

## Unit-II: Solid State Chemistry and Building Materials

Solids are substances characterized by definite shape, definite volume, non-compressibility, very slow diffusion, rigidity and mechanical strength”.

### Properties of solids

- The atoms, molecules or ions are held together by strong chemical forces.
- The nature of bonding is ionic, covalent or intermolecular force.
- They have high melting points.

### CLASSIFICATION OF SOLIDS

Depending on the arrangement of the atoms, molecules or ions, solids are classified into two types

#### Crystalline solids (or True solids)-

- The atoms, molecules or ions are arranged in a definite geometric manner.
- They have a 3-dimensional structural arrangement.
- They have long-range order.
- They exhibit anisotropy- properties varies with direction.
- They have sharp melting points.
- They undergo a perfect cleavage.
- Examples- Sulphur, sugar, sodium chloride, diamond, quartz ,alums.,etc.

#### Amorphous solids-

- The atoms, molecules or ions are arranged in random manner.
- They have short-range order.
- They are also known as super-cooled liquids.
- They exhibit isotropy- Properties same in all directions.
- Compared to crystalline solids, these solids have low melting points.
- They undergo an irregular cut.
- Examples- glass, plastics, bakelite, polyethylene, polystyrene, nylon.,etc.

### BAND THEORY OF SOLIDS

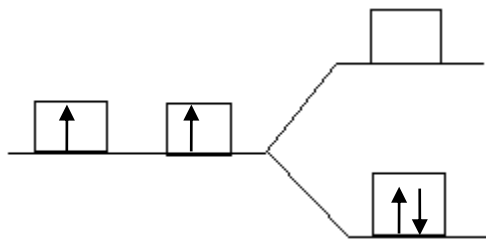
Band theory is extension of Molecular orbital theory of covalent bonds to solids.

#### Salient features of Band theory:

- Solids are made up of giant molecules in which a large number of spherical atoms are arranged in a regular close-packed pattern.
- When atoms are brought together in solids, the atomic orbitals of the valency shells interact forming molecular orbitals.
- During their interaction, their outer shells constitute one single system of electrons, common to entire array of atoms in a crystal.
- Let us take an example of lithium with electronic configuration



- In  $Li_2$  molecule-  $2S_1$  electrons from two Li atoms combine to form one Bonding,  $\sigma 2S_2$  and antibonding orbital,  $\sigma^* 2S_0$ .



- Similarly in  $\text{Li}_n$  molecule,  $n$  number of atomic orbital ( $2S$  of each lithium atom) combine to form a cluster of molecular orbital which are closely placed to each other. Each original energy level becomes a band of very closely spaced levels of small energy differences.



- Depending upon the composition of solids, bands are of two types-
  - Overlapping bands**- Higher band overlap with empty lower band.  
Eg:- Valence  $2S$  band overlap with empty  $2P$  band in Beryllium.
  - Non-overlapping bands**- Higher band do not overlap with lower band.  
Eg:- Valence  $3S$  band do not overlap with empty  $3P$  band in Sodium.

The band of energy levels occupied by valence electrons is called **Valence Band**.

It may be

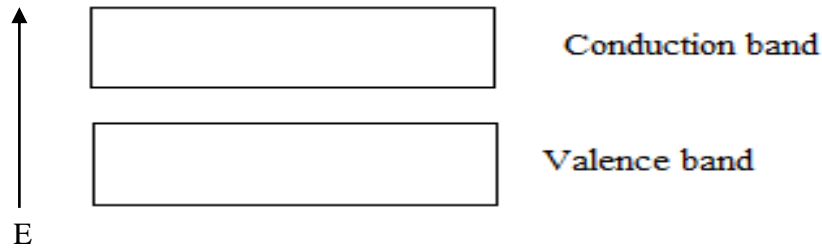
- Partially filled with electrons. Eg:- Na, Cu
- Completely filled with electrons. Eg:- Be, Mg
  - The next higher permitted band above the valence band is called **Conduction band**. The conduction band may be empty or partially filled with electrons which are also called as free- electrons.
  - The gap between the valence band and conduction band is called **Forbidden gap**.

The width of the forbidden gap is called Energy gap ( $E_g$ ). Depending on the  $E_g$ , solids are classified into three types.

- Conductors
- Insulators
- Semi-conductors

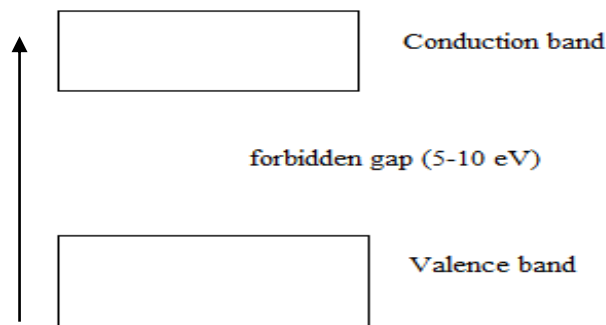
**Conductors**- In these materials, the energy gap is almost negligible.

- When a potential is applied to the half-filled valence band, the free electrons get excited to the empty conduction band and they begin to conduct. Eg:- Na, Al etc.
- In elements like Mg, conduction is mainly due to overlapping of filled valence band with higher empty band.
- Electrical conductivity of a metals decreases with rise in temperature because of the increased thermal vibrations of metal atoms which causes slattering of the electrons. Hence their flow is obstructed.



**Insulators-** In these materials, the energy gap is of order 5-10eV.

- In insulators, the valence band electrons are tightly bound to their parent nuclei and require large amount of electric fields to remove electrons to conduction band.
- They possess a complete valence band and completely empty conduction band.
- Eg:- Diamond, glass, solid NaCl, Plastics, ceramics etc.
- Electrical conductivity increases with increase in temperature. At room temperature, they act as best insulating materials. At higher temperatures, some of the valence electrons acquire sufficient energy to overcome the energy gap and enter the conduction band



**Semiconductors-** In these materials, the energy gap is of order of 1 eV.

- Solids having electrical conductivity in between those of insulators and conductors are called semiconductors.
- They have filled valence band, almost empty conduction band. Eg:- Si, Ge.
- Electrical conductivity increases with increase in temperature. The probability of promotion of electrons from valence band to conduction band decreases with the energy gap and increases with temperature

## SEMICONDUCTORS

- Semiconductors are materials with electrical conductivities that are intermediate between those of conductor's and insulators.
- They acts as insulators at very low temperature, but acts as sizable electrical conductors at room temperature.
- The width of band gap in semiconductors is intermediate to that of insulators and conductors.
- They are used for electronic purposes as they can carry an electric current by electron migration or hole propagation.
- The resistance of semiconductors decreases with increase in temperature- negative temperature coefficient of resistance.
- The resistibility is less than an insulator but more than a conductor.
- When a suitable metallic impurity e.g., arsenic, germanium, gallium, etc is added to a semi-conductor, its current conducting properties change appreciably.

## CLASSIFICATION OF SEMICONDUCTORS

Semiconductors are classified into two types-

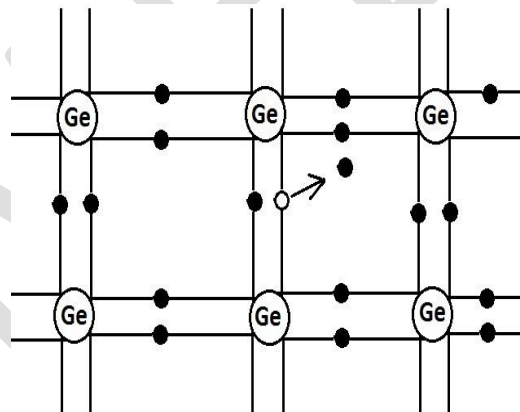
1. **Intrinsic semiconductors**
2. **Extrinsic semiconductors**
  - a) **n-type semiconductors**
  - b) **p-type semiconductors**
3. **Compound Semiconductor**
4. **Defect Semiconductor**
5. **Organic semiconductors**

### 1. Intrinsic semiconductors

These semiconductors are pure enough that impurities do not appreciably affect its electrical behavior. Elements like Silicon, germanium, selenium acts as intrinsic semiconductors which have four valence electrons in their atoms and their band gap is about 1ev.

Conduction Process:-

- When an electron from the valence band is ejected, a covalent bond is broken and a positively charged hole is left in the valence band.
- The hole travels to an adjacent atom by accepting an electron from the latter one.
- This forms a new covalent bond and breaks an existing covalent bond by filling up the previous hole and creating a new hole.
- When electric field is applied, electrons in the conduction band move to the anode and positively charged hole moves to cathode.
- Hence current is produced due to simultaneous movement of conduction band electrons and valence band holes in opposite directions.



### 2. Extrinsic semiconductors-

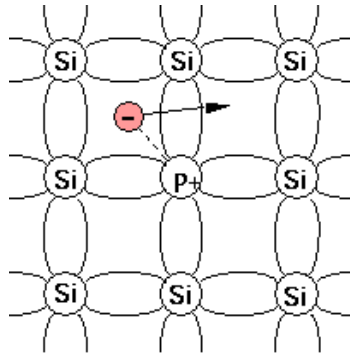
Intrinsic semiconductors when added with extremely small amount of substitutional impurities (doping) are called Extrinsic semiconductors. On adding a doping agent, the energy gap gets reduced and makes the electron flow easy from valence band to conduction band. The conductivity increases by 10,000 times.

Based on the doping agent added, extrinsic semiconductors are classified into two types:-

#### i) **n-type semiconductors-**

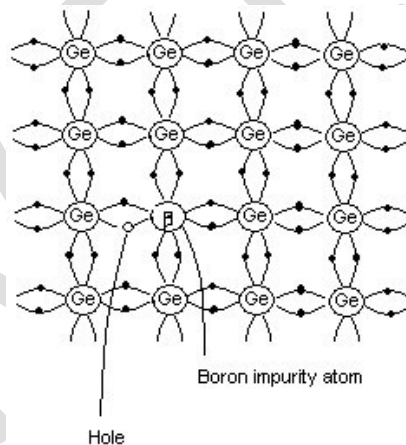
- These semiconductors contain a small quantity of a penta valent element impurity (like phosphorous, arsenic or antimony).
- The doping atom forms four covalent bonds with the surrounding four atoms of intrinsic semiconductor (Germanium, Silicon etc) with the help of its four valence electrons.
- The fifth excess electron remains loosely bound to the donor atom itself. It is easily excited from the valence band to conduction band on applying electric field.

- Thus conduction is due to movement of extra electron in an n-type semiconductor.



## ii) p-type semiconductors

- They contain a small quantity of a trivalent element (like boron, aluminium).
- The three valence electrons present in the trivalent impurity forms three covalent bonds with the surrounding three of the four atoms. So that one bond in one of the four surrounding atom is left incomplete.
- This gives rise to a positive hole.
- On applying an electric field, a hole travels to an adjacent atom by acquiring an electron and establishes a new covalent bond, by breaking an existing covalent bond in the adjacent atom.
- Hence conductivity in p-type semiconductors is due to the movement of positive holes.



## 3. COMPOUND SEMICONDUCTORS

### 4. DEFECT SEMICONDUCTORS

The defects shown in non-stoichiometric compounds behave like a semiconductors are called defect semiconductors.

When the ratio of the number of atoms of one kind to the number of atoms of other kind does not exactly correspond to the ideal whole number implied by the molecular formula of compounds are called non- stoichiometric compounds .

Examples- Oxides and sulphides of Transition elements. FeO, FeS, CuS etc.

The ratio of Fe:O in FeO is Fe<sub>0.84</sub>O – Fe<sub>0.94</sub>O

Electrical conductivity in these compounds is maintained either by having extra electron in the structure or changing the charge on some of the metal ions.

These defects occur in two ways-

- Metal Excess defects
- Metal deficiency defects

### Metal Excess defects-

They occur in two ways-

#### a) Anionic vacancy (F-Centres)

A negative ion may be absent from its lattice site, leaving a hole which is occupied by an electron, thereby maintaining electrical balance.

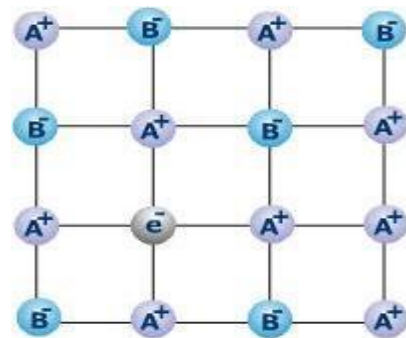
This type of defect is formed by crystals which would be expected to form Schottky defect.

Eg:- NaCl is heated in presence of Na metal, then Cl atom expels from crystal leaving an electron in the anion site.

Anionic site occupied by electrons in this way are called F-Centres.

Solids containing F-centres conduct electricity.

Solids containing F-centres when irradiated with light become Photo conductors.

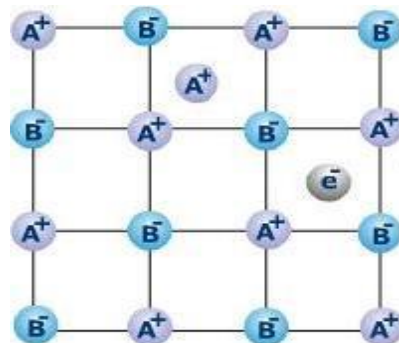


#### b) Extra cation and electron occupying the interstitial position-

The defect is formed in crystals which would show Frenkel defect.

Eg:- ZnO, CdO, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> etc.

In this defect, metal oxide when heated the surface oxygen expels and leaves the electrons, at the same time the metal ion present at the surface enters into the interstitial position of the crystal, increasing its conductivity.



### Consequences of Metal excess defects-

As these defects involve an electron, they act as n-type semiconductors.

These compounds are often colored.

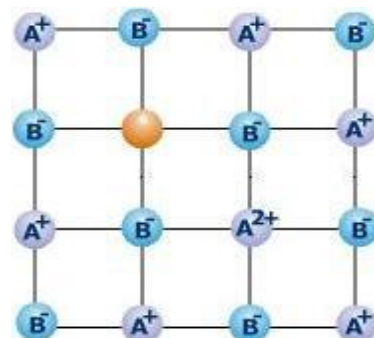
Eg:- ZnO is Yellow when hot, White when cold. Defect NaCl crystal yellow in color

### Metal deficiency defects-

This defect is observed when a positive ion is absent from its lattice site and the charge is balanced by an adjacent metal ion having extra positive charge.

Eg:- FeO, FeS, NiO etc.

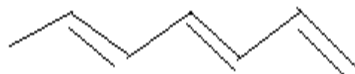
Due to the presence of positive hole, they act as p-type semiconductors.



## 5. ORGANIC SEMICONDUCTORS

Organic semiconductors are conjugated organic polymer materials having very high conductivity. These materials have intrinsic semi-conductivity with an energy gap of 1.0- 2.0 eV.

Conjugated Organic Polymers-



Polyacetylene.



Polyphenylene.

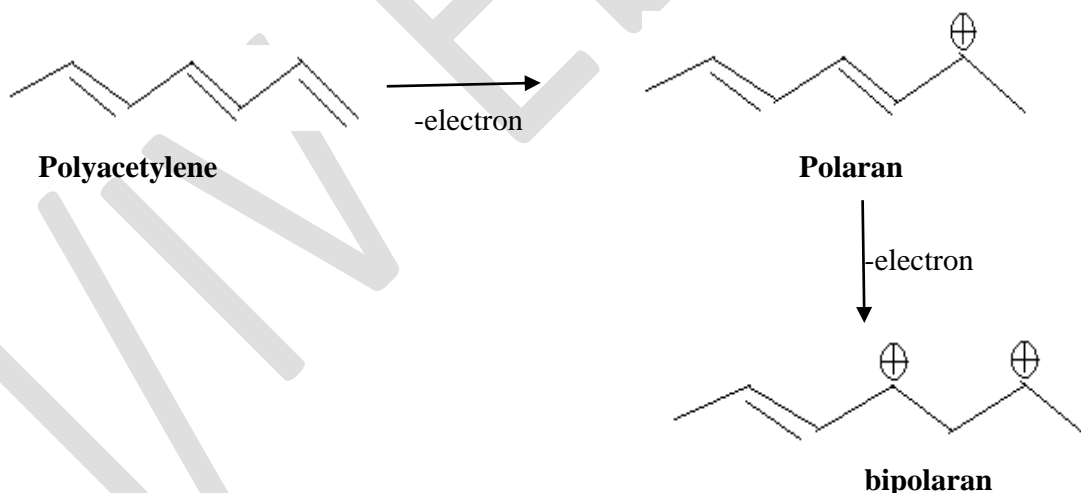
They become more conducting on doping with oxidizing or reducing agents.

If the dopant used is a Lewis acid like  $\text{AlCl}_3$ ,  $\text{I}_2$ ,  $\text{FeCl}_3$  or oxidizing agent or electron withdrawing group etc. then obtained semiconductor is called **p- type semiconductor**.

If the dopant used is a Lewis base like  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  or reducing agent or electron donating group etc. then obtained semiconductor is called **n- type semiconductor**.

**Conducting process-**

- Electron is removed from the valence band by oxidation of the conjugated polymer due to which a vacancy (cation radical) equivalent to hole is formed.
- This partially delocalized cation radical, delocalized over a few monomer units, is called **Polaran**- Breaking of two conjugated bonds and formation of a dispositive radical.
- Low doping gives a polaran and high doping gives a bipolaran.



The polarans and bipolarans are mobile under the influence of electric field.

They can move along the polymer chain as like electrons and holes move in inorganic semiconductors.

**Advantages of organic semiconductors-**

- They are used in photovoltaic cells, electrode photo cells, electro-chromic and memory devices.
- They are also used in communication devices.

## PREPARATION OF SEMICONDUCTORS

For the preparation of semiconductors, the basic materials like Si, Ge should be taken in the purest form.

Following are the steps involved in the preparation of semiconductors.

### 1. Preparation of Pure Si/Ge

#### a) Distillation-

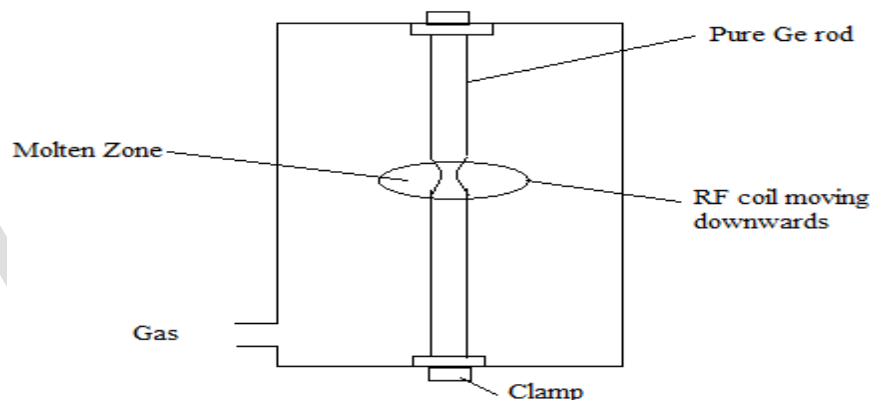
- The method is based on the separation of materials due to difference in boiling points.
- $\text{GeCl}_4$  (used to prepare pure Ge) is taken in a series of distillation stills and a layer of HCl is placed over the charge. This removes the As impurity.
- Chlorine gas is then passed through the charge, which is heated electrically. The vapours distill over in a receiver.
- Pure  $\text{GeCl}_4$  so-obtained is treated with extra pure water to get  $\text{GeO}_2$ , which is subsequently reduced to get pure Ge.

#### b) Zone-refining-

The technique is based on the method of recrystallisation.

Principle- "Impurities are more soluble in the melt than in the solid material".

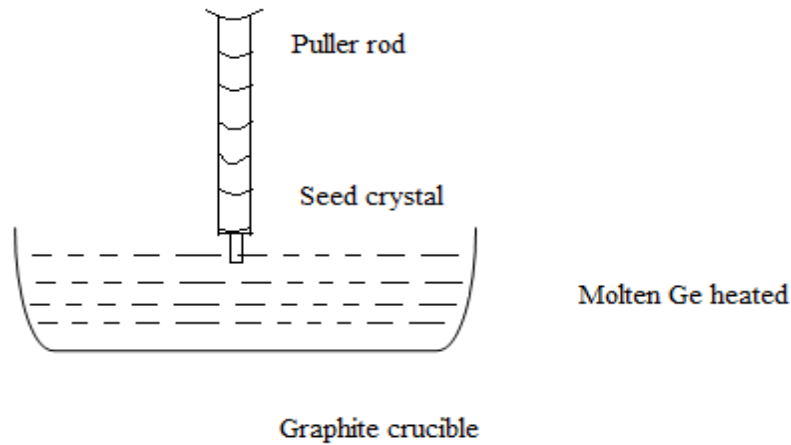
- A rod of purified Ge is clamped vertically and heated to  $1000^\circ\text{C}$  by an RF coil.
- The heating coil is very slowly moved from top towards bottom, the impurities are swept down with molten material. Pure Ge rod solidifies at the upper portion.
- When the purification of upper portion of the rod is complete, the bottom portion (impurities are concentrated) of the rod is separated.
- By repeating the process, the impurity levels can be reduced.



#### c) Czochralski method (or Single crystal growth)-

- Crystals obtained in the above two methods are polycrystalline and contains crystals of different sizes.
- This method involves growing the crystal on a single seed crystal.
- The polycrystalline semiconducting Ge material is taken in a quartz chamber and is heated using RF coil till it melts.
- The temperature is lowered to just above the melting point of Ge. At this stage, single seed crystal of Ge is lowered into the melt, till it is in contact with the molten surface.
- The crystal is rotated slowly and then pulled out.
- The melt in contact with the seed starts solidifying and produces a crystal identical of the seed crystal.





## 2. Doping techniques-

Calculated amount of dopant is added to the melt before crystal pulling stage.

### a) Epitaxial growth-

- It involves in unified crystal growth or deposition of a thin crystal layer on another substrate, often with added dopants.
- The Si or Ge wafer is placed in a long cylindrical quartz tube and is heated by RF induction coil.
- Gaseous compounds of Ge or Si containing calculated quantities of dopant are introduced into the reactor.
- The process is continued till a thin film of dopant over the wafer results.
- For n-type doping,  $\text{PH}_3$  is added as dopant and for p-type doping,  $\text{B}_2\text{H}_6$  is added as a dopant.

b) **Diffusion technique-** The technique involves conversion of a region of semiconductor by solid or gaseous diffusion of impurity atoms into the crystalline lattice of the semiconducting material without any melting.

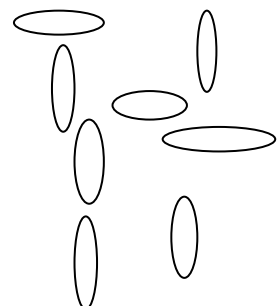
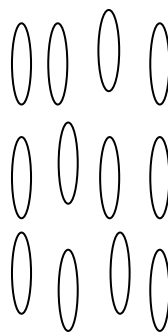
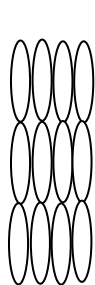
c) **Ion implantation technique-** The technique involves in bombarding the semiconductor material with an electrically controlled beam of high energy ions of Boron or Phosphorous.

3. **Cutting into chips-** The wafers obtained by above methods are then cut into 'chips' by methods like chemical etching, ultrasonic vibrations etc.

## LIQUID CRYSTALS

"Liquid crystals are highly anisotropic fluids that exists between the boundaries of the solid and conventional, isotropic liquid phase."

**SOLID STATE**  $\longleftrightarrow$  **LIQUID CRYSTAL STATE**  $\longleftrightarrow$  **LIQUID STATE**



### Characteristics of liquid crystals-

- Positional order refers to the extent to which an average molecule or group of molecules shows translational symmetry.
- Orientational order represents a measure of the tendency of the molecules to align along the director on a long-range basis.
- Bond orientational order describes a line joining the centres of nearest neighbour molecules without requiring a regular space along that line.

### Classification of Liquid crystals

Liquid crystals are broadly divided into two categories.

1. Thermotropic
2. Lyotropic

**Thermotropic liquid crystals-** They are established singly by the adjustment of temperature. These crystals are of mainly three types-

#### a) **Nematic** –

- They possess rod like molecules with a parallel arrangement to one other along the long molecular axis.
- They are mobile in three directions and possess a one-dimensional structure.
- They possess a significant degree of long-range orientational order.
- When these crystals are heated, they get transformed into isotropic liquid.
- The energy required to deform nematic liquid crystal is very small.
- Eg:- p-azoxyanisole.

#### b) **Cholesteric (or chiral nematic)** –

- These liquid crystals are derivatives of Cholesterol.
- Molecules in the liquid crystal phase contain a chiral center, which produces intermolecular forces that favour alignment between molecules at a slight angle to one another.
- Eg :- cholesteryl nonanoate

#### c) **Smectic-**

- Molecules in the liquid crystal phase show a degree of translational order.
- They possess an increased order which means that smectic state is more solid-like.
- Eg:- p-n-octyloxybenzoic acid.

### Lyotropic liquid crystals-

They occur in concentrated solutions of rodlike molecules in an isotropic solvent, usually water. They are influenced by concentration of solute with temperature.

Eg :- Sodium stearate.

### Applications of Liquid crystals-

- They are used in liquid crystal display (LCD) devices. The principle is also used in digital wrist-watches, calculators, panel meters etc.
- Liquid crystals in medicine- These substances when applied to the surface of skin, are used to locate veins, arteries, infections, tumors.
- In medicines, a lyotropic liquid crystals can coat a drug to keep it from being destroyed in the digestive tract.
- They are also used in making stable hydrocarbon foams.

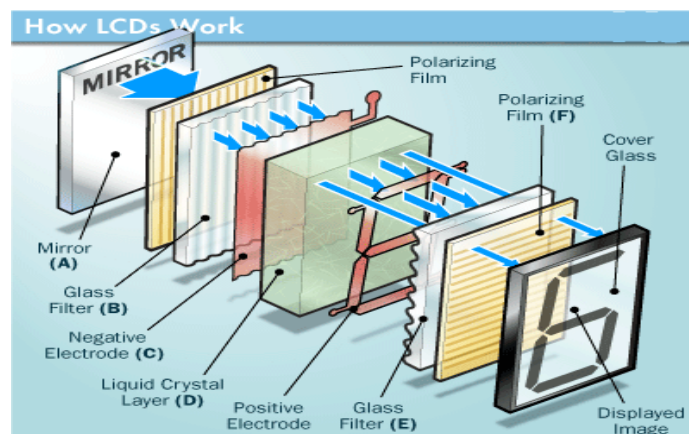
## LCD Displays

### Basic structure of an LCD

A liquid crystal cell consists of a thin layer (about 10  $\mu\text{m}$ ) of a liquid crystal sandwiched between two glass sheets with transparent electrodes deposited on their inside faces. With both glass sheets transparent, the cell is known as *transmittive type cell*. When one glass is transparent and the other has a reflective coating, the cell is called *reflective type*. The LCD does not produce any illumination of its own. It, in fact, depends entirely on illumination falling on it from an external source for its visual effect

**Two types of display available are dynamic scattering display and field effect display.**

- When *dynamic scattering display* is energized, the molecules of energized area of the display become turbulent and scatter light in all directions. Consequently, the activated areas take on a frosted glass appearance resulting in a silver display. Of course, the unenergized areas remain translucent.
- *Field effect LCD* contains front and back polarizers at right angles to each other. Without electrical excitation, the light coming through the front polarizer is rotated 90° in the fluid.
- The main principle behind liquid crystal molecules is that when an electric current is applied to them, they tend to untwist. This causes a change in the light angle passing through them. This causes a change in the angle of the top polarizing filter with respect to it. So little light is allowed to pass through that particular area of LCD. Thus that area becomes darker comparing to others.
- For making an LCD screen, a reflective mirror has to be setup in the back. An electrode plane made of indium-tin oxide is kept on top and a glass with a polarizing film is also added on the bottom side. The entire area of the LCD has to be covered by a common electrode and above it should be the liquid crystal substance. Next comes another piece of glass with an electrode in the shape of the rectangle on the bottom and, on top, another polarizing film. It must be noted that both of them are kept at right angles. When there is no current, the light passes through the front of the LCD it will be reflected by the mirror and bounced back. As the electrode is connected to a temporary battery the current from it will cause the liquid crystals between the common-plane electrode and the electrode shaped like a rectangle to untwist. Thus the light is blocked from passing through. Thus that particular rectangular area appears blank.



## Colour Liquid Crystal Display

- Colour LCDs are those that can display pictures in colours. For this to be possible there must be three sub-pixels with red, green and blue colour filters to create each colour pixel. For combining these sub-pixels these LCDs should be connected to a large number of transistors. If any problem occurs to these transistors, it will cause a bad pixel.

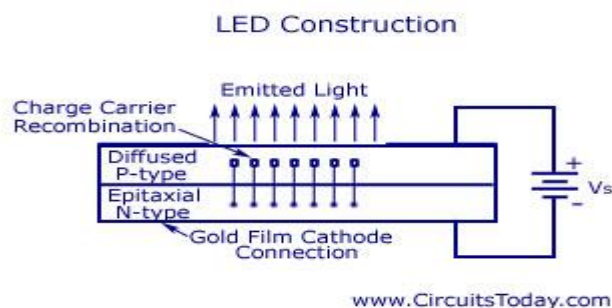
## LIGHT EMITTING DIODE (LED)

A light emitting diode (LED) is known to be one of the best optoelectronic devices out of the lot. The device is capable of emitting a fairly narrow bandwidth of visible or invisible light when its internal diode junction attains a forward electric current or voltage. The visible lights that an LED emits are usually orange, red, yellow, or green.

We know that a P-N junction can convert the absorbed light energy into its proportional electric current. The same process is reversed here. That is, the P-N junction emits light when energy is applied on it. This phenomenon is generally called electroluminescence, which can be defined as the emission of light from a semi-conductor under the influence of an electric field. The charge carriers recombine in a forward P-N junction as the electrons cross from the N-region and recombine with the holes existing in the P-region. Free electrons are in the conduction band of energy levels, while holes are in the valence energy band. Thus the energy level of the holes will be lesser than the energy levels of the electrons. Some part of the energy must be dissipated in order to recombine the electrons and the holes. This energy is emitted in the form of heat and light.

The electrons dissipate energy in the form of heat for silicon and germanium diodes. But in Gallium-Arsenide-phosphorous (GaAsP) and Gallium-phosphorous (GaP) semiconductors, the electrons dissipate energy by emitting photons. If the semiconductor is translucent, the junction becomes the source of light as it is emitted, thus becoming a light emitting diode (LED). But when the junction is reverse biased no light will be produced by the LED, and, on the contrary the device may also get damaged.

The constructional diagram of a LED is shown below.



## Advantages of LED's

- Very low voltage and current are enough to drive the LED.
- Voltage range – 1 to 2 volts.
- Current – 5 to 20 milliamperes.
- Total power output will be less than 150 milliwatts.
- The response time is very less – only about 10 nanoseconds.

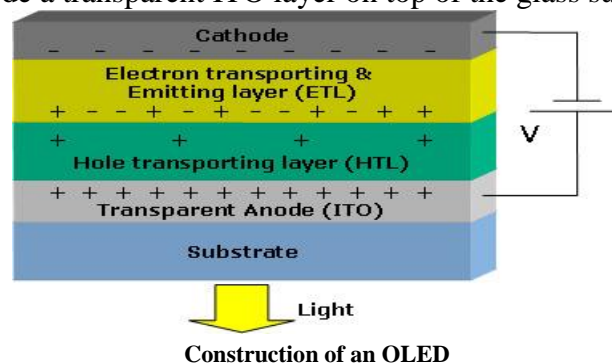
- The device does not need any heating and warm up time.
- Miniature in size and hence light weight.
- Have a rugged construction and hence can withstand shock and vibrations.
- An LED has a life span of more than 20 years.

#### Disadvantages

- A slight excess in voltage or current can damage the device.
- The device is known to have a much wider bandwidth compared to the laser.
- The temperature depends on the radiant output power and wavelength.

### ORGANIC LIGHT EMITTING DIODES

Organic light emitting diodes are a relatively new technology for solid state light sources. A typical OLED consists of two organic layers (electron and hole transport layers), embedded between two electrodes. The top electrode is usually a metallic mirror with high reflectivity and the bottom electrode a transparent ITO layer on top of the glass substrate.



#### Applications and advantages

OLED's can be used for general lighting as well as for displays, backlight sources in LCD displays, signaling (emergency lighting, traffic signals) or automotive applications (dashboard).

#### Applications using OLED's

OLED technology has some major advantages for these applications:

- High efficiency and large area sources.
- High brightness and wide viewing angle.
- Thin, flat and lightweight.
- Low voltage and fast switching technology.
- Form freedom and tunable emission.
- Flexible displays and Low cost production.

# **CEMENT**

Cement may be broadly be described as a material possessing adhesive and cohesive properties, and capable of bonding materials like stones, bricks, building, blocks etc.

The principal constituents of cement used for constructional purposes are compounds of Ca (calcareous) and Al & Si (argillaceous). The cements have property of setting and hardening under water.

## **Manufacture of Portland cement**

Raw materials required for the manufacture of the Portland cement are.

- 1) Calcareous materials, CaO (such as lime stone, chalk, marl etc)
- 2) Argillaceous materials,  $Al_2O_3$  and  $SiO_2$  (such as clay, shale, slate etc.)
- 3) Powdered coal or fuel oil
- 4) Gypsum ( $CaSO_4 \cdot 2H_2O$ )

## **Functions of ingredients of cement**

- 1) **Lime** principal constituent of cement. Its proportion must be properly regulated. However, excess of lime reduces the strength of cement, because it makes the cement to expand and disintegrate.
- 2) **Silica** imparts strength to cement
- 3) **Alumina** makes the cement quick setting. Excess of alumina however weakens the cement.
- 4) **Calcium Sulphate** (Gypsum) helps to retard the setting action of cement.
- 5) **Iron Oxide** provides: Colour, Strength, Hardness to the cement
- 6) **Sulphur trioxide**, in small proportion, is desirable. When present in small amount, it imparts soundness to cement. However, its excess reduces the soundness of cement.
- 7) **Alkalis** if present in excess, cause the cement efflorescent.

Manufacturing of Portland cement involves the following steps:

- 1) Mixing of raw materials can be done either by
  - a) Dry process
  - b) Wet process

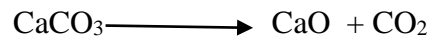
**a) Dry process** The raw materials (lime stone and clay ) are crushed in to roughly 2-5 cm size pieces and dried, ground and mixed in proper proportions. The mixture is then finally powdered and fed on to a rotary kiln of 50 to 80 m long and 3 m in diameter. The kiln kept inclined and is rotated at the rate of about one revolution per minute.

**b) Wet process** The calcareous materials are crushed, powdered and stored in big storage tanks. The argillaceous material is thoroughly mixed with water in wash mills to remove any adhering organic matter and clay is also stored in a storage tank. Powdered lime stone and washed wet clay are allowed to flow in a channel in the required proportions from the channel, the two raw materials are led to grinding mills, where they are mixed to form a paste called slurry. The slurry contains 38-40% water. The slurry is kept ready for feeding in to a rotary kiln.

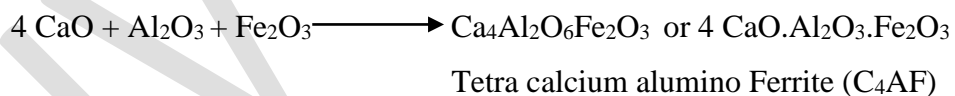
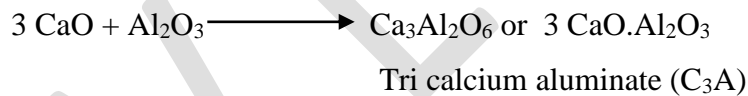
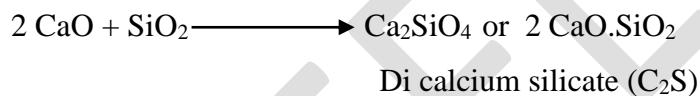
**Process:** The raw mixture or corrected slurry is injected in to the kiln at its upper end. While hot flames is forced in to the kiln from the lower end. Due to slope and slow rotation of the kiln, the materials fed in move continuously towards the hottest end at a speed of about 15m per hour. As the mixture of or slurry gradually descends, the temp. rises.

## 2. Chemistry

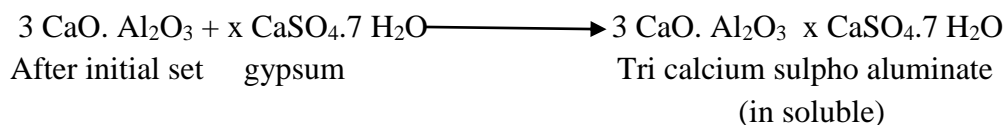
- 1) **Drying zone:** In the upper part of kiln, where the temperature is around 400<sup>0</sup>c, most of the water in the slurry gets evaporated.
- 2) **Calcination zone:** In the central part of kiln, where the temperature is around 1000<sup>0</sup>c, lime stone of dry mixture or slurry under goes decomposition to for quick lime and CO<sub>2</sub> and later escapes out. The material forms small lumps called nodules.



- 3) **Clinkering zone:** In the lower part of the kiln, the temperature is between 1,500 to 1,700<sup>0</sup> c. Here lime and clay undergo chemical interaction or fusion yielding calcium aluminates and silicates. The aluminates and silicates of calcium then fuse together to form small hard, grayish stones called clinkers.



**3) Grinding:** The cooled clinkers are ground to a fine powder in ball mills or tube mills. During final grindings, a small quantity of powdered gypsum is added, so that the resulting cement does not set very quickly, when it comes in contact with water. Gypsum thus acts as a retarding agent for early setting of cement.



**4) Packing:** The ground cement is stored in soils, from which it is fed to automatic packing machines. The cement coming out of the grinding mill is packed and marketed.

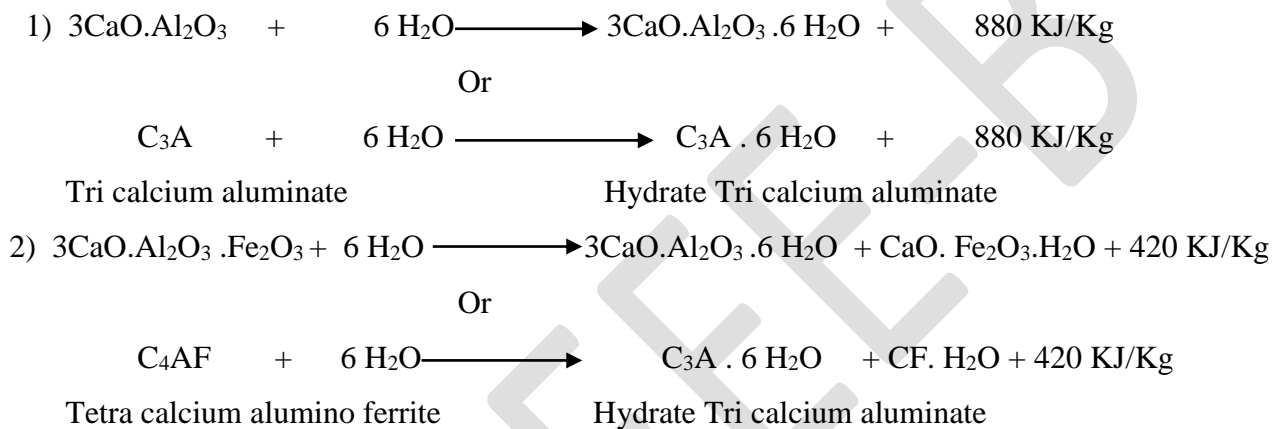
## Setting and Hardening of Port land Cement

Port land cement on mixing with water is converted into a plastic mass called cement paste. It slowly losses its plasticity and become stiff. This is called setting and it is tested with a standard needle.

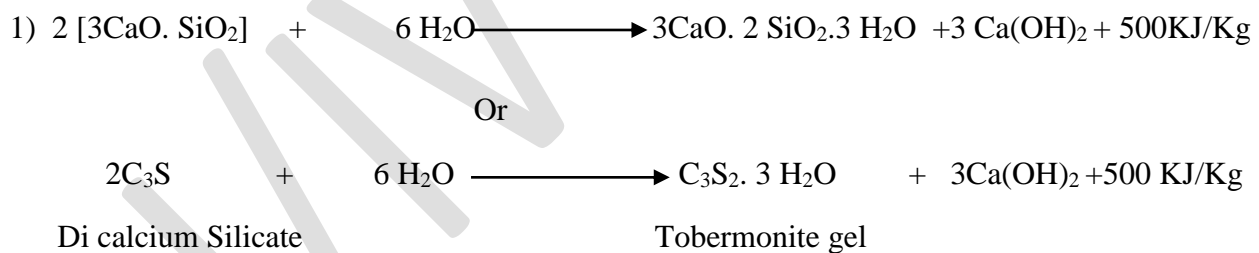
Setting is defined as stiffening of the original plastic mass due to initial gel formation.

Hardening is development of strength due to crystallization setting takes place few hours but hardening takes several years to complete.

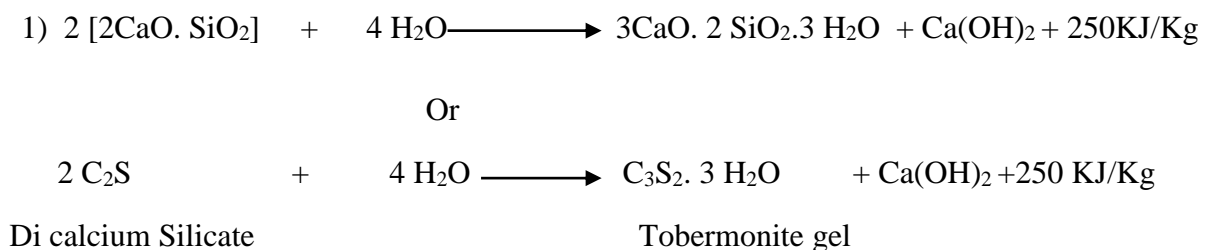
The setting and hardening are mainly due to hydration and hydrolysis reactions. When cement is mixed with water, the paste become quite rigid within short time which is known as initial set or flash set. This is due to  $C_3A$  which hydrates rapidly as follows.



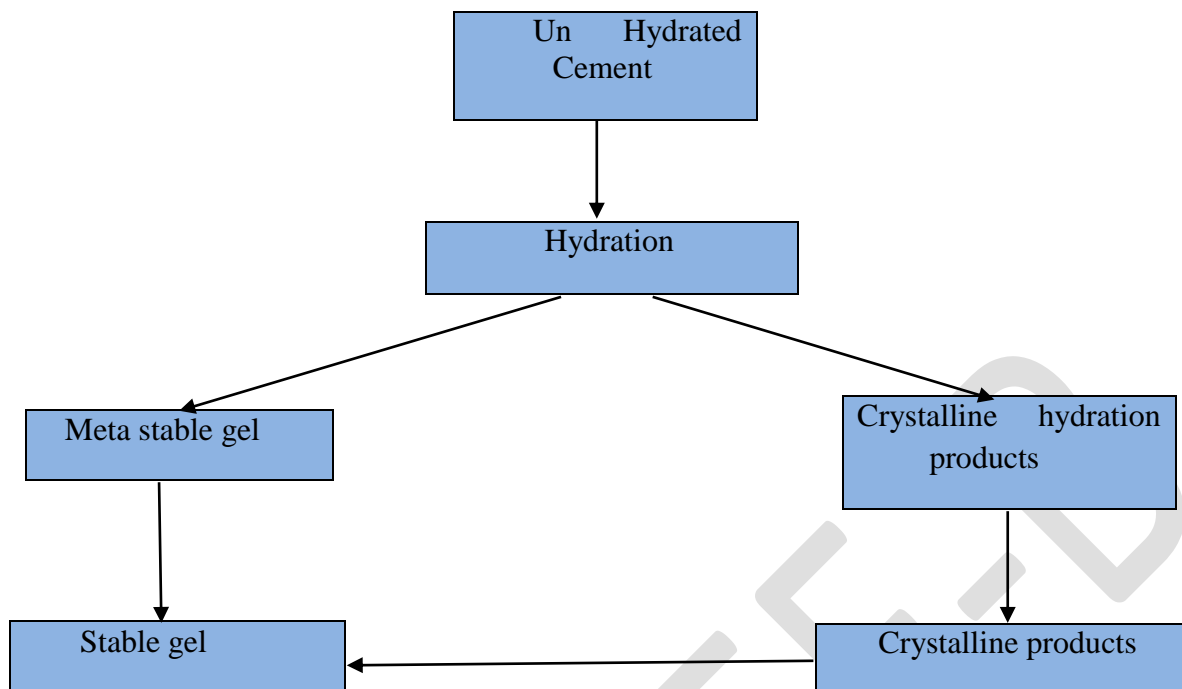
Also Di calcium silicate starts hydrolyzing **Tobermonite gel** ( which possesses a very high surface area and adhesive property ), which also contributes to initial setting.



Final setting and hardening of cement paste is due to the formation of tobermonite gel plus crystallization of  $Ca(OH)_2$  and hydrated tri calcium aluminate







Sequence of chemical reactions during setting and hardening of cement.

Cement + Water paste  $\xrightarrow{1\text{day}}$  Hydration of  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$   $\xrightarrow{7\text{day}}$  Gelation of  $\text{C}_3\text{S}$   $\xrightarrow{28\text{day}}$  gelation of  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$

## Concrete:

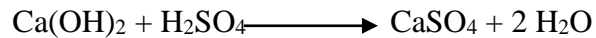
Concrete is a building and structural material, obtained by mixing a binding material (cement or lime), inert mineral aggregates (sand, crushed stone, gravel, broken bricks, slag ) and water in a suitable proportion and which can be readily worked or moulded into almost any desired shape, it is compact, rigid, strong and durable.

**Uses of Concrete:** its typical uses are in roads, buildings, floors, roofs, columns, arches, tanks, foundations, water proof structures and other purposes where compressive strength is required.

**Rein forced concrete construction:** Plain concrete has a great compressive strength, but little ability to with stand tension. Consequently structures which are required to bear tensile stress are rein forced by steel bars of rods. This combination of steel and concrete produces structure called rein forced concrete construction ( RCC)

**Decay of Concrete:** (PCC)

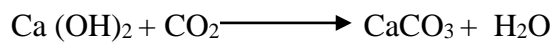
- 1) **Acid attack:** Concrete contains free  $\text{Ca(OH)}_2$ , so in acidic water lime dissolves making the concrete weak.  $\text{P}^{\text{H}}$  value decreased and deterioration of concrete increases.



- 2) **Sulphate attack:** Sulphates are present in soil, ground waters and marine water environment. Sulphates react  $\text{C}_3\text{A}$  to give bulky ettringite causing cracks due to expansion.

### Decay of Concrete: (RCC)

- 1) **Carbon dioxide:** Diffusion of  $\text{CO}_2$  into concrete and conversion of  $\text{Ca(OH)}_2$  to  $\text{CaCO}_3$  is called carbonation. Carbonation depends upon the porosity of concrete. When alkalinity due to  $\text{Ca(OH)}_2$  is lost due to carbonation then reinforcement corrosion starts.



- 2) **Chloride attack:** Chlorine enters concrete through the water used for construction. Then chlorine reaches the reinforcement. Hence less protective and porous oxide layer is formed around iron thereby electrochemical corrosion.

## Refractories

The word refractory implies resistant to melting or fusion. In technology refractory is inorganic material that can withstand high temperature without softening or suffering any deformation in shape. Thus, refractories are used for the construction of furnaces, kilns, ovens, converters, crucibles and retorts.

### Classification of Refractories

#### Acidic refractories :-

These are the refractories, which consist of acidic materials like alumina, silica. They are not attacked by basic materials.

Examples- Alumina (50%  $\text{Al}_2\text{O}_3$ ), Silica and fire clay refractories.

#### Silica Refractories:

Silica refractories contain more than 90% silica. Fine grained quartzite is the principal raw material for this brick.

**Manufacture:** In this silica rock is crushed and ground with lime and water. This mixture is made into bricks by hand moulding or machine pressing. The bricks are dried and fired in kiln. Now quartz converts into cristobalite and tridymite. Which are the more stable allotropes of silica. If this change does not take place then temp. is slowly raised to  $1500^\circ\text{C}$  for longer period.

**Properties:** silica bricks are slightly yellowish in colour with brown specks distributed throughout the mass.

**Uses:** They are used in steel making furnaces and coke ovens. They are also used in glass furnaces.

### **Basic refractories:-**

These are the refractories which consist of basic materials like CaO, MgO etc. These are not attacked by basic materials, but easily attacked by acidic materials.

Examples: magnesite and dolomite refractories.

**Magnesite bricks:-** These are the basic refractories composed of MgO, which is one of the most basic refractory oxides.

The dead burnt magnesite is ground, mixed with water, moulded under pressure, dried and fired to give fire bonded bricks. To obtain the chemically bonded ones, the dead burnt magnesite is mixed with small amount of chromite ore. The mixture is then ground with water and moulded under pressure.

**Uses:** Pea magnesite (about 1cm diameter) is used to make bottoms of the basic furnaces.

### **Neutral refractories:-**

These are made from weakly acidic or weakly basic materials like carbon, chromites and zirconia etc. these are not attacked by either acids or bases.

Examples: graphite, zirconia, carborundum and chromites

**Carborundum :** silicon carbide brick is known as carborundum refractory. It is prepared by fusing together silica (60%) and coke (40%) with small amount of sawdust and salt in an electric furnace. Saw dust burns off and leaves pores in the brick. To obtain bonded refractory is mixed with clay dried and fired and then mixed with bonding agent glue. So self bonded bricks are obtained.

**Properties :** these are having high conductivity and mechanical strength.

**Uses :** they are used in ceramic industries, coke ovens, muffle furnaces.

## **Properties**

**Refractoriness:** It is ability of the refractory material to withstand the heat without any deformation or softening under service conditions. It is indicated by pyrometric cone equivalents. It is generally measured as the softening temp. of the metal.

**Refractoriness under load:** Refractories in use, in industrial furnaces, have invariably to withstand varying loads of the products, being manufactured at higher temps. It is, therefore, essential that refractory materials must also possess high mechanical strengths, even at operating temps, to bear the maximum possible load, without breaking. Some refractories,

like fire clay and high alumina bricks. Soften gradually over a range of temp. but under appreciable load they collapse, far below their true fusion point.

**Dimensional stability:** It can be defined as the resistance of the material to any volume change, which may occur on its exposure to high temp. over a prolonged time. The dimensional change may be reversible or irreversible.

**Thermal expansion:** It affects all dimensions of a body. So, it is necessary that a refractory should have least possible thermal expansion because expansion of refractory decreases the capacity of furnace.

**Thermal Spalling:** It is a breaking, cracking, peeling off or fracturing of a refractory under high temp. so a good refractory show a high resistance to thermal spalling. Spalling is generally due to rapid changes in temp which cause uneven expansion and contraction within the mass of a refractory, there by leading to the development of internal stress and strains.

1. It can be reduce by avoiding sudden temperature changes
2. Using high porosity, low thermal expansion, good thermal conductivity.

**Thermal conductivity:** Thermal conductivity of refractory material depends upon the chemical composition and degree of porosity. Higher porosity leads to a decrease in thermal conductivity because the air entrapped material acts as a bad conductor.

**Chemical Inertness:** A refractory should be chemically inert and does not easily form fusible products with slag's, fuel ashes, furnace gases etc.

### **Failure of Refractories :-**

1. The most common cause for failure of refractory is chemical reaction with the environment in which it is worked. Ex. An acid refractory should not be used in furnaces using basic flues and slag's and vice versa.
2. In the chemical reaction the porosity of the refractory plays an important role. The more porous it is the greater will be the depth to which the slag will penetrate and destroy the refractory porosity also effects the reaction with gases.
3. The deposition of carbon from CO in fire clay refractory's in a blast furnace is an important cause for the failure of a refractory.
4. The higher temp. the faster does the chemical reaction takes place. Sometimes raise in temp. beyond the safe limit quickly brings about the destruction of refractory.

# Ceramics

The word ceramic is derived from the Greek Keramos means burnt stuff. In modern usage ceramics are polycrystalline inorganic metallic or non metallic materials that are processed and used at high temp. Ceramic materials include a wide range of silicates, metallic oxides and combination of silicates and metal oxides.

## Characteristics of Ceramics :

1. They are usually hard and brittle in nature and generally being in the form of amorphous or solids.
2. The atomic bonding in these materials is of mixed ionic or covalent character.
3. They have high temp. resistance
4. They have good electrical resistance and act as insulators
5. They have good resistance to chemical attack and weathering
6. They have compressive strength and tensile strength

## Ceramics generally consists of the following major components

1. **Plastic portion:** This is usually provided by clay, which imparts the necessary plasticity and workability.
2. **A non plastic refractory crystalline portion :** This is generally provided by feldspar ( $K_2O \cdot Al_2O_3 \cdot 6H_2O$ ) which helps in bonding & cementing

## Classification of Ceramic materials

Generally ceramic materials are three types based on the characteristic properties. They are

- i. Clay products
- ii. Refractories
- iii. Glasses

## Functional classification of Ceramics

<u>Group</u>	<u>Example</u>
1. Abrasives	Alumina, carborundum
2. Pure oxide ceramics	MgO, $Al_2O_3$ , $SiO_2$
3. Fire clay products	Porcelain, bricks, tiles etc.
4. Inorganic glasses	Hard glass, window glass.
5. Cementing materials	Lime, Portland cement etc.

- |                 |                                 |
|-----------------|---------------------------------|
| 6. Rocks        | Granite, sand stone etc.        |
| 7. Refractories | Silica bricks, magnesite bricks |

### Structural classification of Ceramics

<u>Group</u>	<u>Example</u>
1. Crystalline ceramics	Single phase like MgO or multiphase from MgO to Al <sub>2</sub> O <sub>3</sub>
2. Non crystalline ceramics	Natural and synthetic inorganic glasses
3. Glass bonded ceramics	Fire clay products, crystalline phases are held in glassy matrix.
4. Non crystalline phases	Cement

### Engineering Applications

1. The older ceramics refer to white wares and are widely used in tiles, sanitary ware, insulators and high frequency applications.
2. White wares also used in chemical industries as crucibles, jars and compounds of chemical reactors.
3. Pyrometer tube, burner, burner tips and radiant heater supports are somewhat heat resistant items, which are also used as white wares.
4. The newer ceramics have high hardness and high resistant to heat and oxidation. Therefore they are used in applications such as refractories for industrial furnaces
5. Ceramics are now being used in electrical and electronic industries for insulators, semi conductors, super conductors, glass, porcelain, alumina, quartz, mica etc.,
6. Yattrlox is a type of ceramic. It is useful in optical applications, because it is transparent as window glass and can resist very high temp.
7. Ceramic materials are also used as cutting tools.