

## 4.4 CERAMICS

"Ceramic materials" are defined as those containing phases that are compounds of metallic and nonmetallic elements.

### 1. Functional Classification

- (i) Abrasives : Alumina, carborundum
- (ii) Pure oxide ceramics : MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>
- (iii) Fire-clay products : Bricks, tiles, porcelain etc.
- (iv) Inorganic glasses : Window glass, lead glass etc.
- (v) Cementing materials : Portland cement, lime etc.
- (vi) Rocks : Granites, sandstone etc
- (vii) Minerals : Quartz, calcite, etc.
- (viii) Refractories : Silica bricks, magnesite, etc.

### 2. Structural Classification

- (i) Crystalline ceramics: Single-phase like MgO or multi-phase form the MgO and Al<sub>2</sub>O<sub>3</sub> binary system.
- (ii) Non-crystalline ceramics: Natural and synthetic inorganic glasses.
- (iii) "Glass-bonded" ceramics: Fire clay products-crystalline phases are held in glassy matrix.
- (iv) Cements: Crystalline and non-Crystalline moderators, and controls and shielding.

- Internal combustion engines and turbines, as armor plate
- Electronic packaging
- Cutting tools
- Energy conversion, storage and generation

Ceramics can also be classified into three categories as

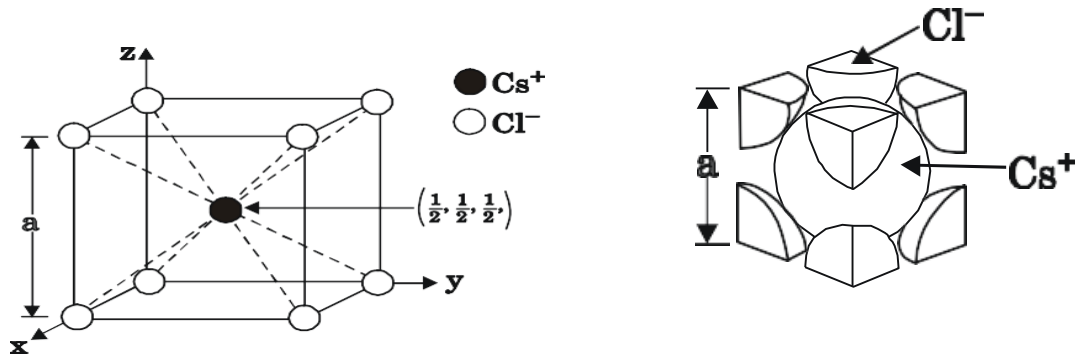
- (i) **Crystalline ceramics**
- (ii) **Non-crystalline (Amorphous) ceramics**
- (iii) **Bonded ceramic**

## **CRYSTALLINE CERAMICS**

These have simple crystal structure, such as aluminium oxide (corundum), magnesium oxide, silicon carbide. Most of the oxides can be considered packing of oxygen ions with the cations occupying the tetrahedral and / or octahedral sites in the structure. Magnesium oxide is used in refractory furnace lining for steel making. Silicon carbide is used for cutting tools. The crystal structure of ceramic is, more complex, since atom of different size and electronic configuration are assembled together. Common crystal structures found in crystalline ceramics particularly those of the oxide type are briefly described below:

### **Cesium Chloride Structure**

It is possible for ceramic compounds to have simple cubic structure that are not found among metals. Cesium chloride is a prototype for this case.

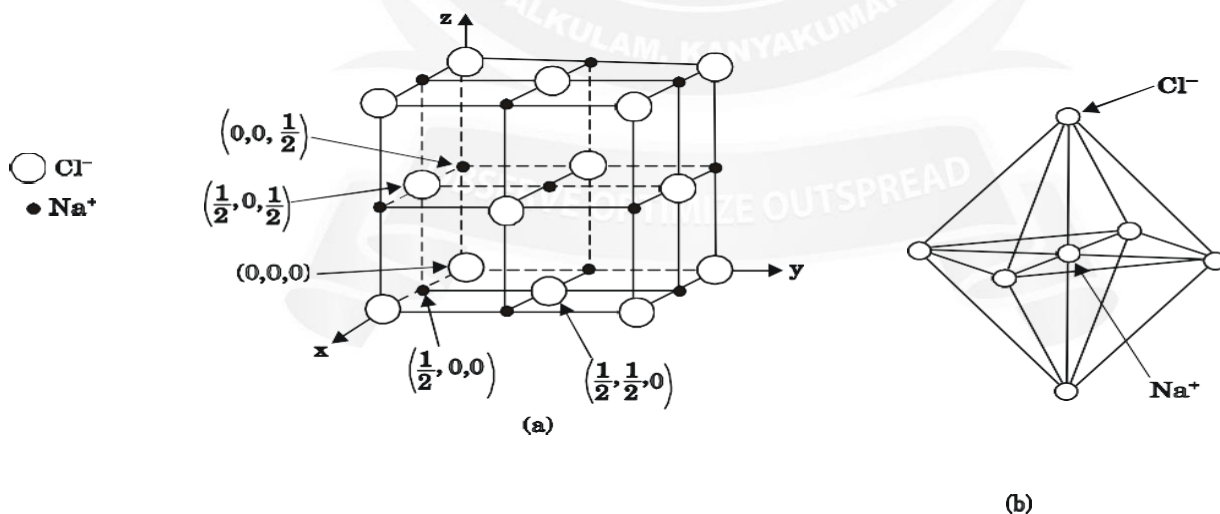


**Fig. 4.4.1 A unit cell for the cesium chloride (CsCl) crystal structure**

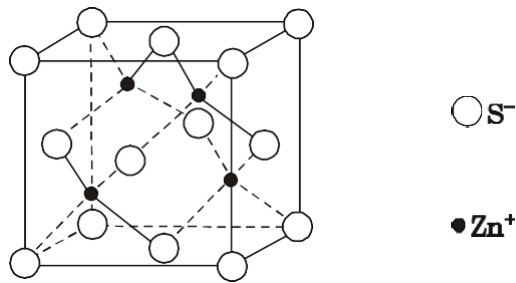
### Rock Salt Structure

Most of the oxides and halides crystallize in the closed packed cubic structure similar to that of a rock salt (sodium chloride). The structure can be considered as consisting of the fcc anions with smaller cations filling all available interstitial positions.

Here, each metal atoms is surrounded by six non-metallic atoms and vice versa (Fig. 4.15). Thus, atomic coordination (CN) is the 6. Other examples include this are MgO, CaO, BaO, CdO, MnO, FeO, CeO and NiO.



**Fig. 4.4.2- A unit cell for the rock soil, or sodium chloride (NaCl), crystal structure**



*Fig. 4.4.3- A unit cell for the zinc blende (ZnS) crystal structure.*

## NON - CRYSTALLINE CERAMICS

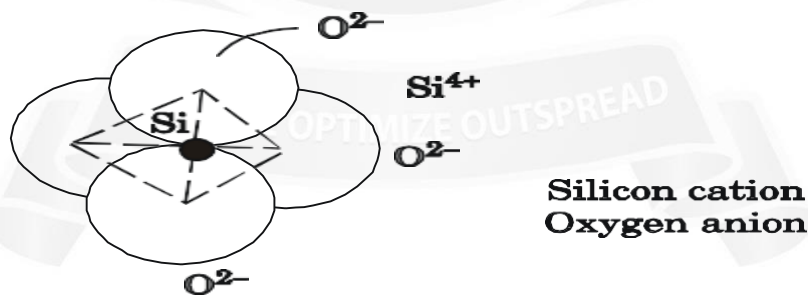
These are usually regarded super, cooled liquids. Their molecules are not arranged in regular geometric shapes. *e.g.* amorphous or fused  $\text{SiO}_2$  has each Si bonded to four O and each O is bonded to two Si.

This type of ceramics is used for mirrors, optical lenses, reinforcement fibres for GRP and optical fibres for data transmission.

### Silicates and Silica

Silicates are composed of silicon and oxygen, which are abundantly available in the Earth's crust. For example, rocks, soils and clay come under the classification of silicates.

A unit cell of silicate is a tetrahedron on which each atom of silicon is bounded to four atoms of oxygen as shown in figure 4.4.5.



*Fig. 4.4.4- Silicate Structure*

## BONDED CERAMICS

These ceramics contain both crystalline and non-crystalline materials which are bound together by a glassy matrix after firing. This group includes the lining and

clay products.

Bonded ceramics are used as electrical insulators, refractory for furnace, spark plugs etc.

## CERAMIC MANUFACTURING METHODS

The various steps to be considered for the processing are

- (i) **raw material processing,**
- (ii) **fabrication**
- (iii) **densification.**

The raw material powder is thoroughly mixed with water and other ingredients to obtain flow characteristic depending on particular processing technique. The different fabrication processes that are used for many years are

- (a) **casting,**
- (b) **extrusion**
- (c) **dry processing.**

## SLIP CASTING

*Casting* is a familiar process used for ceramic forming. In this process, the raw materials are mixed with a stable suspension of fluid like water in the range of

25 - 30 vol.%. **This suspension is known as slip.**

The slip is poured into a porous mold which is made of plaster of paris. The slip is absorbed into the mold wall leaving behind a solid layer on the mold.

The thickness of solid layer depends on the length of time in mold. This process is continued until the entire mold cavity becomes solid. **This process is known as slip casting** and the various stages are shown in Fig. 4.21.



*Fig. 4.4.5- Solid slip casting*

### **Advantages:**

The main advantage of slip casting is the ability to form intricate shapes at relatively low cost.

The complex ceramics shapes which are produced using slip casting include turbine engine rotors, automobile wings, etc.

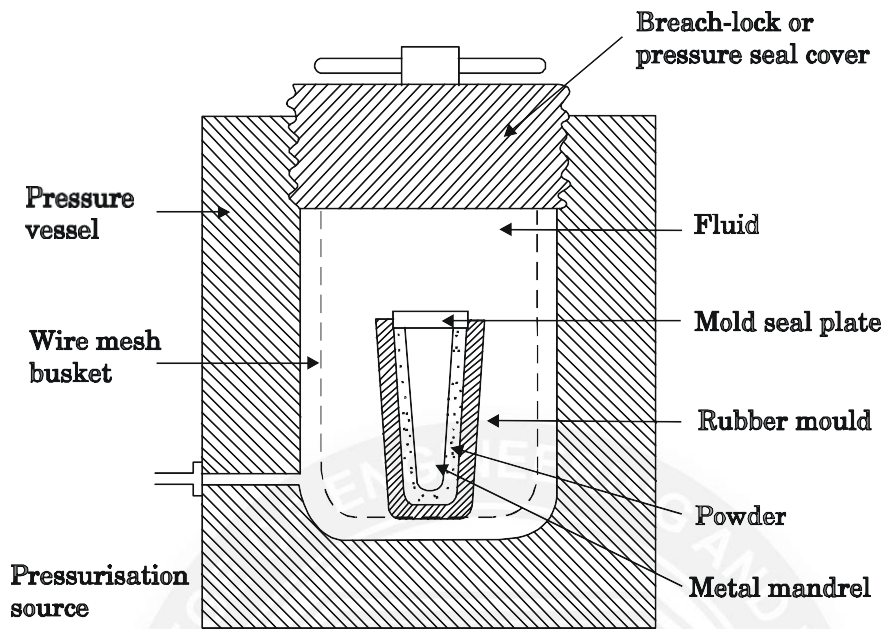
### **ISOSTATIC PRESSING**

In *isostatic pressing method*, a uniform pressure is applied on all sides.

The raw material is filled in rubber mold and it is sealed with plate and metal mandrel. The sealed rubber mold is inserted into liquid. The liquid is kept inside the pressure vessel and preferably non compressible.

The top of the pressure vessel is closed after inserting the rubber mold.

A hydraulic pressure is applied to the liquid and hence, the uniform pressure is experienced by the rubber mould in all directions. The friction of rubber mould with the walls is eliminated, which results in a uniform density of compacted material.



*Fig.4.4.6 Wet-bag isostatic pressing system*

By removing the pressure, the rubber mould is taken out. The compacted material is removed by removing the mould sealed plate and metal mandrel.

The compacted materials are then subjected to densification resulting in more uniform shrinkage with less warping and cracking.

There are two different methods of isostatic pressing process

- (i) **wet-bag and**
- (ii) **dry-bag processing.**

In wet-bag processing method, raw material is filled in flexible rubber mold, sealed and then poured isostatically. The experimental set-up is shown in Fig. 4.22. The pressure applied in laboratory experiment process ranges from 35 to 1380 MPa.

However, in industry, the production units normally operate at a pressure of 400 MPa or even less.

This method is widely used for production of variety of products and sizes. The main disadvantages of this method are long cycle time, high labour

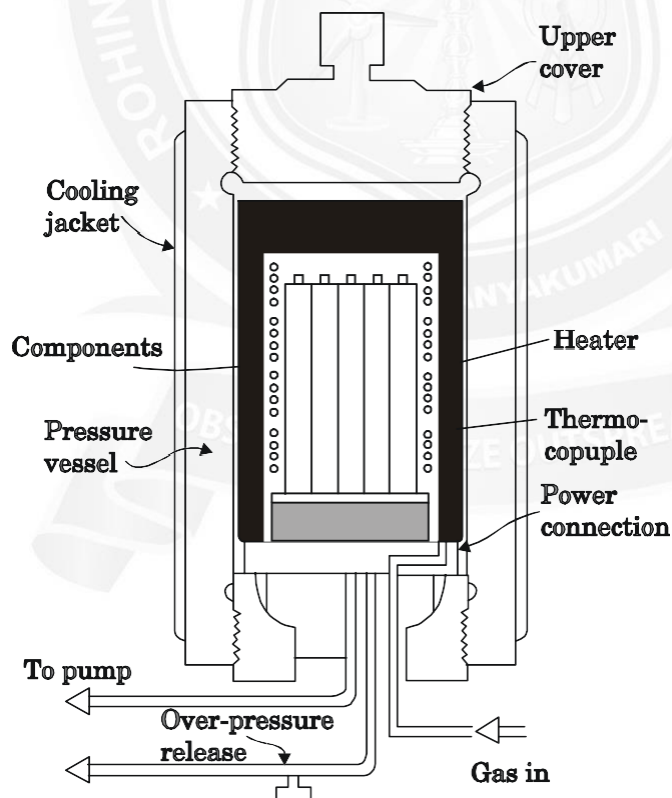
requirements and low production rates.

## **GAS PRESSURE BONDING:**

### **Hot isostatic pressure :**

The hot isostatic press (HIP) uses the simultaneous application of heat and pressure. We refer to this process as HIPing and the product as being HIPed. A furnace is constructed within a high-pressure vessel and the objects to be pressed are placed inside. Figure

Temperatures can be up to  $2000^{\circ}\text{C}$ , and pressures are typically in the range 30-100 MPa. A gas is used as the pressure medium — unlike in the CIP where a liquid is often used. Argon is the most common gas used for HIPing, but oxidizing and reactive gases can be used. Note that the high-pressure vessel is not inside the furnace



*Fig. 4.4.7- Hot isostatic pressing apparatus*

There are two variants of HIPing.



- Encapsulated: using a deformable container
- Not encapsulated: shape and sinter first, then HIPed
- Now HIPing is used for a wide variety of ceramic (and metallic) components, such as alumina-based tool bits and the silicon nitride nozzles used in flue-gas desulfurization plants by the utility industry.

The advantages of the HIPing process are becoming more important as interest in structural ceramics (e.g.,  $\text{Si}_3\text{N}_4$ ) grows.

- Nonoxide ceramics can be HIPed to full density while keeping the grain size small and not using additives. Very high densities combined with grain sizes (because of the relatively low temperatures) leads to products with special mechanical properties.

HIPing has also been applied to the formation of piezoelectric ceramics.

### **Properties of ceramics**

#### **• Thermal Properties**

Since the ceramic materials contain relatively few electrons, their thermal properties differ from that of metals. The most important thermal properties of ceramic materials are.

- (i) **Thermal capacity**
- (ii) **Thermal conductivity**
- (iii) **Thermal shock resistance**

#### **(i) Thermal capacity**

- The specific heats of fine clay bricks are 0.25 at  $1000^\circ\text{C}$  and 0.297 at  $1400^\circ\text{C}$
- Carbon bricks possess specific heats of about 0.812 at  $200^\circ\text{C}$  and 0.412 at  $1000^\circ\text{C}$ .

#### **(ii) Thermal conductivity**

- The ceramic materials possess a very low thermal conductivity since they do not have enough free electrons.
- The impurity content, porosity and temperature decrease the thermal conductivity.
- The ceramic materials possess low thermal conductivity due to its low density.

### (iii) **Thermal Shock**

“*Thermal shock resistance*” is the ability of a material to resist cracking or disintegration of the material under sudden changes in temperature.

- *Lithium compounds* are in many ceramic compounds to *reduce thermal expansion* and *provide excellent thermal shock resistance*.

### • **MECHANICAL PROPERTIES OF CERAMICS**

The mechanical behaviour of ceramic phases is determined in a number of ways depending upon how the force is applied: compressive, tensile, transverse, torsional shear or impact.

- **Compressive strength.** Compressive strength in ceramics in general is many times greater than tensile strength. Therefore, ceramics like brick, cement, and glass are always used in the compression and not in tension.
- **Shear strength.** High shear strengths and low fracture strengths are generally characteristics of ceramics. Therefore, they commonly fail nonductilely, *i.e.* in a brittle manner by fracture.
- **Tensile strength.** Tensile strength in ceramics are theoretically high, but in practice are usually quite low. Failures are often due to stress concentrations at the pores, grain corner or microcrack.
- **Transverse strength or modulus of rupture.** Transverse strength is difficult to ascertain in ceramic materials. Ceramics are, therefore not used in places where transverse strength of materials is an important criterion.

- **Torsional strength.** Torsional strength is seldom considered as a critical property of ceramics since tensile and cantilever requirements will show the torsional strength of material.
- **Modulus of elasticity.** Ceramic materials have high modulus of elasticity ranging from  $7 \times 10^{10}$  to  $42 \times 10^{10}$  N/m<sup>2</sup> which indicates the strength of the bond.
- **Plastic deformation.** Due to the restricted slip, most of materials does not permit plastic deformation. The ceramic materials have greater resistance to slip than do meta
- Toughness of Ceramic Materials

Due to presence of covalent-ionic bonding, ceramics have low toughness.

## • ELECTRICAL PROPERTIES

Electrical properties depends upon composition, texture, size and density of material and also on temperature and time. These factors greatly influence the electrical behavior of a ceramic material.

Ceramic materials are used as insulators, conductors, semiconductor and dielectrics. Ceramics are also used as ferroelectric and piezoelectric materials.

- Ceramics are generally poor conductors of electricity because the electrons associated with the atoms ceramics are shared covalent or ionic bonds. The electrical properties of ceramics mainly depend on the following factors.

- (i) volume resistivity,      (ii) dielectric strength,
- (iii) dielectric constant, and (iv) dissipation factor (or lossfactor).

## Ceramic insulator

Ceramic materials are used in an electrical circuit both as the electrical insulators

and as its functional parts.

Porcelains are very commonly used as electrical insulators and resistors.

### **Dielectric ceramics**

Ceramic materials have good dielectric capacity.

Porcelain and high grade fire clays have high dielectric strength. The dielectric varies with temperature.

### **Ceramic semiconductor**

Although ceramic compounds are normally insulators, they become semiconductors if they contain multivalent transition elements.

## **• CHEMICAL PROPERTIES**

### ***Chemical resistance***

- The great majority of ceramic products, are highly resistant to all chemicals except hydrofluoric acid and to some extent, hot caustic solutions.
- Organic solvents do not affect the ceramics.
- Oxidic ceramics are completely resistant to oxidation, even at very high temperatures.
- Magnesia, zirconia, porcelain, graphite, alumina, etc., are resistant to certain molten metals. They are used for making crucibles and furnace linings.
- Ceramics like glass are employed where resistance to attack from acids, bases and salt solutions is required.

### **Applications of Ceramics**

The applications of ceramics are listed below

1. **Whitewares (older ceramics):** are largely used as:

- Tiles
  - Sanitary wares
  - Low and high voltage insulators
  - High frequency applications
  - Chemical industry - as crucibles, jars and components of chemical reactors;
  - Heat resistant applications as pyrometers, burners, burner tips, and radiant heater supports.
2. **Newer ceramics:** (e.g., borides, carbides, nitrides, single oxides, mixed oxides, silicates, metalloid and intermetallic compounds) which have the high hardness values and heat and oxidation values are largely used in the following applications.
- Refractories for industrial furnaces
  - Electrical and electronic industries as inductors, semiconductors, dielectrics, ferro-electric crystals, piezo-electric crystals, glass, porcelain alumina, quartz and mica etc.