**5- Perovskite Structure**

The chemical formula of perovskite is CaTiO3. The structure is shown in Figure 1.14. Let us apply Pauling’s rule to this structure. The strength of Ti–O bond = 2/3, and that of Ca–O bond = 1/6. Since each O2− is coordinated with 2 Ti4+ and 4 Ca2+, the total bond strength becomes (4/3) + (4/6) = 2, which is the same as the anion oxide valency. Hence, Pauling’s rule is satisfied. Other examples for compounds having perovskite structure are BaTiO3, SrTiO3, SrSnO3, and CaZrO3.

 This structure type is based on CCP of oxygen, with one quarter of the oxygen replaced by a large A cation. This large cation position is in 12 coordination with the surrounding oxygen. The B cations occur in octahedrons that share only apices. The valence of the A and B ions is not specified; however, the total valence of both ions (A+B) must be equal to 6 (to balance the O3ˉ2 in the formula ABO3).

***FIGURE 1.14 Perovskite structure (idealized).***

**6- Spinel**

The general formula for spinel structure is AB2O4. An example for a ceramic possessing this structure is magnesium aluminate (MgAl2O4). Thus, A represents divalent cations, and B, trivalent ones. The structure is cubic, having rock salt and zinc blende structures combined. A subcell of this structure is formed by O2− ions in FCC packing (Figure 1.15). The figure shows four octahedral interstices and eight tetrahedral interstices. Out of the four octahedral sites, only two will be filled in the spinel structure, and out of the eight tetrahedral sites, only one will be filled. Eight elementary cells are arranged to form a unit cell. There are two types of spinel: normal and inverse. In normal spinel, the A2+ ions are in tetrahedral sites and B3+ ones in octahedral sites. The examples for normal spinel are ZnFe2O4, CdFe2O4, MgAl2O4, CoAl2O4, MnAl2O4, and ZnAl2O4.

In inverse spinel, A2+ and half B3+ will be in octahedral sites and the other half in tetrahedral sites. The arrangement can be represented as B (AB) O4. These compounds are more common than the normal one. Examples are Fe (MgFe) O4, Fe (TiFe) O4, Fe3+ (Fe2+Fe3+) O4, Fe (NiFe) O4, and many other magnetic ferrites.

In fact very few spinels have exactly the normal or inverse structure, and these are sometimes called mixed spinels. The cation distribution between the two sites is a function of number of parameters, including temperature. This variability is described by an occupation factor λ which gives the fraction of B3+ cation in tetrahedron positions. A normal spinel is characterized by value of λ of 0, and an inverse spinel by a value of λ 0.5. The spinel MgAl2O4 has a value of λ of 0.05 and so is quite a good approximation to the normal spinel



***FIGURE 1.15 Subcell of spinel structure*.**

**7- Alumina Structure**

Al2O3 has a common structural arrangement shared by many oxides of the transition metals with the formula A2O3. In Al2O3, the preferred CN for Al3+ is 6, so bond strength becomes equal to 1/2; hence, there should be four Al3+ adjacent to each O2− to give the total bond strength equal to the valency of oxide anion. This is possible when the unit cell is hexagonally closed packed (HCP) of O2−, with Al3+ filling two-thirds of octahedral sites. The structure is called Corundum Structure as shown in Figure1.16.



***FIGURE 1.16 Unit cell of alumina crystal.***

**8- Rutile Structure**

Rutile’s chemical formula is TiO2.AX2 compounds that exhibit RA:RX ratio between about 0.73 and 0.41 may adopt the rutile structure in which the A cation is octahedral coordination to the X anion. The oxygen anions are coordinated by three cations in a triangular array.

In its structure, the CN for Ti is 6, its valence is +4, and therefore the bond strength becomes 2/3. This gives rise to threefold coordination for O2−. Cations fill only half the available octahedral sites, and the closer packing of O2− around filled cation sites leads to distortion of anion lattice, which is FCC. In Figure 1.17, the cationic lattice is shown. Other examples for compounds possessing rutile structures are GeO2, PbO2, SnO2, and MnO2.

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***FIGURE 1.17 the cationic lattice of rutile*.**