**1.3-2 Covalently Bonded Solids**

Covalent bonds arise by electron sharing. Many predominantly covalently bonded ceramics, especially Si-based ones, such as SiC, Si3N4, and silicates, are composed of Si atoms simultaneously bonded to four other atoms in a tetrahedral arrangement. Ground state configuration of Si has the valence electron in 3s23p2 configuration, as shown in Figure 1.9 a. It shows that Si can have two primary bonds when it combines with another element atom, because Si atom has two unpaired electrons.

In reality, there are four primary bonds associated with each Si atom. This can happen by *hybridization* between s and p wave functions. The s orbital hybridizes with all the three p orbitals to form *sp3 hybrid orbitals* (Figure 1.9b). Hybrid orbitals possess both s and p character, and directionally reaches out in space as lobes in a tetrahedral arrangement with a bond angle of 109° (Figure 1.9c). Each orbital is populated by one electron (Figure 1.9b). Now, each Si can bond to four other Si atoms or any other *four* atoms to give three-dimensional structures.



***FIGURE 1.9 (a) Ground state of the Si atom; (b) electronic configuration after hybridization; (c) directionality of sp3 bonds.***

**1.3-3 Metallic bond**

The cohesive force between positive nuclei and electrons cloud. There are two theories explain the nature of metallic bond: First, free electron theory arise from free movement of electrons in the structure. Second, tight-binding theory results from spread-out or delocalization of covalent bonds. Properties of crystals have metallic bonds: High plasticity and ductility, Well conduct for heat and electrical current and Low hardness. In minerals, it is only native minerals show metallic bonds.

**1.3-4 Van der Waals Bond**

It is the weak electrostatic force between atoms or molecules. For any atom or molecule, there is a fluctuating dipole moment, which varies with the instantaneous positions of electrons. The field associated with this moment induces a moment in neighboring atoms, and the interaction of induced and original moments leads to an attractive force (0.1 eV).

**1.3-5 Intermediate bond Types**

Although the structure of KCl can be regarded as almost completely ionic and that of H2 as completely covalent, there are many intermediate types in which a bond may be characterized by an ionic electron configuration associated with an increased electron concentration along the line between atom centers. Pauling has derived a semiempirical method of estimating bond type based on electronegativity scale. The electronegativity value is a measure of an atom's ability to attract electrons and is roughly proportional to the sum of the electron affinity (energy to add an electron) and ionization potential (energy to remove an electron). [Amount of ionic character =1-e-1/4 (xa-xb)]where xa is electronegativity of element a, xb is electronegativity of element b. Compounds between atoms with a large difference in electronegativity are largely ionic, whereas compounds in which atoms have about the same electronegativity are largely covalent.

**1.3- 7 Coordination Number**

 A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii. CN is determined by the radius ratio:

A given CN is stable only when the ratio of cation to anion radius is greater than some critical value. The derivation of these limits is strictly geometric as shown in Figure 1.9-9. Why are the radius ratio and CN related?

Coulomb interactions mean that, as signs should be as far apart as possible and opposite signs as close together as possible. Crystal structures are thus at their most stable when the cations have the maximum CN allowed by *r*X. In many well-known ceramics, the cation coordination polyhedron is the basic building block.



***FIGURE 1.9 Geometric method for calculating limiting radius ratios.***