy levels are emitted from the specimen surface as a result of the electron beam. By interacting with the specimen, the electron beam generates signals that provide details about the specimen's surface topography and composition.
- Even air-dried samples can be analysed without extra preparation in order to visualise the specimen under the SEM. However, in order to preserve the structural characteristics of the cells and prevent cell collapse when exposed to the high vacuum of the microscope, microbial specimens require fixation, dehydration, and drying.
- To enable spatial dispersion of electric charges on the surface of the specimen, the samples are mounted and coated with a thin coating of heavy metal components. This improves picture creation and increases image quality.
- This microscope scans by tapering an electron beam back and forth over a small area of the microscope. Secondary electrons are a small cluster of electrons that are released by the specimen's surface when electrons strike it. These secondary electrons are then captured by a specialized detection device.
- The secondary electrons hit a scintillator as soon as they enter the detector and get there (a luminescence material that fluoresces when struck by a charged particle or high-energy photon). This produces brief light bursts, which are transformed into an electric current via a photomultiplier and sent to the cathode ray tube as a signal. This creates a viewable and photographable image that resembles a television image.
- The nature of the specimen, i.e., raised surfaces to receive high quantities of secondary electrons entering the detector while depressed surfaces have fewer electrons reaching the surface and therefore fewer electrons enter the detector, strongly influences the quantity of secondary electrons that enter the detector.
- As a result, on the screen, elevated objects will seem brighter and depressed areas darker.

Parts of a Scanning Electron Microscope (SEM):

The following are main parts of the scanning electron microscope (Figure 9.8):

Electron source**:** This is where electrons are created at a voltage between 1 and 40 kV while being heated thermally. In order to create a picture and conduct analysis, the electrons condense into a beam. There are three different kinds of electron sources that can be used: tungsten filament, lanthanum hexaboride, and field emission gun (FEG).

Lenses**:** The FEG has several condenser lenses that focus the electron beam from the source through the column to form a focused beam of electrons that forms a spot known as a spot size.

Scanning Coil : they are used to deflect the beam over the specimen surface.

Detector: It's made up of several detectors that are able to differentiate the secondary electrons, backscattered electrons, and diffracted backscattered electrons. The functioning of the detectors highly depends on the voltage speed, the density of the specimen.

The display device (data output devices)

Power supply

Vacuum system

Scanning electron microscope should be free from vibrations and any electromagnetic elements, just like the TEM.

Limitations:

1. They are very costly.
2. They are heavy to transport.
3. They must be utilized in spaces free of electromagnetic interference and vibration.
4. They need to be kept at a constant voltage.
5. They ought to have access to cooling systems for maintenance.

By combining the operating concepts of the scanning electron microscope (SEM) and the transmission electron microscope (TEM), scanning-transmission electron microscope (STEM) was created. STEM focuses a probe on the specimen using a convergent electron beam, and then scans the probe's surface to capture signals that are then collected as point-to-point to create a picture.

(SAS.1). Why do we need a microscope?

(SAS.2). How does a microscope work?

(SAS.3). What is the best resolution one can obtain by an optical microscope?

(SAS.4). Is there any limitation on the number of lenses to build a microscope? Why?

(SAS.5). What is the difference between simple and compound microscope?

(SAS.6). What is the difference between light microscope and electron microscope?

(SAS.7). What are the uses of Microscope

9.7 Heat treatments

Heat treatments are used to change a metal's and metal alloys's physical and mechanical properties without affecting its shape. They are important processes in metal and metal alloys fabrication because they improve the desirable properties of metal while allowing for additional processing.

The heating and cooling of metal is carefully managed in various heat treatment methods. Steel, for example, is frequently heat treated for a variety of commercial purposes.

Purpose of heat treatment

- To increase ductility, strength, toughness
- Increase machinability
- Relieve internal stresses
- To improve corrosion resistance and hardness

Process of heating consists of three steps **(**Figure 9.9**):**

1. Heating
2. Soaking
3. Cooling

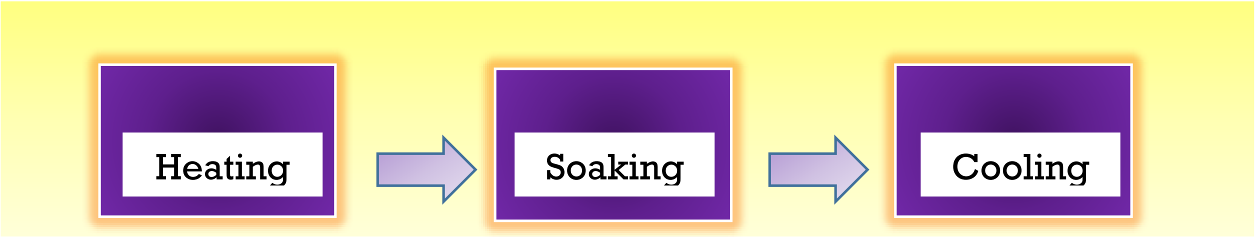

Figure 9.9: Schematic diagram of Process of heating.

Depending on the metal and technique, the cooling stage has distinct impacts. Steel hardens when it is swiftly cooled, whereas aluminium softens during the rapid cooling step of solution annealing.

Benefits of Heat Treating

- *Heat treatment soften a metal or plastic by the process of annealing*
- *It harden a metal through case hardening, hardening, Nitriding, carburizing*
- *It harden or soften just one area of a metal part through induction hardening*
- *It homogenize plastic parts that are injection molded through annealing*
- *It remove stress from extruded, formed, bent or cut material through stress relief*
- *It add resilience to a metal*
- *It change the magnetic permeability*
- *Enhancing workability and machinability with heat treatment:*

  Heat treatment improves manufacturability by eliminating internal tensions. For instance, if a metal is too hard to bend or process, the hardness can be reduced by stress relief or annealing. After machining, a plastic that deforms can be prevented from deforming by being annealed or stress relieved. Only a small portion of a component may be softened by induction flame heat treatment; the remainder of the item remains unaltered.
- *Heat treatment increases durability and wear resistance:*

A part's wear resistance can be increased by heat treating it by hardening it. Metals can be surface- or all-hardened to increase their strength, toughness, durability, and wear resistance.

- *Heat treatment increases toughness and tensile strength:*
  Strength and toughness are trade-offs; as strength increases, toughness may decline, leading to brittleness. Tensile strength, yield strength, and fracture toughness are three properties that heat treatment particularly affects. Case hardening enhances strength, but to reduce brittleness, the pieces must be tempered or pulled back. The intended final strength of the material dictates how much tempering is applied.
- *Magnetic characteristics are enhanced by heat treatment:*
  Most materials, have a tendency to become more magnetic after being work-hardened. The magnetic permeability is decreased by using a particular annealing procedure, which is crucial if the component will be employed in an electronic environment.

Heat treatment applications

The most common application of heat treatment is in metallurgy. The following are some examples of the applications for heat-treated parts:

- Automobiles
- Aerospace
- Computers
- Metalworking
- Machinery
- Construction
- Others

The global automotive industry has been a large player in the market of heat-treated metals recently. In terms of materials, steel dominates the industry, but the forecast is for aluminium and other metals for manufacturing automobiles and aircraft to drive market growth.

9.7.1 HEAT TREATING PROCESSES:

Common types of heat treating methods include annealing, hardening, quenching, and stress relieving, each of which has its own unique process to produce different results. Heat treatment, annealing and tempering are two of the most common.

9.7.1.1 Annealing:

Annealing is a metal heat treatment procedure that gradually raises the temperature of the metal. Then it's kept for a long period and cooled at an adequate rate. The goal is to bring the metal's internal structure as close as possible to equilibrium. Good process and application performance. Alternatively, prepare the structure for more quenching.

Complete annealing, incomplete annealing, and stress relief annealing are the three types of annealing.

Purpose of Annealing:

During the annealing process, manufacturers heat the material to the ideal temperature and then hold it there for a certain period of time. Additionally, annealing has a very sluggish cooling rate. Imagine if the timer went off while you were baking something in the oven. The idea behind annealing would be similar if you let it cool down within the oven rather than taking it out.

Manufacturers anneal a material primarily to decrease its hardness for easier machining. Additionally, manufacturers could want a higher level of electrical conductivity from the metal, which can be achieved by annealing.

The three stages of annealing

The annealing process includes three distinct stages:

- Recovery
- Recrystallization
- Grain Growth

Let's take a closer look at what happens during each stage.

ANNEALING STAGE 1: RECOVERY

Recovery is the first step in the annealing process. Manufacturers completely heat the metal during recovery. For this kind of metal treatment, a furnace is most frequently used. The aim of the recovery step is to heat the metal to a temperature where the metal may relax and become malleable, and this might be accomplished using a gas, electric, or induction furnace. Which can also be created using annealing.

ANNEALING STAGE 2: RECRYSTALLIZATION

At this stage of the procedure, the distinctions between tempering and annealing steel become apparent. Manufacturers raise the temperature to a crucial level during recrystallization. The ideal temperature is one that is above the metal's recrystallization temperature but below its melting point.

The development of new grains inside the internal structure of the metal starts when the material is kept in this ideal range, free from the development of existing tensions.

ANNEALING STAGE 3: GRAIN GROWTH

Grain growth is the third step in the annealing process. During this last stage, grains from the second stage can mature entirely. A more ductile, less hard material is produced by regulating the cooling process and maintaining a specified pace.

9.7.1.2 Quenching

Quenching is a metal heat treatment technique. The metal work piece is heated to an appropriate temperature and held there for a period of time during the procedure. Then it was quickly cooled in a quenching medium.

The process of quench hardening is mechanical. The work piece was reinforced and toughened during this procedure. Ferrous metals and alloys, steel, and cast iron alloys are among these metals. The material is routinely tempered after that to reduce any brittleness that may have developed as a result of the quench hardening process. Gears, shafts, and wear blocks are examples of products that can be quenched.

In addition, aluminum alloys, copper alloys, titanium alloys, tempered glass, and other materials undergo solution treatment. Quenching is another term for the heat treatment procedure that involves rapid cooling.

Types of Quenching: Quenching is basically of three types

i) Fog Quenching, ii) Selective Quenching, iii) Direct Quenching

1. **Fog Quenching:** When quenching process is done in the presence of the mist or vapour then, it is called as a fog quenching.
2. **Selective Quenching:** When only certain part of metal is gone through quenching then, it is termed as a selective quenching.
3. **Direct Quenching:** When quenching is practiced with the help of other heat treatment techniques like carburization, etc. then, it is called as a direct quenching.

Advantages of quenching:

There are several benefits to it. The advantages of the quenching process are as follows:

- The material that is properly passed through quenching is more durable and has more tensile strength. Hence, quenching enhances the durability of the metal.
- Compared to other heat treatment methods, quenching is a fairly straightforward and uncomplicated operation.
- Quenching is the most effective procedure when done correctly and requires very little time.

9.8 Radiation Damage

Radiation is a term that includes alpha particles, beta particles, gamma, X-rays, photon of light, protons, neutrons, electrons, microwave and all the different types electromagnetic waves that can be produced.

Materials used in nuclear power plants are exposed to a variety of radiation types, including neutrons, gamma, beta and alpha. Some of them have the potential to seriously harm a material's crystalline structure. Energy from nuclear radiation is concentrated in a very small region. This energy interacts with the nuclei and circling electrons, causing damage. These energy exchanges can change the crystal structure. As a result, we can anticipate changes in the bulk material's mechanical characteristics. It is crucial to keep in mind that materials in our reactors, particularly those in the core, are bombarded by all forms of radiation at once.

As a result, the damage suffered might be exceedingly intricate. We will examine each form of radiation and its effects on material independently to make it easier to comprehend this harm.

9.8.1 Effects of ionizing radiation on types of atomic bond

Gamma, beta and alpha are classed as ionizing radiation because they interact only with electrons surrounding nuclei. When particles such as α^{2+} and β^- particles pass through matter, they can cause damage by interacting with the atoms through electrical forces and thereby ionizing them. When α^{2+} particles passes it attracts the electron of one of the nuclei. It becomes electron deficient and this causes it to repel from the nearby atoms disrupting bonding between them. Particles that do not have net charge, such as gamma and X-rays can also cause much damage to the atoms. For example a gamma ray can collide and ionising the atoms. This in turn disrupt the bonding in the material. A moving neutron can also cause considerable damage by colliding with the actual nucleus of the atom, leading to a nuclear reaction and altering the atom.

Ionizing radiation produces charged ions in the form of nuclei by removing electrons from the atoms' outermost orbitals. The atomic bonding of materials is broken by this ionisation. The removed electrons may continue to cause more harm. Let's think about the different kinds of atomic bonding to provide further context. Atoms are kept together by covalent bonds, which result from the sharing of electron pair energy. Ionizing radiation can split up electron bond pairs by removing electrons from their atoms. This results in a chemical change, or the dissolution of the original molecules and the production of new and different ones. Ionizing radiation causes severe damage to organic materials including oils, polymers, and rubber (both natural and manmade), which almost entirely include covalent bonds.

Ionic bonds are created when oppositely charged ions are kept together in a crystal lattice only by electrostatic attraction, keeping all of the compound's electrons in certain atoms' orbits. An ionic link is not nearly as vulnerable to ionising radiation damage as a covalent one. The removal of electrons from an atom may change the electrical charge on specific ions, but electrostatic attraction will still exist between pairs of oppositely charged ions. A dislocated electron could ultimately find its way to another spot lacking in electrons, causing no net harm. However, if the electron is caught in a flaw in the crystal lattice, we have what is known as an F centre. Changes in colour may result from this, but has no impact on the material's mechanical qualities. When subjected to ionising radiation, for instance, glass quickly becomes black, despite the fact that its structural characteristics are essentially unaffected. Since all accessible electron sites are occupied and there is hardly any electron mobility from site to site, the bulk of inorganic materials, aside from metals, display ionic bonding and are hence nonnatively excellent insulators. The resistivity of these materials is decreased during irradiation because ionising radiation results in electron migration enhancing their conductivity.

For the purposes of considering the effects of ionising radiation on metallic bonding, a straightforward perspective of the bonding configuration is most useful. Positive ions locked in fixed locations (a crystal lattice) and enveloped by an ocean of electrons make up metals. The electrons migrate from atom to atom under a variety of circumstances since they are very mobile and not linked to any specific atoms. Metals will only have a temporary impact from ionising radiation because any lost electrons may be easily replaced by other electrons moving freely.

9.8.2 Effects of fast neutron radiation

Neutrons with enough energy can alter the crystal structure or atomic structure of materials. Atoms are moved around in a substance by fast neutrons, resulting in structural damage and perhaps momentary localized hot spots. Metals are more susceptible to structural deterioration due to their relative resistance to ionizing radiation damage. Thus, even though we focus on the effects of fast neutrons on metals in the discussion that follows. We must understand that they can affect all materials in a similar way.

9.8.3 Effect of thermal neutrons

Thermal neutrons may be trapped by the irradiated material's nuclei, thereby altering their composition. When a neutron is added to a nucleus, the atomic mass number of the resulting isotope is altered. It is possible for this isotope to be radioactive and eventually decay into a stable nucleus that is a different element, or it may be stable like the original nucleus. For instance, when Cobalt 59 absorbs a neutron, radioactive Cobalt 60 is produced. However, aluminium absorbs neutrons to create a radioactive silicon isotope that eventually decays to a stable silicon isotope. The majority of iron atom neutron captures result in a heavier stable isotope of iron.

Although the UO_2 fuel is not a metal, it should be noted that during the radioactive decay and neutron capture processes, gases may be produced. Multiple gaseous fission products are produced during the fission process, which is started by thermal neutrons (eg. krypton, xenon and iodine). The gas atoms which are typically kept at the grain boundaries—move and combine to produce gas bubbles when the fuel is run at temperatures higher than those for which it is rated. As more of these bubbles form, the pressure inside the fuel sheath rises.

When compared to fast neutrons, thermal neutrons cause less structural deterioration to the crystal lattice of a metal. In most cases, the nucleus that the neutron was grabbed by just moves. Because this nucleus is stimulated or in a high-energy state, it releases surplus energy by releasing high-energy gamma rays, which causes the emitting nucleus to recoil and move. It is significant to highlight that metal components within the reactor or in nuclear process systems will be activated and must be treated as radioactive material when removed, independent of any physical damage brought on by neutron exposure.

SAS 1. Explain why ionizing radiation has little effect on metals and their mechanical properties, but creates significant damage in non-metals.

SAS 2. Describe the damage created in metals subjected to fast neutron irradiation.

SAS 3. Describe how fast neutron damage affects the mechanical properties (ie, strength, hardness and ductility) of metals.

SAS 4. Explain how elevated operating temperatures reduces the effects of fast neutron damage.

9.9 Conclusion

Throughout the present chapter, we have studied the "microscope", instrument that produces enlarged images of small objects and their various types such as; simple, compound, optical, stereo microscope in detail. After that, we have dealt with another type of microscope "Electron Microscope" which uses a beam of electrons in its image formation. Its principle application and its various types have been discussed in detailed. Microscopes are essential tools for scientific research and have made many important contributions to our understanding of the natural world. They have helped to reveal the existence of microorganisms, enabled the study of cells and tissues, and opened up new areas of research that have led to many of the scientific and medical advances we enjoy today. Then we have extended our discussion to "Heat treatment" and their various techniques. Heat treatment techniques offers unique outcomes when applied. Therefore, while choosing a heat treatment technique, the phases involved in each heat treatment procedure as well as the requirements mentioned must be taken into account in order to produce a good product with the needed attributes. Beside this heat treatment "Radiation Damage" is also discussed in detail.

9.10 Glossary

Microscope	A piece of equipment that makes very small objects look big enough for you to be able to see them
Magnification	the process of making something look bigger than it is
Resolving power	The ability of a microscope, telescope, or other optical instrument to produce separate images of closely placed objects.
Radiation	Powerful and very dangerous rays that are sent out from certain substances
Compound	Something that consists of two or more things or substances combined together
Heat treatment	To treat (a material, such as metal) by heating and cooling in a way that will produce desired properties.

Annealing	Heat (metal or glass) and allow it to cool slowly, in order to remove internal stresses and toughen it.
Quenching	The process of plunging hot metal into water
Electromagnetic waves	Waves that are created as a result of vibrations between an electric field and a magnetic field.
Optical microscope	A type of microscope that uses visible light and a system of lenses to magnify images of small samples.

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9.12 Suggested reading

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2- Michael Hoppert, Cambridge University Press; 4 edition (April 13, 2000), Microscopic Techniques in Biotechnology 1st Edition

3- ASM'S Curriculum Recommendations: Microbiology Majors Program.

9.13 Terminal questions

Short type questions:

1. What are the types of microscopes?
2. What is a simple microscope?
3. Define a compound microscope.
4. How many eyepieces are there in a compound microscope?
5. List three uses of a compound microscope.
6. What is a microscope?
7. What are the parts of a microscope?
8. What are the advantages of the SEM over optical microscopy?
9. List various applications of the SEM.
10. Why the scanning electron microscope is so named?
11. Define the term ‘heat treatment’.
12. List some of the important heat treatment operations widely used.
13. What is meant by annealing?
14. What are the purposes of annealing?
15. What is quenching?

Multiple choice questions:

1. Which of the following is used in electron microscope:

   a. Electron beams

   b. magnetic field

   c. light waves

   d. electron beams and magnetic field

2. Electron microscope can give magnification upto

   a. 400,000X

   b. 100,000X

   c. 15000X

   d. 100X

3. Which among the following helps us in getting a three dimensional picture of the specimen?
   a. Transmission Electron Microscope
   b. Scanning Electron Microscope
   c. Compound Microscope
   d. Simple Microscope

4. The secondary electrons radiated back in scanning microscope is collected by?
   a. Specimen
   b. anode
   c. vacuum chamber
   d. cathode

5. Where do we obtain the magnified image of the specimen in SEM?
   a. cathode ray tube
   b. phosphorescent screen
   c. anode
   d. scanning generator

6. What is the effect of heat treatment on a metal?
   a. Improvement in availability
   b. improve physical properties
   c. Decreased color
   d. Decreased availability

7. What are the various stage of heat treatment?
   a. Heating, cooling, and quenching
   b. Heating, soaking and quenching
   c. quenching, cooling and heating
   d. soaking, quenching and cooling
8. Resolving power of a microscope depends upon

a. The focal length and aperture of the eye lens
b. The focal length and objective of the eye lens
c. The apertures of the objective and the eye lens
d. The wavelength of light illuminating the object

9. The magnification power of a compound microscope does not depend upon
a. The focal length and aperture of the eye lens
b. The apertures of the objective lens
c. Tube length of the microscope
d. None of the above

10. Which component of the compound microscope aids in the collecting and focussing of light rays on the material to be examined?
a. Lens for the eyepiece
b. A lens that is objective
c. A lens with a condenser
d. The use of a magnifying lens

11. In compound microscope, as compare to eye piece, objective lens has
a. negative focal length
b. zero focal length
c. small focal length
d. large focal length

12. As compared to the single lens, a compound microscope gives
a. smaller magnification
b. greater magnification
c. no magnification
d. equal magnification

Answer: 1 d); 2 a); 3 b); 4 b); 5 a); 6 b); 7 b); 8 d); 9 b); 10 c); 11 c); 12; b)

UNIT 10 OPTICAL SPECTROSCOPY

Structure

10.1 INTRODUCTION

Spectroscopy is the study of the interaction of light (electromagnetic radiation) with matter. Electromagnetic radiation covers a wide range of frequencies from gamma rays to radio frequencies. Depending on the frequency of radiation interacting with the matter, one can have different forms of spectroscopy. These spectroscopic techniques allow us to monitor the structural properties of matter. For example, information on moment of inertia (and hence bond length) can be obtained from rotational spectrum. Similarly, vibrational spectrum provides information on the force constant, i.e. the strength of a chemical bond. Besides providing information on molecular structure, spectroscopic techniques can also be used for quantitative estimation of a substance making spectroscopy an important analytical tool. Further, a spectroscopic transition is characterized by a definite timescale and this can provide information on molecular dynamics.

This chapter deals the interactions of ultraviolet, visible, and infrared radiations with matter. Along this, Raman Spectroscopy, X-ray photoelectron, Nuclear Magnetic Resonance (NMR), Electron Spin Resonance (ESR) Spectroscopy is also discussed. Irrespective of differences in the instrumentation, all spectroscopic techniques have many common attributes. The similarities as well as differences between various spectroscopic techniques have been outlined. Application of these different spectroscopic methods for the elucidation of molecular structure will also be discussed.

10.2 OBJECTIVE

After studying this unit you should be able to:

- Define the term Spectroscopy and uunderstand the basis on spectroscopy
- Describe the types of Spectroscopy.
- Gain knowledge about the basic elements of Spectroscopy.
- Know about the UV-Vis spectroscopy, Fourier Transform (FT-IR) spectroscopy, X-ray photoelectron spectroscopy, NMR, ESR, Raman, Mossbauer spectroscopy and Positron annihilation spectroscopy.

- Know about the Instrumentation and sample handling in FTIR, UV absorption, emission, ESR and Raman spectra.

10.3 OPTICAL SPECTROSCOPY

Sir Isaac Newton originally used the word "spectroscopy" in 1666 when he showed how white light could be split into several hues using a prism.

Basically, spectroscopy is the study of how light interacts with diverse materials. We can identify a sample's composition and quantity by examining how much light is absorbed or emitted by it. Long-wavelength radio waves, microwaves, infrared light, visible light (a very small portion of the electromagnetic spectrum), ultraviolet light, higher energy X-rays, gamma rays, and cosmic rays are all included in the electromagnetic radiation spectrum (Figure 10.1).

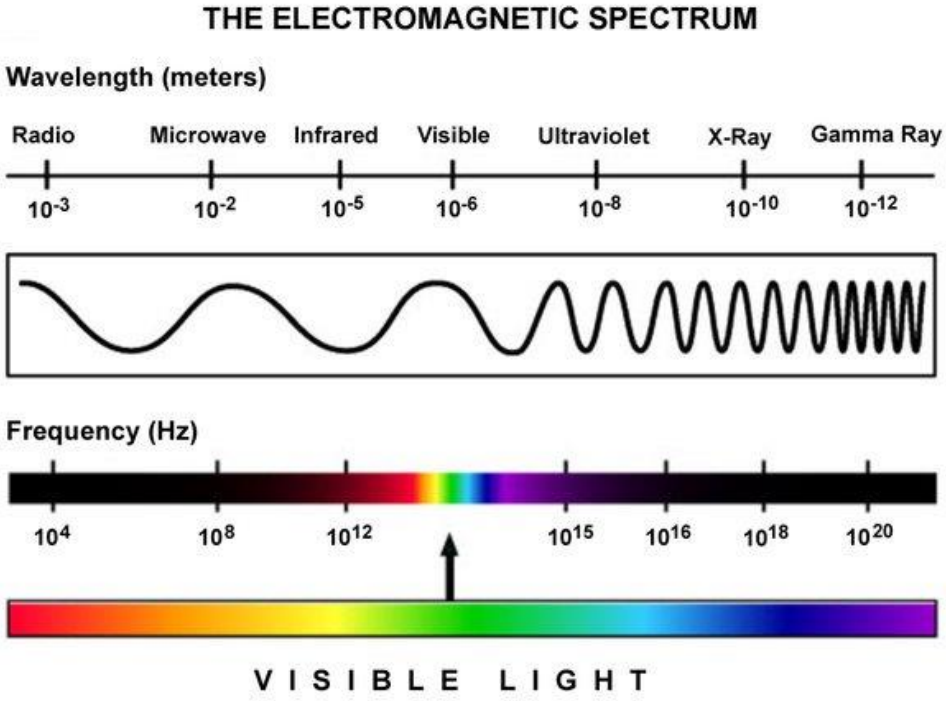


Figure 10.1: The electromagnetic spectrum covers many orders of magnitude in frequency and wavelength.

Basically, when light strikes a sample, two things can happen. Either absorption occurs, or emission occurs. The sample absorbs part of the light's energy during absorption, which is what happens when your sunglasses block the sun's UV rays from reaching your eyes. When we shine light on a sample, emission happens when the sample emits light at a different wavelength. The effect of light on a sample depends on the wavelength of the light, the intensity of the light, and what it’s doing to the molecules or atoms of the sample.

Spectroscopy/spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them. “A spectrometer is an instrument for making relative measurements in the optical spectral region, using light that is spectrally dispersed by means of a dispersing element”. A basic schematic for a spectrometer is shown in the Figure 10.2. First, we have a light source, second, we have a gadget that can choose a certain wavelength for that light. It may be a filter, interferometer, monochromator, polychromator, or even something as straightforward as that. Third, we have a method for delivering our sample to the spectrometer.

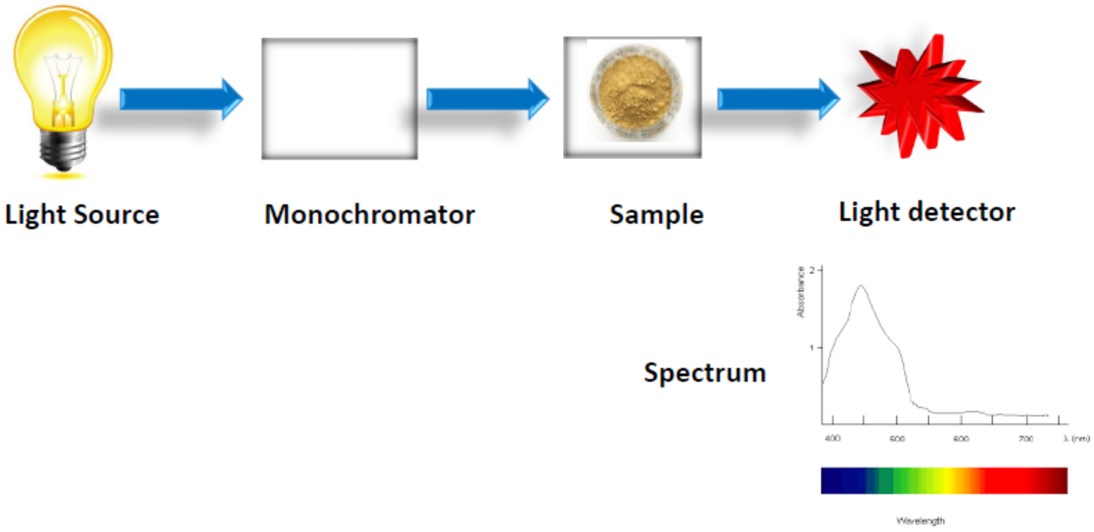


Figure 10.2: Schematic of a spectrometer.

We direct the light onto the sample. We know the light's wavelength and intensity. After that, we measure the output using a detector of some kind. A spectrum will be observe. As we go throughout the spectrum and alter the wavelength, we see a change in the absorption or intensity of that light.

As scientists and engineers, we may use a variety of different spectroscopic approaches based on these basics.

10.4 ATOMIC SPECTROSCOPY

10.4.1 Atomic absorption spectroscopy (AA): The first of these is atomic absorption spectroscopy. The first of these is atomic absorption spectroscopy. Atomic absorption is based on the fact that an atom in the vapour state will absorb light of certain frequencies as a unique characteristic of that specific atom (Figure 10.3). We begin with a hollow cathode lamp, which is essentially a glass light with a metal cathode inside of it. It emits lines at a certain wavelength after being heated successfully. The cathode material exhibits these wavelengths as a characteristic. For example, if it is copper, it will emit lines in a range of copper-specific wavelengths.

Then, we nebulize our sample, which is typically in a liquid solution. We atomize the sample by sucking it up into a flame that is several thousand degrees hot. Currently, we are passing gaseous atoms via the spectrometer's light path. These wavelength lines will be absorbed if those atoms are copper. Because the atoms are absorbing light, we will see a decrease in intensity as we aspirate the sample. That drop in intensity is related to a concentration drop. And that's how we assess the sample's contents.

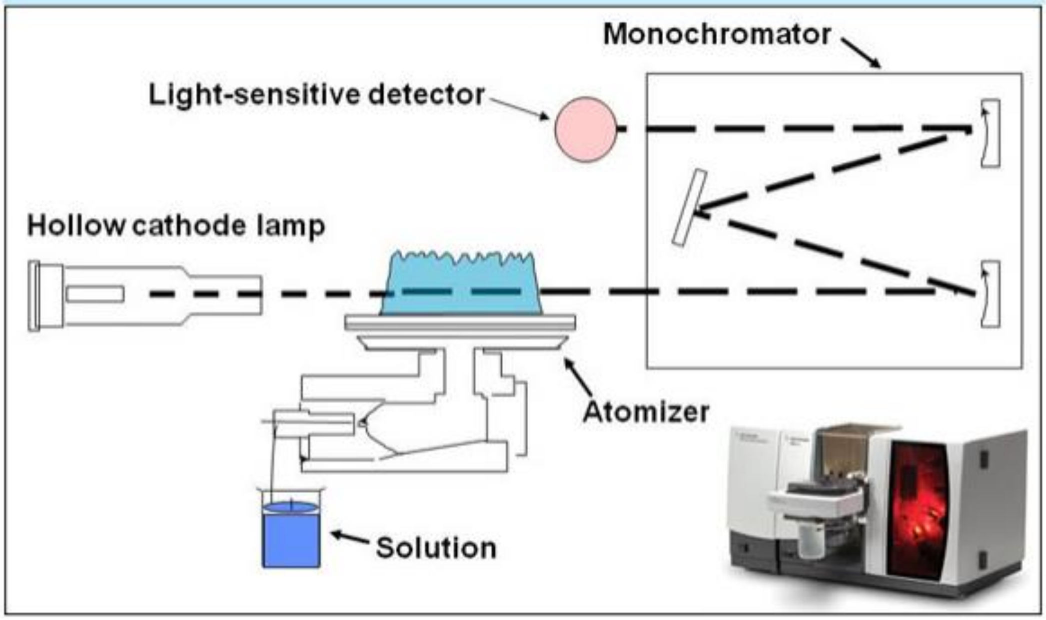


Figure 10.3: atomic absorption spectroscopy.

Atomic absorption is a fairly reliable method. The mining and mineral industries make extensive use of it. Atomic absorption is a suitable method to use if you want to determine the concentration of an element, such as calcium, zinc, or copper.

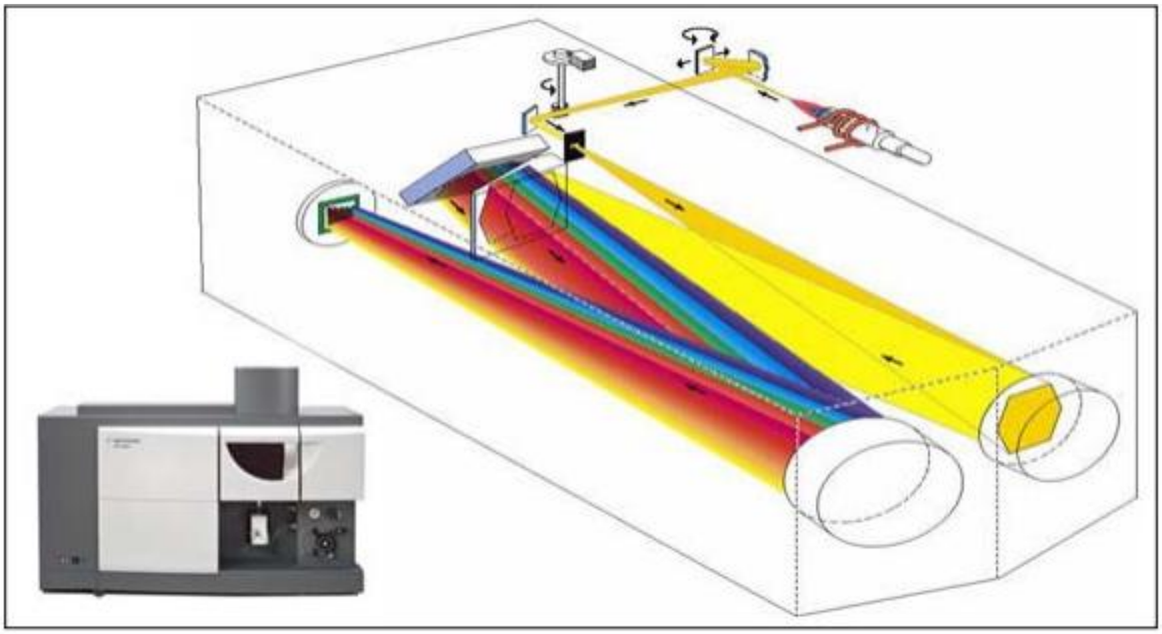


Figure 10.4: Inductively coupled plasma optical emission spectroscopy.

10.4.2 Inductively coupled plasma optical emission spectroscopy (ICPOES)

Inductively coupled plasma optical emission spectroscopy (ICPOES) is another analysis technique. It generally uses an argon plasma to excite the atoms in solution. We nebulize a liquid sample that we have collected. We absorb it and spray it into a plasma that has a temperature that is roughly double that of the flames employed in atomic absorption. The sample is introduced into the very hot plasma. After absorbing that energy, it produces light. Again, based on the nature of the sample, we can predict the wavelengths it will emit. We can set up our polychromator to look for those wavelengths and measure how much of the material we're looking for is there (Figure 10.4). We can relate the intensity of the wavelengths to the concentration in the sample.

Advantages of ICPOES over AA:

We can measure more elements with ICP than with AA, and we can measure them all at once. Atomic absorption is a sequential method; by switching lamps, we must measure each element in turn. With ICP, we may test a wide variety of compounds simultaneously as long as our polychromator and detector have the same wavelength range.

10.5 MOLECULAR SPECTROSCOPY

This spectroscopy deals with the interaction of electromagnetic radiations with molecules. This interaction results in transition between rotational, vibrational and electronic energy levels. Molecular spectra are more complicate than atomic spectra. When a molecule absorbs or emit a photon, following changes may occur:

1) There may be change in rotational quantum number which gives rise to rotational spectra. This takes place in far infrared region and microwave regions of electromagnetic spectra.

2) There may be change in vibrational quantum number along with the change in rotational quantum number which gives rise to other spectra known as vibrational-rotational spectra. This spectrum occurs in near infrared region of electromagnetic spectra.

3) There may be change in electronic energy level which is accompanied by change in vibrational and rotational energy levels which give rise to electronic spectra. This spectra occurs in visible and ultra-violet regions of electromagnetic spectra.

4) There may be change in the direction of nuclear spin quantum number in the presence of magnetic field, this give rise to type of molecular spectra known as nuclear magnetic resonance (NMR).

5) There may be change in the direction of the resultant spin in the presence of a magnetic field, this give to electron spin resonance (ESR) type of molecular spectra. This type of spectra occur in microwave region of electromagnetic spectra.

6) There may occur nuclear transition which gives rise to spectra known as Mossbauer spectra which occur in gamma rays region of electromagnetic spectra.

It is clear from above discussion that a molecule possesses translational energy (E_{trans}), rotational energy (Erot), vibrational energy (Evib), electronic energy (Eel), spin energy (Espin) and nuclear energy (Enuclear). Thus the total energy (Etotal) is given by:

Etotal = Etrans + Erot + Evib + Eel + Espin + Enuclear

All these energies are quantized except translational energy. Due to large difference in mass between electron and nucleus, it is permissible as approximation to consider the respective motion as mechanically separable. This approximation is known as Born-Oppenheimer approximation. According to Born-Oppenheimer approximation: Etotal = Erot + Evib + Eel .This expression do not contain translational energy because it is negligibly small.

Now let's discuss different types of molecular techniques in detail:

10.5.1 UV-Vis spectroscopy

UV-Vis spectroscopy refers to spectroscopy in the UV-Vis regions of EM. In this region of the EM spectrum, molecules undergo electronic transitions. When an incident photon hits a molecule in its ground state, the molecule moves up into its excited state by absorption of that photon. Absorption of energy takes place only if the photon energy equals the energy gap between the ground and excited state. There are two fundamental laws of absorption namely Lambert's law and Beer's law.

Lambert's law: This law was formulated by Johann Heinrich Lambert and according to this law "When a monochromatic light (light of single wavelength) is passed through a pure homogeneous medium, the decrease in the intensity of light with the thickness of the absorbing medium at any point is proportional to the intensity of the incident light". Mathematically the laws says:

$-dI/dx \propto I$

Where I is intensity of incident radiation or light before entering the medium of small thickness dx,–dI/dx is decrease in the intensity of light on passing through small thickness dx.

$-dI/dx = k\,I$ (k = constant of proportionality = absorption coefficient)

This coefficient depends upon the nature of the absorbing medium. Now in order to obtain integrated absorption coefficient, we have to integrate the above equation:

$$dI/dx = k\,I$$

$$dI/I = -k\,dx$$

$$\text{when } x = 0,\ I = I_0$$

$$\int_{I_0}^{I} \frac{dI}{I} = \int_{x=0}^{x=x} -k dx$$

$$\ln I/I0 = -kx$$

$$2.303 \log I/I_0 = -kx$$

$$\log I/I_0 = -kx / 2.303$$

$$\log I/I_0 = -k^1x \ (k1 = k/ 2.303)$$

The above equation is integrated form of Lambert's law where k^1 is integrated absorption coefficient or extinction coefficient of the substance or absorptivity of the substance.

Beer's law: This law was formulated by August Beer and according to this law of absorption "When a monochromatic light is passed through a solution, there is decrease in the intensity of light with the thickness of the solution is directly proportional to the intensity of incident radiation or light along with the concentration of the solution”. Mathematically the laws says:

$$-dI/dx \propto I\,c$$

Where c is the concentration of solution, $-dI/dx$ is decrease in the intensity of light on passing through solution of thickness dx.

$$-dI/dx = \varepsilon\, I\, c \quad (\varepsilon = \text{constant of proportionality} = \text{molar absorption coefficient})$$

The value of molar absorption coefficient depends on the nature of the absorbing medium along with the wavelength of light used. Now in order to obtain integrated absorption coefficient, we have to integrate the above equation:

$$-dI/dx = \varepsilon\, I\, c$$

$$dI/I = -\varepsilon\, c\, dx$$

$$\text{when } x = 0,\ I = I_0$$

$$\int_{I_0}^{I} \frac{dI}{I} = \int_{x=0}^{x=x} -\varepsilon\, c\, dx$$

$$\ln I/I_0 = -\varepsilon\, c\, x$$

$$2.303 \log I/I_0 = -\varepsilon\, c\, x$$

$$\log I/I_0 = -\varepsilon\, c\, x / 2.303$$

$$\log I/I_0 = -\varepsilon^1 c\, x \quad (\varepsilon^1 = \varepsilon/2.303)$$

The above equation is integrated form of Beer’s law where ε1is integrated absorption coefficient or molar extinction coefficient of the absorbing solution or molar absorptivity of the absorbing solution.

Lambert- Beer’s law: Lambert- Beer’s law is also known as Beer- Lambert-Bouguer law or simply Beer’s law. According to this law “For a given material, the thickness and concentration of the absorbing medium (solids) are directly proportional to the absorbance of the light”. Mathematically:

$$\text{Absorbance} \propto c\, x$$

$$\text{Absorbance (A)} = \varepsilon^1 c\, x$$

$$A = \log I_0/I = \varepsilon^1 c\, x$$

Where c is concentration of the absorbing medium, x is the thickness, ε^1 is extinction coefficient of the absorbing medium and is defined as the log of the ratio of intensity of incident light to the transmitted light. According to Lambert- Beer's law, the absorbance is directly proportional to the concentration of the absorbing medium (solution).

Principle: Ultraviolet (UV) spectroscopy is an essential physical instrument that uses light in the ultraviolet, visible, and near infrared ranges of the electromagnetic spectrum. The Beer-Lambert law provides a linear connection between absorbance, the concentration of absorbers (or absorbing species) in the solution, and the route length. As a result, given a fixed route length, UV-Vis spectroscopy may be used to determine the concentration of the absorbing species. This method is incredibly straightforward, adaptable, quick, precise, and economical.

In this spectroscopy, the wavelength of the light that reaches the detector after travelling through an item in a light beam is measured. By measuring the wavelength, some important details regarding the chemical structure and amount of molecules are revealed. As a result, information that is both quantitative and qualitative may be acquired. The transmittance, absorbance, or reflectance of light in the range of 160 to 3500 nm can be used to gain information. The absorption of incident energy promotes electrons to excited states or the anti-bonding orbitals. For this transfer to occur, photon energy must match the energy needed by electron to be promoted to next higher energy state. This process forms the basic operating principle of absorption spectroscopy. There might be three different kinds of ground state orbitals at play:

1. σ (bonding) molecular orbital
2. π (bonding) molecular orbital
3. n (non-bonding) atomic orbital

Along this the anti-bonding orbitals are:

i. σ* (sigma star) orbital

ii. π* (pi star) orbital

σ to σ* transition involves excitation of an electron from its s bonding orbital to its σ anti-bonding orbital Figure (10.5). The excitation of an electron from a lone pair (a non-bonding electron pair) to an antibonding π orbital is represented by the symbols π to π*. The following electronic transformations take place as a result of UV and visible light absorption:

σ to σ*;
n to σ*;
n to π*;
π to π*.

The transitions from s to σ* and n to σ* typically take place in the far UV region or weakly in the 180 to 240 nm range that involve higher energies. Therefore, saturated groups do not exhibit substantial UV absorption. Molecules with unsaturated centres undergo n to π* and π to π* transitions; these transitions involve lesser energies and thus occur at longer wavelengths than transitions to σ* anti-bonding orbitals.

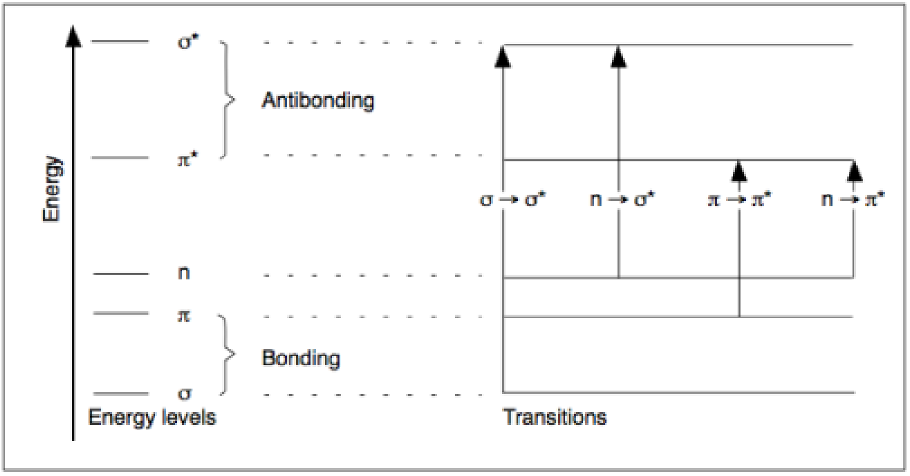


Figure 10.5: Electron transitions in UV-Vis spectroscopy.

A certain wavelength and energy is directed at the sample, it absorbs some of the incident wave. A photodetector monitors the energy of light that is transmitted from the sample and records the sample's absorbance. The absorption or transmission spectrum of the light absorbed or transmitted by the sample against the wavelength is formed. Lambert−Beer rule is basic principle of quantitative analysis, and it states that a solution's absorbance scales directly with the concentration of analytes.

Lambert-Beer’s law with c, the sample concentration and b, the optical path length and with ε(λ), molar absorptivity (A) can be expressed as:

$$A = a.b.c$$

The UV-visible and near-infrared (NIR) spectrometer can measure absorbance or transmittance in UV-visible range. The relationship between incident light of intensity "I_o" and transmitted light of intensity 'I' is described as follow.

Optical band gap measurement

The optical band gap is defined as the minimal photon energy necessary to move an electron from the top of the valence band to the bottom of the conduction band. It is one of the major factors determining the conductivity of a given sample. The values of the absorbance coefficient displayed as a function of wavelength were used to determine the band gap of the thin films that were deposition.

$$\alpha = [\ln(1/T)/t$$

where T is the transmittance and t is the film thickness. The relation between absorption coefficient and energy band gap for a direct band gap material can be written as follows:

$$\alpha h\vartheta = const\ (h\vartheta - E_g)^{1/2}$$

where E_g is the sample's direct optical band gap and $h\vartheta$ is the energy of the incident photon. The band gap is calculated by extrapolating the linear portion of the Tauc plot on the energy axis from a graph (Tauc plot) between$(\alpha h\vartheta)^2$and $h\vartheta$.

Instrumentation:

The UV-Vis spectrum can by recorded via the following types of absorbance instruments (Figure 10.6, 10.7, 10.8):

a. Single beam spectrometer

b. Double beam spectrometer

c. Simultaneous spectrometer

The four fundamental parts of a spectrometer are light source (UV and visible), monochromator (wavelength selection), sample stage, and detector. Typically, a continuous tungsten filament spanning the UV spectrum is utilised as the light source. The typical detector is a photodiode or CCD. In order to filter light of a specific wavelength before it is supplied to the detector, photodiodes are used with monochromators. By keeping an eye on UV spectrum absorption, Holder for thin films Assembly for a reflection sample holder Assembly for liquid sample holders.

The visible lamp must be turned off, and vice versa, for the sample mounting carousel. Below figure 10.6 includes schematic UV−Vis−NIR Spectrometer.

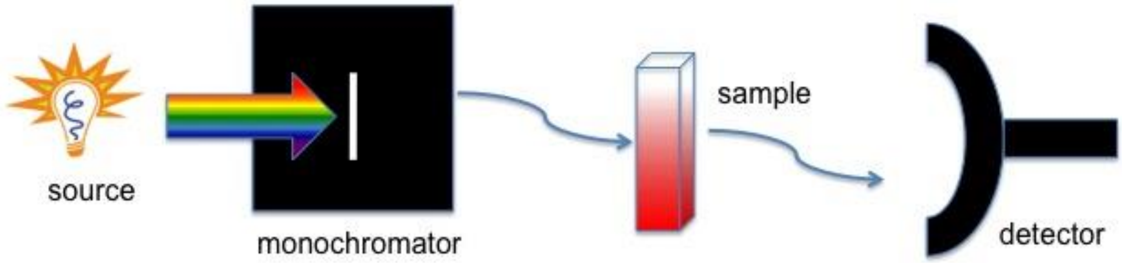


Figure 10.6: Schematics of a single beam UV-Visible spectrometer.

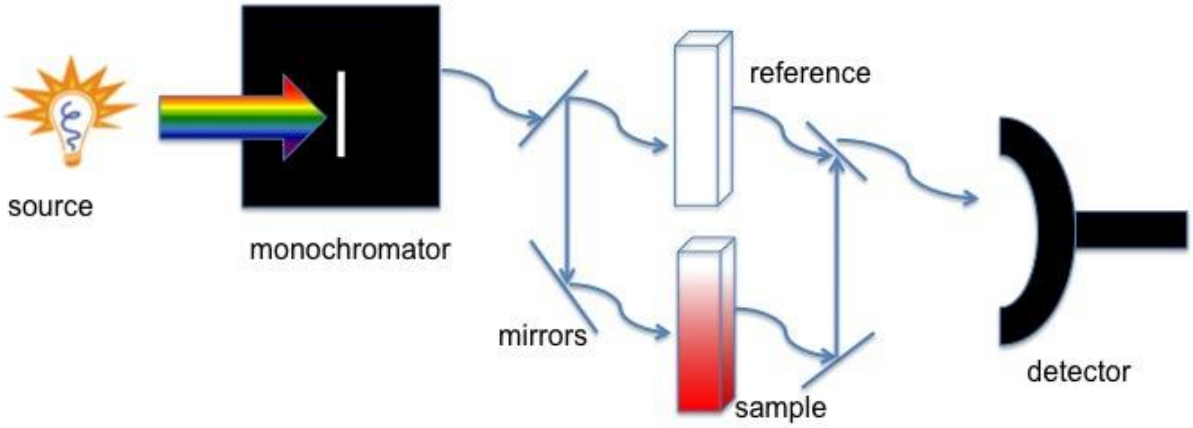


Figure 10.7: Schematics of a double beam UV-Visible spectrometer.

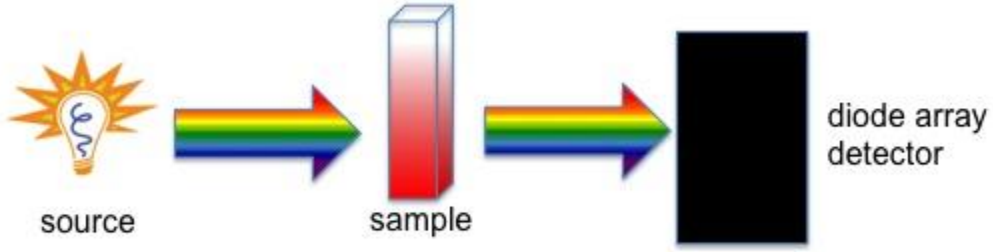


Figure 10.8: Simultaneous UV-Visible spectrometer.

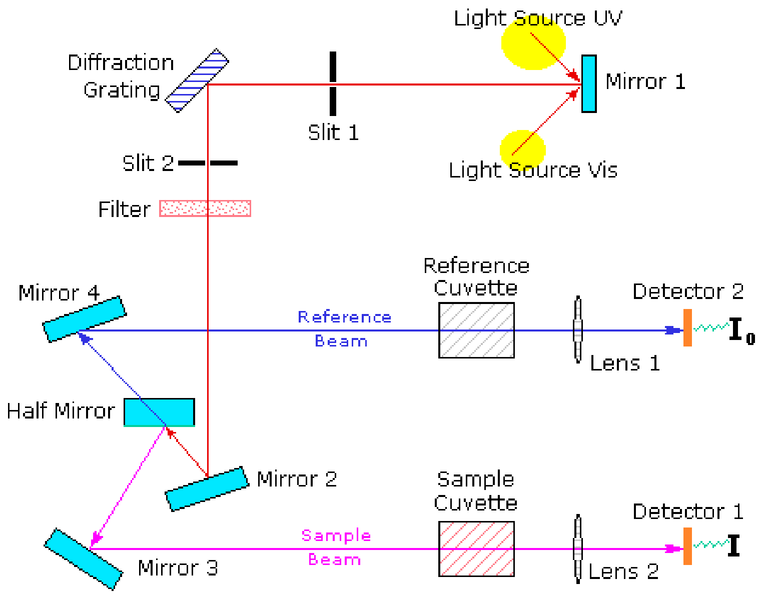


Figure 10.9: Schematic of an UV-Vis spectrometer.

Components: The Schematic diagram of an UV-Vis spectrometer is shown in the Figure 10.9. The different components of UV-Vis spectrometer are given as:

1. *UV Source*

The power of radiating source should not vary in its operating wavelength range. When deuterium or hydrogen is electrically excited at low pressures, a continuous UV spectrum is created. An excited molecular species is produced as part of the UV light generating process, and this species then splits into two atomic species and a UV photon. Both deuterium and hydrogen lamps emit light with wavelengths between 160 to 375 nm. Due to flaws in the obtained absorption spectra, the cuvettes' material must be chosen so that it does not absorb the light that is incident. Consequently, quartz is frequently employed.

2. *Visible Light Source*

The visible light source is a tungsten filament bulb. This lamp has a wavelength range of 350 to 2500 nm. Energy output from a tungsten filament lamp is proportional to the operating voltage raised to the fourth power. Thus, a highly stable voltage must be provided to the lamp in order to obtain stable emission. Transformers with constant voltage or electronic voltage regulators are used to maintain voltage stability. Little amounts of iodine are incorporated within a quartz "envelope," which also houses the tungsten filament, in tungsten/halogen lights. Iodine combines with sublimated gaseous tungsten to create the volatile chemical WI2. When WI2 molecules collide with the filament, they break down and re-deposit tungsten there. The lifetime of tungsten/halogen lights is often twice that of a traditional tungsten filament lamp.

Modern spectrophotometers use tungsten/halogen lamps because of their great efficiency and output that extends to the UV range.

3. Cuvettes

It uses a monochromator source, which is separated into two halves of equal intensity by a half-mirror splitter before it reaches the sample. One component (or sample beam) moves through the cuvette containing the substance to be investigated in a clear solvent solution. Another beam, known as the reference beam, travels through a cuvette that contains only solvent. Containers for reference and sample solutions must be transparent to the passing beam.

4. *Detectors*

A detector measures the amount of light that cuvettes emit, and it communicates this information to a metre so that it can record and show the values. The intensities of light beams are calculated and compared by electronic detectors. A number of UV-Vis spectrophotometers feature two detectors, a phototube and a photomultiplier tube, and simultaneously monitor the reference and sample beams. In UV-Vis equipment, the photomultiplier tube is the detector that is most frequently utilised. It consists of an anode, many dynos, and a photoemissive cathode that emits electrons when photons touch it. Dynos also emit several electrons when a single electron strikes them.

Charge-Coupled Devices (CCDs) are similar to diode array detectors in that they use an array of photocapacitors in place of diodes. The intensity of the reference beam is I0, while that of the sample beam is I. The reference beam should absorb very little or not at all. All wavelength components are quickly analysed by the spectrophotometer automatically. The concentration as well as molecular structure or structural changes can be evaluated using this method. The energy levels of vibration and conformation that change prior to and following an interaction with a substrate or molecule may also be examined using this method.

UV-VIS spectroscopy applications:

Here is a quick list of some typical UV-VIS spectroscopy applications:

1. Detection of impurity: UV-VIS spectroscopy is used for the determination of impurities in the organic molecules. Additional peaks can be observed due to the impurities in the sample and it can be compared with the standard raw material.

2. Structure elucidation of organic compounds: UV-VIS spectroscopy is useful in the structure elucidation of organic compounds, the presence or absence of unsaturation or the presence of hetero atoms.

3. Qualitative Analysis: UV-VIS spectroscopy can be used for the qualitative determination of compounds that absorb UV radiation.

3. Quantitative Analysis: UV-VIS absorption spectroscopy can characterize those types of compounds which absorbs UV radiation. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

4. Chemical Kinetics: Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passes through the reaction cell and the absorbance changes can be observed.

5. Detection of functional groups: This technique is used to detect the presence or absence of functional group in the compound. Absence of a band at particular wavelength regarded as an evidence for absence of particular group.

6. Quantitative analysis of pharmaceutical substances: Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

7. Examination of polynuclear hydrocarbons: Benzene and polynuclear hydrocarbons have characteristic spectra in ultraviolet and visible region. Thus identification of polynuclear hydrocarbon scan be made by comparison with the spectra of known polynuclear compounds.

8. Molecular weight determination: Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.

1. What is a UV-Vis spectrophotometer?
2. **What is the principle of UV visible spectroscopy?**
3. What information can be obtained from UV-Vis spectra?
4. How is beer Lambert law used in spectroscopy?
5. What is a fundamental difference between IR detectors and UV/vis detectors?
6. Write down some applications of UV-Visible spectroscopy.

7. How does delocalisation of electron helped in getting a molecule to absorb UV-Visible radiation and displaying the UV-Visible absorption spectra?
8. Explain in short non-bonding electron excitation and UV spectra.
9. What is the range of UV Visible Spectroscopy?
10. Write a brief note on vibrational, rotational and electronic spectra.

10.5.2 Fourier Transform (FT-IR) spectroscopy

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

So, what information can FT-IR provide?

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the number of components in a mixture

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks that correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, an infrared is an excellent tool for quantitative analysis. The original infrared instruments were of the dispersive type. These instruments separated the individual frequencies of energy emitted from the infrared source. This was accomplished by the use of a prism or grating. An infrared prism works exactly the same as a visible prism which separates visible light into its colors (frequencies). A grating is a more modern dispersive element that better separates the frequencies of infrared energy. The detector measures the amount of energy at each frequency that has passed through the sample. This results in a spectrum which is a plot of intensity vs. frequency. Fourier transform infrared spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for several reasons:

- It is a non-destructive technique
- It provides a precise measurement method that requires no external calibration
- It can increase speed, collecting a scan every second
- It can increase sensitivity – one-second scans can be co-added together to ratio out random noise
- It has greater optical throughput
- It is mechanically simple with only one moving part

Use of FT-IR

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter that takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism that allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.

This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal cannot be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

Components of FT-IR

The normal instrumental process is as follows:

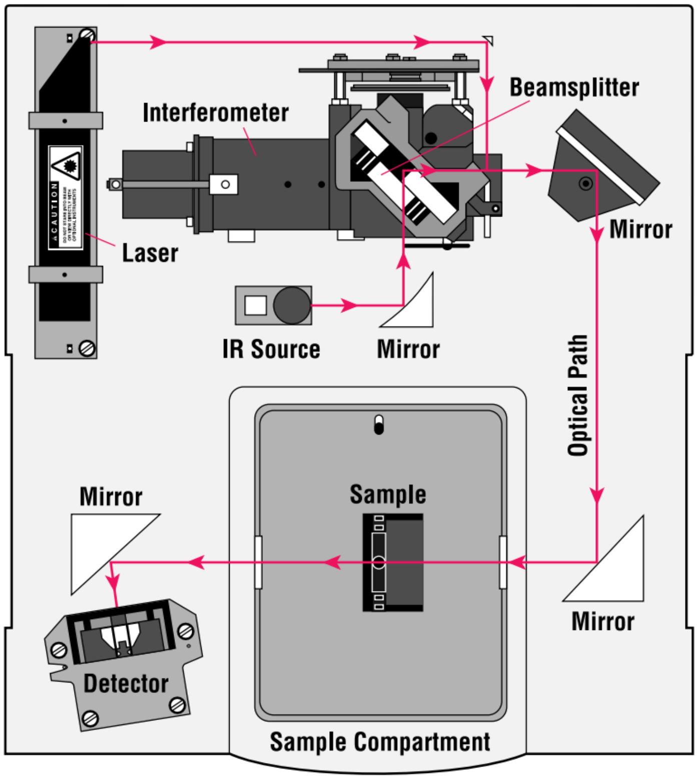
1. The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture that controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. The Interferometer: The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer.

3. The Sample: The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

4. The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

5. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for the interpretation and any further manipulation.



Advantages of FT-IR

Some of the major advantages of FT-IR over the dispersive technique include:

- Speed: Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Felgett Advantage.

- Sensitivity: Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the coaddition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

- Mechanical Simplicity: The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

- Internally Calibrated: These instruments employ a HeNe laser as an internal wavelength calibration standard (referred to as the Connes Advantage). These instruments are self-calibrating and never need to be calibrated by the user.

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. Thus, it is a very reliable technique for the positive identification of virtually any sample. The sensitivity benefits enable the identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it be batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FT-IR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis. Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

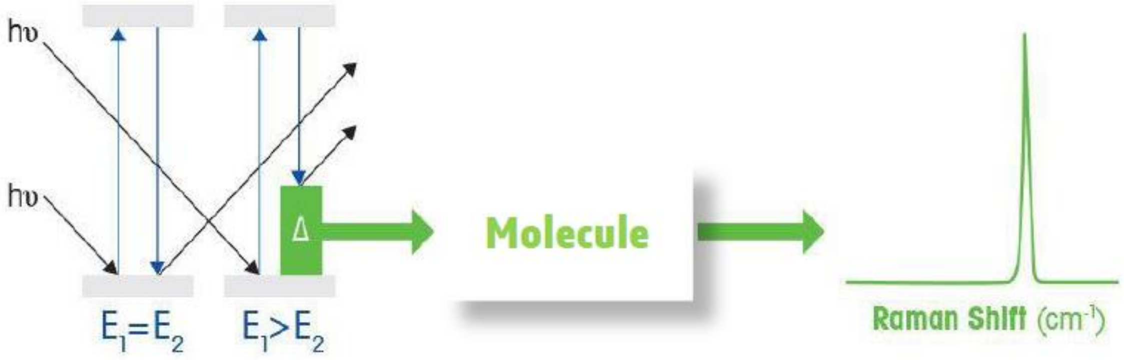
10.5.3 Raman Spectroscopy

Raman spectroscopy is a molecular spectroscopic method that uses the interaction of light and matter to know more about a material's composition or properties. Raman spectroscopy uses light scattering to provide its information. Raman spectroscopy can add to our understanding of a process by revealing information about intra- and intermolecular vibrations. Raman spectroscopy offer a spectrum indicative of the distinct vibrations of a molecule (a "molecular fingerprint") thus are useful for identifying a material. Raman spectroscopy, however, can provide additional details on lower frequency modes and vibrations that shed light on the molecular backbone and crystal lattice.

The Raman Spectroscopy Principle:

The majority of photons that are dispersed or scattered when light interacts with molecules in a gas, liquid, or solid have the same energy as the incident photons. Elastic scattering or Rayleigh scattering is the term used to explain this. A tiny fraction of these photons, around 1 in 10 million, will scatter at a frequency distinct from the incoming photon. The Raman effect, which was discovered by Sir C.V. Raman and for which he received the 1930 Nobel Prize in Physics, is a phenomenon known as inelastic scattering. Since then, Raman has been used in a wide range of fields, including material research, reaction analysis, and medical diagnostics.

Raman enables the user to gather a molecule's vibrational signature, revealing details about its composition and interactions with molecules nearby.



Raman Scattering Process

According to quantum physics, the Raman Scattering Process occurs when photons interact with molecules, which might move the molecule to a higher energy, virtual state. There might be a variety of effects from this greater energy level. One such result would be a photon with a different energy level being produced as the molecule relaxes to a vibrational energy level that is different from its initial condition. The Raman shift is the term used to describe the energy gap between the incoming photon and the scattered photon.

Stokes scattering is the term for scattering when the energy change of the scattered photon is smaller than the incident photon. When certain molecules are advanced to the higher energy virtual state from a vibrationally excited state, they may relax to a final energy level with a lower energy than the original excited state. Anti-Stokes is the name of this dispersion.

Raman Spectroscopy Basics

Raman spectroscopy looks at changes in a molecular bonds polarizability. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a change of polarizability occurs, giving rise to Raman active modes. For example; molecules that contain bonds between homonuclear atoms such as carbon-carbon, sulfur-sulfur, carbon-carbon and nitrogen-nitrogen bonds undergo a change in polarizability when photons interact with them. These are examples of bonds that give rise to Raman active spectral bands.

The optical components of a Raman Spectrometer must be perfectly matched and adjusted since Raman is an intrinsically weak effect. Furthermore, longer wavelength monochromatic excitation sources, such solid state laser diodes that emit light at a wavelength of 785 nm, are often employed since organic molecules may have a stronger propensity to glow when lower wavelength radiation is used.

Fundamental components of Raman spectrophotometer: The schematic diagram of Raman spectrophotometer is shown in the Figure 10.10.

1. Excitation source (Laser)
2. Optics for sample illumination and light collection
3. Wavelength selector (Filter or Spectrometer)
4. Detector (Photodiode array, CCD or PMT)

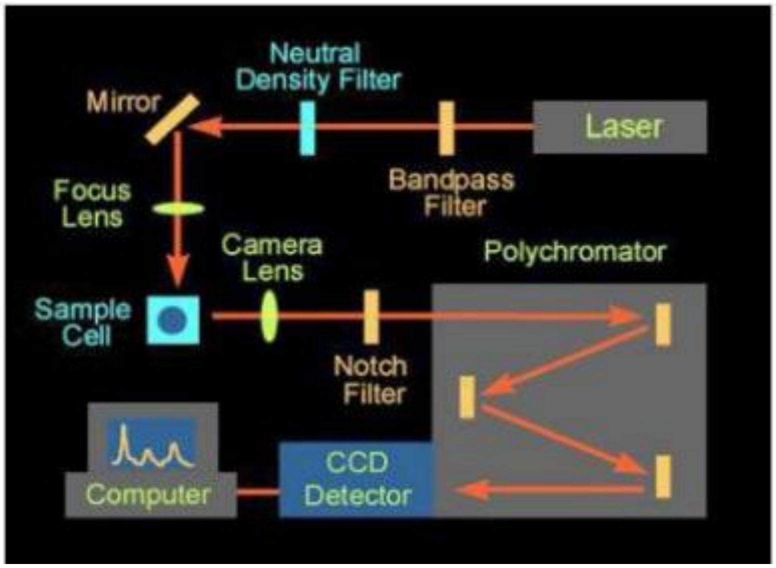


Figure 10.10: Schematics of the set of Raman spectroscope.

Excitation source (Laser): In early Raman spectrometers until the 1960s, a 435.8 nm line of a coiled low-pressure mercury arc lamp was utilised as light source. When laser sources were made accessible in the late 1960s, the mercury lamp was totally phased out. The radiation beam produced by these laser sources is steady and powerful. It is possible to employ a wide range of lasers, including Argon ions (488 and 514.5 nm), Krypton ions (530.9 and 647.1 nm), Helium-Neon (He-Ne) (632.8 nm), Near Infrared (IR) diode lasers (785 and 830 nm), Neodymium-Yttrium Aluminum Garnet (Nd:YAG), and Neodymium-Yttrium Ortho Argon ion and krypton ion lasers, for example, produce significant fluorescence and cause the specimen to photodegrade.

(SAS.1) What are the phenomena that occur when the light interacts with materials?

(SAS.2) What are the conditions to be satisfied for absorption?

(SAS.3) What is the advantage of double-beam spectrophotometers over single-beam spectrophotometers?

(SAS.4) Why is UV spectroscopy used in pharmaceutical analysis?

(SAS.5) What are the applications of spectrophotometry?

(SAS.6) What is the range of UV spectroscopy?

(SAS.7) Which lamp is used in UV spectroscopy?

(SAS.8) What is the IR principle?

10.5.4 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance is referred to by the acronym NMR. NMR device enables the analysis of a material's molecular structure by viewing and quantifying the interaction of nuclear spins when they are subjected to a strong magnetic field. Electron microscopes and X-ray diffraction tools can also be used to analyse molecule structure at the atomic level, however NMR has the benefit of non-destructive sample measurements and requiring less sample preparation. NMR is now a crucial analytical technique in domains of cutting-edge research and technology. t is the study of interaction of magnetic nuclei having resultant nuclear spin (^{1}H, ^{19}F, ^{31}P ^{13}C etc.) with electromagnetic radiations in radio frequency region under the influence of an appropriate magnetic field. The study of hydrogen nuclei comes under the preview of 1H NMR spectroscopy or proton magnetic resonance (PMR) spectroscopy. Combined with 13C NMR, 1H NMR (PMR) can be used to reveal most of the structural and stereochemical features of an organic compound. By studying a compound by 1H NMR (PMR) spectroscopy, one can obtain the following types of information regarding the compound:

(i) The number of types of hydrogen atoms in a molecule.

(ii) The chemical environment of hydrogen atoms.

(iii) The number of hydrogen atoms in a given chemical environment.

(iv) The molecular structure and its stereo chemical features.

Basics of NMR:

NUCLEAR SPIN (MAGNETIC AND NON-MAGNETIC NUCLEI): Atomic nuclei are made up of positively charged protons and electrically neutral neurons. Like electrons, protons and neutrons also spin about their own axes, each with spin quantum number equal to 1/2. Each nucleus has a total spin quantum number (I) which results from the vector addition of the spins of its constituent protons and neutrons. Based on experimental observations, some empirical rules regarding the value of the resultant spin quantum number (I) of nuclei have been formulated. These empirical rules are as follows:

(i) Nuclei having even number of protons and neutrons both have zero resultant nuclear spin quantum number (I).
For example: ${}_2He^4$ (p=2, n=2), I=0
Such nuclei with I = 0 are called non-magnetic nuclei.
(ii) Nuclei with odd number of protons and neutrons both have integral nuclear spin quantum number (I).
Examples: ${}_1H^2$ (p = 1, n=1), I=1

(iii) Nuclei having odd-even combination of protons and neutrons have half integral resultant nuclear spin quantum number (I). Such nuclei have odd mass number and even or odd atomic number.
Examples: ${}_1H^1$ (p = 1, n=0), I=1/2
Or ${}_{17}Cl^{35}$ (p =17, n =18), I = 3/2
Nuclei having non-zero value of resultant nuclear spin quantum number (I) are said to be magnetic nuclei. Thus, when
(a) I = 0, non-magnetic nuclei
(b) $I \neq 0$, magnetic nuclei

Angular momentum of the nucleus

The magnitude of angular momentum vector (L) associated with the spinning nucleus having resultant nuclear spin quantum number I is given by

$$L = \sqrt{I(I+1)}\,\frac{h}{2\pi}$$

The angular momentum vector associated with the spinning nucleus cannot orient in any arbitrary direction in space. It can orient itself in those directions only in which its components along the direction of an applied magnetic field have quantized values, integral (when I is integral) or half-integral (with I is half-integral). The direction of applied magnetic field is usually taken along Z-axis (reference direction). The allowed values of components of the angular momentum vector along the z-axis are given by the expression $m_I \frac{h}{2\pi}$, here m_I can take following values:

a) When I is integral

$$m_I = I, (I-1), \ldots..0, \ldots\ldots.-(I-1), -I$$

b) When I is half integral

$$m_I = I, (I-1), \ldots..+\frac{1}{2}, -\frac{1}{2}\ldots\ldots.(I-1), -I$$

Thus, there are a total of (2I + 1) orientations that the nuclear spin angular momentum vector can take in an applied magnetic field. These orientations are degenerate, i.e., have same energy in the absence of an external magnetic field. However, the degeneracy of these orientations is destroyed in the presence of the applied magnetic field. The NMR spectrum is basically the result of the lifting up of the degeneracy of these energy states.

Instrumentation:

There are two different experimental setups available for capturing NMR spectra. We may either apply a fixed magnetic field to a set of identical nuclei so that their Larmour frequencies are all equal, say, 100 MHz; and the frequency of the radiation beam is then swept over a range including 100 MHz. This will result in resonance absorption at precisely that frequency. On the other hand, we could expose the nuclei to radiation of a fixed frequency of 100 MHz and sweep the applied magnetic field over a range until absorption occurs. In common NMR instruments, the frequency of the radiation is kept constant and the strength of magnetic field is varied until all types of nuclei come into resonance with the incoming radiation. Figure 10.11 illustrates the basic elements of a classical 100 MHz NMR spectrometer.

The sample is dissolved in a solvent containing no interfering protons (CCl_4, CDC_{l3}, d_{6-} DMSO etc. and a small amount of TMS is added to serve as an internal reference. The sample cell is a small cylindrical glass tube that is suspended in the gap between the faces of the pole pieces of the magnet. The sample is spun around its axis to ensure that all parts of the solution experience a relatively uniform magnetic field. The sample tube is surrounded by a coil attached to a 100 MHz radiofrequency generator. This coil supplies the electromagnetic energy used to change the spin orientations of protons. There is a detector coil perpendicular to the radiofrequency coil. When no absorption of energy is taking place, the detector coil picks up no energy given off by the radiofrequency oscillator coil. However, when the sample absorbs energy, the reorientation of nuclear spin induces a radiofrequency signal in the plane of the detector coil, and the instrument responds by recording it as a resonance signal or, peak.

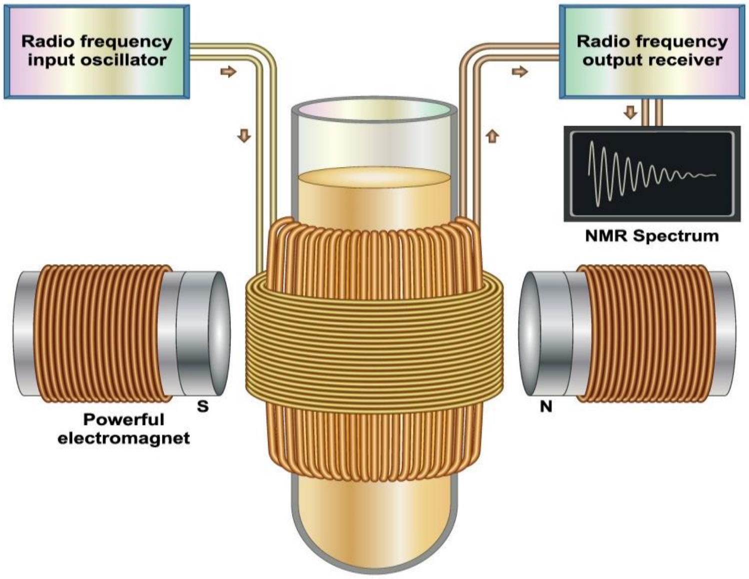


Figure 10.11: The basic elements of a classical nuclear magnetic Resonance spectrometer.

At a constant field strength, the different types of protons in a molecule precess at slightly different frequencies depending on their electronic environments. As the strength of magnetic field is increased, the precessional frequencies of all the protons increase. When the precessional frequency of a given type of protons reaches 100 MHz, resonance occurs and energy is absorbed from the radiofrequency source giving rise to an NMR signal. Thus by varying the magnetic field strength keeping the frequency of the radiofrequency oscillator fixed, all types of protons are made to resonate with recording of corresponding NMR signal. The magnet with variable field strength is a two part device. There is a main magnet with a strength of 2.3487 T, which is capped by electromagnet pole pieces. By varying the current strength through the pole-pieces, the strength of the main field can be increased as much as 20 ppm.

Chemical shift in NMR spectroscopy

A spinning charge generates a magnetic field that results in a magnetic moment proportional to the spin. When a molecule is placed in an external magnetic field, the valence electrons around protons are made to circulate. This circulation generates a **local diamagnetic current** and produces a counter magnetic field which opposes the applied magnetic field. The field experienced by the proton is thus diminished and the proton is said to be shielded. This effect is called **diamagnetic shielding** or **diamagnetic anisotropy**.

Circulation of electrons, specifically π-electrons, about nearby nuclei generates a field that can either oppose or reinforce the applied magnetic field at the proton, depending on the location of the proton. If the induced field opposes the applied field, the proton is shielded. However, if the induced field reinforces the applied field, the proton experiences greater magnetic field than the applied one and it is said to be deshielded.

Compared with a naked proton, a shielded proton requires a higher magnetic field while a deshielded proton requires a lower applied field in order to come to resonance with a fixed radiofrequency radiation. Shielding thus shifts the absorption upfield and deshielding shifts the absorption downfield. Such shifts in the position of NMR absorptions, arising from shielding or deshielding of nuclei by surrounding electrons, are called **chemical shifts**.

Chemical shift is characterized as the difference between the resonant frequency of the spinning protons and the signal of the reference molecule. Nuclear magnetic resonance chemical change is one of the most important properties usable for molecular structure determination. There are also different nuclei that can be detected by NMR spectroscopy, 1H (proton), 13C (carbon 13), 15N (nitrogen 15), 19F (fluorine 19), among many more. 1H and 13C are the most widely used. The definition of 1H as it is very descriptive of the spectroscopy of the NMR. Both the nuts have a good charge and are constantly revolving like a cloud. Through mechanics, we learn that a charge in motion produces a magnetic field. In NMR, when we reach the radio frequency (Rf) radiation nucleus, it causes the nucleus and its magnetic field to turn (or it causes the nuclear magnet to pulse, thus the term NMR).

Measurement of chemical shift

The unit in which a chemical shift is expressed is parts per million (ppm) of the total applied magnetic field. Since shielding and deshielding arise from induced secondary fields, the magnitude of the chemical shift is proportional to the strength of the applied field and consequently to the radiofrequency, the field must match. However, if it is expressed as a function of the applied field, that is, if the observed shift is divided by the particular radiofrequency used, the chemical shift has a constant value that is independent of the Radiofrequency and the magnetic field that the NMR spectrometer employs.

Reference for measuring chemical shift

The reference point from which chemical shifts are measured. For practical purpose we use tetramethyl silane (TMS), $(CH_3)_4Si$ for reference measurement**.** Reasons for using TMS as reference for measuring chemical shifts:

1. Its resonance is sharp and intense since all the twelve protons are equivalent and absorb at exactly the same applied field.
2. Due to the lower electronegativity of silicon than that of carbon, the shielding of protons is greater in TMS than in most organic molecules. So, the protons of TMS absorb too upfield and can be easily recognized. Protons in most of the organic molecules absorb downfield with respect to the protons of TMS.
3. TMS is a low boiling liquid (b.p. 27ºC) and hence it can be easily recovered from most samples after use.

Thus, if about five percent of TMS is added to a sample and the complete NMR spectrum is produced, the sharp, upfield signal of TMS is easily recognized and can be used as a standard. The signal from TMS is often exhibited towards the far right since the field of an NMR spectrum increases from left to right.

The most commonly used scale for measuring chemical shifts is the δ (delta) scale.

The position of the TMS signal is taken at δ = 0.0ppm. Most chemical shifts have δ values between 0 and 10. A small δ value indicates a small downfield shift while a large δ value represents a large downfield shift. An NMR signal from a particular proton appears at a different field than the signal from TMS. The chemical shift (δ) is defined as

$$\delta = \frac{(\nu_{sample} - \nu_{reference})}{operating\ frequency\ of\ the\ instrument\ (\nu_0\,)\ Hz}\ X\ 10^6\ ppm$$

$$\delta = \frac{\Delta\nu\ \ (Hz)}{(\nu_0\,)\ Hz}\ X\ 10^6\ ppm$$

Chemical shift in δ units expresses the amount by which a proton resonance is shifted from TMS, in parts per million, of the spectrometer's basic operating frequency. Value of δ for a given proton is always the same irrespective of whether the measurement was made at 60 MHz (B_Z = 1.41T) or at 100 MHz (B_Z = 2.3487T). For example, at 60 MHz the shift of the protons in CH_3Br is 162 Hz while at 100 MHz, the shift is 270 Hz from TMS. However, both of these correspond to the same value of δ = 2.70 ppm.

$$\delta = \frac{162\ \ (Hz)}{60\ X\ 10^6\ \ Hz}\ X\ 10^6\ ppm$$

$$\delta = \frac{270\ \ (Hz)}{100\ X\ 10^6\ \ Hz}\ X\ 10^6\ ppm$$

$$\delta = 2.70\ \text{ppm}$$

There are a number of factors the values of chemical shifts, such as electronegativity effects, hybridisation effects, hydrogen bonding, magnetic anisotropy etc.

Applications of NMR spectroscopy

NMR spectroscopy is a non-destructive and non-invasive technique that is used to determine molecular structure and dynamics. The applications of NMR are diverse and include the following research areas and industries:

- In biology, NMR is applied to study macromolecules, such as proteins, lipids and nucleic acids. ^{13}C, ^{1}H, ^{15}N, ^{31}P, ^{23}Na, and ^{19}F are the most biologically relevant NMR-active nuclei, used to understand biochemical pathways involved in amino acid, lipid and carbohydrate metabolism.

- In chemistry, it's widely used for both qualitative and quantitative analysis to monitor reactions, identify structures and assess purity.
- In polymer science, to analyze monomer ratio, molecular weight, tacticity, sequencing, chain length and branching, and to determine end groups.
- In the pharma industry, to determine the purity and quantity of active ingredients, excipients and impurities in pharmaceutical products
- In the petroleum industry, to assess hydrocarbons of raw petroleum and its products.
- In medicine, magnetic resonance imaging (MRI) is an application of NMR used for soft tissue analysis to identify the damaged or diseased tissues.
- Identification of structural isomers.
- Distinction between cis-trans isomers and conformers: A cis isomer can easily be distinguished from its trans-isomer as cis and trans protons have different coupling constants. trans-protons have higher coupling constant than cis-protons.

SAS:

1. What is NMR spectroscopy?
2. What is proton NMR used for?
3. What does resonance mean in NMR?
4. How is NMR used in medicine?
5. How is NMR used in MRI?
6. What is the reason of using radio frequency in NMR spectroscopy?
7. What down the various factors that affect the NMR spectra?
8. Define a chemical shift?
9. Why is carbon tetrachloride used in NMR?

10.5.5 Electron Spin Resonance (ESR)

Electron spin resonance (ESR) also known as electron paramagnetic resonance (EPR), uses microwave radiation to examine species containing unpaired electrons, such as radicals, radical cations, and triplets. ESR is a technique for detecting how electrons behave (dynamically) inside of a suitable molecule and for investigating various processes by determining the electron environment. Quantities, types, nature, environments, and behaviours of unpaired electrons may all be learned via ESR observations. The sole method for non-destructively and selectively detecting free radicals in any sample phase is through the use of ESR devices (gas, liquid or solid).

Difference between ESR and NMR:

ESR and NMR both include magnetic resonance phenomena, but ESR's is of a different type due to the magnetic dipole moment of the involved nucleus. Because of the difference in mass, the nuclear magnetic moment is lower than the electron's. The resonance occurs in the radio frequency range and has a correspondingly lower frequency. The constraint to molecules with unpaired electrons no longer exists, which is a significant departure from ESR. The NMR spectrum is produced by every molecule having a magnetic nucleus. The NMR and ESR are similar in the sense that NMR deals with nuclear ground state while ESR deals with electronic ground state.

Historical Development of ESR

In 1896, a Dutch physicist, Zeeman discovered the line splitting in optical spectra under a static magnetic field. Stern and Gerlach discovered the inherent angular momentum of electrons and atoms in the 1920s when they ran a beam of silver atoms through an inhomogeneous magnetic field and observed the beam divide into two different sections. The electrons' angular momentum was then postulated by Uhlenbeck and Goudsmit. Isidor Rabi detected the magnetic resonance absorption of the molecules of lithium chloride in 1938, allowing him to measure several resonances to obtain more precise details on molecular structure. The broad availability of microwave instruments following World War II hastened the development of electron paramagnetic resonance (EPR). In 1944, Soviet researcher Zavoisky discovered the first magnetic resonance signal in a number of salts, including hydrous copper chloride, copper sulphate, and manganese sulphate. The Oxford Group later put forward the fundamental theory of magnetic resonance. EPR was widely researched thanks to the work of several researchers, including Cummerow & Halliday and Bagguley & Griffiths. Between 1960 and 1980, Bell laboratories were primarily involved in the development of continuous wave (CW) EPR and the study of pulsed EPR. Typically, EPR was used to combat organic free radicals. The first commercial pulsed EPR spectrometer hit the market in the 1980s, and it has since been widely employed in the fields of biology, medicine, active oxygen, and other fields. EPR is a flexible research tool that is now accepted.

Principle behind ESR Spectroscopy:

The basis for ESR spectroscopy is the unpaired electron's ability to absorb microwave radiation when subjected to a high magnetic field. The atom's or molecule's electrical energy levels will divide into many levels. Magnetic resonance absorption is the term for such an excitation. A static/magnetic field and microwave are utilised in an ESR apparatus to investigate the behaviour of unpaired electrons in the substance under study. In theory, ESR detects paramagnetic centres (such as radicals) that may or may not be caused by radiation. An applied microwave energy is absorbed in resonance when a strong external magnetic field produces a difference between the energy levels of the electron spins, $m_s = +1/2$ and $m_s = -1/2$.

An electron spins on its own axis and its spin quantum number, S=1/2. An electron's spin motion results in spin angular momentum, S, which is given by:

$$\vec{S} = \sqrt{S(S+1)}\,\frac{h}{2\pi}, where\ S = \frac{1}{2}$$

$$\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\frac{h}{2\pi} = \frac{\sqrt{3}}{2}\,\frac{h}{2\pi}$$

In the presence of an external magnetic field, this spin angular momentum vector can only take those orientations in which its components along the direction of the external magnetic field (along the z-axis) are half-integrals (Figure 10.12).

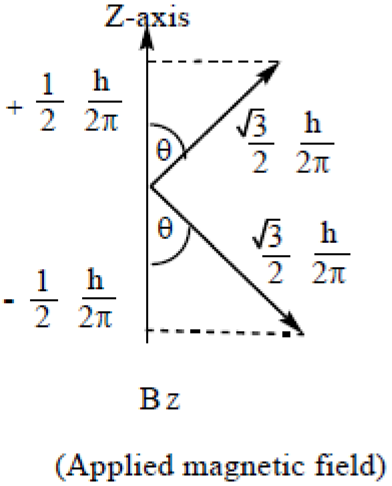


Figure 10.12: Two orientations of spin angular momentum vector in a magnetic field.

The z-component of the spin angular momentum vector is:

$$m_s \frac{h}{2\pi}$$

where the value of m_s is either $+\frac{1}{2}$ (spin-α) or $-\frac{1}{2}$ (spin-β). Thus, in the presence of an external magnetic field (B_Z), the spin angular momentum vector can only take two orientations in space.

Thus the orientation angle θ can be given as:

$$\left(\sqrt{S(S+1)}\ \frac{h}{2\pi}\right) cos\theta = m_s \frac{h}{2\pi}$$

Or we can write this equation as:

$$\left(\sqrt{S(S+1)}\ \right) cos\theta = m_s$$

An electron spinning on its own axis produces a magnetic field, which causes it to act like a miniature bar magnet. The spinning electron's magnetic moment is determined by

$$\mu = -g(\frac{e}{2m})\sqrt{S(S+1)}\ \frac{h}{2\pi}$$

$$= -g(\frac{eh}{4m\pi})\sqrt{S(S+1)}$$

$$= -g\mu_B\sqrt{S(S+1)}$$

In the above equation g is known as Lande splitting factor, a dimensionless constant and its value for the free electron is 2.0023. μ_B is the basic unit of magnetic moment of the electron, known as Bohr magnetron.

$$\mu_B = \frac{eh}{4m\pi}$$

On putting the values of e, h, m and π, we will find the value of μ_B as 9.2741 × 10–24 JT^{-1}.

The spin angular momentum vector and associated magnetic moment vector orient in opposite directions (Figure 10.13).

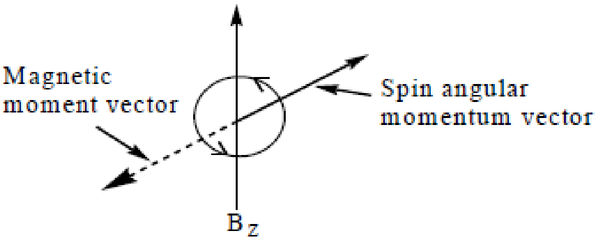


Figure 10.13: The orientation of magnetic moment vector relative to spin angular momentum vector.

The energy of interaction between the magnetic moment vector associated with the spinning electron and the magnetic field is given by when a spinning electron is put in a magnetic field (B_Z).

$$E = \mu_Z B_Z = \mu \cos\theta \; B_Z$$

On putting the value of μ from the above equation, we will get:

$$E = -\left(-g\mu_B\sqrt{S(S+1)}\right)\cos\theta \; B_Z$$

$$= g\mu_B B_Z \sqrt{S(S+1)}\cos\theta$$

Substituting the value of $\sqrt{S(S+1)}\cos\theta = m_s$, we will get:

$$E = g\mu_B B_Z m_s$$

As m_s can take two values $+\frac{1}{2}$ and $-\frac{1}{2}$, the equation can be written as:

$$E_{+\frac{1}{2}} = +\frac{1}{2} g\mu_B B_Z \qquad \text{for } (m_s = +\tfrac{1}{2})$$

$$E_{-\frac{1}{2}} = -\frac{1}{2} g\mu_B B_Z \qquad \text{for } \left(m_s = -\tfrac{1}{2}\right)$$

Where $m_s = +\frac{1}{2}$ corresponds to higher energy state whereas $m_s = -\frac{1}{2}$ corresponds to lower energy state. It is evident from above equations that an increase in magnetic field strength causes a rise in $E_{+\frac{1}{2}}$ while decrease in $E_{-\frac{1}{2}}$ (Figure 10.14)

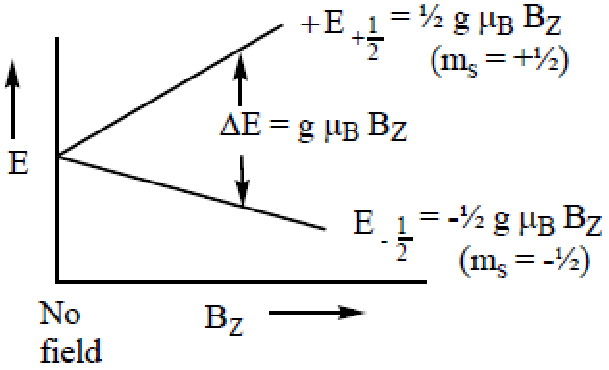


Figure 10.14. Effect of magnetic field strength on the energy of spinning electron.

In the presence of a magnetic field, the energy difference between an electron's two spin states is given by:

$$\Delta E = E_{+\frac{1}{2}} - E_{-\frac{1}{2}}$$

On putting the values of $E_{+\frac{1}{2}}$ and $E_{-\frac{1}{2}}$. We have:

$$\Delta E == +\frac{1}{2} g\mu_B B_Z - (-\frac{1}{2} g\mu_B B_Z\ )$$

$$\Delta E = g\mu_N B_Z$$

If electromagnetic radiation of frequency ν satisfying the condition.

$$h\nu = g\mu_N B_Z$$

is present, transition of electron from lower energy spin state ($m_s = -\frac{1}{2}, \beta - spin$) to higher energy spin state ($m_s = +\frac{1}{2}, \alpha - spin$) takes place with the absorption of this much amount of energy giving rise to ESR spectrum. Equation $h\nu = g\mu_N B_Z$ gives the resonance condition for ESR spectrum. In a magnetic field of strength 0.34 T, the resonance frequency (ν) is given as:

$$\nu = \frac{g\mu_N B_Z}{h}$$

On putting the values of each terms in the above equation we will get:

$$= \frac{(2.0023)(9.274X10^{-24}\,JT^{-1})\ (0.34\,T)}{6.626\,X\ 10^{-34}\,JS}$$

$$= 9.530 \times 10^9 \text{ Hz} = 9530 \times 10^6 \text{ Hz} = 9530 \text{ MHz}$$

The frequency is in the electromagnetic spectrum's microwave range. Therefore, it is necessary to use microwave sources and procedures to record ESR spectra.

It is necessary to meet equation: $h\nu = g\mu_N B_Z$, for the frequency (ν) and magnetic field (B_Z) in order to successfully see the ESR spectrum. The calculated value of for a magnetic field of 0.34 T is 9530 MHz. Spectrometers operating around this frequency are referred to as X-band spectrometers. There are other spectrometers that operate at greater magnetic fields (B_Z = 1.3 T) and higher microwave frequencies (35000 MHz). They are known as spectrometers in the Q-band.

Instrumental Technique in ESR Spectroscopy:

Normally, there are two approaches to record the ESR spectrum. Either the frequency (ν) is changed while the magnetic field is changed (B_Z) or the magnetic field is changed while maintaining a constant frequency (B_Z). The latter method is typically used because it is simpler to control the magnetic field while maintaining extremely high levels of stability. The magnetic component of electromagnetic radiation interacts with the magnetic dipole connected to the unpaired electron in the ESR Experiment. Only the energy level oscillates and not the electron magnetic moment when the oscillating magnetic field vector of the radiation is parallel to the applied magnetic field. Only when the electron magnetic moment is reoriented will there be a transition between the levels. Therefore, the oscillating magnetic field of the radiation must be perpendicular to the applied magnetic field for ESR absorption to be successful.

The fundamental parts of an X-band ESR spectrometer are:

(a) A electromagnet that can produce a homogeneous magnetic field that can be varied linearly on either side of the magnetic field.

(b) A source of microwave radiation with a 9.5 GHz range.

(c) A suitable sample cavity.

(d) Arrangements for delivering the radiation energy to the sample cavity are listed in item

(e) A detector that tracks changes in microwave power.

(f) An appropriate recorder or oscilloscope.

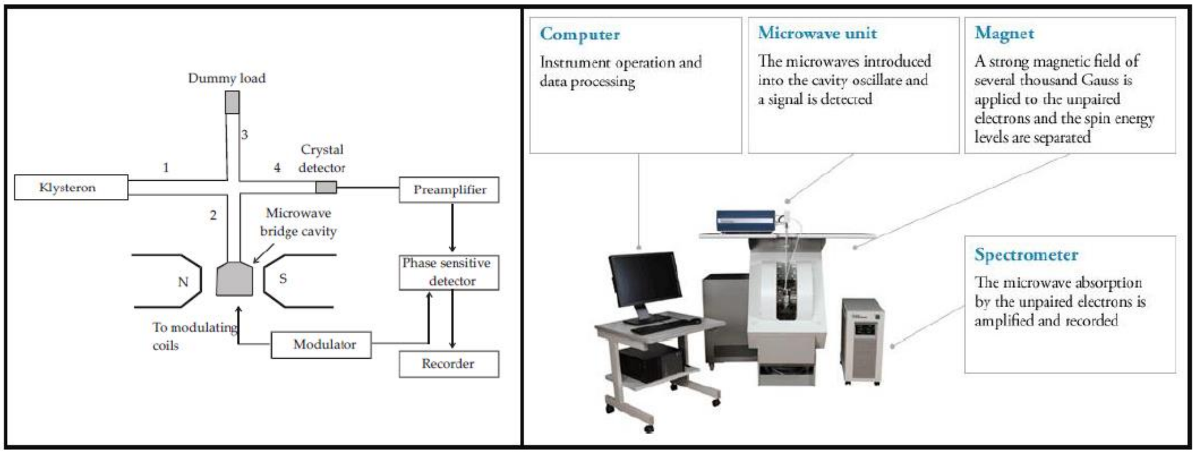


Figure 10.15: Electron Spin Resonance (ESR) instrument composition.

A simple block diagram of a balanced bridge ESR spectrometer is given in Figure 10.15. The typical source of microwave radiation is a klysteron oscillator, which produces monochromatic radiation at the necessary frequency. A microwave impedance bridge transmits the source's radiation to the sample cavity. The sample is stored inside a rectangular microwave cavity that is sandwiched between the electromagnet's pole parts. The third arm of the microwave bridge is used to hold a dummy load, while the fourth arm is used to hold a semiconducting crystal. The crystal picks up the radiations that enter the fourth arm. After being amplified, it is sent into an appropriate recorder. ESR signals are often depicted as absorption or first derivative curves, and they are typically detected using phase sensitive detectors. By adjusting the current in a pair of sweep coils positioned on the hollow walls, the magnetic field is swept within a narrow range spanning the resonance state.

Microwave power only flows in two arms when the bridge is balanced: one arm goes to the cavity (arm -2), and the other one goes to the dummy load (arm 3). The 4th arm won't have any power. Only when the bridge is unbalanced will the 4th arm have power. Only two arms of microwave power flow when the bridge is balanced: one goes to the cavity (arm -2), and the other goes to the dummy load (arm 3). The power in the fourth arm won't exist. Only when the bridge is unbalanced will there be power in the fourth arm. When the bridge is in a balanced position, microwave power flows only in two arms - the one to the cavity (arm -2) and the other to the dummy load (arm 3). There will not be any power in the 4th arm. Power in the 4th arm will be there only when the bridge is not balanced.

ESR spectrum of benzene anion ($\dot{C}_6H_6^-$)

By reacting an alkali metal with benzene in a solvent like tetrahydrofuran, benzene anion can be created (THF). When an electron is transferred from the alkali metal atom to the benzene molecule, the outcome is a benzene anion. Seven peaks in the $\dot{C}_6H_6^-$ measured ESR spectrum (Figure 10.16) indicate that the system's unpaired electron density is evenly distributed across its six protons.

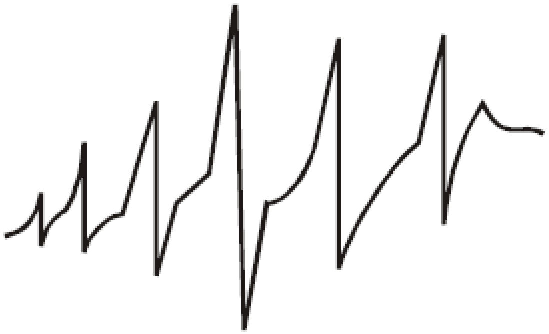


Figure 10.16: ESR spectrum of benzene anion.

Given that benzene anion has six equivalent protons, the anticipated number of ESR signals = (2n I+1)

$$2 \times 6 \times \frac{1}{2} + 1 = 7$$

Seven lines with the intensity ratio. 1 : 6 : 15 : 20 : 15 : 6 : 1, are actually observed in the ESR spectrum of $\dot{C}_6 H_6^-$. The hyperfine coupling constant (a), which is 3.76 gauss, is determined by the distance between the lines.

Benefits of ESR:

- A variety of irradiated food kinds may be recognised using ESR Spectroscopy.
- In a range of materials, it can find free radicals and paramagnetic ions.

ESR applications:

There are a number of applications of ESR.

1 Free Radical Study

- This allows us to research free radicals. ESR spectroscopy allows us to analyse free radicals even in extremely low quantities.
- It is possible to determine the structure of organic and inorganic free radicals.
- The triplet state of molecules can also be studied.
- The spin label informs the reader of the polarity of its surroundings.

2. Structural Determination

- In some situations, ESR offers information on the shape of the radio waves.

3. ***Detection of radioactively contaminated food***

4. Utilising lattice flaws to determine the age of fossils and geological features

5. To determine the rate of catalysis

6. To know about the active site geometry

10.5.6 Mossbauer spectroscopy

Mossbauer spectroscopy deals with the interaction of γ rays with the atoms/molecules. It is also known as Nuclear Gamma Resonance Spectroscopy. In this method nucleus absorbs a gamma ray photon and undergoes transition. γ rays being highly energetic, interact with only the nucleus of the atoms. Wherein information about the chemical environment and oxidation states of the atoms can be obtained. For example a compound $Fe^{3+}[Fe^{III}(CN)_6]$, there are two iron atoms in 3+ oxidation state. Both of them are in different chemical environment. One of the atom is in the coordination sphere and another is outside. From the help of Mossbauer spectroscopy it is possible to identify this. Elements used Mössbauer spectroscopy are ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{129}I, etc.

Mossbauer Nuclei:

To obey the Mossbauer spectroscopy one nuclei must obey

1. The element which is to be investigated must have a source of gamma ray emission
2. The parent nuclei must have larger half-life time.
3. The emission energy must lies in few keV to lower value of hundreds keV.
4. The life time of isomer excited level must ranges in 10^{-3} to 10^{-6} s. If larger then it will decrease the width to energy ratio resulting to diminishing resonance selectivity.

Advantage: Mössbauer spectroscopy can be applied to many branches of study, including physics, chemistry, biology, and metals. It can provide incredibly accurate details regarding a material's chemical, structural, magnetic, and time-dependent properties. It also gives very accurate information about the chemical environment of similar atoms present in a molecule and their oxidation states.

Disadvantage: Resonance absorption of γ rays, unlike other radiations, is not possible. Also in order to have a γ ray source, an atom should be radioactive with enough half-life. Hence, this method cannot be employed to study all the molecules.

Basic principle:

It involves recoil-less emission & absorption of γ rays by nuclei. Atoms in source emitting γ rays must be of same isotope as atoms in sample absorbing them.

Recoil effect:

Whenever a high energy particle is released from a body at rest, the releasing body feesls a back-kick, i.e., it is pushed backward (just like gun). This is called recoil effect (Figure 10.17). So the energy of the γ rays is slightly less than natural energy of transition. Similarly for a nucleus at rest to absorb γ ray, the energy of γ rays should be slightly less than natural energy.

Energy of recoil (E_R) $=\frac{E_\gamma^2}{2mc^2}$

E_γ = Energy of γ ray (energy betweenground state and excited state)

M=mass of nucleus

C=velocity of light

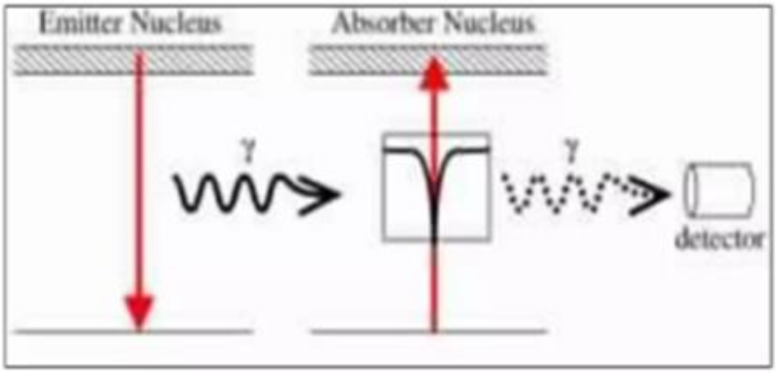


Figure 10.17: Recoil effect.

Recoiling effect depends upon the effective mass. So as mass increases, the recoiling effect decreases. So for the free nuclei this nuclear resonance, i.e. absorption and emission of γ rays by identical nuclei, is not observable. But when nuclei is present in solid crystal, there is very little loss as recoil energy. If the free nuclei this nuclear resonance i.e. absorption and emission of γ rays by identical nuclei, is not observable. But when nuclei is present in solid crystal, there is very little loss as recoil energy. If the emitting and absorbing nuclei were in identical chemical environment then the transition energies would be equal and nuclei resonance. But if the chemical environment is different, it will cause the shift in nuclear energy less. To bring the nuclei in the resonance the energy of γ-rays is slightly changed Doppler effect.

Mossbauer Effect:

Mossbauer effect involves the resonant and recoil free emission and absorbtion of gamma radiation by atomic nuclei bound in a solid. Mossbauer effect cannot be observed in the liquid and gases because the recoil energy cannot be dissipated in these sattes in matter. In a mossbauer effect, a narrow resonance for the nuclear gamma emission and absorbtion results from the momentum of recoil being delivered to a surrounding crystal lattice rather than to the emitting or absorbing nucleus alone. When this occurs, no gamma energy is lost to the kinetic energy of recoiling nuclei at either the emitting or absorbing end of a gamma transition: emission and absroption occur at the same energy resulting in strong, resonant absorption.

Instrumenation:

The main components of the Mossbauer spectroscopy are (Figure 10.17):

***Mossbauer Driver*:** It is used to move the source relative to the sample.

Source: ^{57}Co source of γ-ray emission. Enerally kept at RT.

Collimator: This is used to narrow the γ-rays.

Sample: The sample must be in solid phase and in crystalline. Usually sample requies in a large amount and applied as a thin layer on sample holder and irradiated.

Detector: The choice of the detector depends upon the γ-ray energies . It cannot be seen using traditional examinatio methods of electromagnetic raditaion. The distance and angle of the detctor plays a crucial role. Basically it is two types:

1. Gas fileed
2. Scintillation

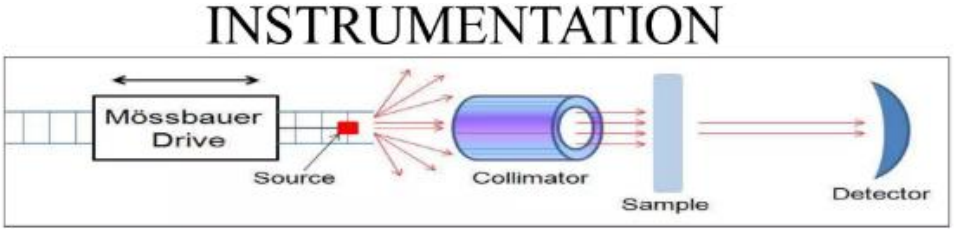


Figure 10.18: Experimental set up for Mossbauer spectroscopy

Mössbauer Spectroscopy characteristic:

- It is cheap.
- It is fast.
- It is sensitive to magnetic transitions, phase purity.
- It can give some information about the nature of the magnetic phase
- It is reasonably easy to use T, P, H as variables

10.5.7 Positron annihilation spectroscopy

Positron annihilation spectroscopy (PAS) is particularly suitable for studying vacancy-type defects in semiconductors. The method is based on the idea that positrons or positronium will disintegrate when they come into contact with electrons. The duration between the production of positrons from a radioactive source and the detection of gamma rays as a result of annihilation correlates to the lifetime of the positron or positronium.

PAS is based on the detection of gamma radiation after annihilation of positron with an electron in the studied sample, using either positron lifetime or annihilation gamma ray information, such as energies or angles of detected gamma rays, to extract basic structural features of studied samples. P. Dirac predicted the positron as the electron anti-particle in 1928, and as a first antiparticle was discovered by C. Anderson in cosmic rays in 1932. Analogous to proton and electron which are bound in hydrogen atom, S. Mohorovičić has predicted that positron and electron can form bound state, later called positronium, and which was discovered by M. Deutsch in 1951.

Beside the fundamental research with positrons in investigations of quantum electrodynamics laws, e.g., already at the end of forties it was realized that information carried by gamma rays after annihilation of positrons can be used to study structural properties of various samples, and since then various techniques of PAS have been successfully employing in various fields of research and applications. Initial investigations which have used radioactive positron sources have been recently complemented with slow positron beams as well, available also as table-top beam systems. One of the most useful and productive applications of PAS has been in material properties research, for some general reviews of applications and techniques. The other outstanding field of application of positron annihilation detection is medical imaging. Positron annihilation is used in various imaging systems such as gamma camera, PECT, PET, CT-PET, etc. This technique is of great importance for nano-scale investigations of some technology important materials like metallic layers, thin films, layered semiconductors, porous materials etc. providing information on native or induced defects and surface structural imperfections. Also new detection methods based on the novel detectors and electronics are opening new possibilities through combination of various PAS techniques in unified measuring systems, which can provide correlations of, previously also accessible, but uncorrelated, data.

Positron Annihilation Spectroscopy Techniques

There are three main techniques of positron annihilation spectroscopy and which can be used both with the positrons from sources and slow positron beams: 1) positron annihilation lifetime spectroscopy (PALS), 2) Doppler broadening spectroscopy and 3) angular correlations measurements.

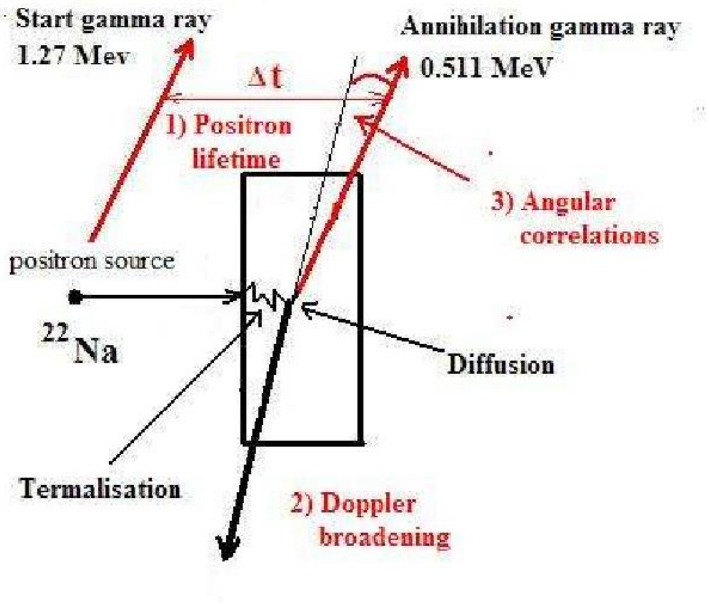


Figure 10.19. Principles of three main techniques in positron annihilation spectroscopy (here presented with ^{22}Na positron source): 1) Positron annihilation lifetime spectroscopy, 2) Doppler broadening spectroscopy and 3) Angular correlations measurements.

The principles of these techniques are illustrated in Fig. 10/19. In the positron annihilation lifetime spectroscopy, when used with radioactive sources, ^{22}Na is usually used as positron source. In this case PALS is based on the measurements of the time difference between 1.274 MeV γ-ray, emitted from the daughter ^{22}Ne nucleus almost immediately after positron emission from the ^{22}Na, and one of the annihilated 0.511 MeV γ-rays emitted in positron annihilation. The collected time spectra contain various lifetime contributions and decomposition in individual time components and corresponding intensities can yield information about holes in the sample and their concentrations. This technique, when used with slow positron beam, should include some gating from the incoming positrons in beam, but with the definite positron energy, the exact penetration depth can be determined. In Doppler broadening spectroscopy the precision measurement of energy shift of the annihilated 0.511 MeV γ-ray as a consequence of non-zero momentum of annihilated positron and electron pairs is used to extract information about electron distributions in the investigate sample. One can detect either only one annihilated gamma ray (single Doppler broadening spectroscopy) or, in order to reduce the background, coincidence between the two outgoing 0.511 MeV γ-rays can be used (coincidence Doppler broadening spectroscopy). This non-zero momentum of annihilated positron-electron pairs causes also deviation from co-linearity of the two outgoing γ-rays, and these angular deviations can be registered in γ- γ coincidence measurements in one or two dimensions, and form basis of angular correlation measurements. But to achieve required angular resolution in these measurements gamma ray detectors should be several meters apart and require special laboratory arrangements

10.6 SUMMARY:

In this unit, we have discussed about the concept of spectroscopy and its different types. The characteristics of electromagnetic radiations were discussed with reference to wavelength, frequency, wave number and velocity. In addition to this, the fundamental laws of absorption were taken into account that includes Lambert's law and Beer's law. Then we have extended our discussion to IR spectroscopy, NMR, ESR, Mossbauer and Positron annihilation. We have observed that these spectroscopy techniques are extensively used in different areas of industry.

10.7 Glossary

Spectroscopy	Interaction between electromagnetic radiations and matter.
Monochromatic Light	Light of single wavelength.
Spectrophotometer	Instrument used to measure the relative energy that is emitted, transmitted or reflected
Atomic Spectroscopy	Interaction of electromagnetic radiations with atoms.
Molecular Spectroscopy	Interaction of electromagnetic radiations with atoms.
Electromagnetic Radiations	Waves of high and low frequency having oscillating electric and magnetic field perpendicular to each other.
Atomic Spectroscopy	Interaction of electromagnetic radiations with atoms.

NMR	Nuclear magnetic resonance
Electromagnetic Spectrum	Arrangement of electromagnetic radiations in order of their decreasing frequencies
Anhilation	Being completely destroyed or obliterated
Positron	A subatomic particle with the same mass as an electron and a numerically equal but positive charge.

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10.9 Suggested readings

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10.10 Terminal question

1. Define electromagnetic spectrum and explain the characteristics of electromagnetic radiations.
2. Explain spectroscopy along with the fundamental laws of absorption
3. What is Raman spectroscopy?
4. What's the time needed to obtain a Raman spectrum?
5. Explain the applications of Raman spectroscopy.
6. What information is provided by Raman spectroscopy?
7. Explain the mechanism of Raman excitation.
8. What is the full form of ESR?
9. What is the use of Electron Spin Resonance Spectroscopy?
10. Discuss the principle behind ESR spectroscopy. What type of species are studied by this technique?
11. Discuss the principle behind ESR spectroscopy. What type of species are studied by this technique?

12. What is the difference between ESR and NMR spectroscopy?
13. Describe the experimental technique for recording ESR spectrum.
14. What is the principle of positron annihilation spectroscopy?

Objective Questions:

1. Absorption occurs at...
   a) All wavelengths in the spectrum.
   b) A characteristic wavelength dependent on the molecule
   c) The UV region
   d) The visible region

2. The sample path length and concentration of the sample are directly proportional to the _____.
   a) Reflection of light
   b) Refraction of light
   c) Absorbance of the light
   d) Intensity of the light

3. UV-Visible spectrometer uses a prism to...
   a) Focus all wavelengths on the sample simultaneously
   b) Separate radiation into its constituent wavelengths
   c) Reduce the amount of radiation passing through the sample
   d) Stop any radiation going through the sample

4. The Mossbauer Spectroscopy uses -------radiation.
   a) γ radiation
   b) β Radiation
   c) α Radiation
   d) μ Radiation

5. The Mossbauer effect based on
    a) Doppler effect
    b) Beer-Lamberts law
    c) Mössbauer effect
    d) Spin effect

6. Stokes lines are frequently much more __________ than the anti-Stokes' lines.
    a) thinner
    b) broader
    c) weaker
    d) intense

Answer: 1: b), 2: c), 3: b), 4: a), 5: c), 6: d)