4.4 Ceramic materials

"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, Al2O3, SiO2

(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) Crstalline ceramics: Single-phase like MgO or multi-phase form the MgO and Al2O3binary 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

Properties of ceramic materials

Mechanical properties

(i)The compressive strength is several items more than the tensile strength.

(ii)Non-ductile/brittle. Stress concentration has little or no effect on compressive strength

(iii) The ceramic materials possess high modulus of elasticity due to ionic and covalent bonds.

(iv) At high temperature, rigidity is high.

Electrical properties

(i)Ceramic exhibits low dielectric constant contributes to low power loss and low loss factor.

(ii)Porcelain has large positive temperature coefficient.

(iii)Rutile bodies have large negative coefficients,

(iv)The specific values of dielectric strength vary from 100 V per mil for low -tension electrical porcelain to 500 V per mil for some special ceramics.

(v)Rutile bodies show higher breakdown strength at higher frequencies.

Thermal properties

Since the ceramic materials contain relatively few electrons, and ceramic phases are transparent to radiant type energy, their thermal properties differ from that of metals. The following are the most important thermal properties of ceramic materials.

1. Thermal capacity

- The specific heats of fine clay bricks are 0.25 and 0.297 at 1000˚C and 1400˚C respectively.
- Carbon bricks possess specific heats of about 0.812 at 200˚C and 0.412 at 1000˚C

2. Thermal conductivity

- The ceramic material possesses a very low thermal conductivity since they do not have enough free electrons.
- The impurity content, porosity and temperature decrease the thermal conductivity.
- In order to have maximum thermal conductivity, it is imperative to have maximum density which most of the ceramic materials do not possess.

3. Thermal shock

- "Thermal shock resistance" is the ability of a material to resist cracking or disintegration of the material under abrupt or sudden changes in temperature.
- Lithium compounds are used in many ceramic compounds to reduce thermal expansion and to provide excellent thermal shock resistance.
- Common ceramic materials graded in order of deceasing thermal shock resistance are given below:

1. Silicon nitrite
2. Fused silica
3. Cordierite
4. Zircon
5. Silicon carbide
6. Beryllia
7. Alumina
8. Porcelain

9. Steatite

Chemical properties

1.Several ceramic products are highly resistant to all chemicals except hydrofluoric acid and to some extent, hot caustic solutions. They are not affected by the organic solvents.

2.Oxidic ceramics are completely resistant to oxidation, even at very high temperatures.

3.Zirconia, magnesia, alumina, graphite etc., are resistant to certain molten metal and are thus employed for making crucibles and furnace linings.

4.Where resistant to attack from acids, bases and salt solutions is required, ceramics like glass are employed.

Optical properties

1.Several types of glasses have been employed for the production of windows, subjected to high temperatures and optical lenses.

2.Special glasses used for selective transmission or absorption of particular wavelength such as infrared and ultra violet.

Nuclear properties

As ceramics are refractory, chemically resistant and its different compositions offer a wide range of neutron capture and scattering characteristics. They are finding nuclear applications such as fuel elements, moderators, and controls and shielding.

Classification of Ceramic Products

A general classification of 'ceramic products' is difficult to make because of the great versatility of these materials, but the follwing list includes the major groups.

1. Whitewares
2. Bricks and tiles
3. Chemical stoneswares
4. Cements and concretes
5. Abrasives
6. Glass
7. Insulators
8. Porcelain enamel
9. Refractories

10. Electrical porcelain
11. Mineral ores
12. Slags and fluxes

Advantages of Ceramic Materials

The ceramic materials have the following advantages

1. The ceramic are hard, strong and dense.
2. They have high resistance to the reaction of chemicals and to the weathering.
3. Possess a high compression strength compared with tension.
4. They have high fusion points.
5. They offer excellent dielectric properties.
6. They are good thermal insulators.
7. They are resistant to high temperature creep.
8. Cheaply available.

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.

- Nuclear applications - as fuel elements, fuel containers, moderators, control rods and structural parts. Ceramics such as UO_2, UC, UC_2 are employed for all these purposes.
- Ceramic metal cutting tools-made from glass free Al_2O_3
- Optical applications- ceramic material are useful as window glass and can resists very high temperature

3. **Advanced ceramics**: (e.g., ZrO_2, B_4C, SiC, TiB_2etc)

The advanced ceramics are used in the following areas.

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

Structure of crystalline ceramics

Most ceramic phases, like metals, have crystalline structure. Ceramic crystals are formed by the pure ionic bond, a pure covalent bond or both the ionic and covalent bonds.

- Ionic bonds give ceramic materials of relatively high stability. They are also harder and more resistant to chemical reactions.
- Covalent bond usually gives high hardness, high melting point and low electrical conductivity at room temperature.
- The ceramic crystals structures are, however, invariably more complex as compared to those of metals, since atoms of different sizes and electronic configurations are assembled together

Common crystal structure found in crystalline ceramics particularly those of oxide type are:

1.Rock salt structure

2. Cerium chloride structure

3.Zinc blend structure

4.Wurzite structure

5. Spinal structure

6. Fluorite structure

7. Ilmenite structure

Classification of ceramics

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.

In this structure, chlorine ions are arranged in a simple cubic structure and all intertices are occupied by cesium ions. The co-ordination number is eight ig.4.4.1).

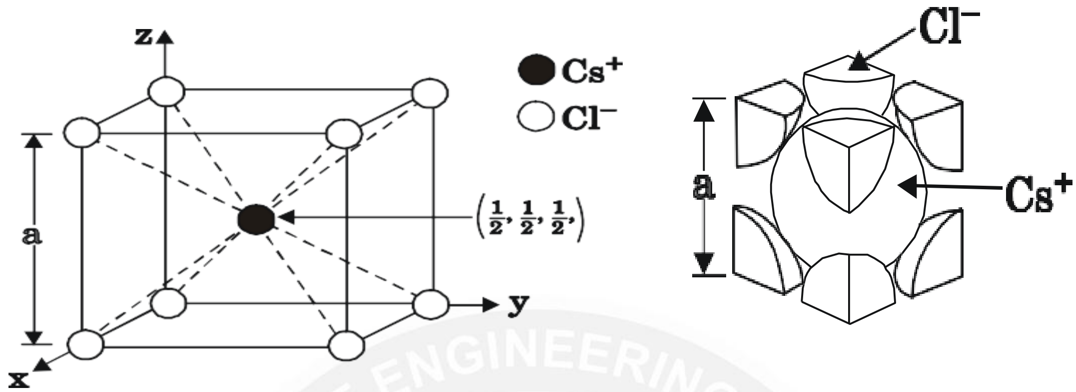

Fig. 4.4.1 A unit cell for the cesium chloride (CsCl) crystal structure

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.

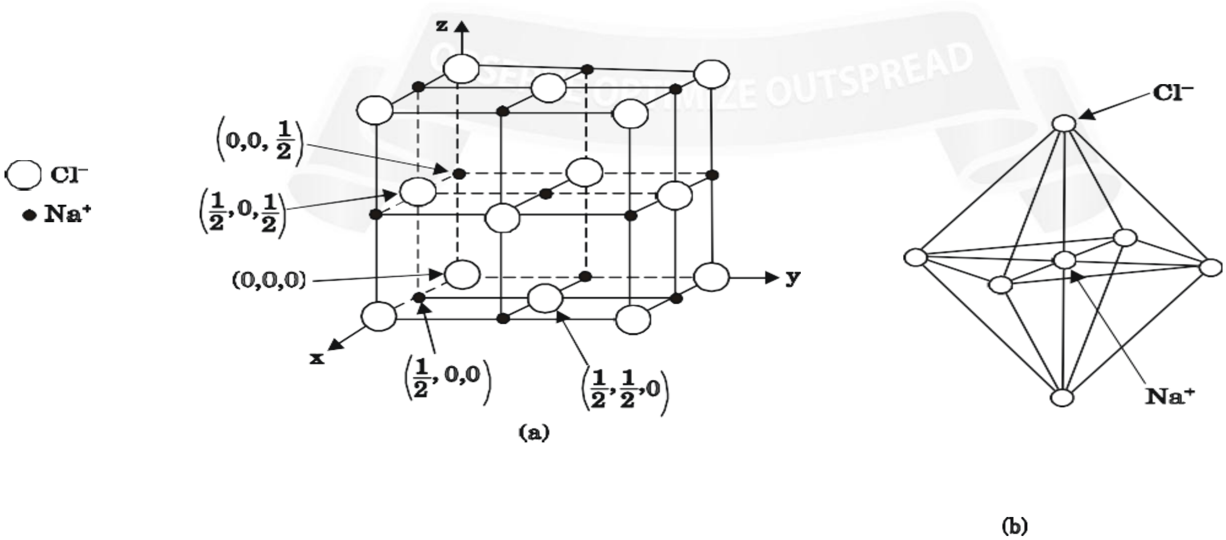

Fig. 4.4.2- A unit cell for the rock soil, or sodium chloride (NaCl), crystal structure

Zinc Blende Structure

Two of the more cubic ceramic compounds which have atoms in the 4-fold sites, are zinc blende (ZnS), silicon carbide (β-SiC). The atomic coordination is 4. (Fig. 4.4.3)

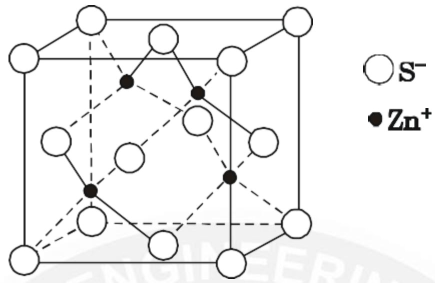

Fig. 4.4.3- A unit cell for the zinc blede (ZnS) crystal structure.

- Each type of atom form an fcc structure of its own.
- Only half of the available tetrahedral interstices are filled with the small cations.
- The structure is the same as the diamond cubic except that alternate atoms are of different elements.

This structure also includes cadmium sulphide (CdS) and aluminium phosphide (AlP).

Perovskite Crystal Structure

It is also possible for ceramic compounds to have more than one type of cation. For example Barium titanate ($BaTiO_3$),

having both Ba^{2+} and Ti^{4+} cations, falls into this classification.

This material has a ***perovskite crystal structure***. A unit cell of this structure is shown in fig. 4.17. Ba^{2+} ions are situated at all eight corners of the cube and a single Ti^{4+} is at the cube center. The O^{2-} ions located at the center of each of the six faces of the unit cell.

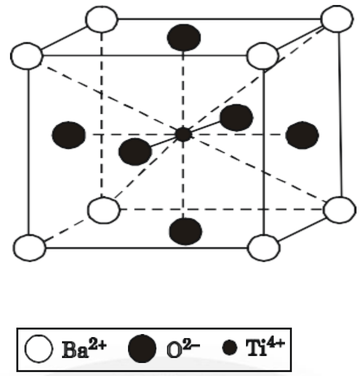

Fig. 4.4.4- A unit cell for the perovskite crystal structure

NON - CRYSTALLINE CERAMICS

These are usually regarded super, cooled liquids. Their molecules are not arranged in regular geometric shapes. *e.g.* amorphous or fused 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 crest. 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.

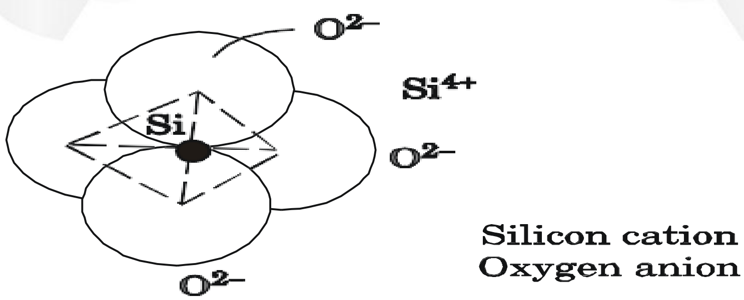

Fig. 4.4.5- Silicate Structure

Oxygen atoms are located on the edges of a tetrahedron structure and silicon atoms are located at the centre.

This basic unit of silicate is treated as negatively charged.

There is a covalent bond between Si and O, i.e. Si-O.

Silica

Silica (SiO_2) is the simple form of silicate. This is a three-dimensional network of tetrahedron where every corner oxygen atom is shared by adjacent tetrahedral. This material becomes electrically neutral but electronically stable.

Under this arrangement, the ratio of Si to O becomes 1:2 as given by chemical formula, SiO_2.

There are three polymorphic forms of silica: (1) quartz, (2) cristobalite and (3) tridymite. Silica is used in the manufacture of different varieties of glasses.

Structure of glasses

Generally, solids have three-dimensional periodic structures as shown in figure 4.4.6. This is a crystalline structure.

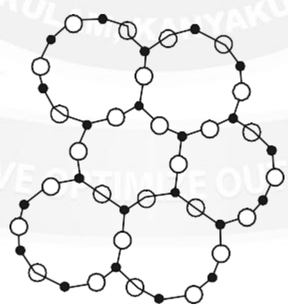

Fig. 4.4.6- Crystalline Structure (Orderly Repeated)

The materials, which do not have three-dimensional structures, but random structure as shown in figure 4.4.6 are said to be amorphous or glassy.

Many metal alloys, oxide compounds and non-oxide compounds form glassy structure. Fused silica or vitreous silica has high degree of atomic randomness.

Similarly, oxide as $B_2 O_3$ and GeO_2 may also form glassy structure.

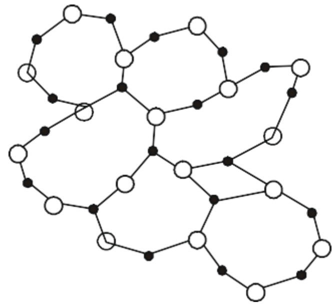

Fig. 4.4.7- Random Structure (Amorphous)

The glasses that are used containers and windows are silica glasses in which oxides such as CaO and Na_2O are added.

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.