**1.4 STRUCTURES OF CERAMICS**

The structure of ceramics can be considered by dividing them into three groups—oxides, silicates, and glasses. Both oxides and silicates can form crystalline and amorphous structures. The crystalline form will be considered separately for oxides and silicates. The amorphous forms of both will be considered under glasses.

**1.4.1 Oxide Structures**

Oxide ceramics are those in which the nonmetal is oxygen. These ceramics Possess different structures. These structures are discussed in the following text.

**1- Rock Salt Structure**

In this structure, the large anions are arranged in cubic close packing, and all the octahedral interstitial positions are filled with cations. The structure is shown in Figure 9.1. Oxides having this structure are MgO (Mg2+/O2− = 0.51), CaO, SrO, BaO, CdO, MnO, FeO, CoO, and NiO. For stability, the radius ratio should be between 0.732 and 0.414, and the anion and cation valences should be the same.

Na+ ion has an ionic radius of 0.102 nm (1.02 Aº); Cl- has a radius of 0.181 nm (1.81 Aº). This large anion to cation size ratio is typical of many common ionic structures. This size difference is large enough so that Na+ cations fit comfortably in all octahedral interstices of the closed Cl- sublattice. The lattice constant for this structure is predicted to be ɑ = 2(RNa + RCl) = 0.566 nm (5.66 Aº).

The only coordination polyhedron present in the NaCl structure is the octahedron. It is apparent that all octahedral share all 12 edges. The large coordination number 6 helps to explain deviations from Pauling′s rule as to edge-rather than vertex sharing polyhedra. The strength of the anion-cation bond and the bond sum are s = 1/6 and Ʃs = 6(1/6) = 1.

Because both Na and Cl have CN = 6, we expect the rocksalt structure to form with cation/anion radius ratio between: 0.414 < R+/R- < 2.41.



***FIGURE 1.10 Crystal structure of sodium chloride.***

***Smaller spheres represent Na+, and larger spheres***

***Cl− ions. Shows locations of the ions in the FCC***

***Structure.***

**2- Zinc Blende Structure**

The structure of zinc blende has tetrahedral coordination. A BeO polymorph at high temperature has this structure. The structure is shown in Figure 1.11.

The radius ratio, Rzn: Rs = 0.32 (radius of Zn+2 = 0.6 Aº in four coordination; S-2 = 1.84 Aº in 4-coordination) predicts that Zn2+ is in tetrahedral coordination with neighboring S2-.

***FIGURE 1.11 Zinc blende (ZnS) structure.***

**3- Cesium Chloride Structure**

The radius ratio between cesium and chloride ions requires eightfold coordination. From this, we can find that the bond strength is 1/8. These two criteria give rise to simple cubic (SC) array for Cl− ions. All the body center positions are filled with Cs+ ions. The structure is shown in Figure 1.12.

The Cesium chloride structure instead of the NaCl structure is adopted by AX compound when the radius ratio RA:RX is greater than 0.73. Therefore, the anions (X) are in simple cubic packing (SCP) and the cations fill the large interstices between them. The overall structure is made up of centered cubes that share faces with six other neighboring cubes. This feature makes this structure an unattractive choice for highly charged cations (see Pauling′s Rule 3). Examples of AX compounds that exhibit this structure are: CaCl, CsBr, CsI, (NH4) Cl, and (NH4) Br.

***FIGURE 1.12 Cesium chloride structure.***

**4- Fluorite and Antifluorite**

For AX2 compounds in which the radius ratio RA:RX exceeds 0.73, the fluorite structure mat be adopted. In this structure the Ca+2 ions are arranged at the corner and face centers of a cubic unit cell. The two fluorine atoms motifs at 1/4,1/4,1/4 and -1/4, -1/4, -1/4 for each lattice point. Each Ca+2 is surrounded by eight Fˉ in cubic coordination, and each Fˉ is surrounded by four Ca+2 at the corners of a tetrahedron. This leaves alternate cubic interstices vacant and results in the octahedral cleavage of fluorite and iso-structural minerals. The cubic coordination of Fˉ about a central Ca2+ is the result of the radius ratio of RCa : RF ̴ 0.75. These cubic coordination polyhedral share edges only; similarly, the tetrahedral coordination polyhedral share only edges. This arrangement allows for the maximum separation of the Ca2+ cations from each other. Because the cation has double the charge of the anion, the number of anions in the structure must be double that of the cations in order to achieve electrostatic neutrality.

Examples: Halides = CaF2, SrF2, BaF2, CdF2, SrCl2, BaCl2. Oxides = ZrO2, HfO2, CeO2, UO2.The example for an oxide-possessing fluorite (CaF2) structure is thoria (ThO2). The charge on Th4+ is large. This gives rise to the largest coordination number (CN) of 8. Therefore, the bond strength comes to 1/2. The number of valence bonds becomes four to satisfy the valency of 4 of Th4+ to each O2− ion. Thus, there will be simple cubic packing for O2− with Th4+ in half the sites with eight fold coordination. This is the structure of fluorite (CaF2), shown in Figure 1.13. The cation lattice is face-centered cubic (FCC), with all the tetrahedral interstices filled with anions.

Antifluorite structure is the reverse of a fluorite structure having a cubic close-packed array of O2− with cations in the tetrahedral sites. Examples of oxides with this structure are Li2O, Na2O, and K2O.



***FIGURE 1.13 Fluorite structure.***