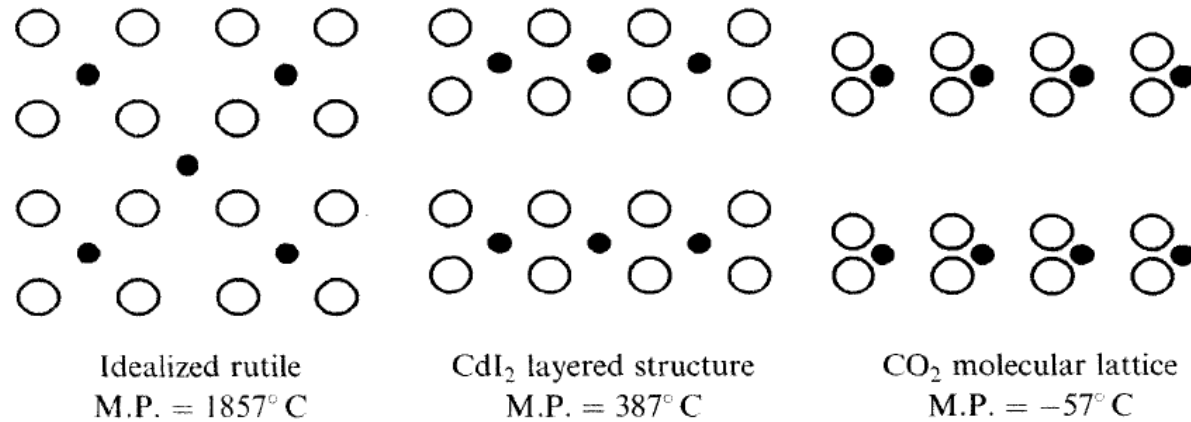


خواص سرامیک ها از جنبه تئوری

4.2.1 Factors Affecting Melting Points of Ceramics that are Predominantly Ionically Bonded

Ionic charge



Polarizing power of cation. High charge and small size increase the polarizing power of cations. Over the years many functions have been proposed to quantify the effect, and one of the simplest is to define the **ionic potential** of a cation as:

$$\phi = \frac{z^+}{r}$$

where z^+ is the charge on the cation and r its radius. The ionic powers of a few selected cations are listed in Table 4.2, where it is clear that high charge and small size greatly enhance ϕ and consequently the covalent character of the bond.

To illustrate compare MgO and Al₂O₃. On the basis of ionic charge alone, one would expect the melting point of Al₂O₃ (+3, -2) to be higher than that of MgO (-2, +2), and yet the reverse is observed. However, based on the relative polarizing power of Al³⁺ and Mg²⁺, it is reasonable to conclude that the covalent character of the Al-O bond is greater than

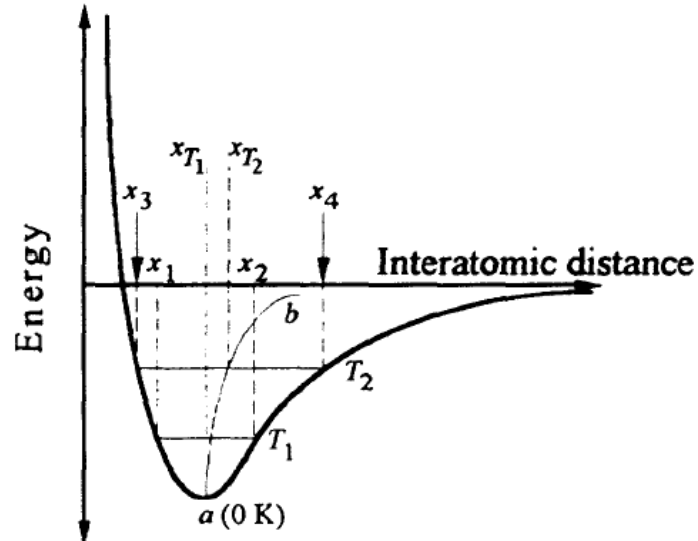
4.3 Thermal Expansion

It is well known that solids expand upon heating. The extent of the expansion is characterized by a **coefficient of linear expansion** α , defined as the fractional change in length with change in temperature at constant pressure, or

$$\alpha = \frac{1}{l_0} \left(\frac{\partial l}{\partial T} \right)_p \quad (4.2)$$

where l_0 is the original length.

The origin of thermal expansion can be traced to the anharmonicity or asymmetry of the energy distance curve described in Chap. 2 and reproduced in Fig. 4.3. The asymmetry of the curve expresses the fact that it is easier to pull two atoms apart than to push them together. At 0 K, the total energy of the atoms is potential, and the atoms are sitting at the bottom of the well



4.4 Young's Modulus and the Strength of Perfect Solids

In addition to understanding the behavior of ceramics exposed to thermal energy, it is important to understand their behavior when they are subjected to an external load or stress. The objective of this section is to interrelate the shape of the energy versus distance curve $E(r)$, discussed in Chap. 2, to the elastic modulus, which is a measure of the stiffness of a material and the theoretical strength of that material. To accomplish this goal, one needs to examine the forces $F(r)$ that develop between atoms as a result of externally applied stresses. As noted in Sec. 2.4, $F(r)$ is defined as

$$F(r) = \frac{dE(r)}{dr} \quad (4.3)$$

From the general shape of the $E(r)$ curve, one can easily sketch the shape of a typical force versus distance curve, as shown in Fig. 4.6. The following salient features are noteworthy:

- The net force between the atoms or ions is zero at equilibrium, i.e., at $r = r_0$.
- Pulling the atoms apart results in the development of an *attractive restoring force* between them that tends to pull them back together. The opposite is true if one tries to push the atoms together.
- In the region around $r = r_0$ the response can be considered, to a very good approximation, linear (inset in Fig. 4.6). In other words, the atoms act as if

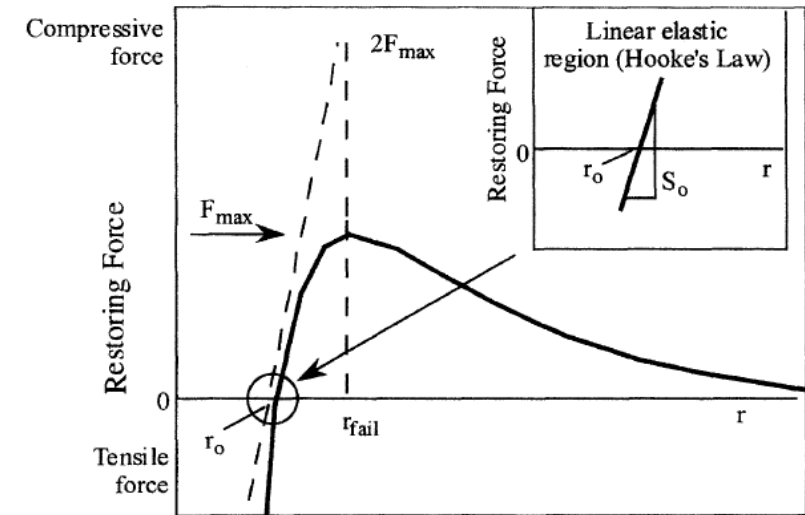


Figure 4.6 Typical force–distance curve. Slope of line going through r_0 is the stiffness of the bond S_0 . It is assumed in this construction that the maximum force is related to the stiffness as shown. This is quite approximate but serves to illustrate the relationship

$$\sigma = Y\varepsilon \quad (4.4)$$

where Y is Young's modulus and ε is the **strain** experienced by the material, defined as

$$\varepsilon = \frac{L - L_0}{L_0} \quad (4.5)$$

Here L is the length under the applied stress, and L_0 is the original length.

Refer once more to the force/distance curve shown in Fig. 4.6. In the vicinity of r_0 , the following approximation can be made:

$$F = S_0(r - r_0) \quad (4.6)$$

where S_0 is the **stiffness** of the bond, defined as

$$S_0 = \left(\frac{dF}{dr} \right)_{r=r_0} \quad (4.7)$$

Note that Eq. (4.6) is nothing but an expression for the extension of a linear spring.

Dividing Eq. (4.6) by r_0^2 and noting that F/r_0^2 is approximately the stress on the bond, while $(r - r_0)/r_0$ is the strain on the bond, and comparing the resulting expression with Eq. (4.4), one can see immediately that

$$\boxed{Y \approx \frac{S_0}{r_0}} \quad (4.8)$$

Theoretical strengths of solids

The next task is to estimate the theoretical strength of a solid or the stress that would be required to *simultaneously* break all the bonds across a fracture plane. It can be shown (see Prob. 4.2) that typically most bonds will fail when they are stretched by about 25%, i.e., when $r_{\text{fail}} \approx 1.25r_0$. It follows from the geometric construction shown in Fig. 4.6 that

$$S_0 \approx \frac{2F_{\text{max}}}{r_{\text{fail}} - r_0} \approx \frac{2F_{\text{max}}}{1.25r_0 - r_0} \quad (4.10)$$

Dividing both sides of this equation by r_0 and noting that

$$\frac{F_{\text{max}}}{r_0^2} \approx \sigma_{\text{max}} \quad (4.11)$$

i.e., the force divided by the area over which it operates, one obtains

$$\sigma_{\text{max}} \approx \frac{Y}{8} \quad (4.12)$$

4.5 Surface Energy

The **surface energy** γ of a solid is the amount of energy needed to create a unit area of new surface. The process can be pictured as shown in Fig. 4.7a, where two new surfaces are created by cutting a solid in two. Given this simple picture, the surface energy is simply the product of the number of bonds N_s broken per unit area of crystal surface and the energy per bond E_{bond} , or

$$\gamma = N_s E_{\text{bond}} \quad (4.15)$$

For the sake of simplicity, only first-neighbor interactions will be considered here, which implies that E_{bond} is given by Eq. (2.15). Also note that since N_s is a function of crystallography, it follows that γ is also a function of crystallography.

To show how to calculate surface energies by starting with Eq. (4.15), consider cleaving a rock salt crystal along its (100) plane,⁴¹ shown in

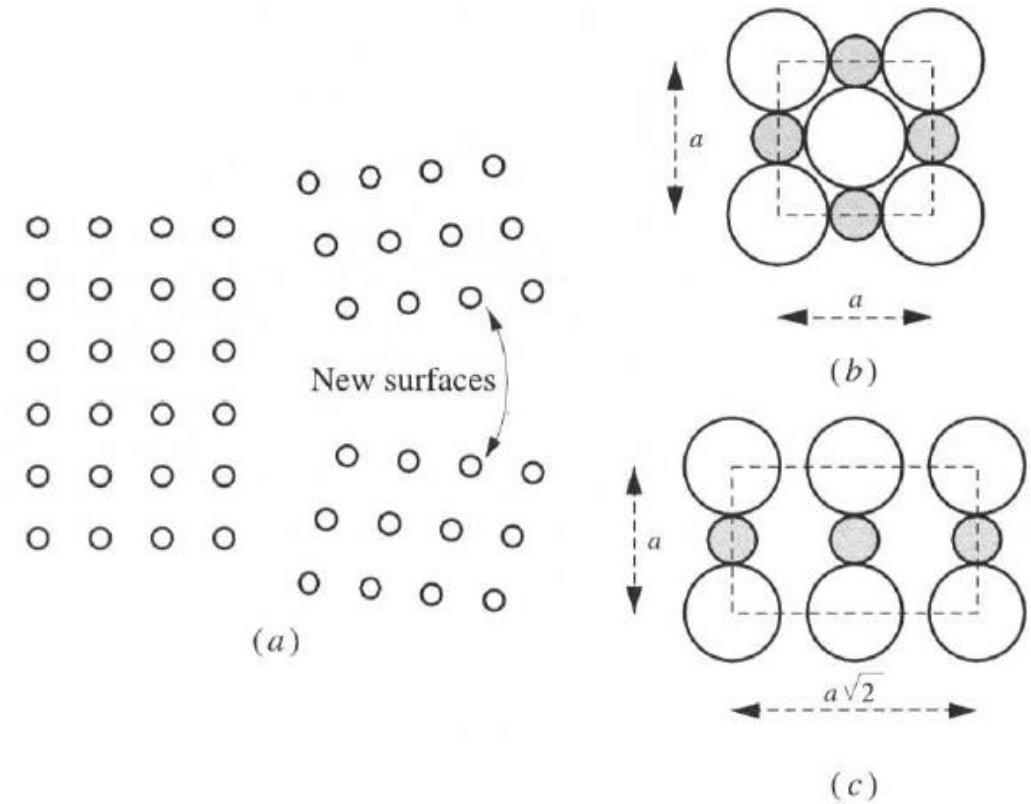


Figure 4.7 (a) The creation of new surface entails the breaking of bonds across that surface. (b) Structure of (100) plane in the rock salt structure. (c) Structure of (110) plane in same structure. Note that the coordination number of ions in this plane is 2, which implies that to create a (110) plane, only two bonds per ion would have to be broken.

Experimental Details

Melting points

Several methods can be used to measure the melting point of solids. One of the simplest is probably to use a **differential thermal analyser** (DTA for short). The basic arrangement of a differential thermal analyser is simple and is shown schematically in Fig. 4.8*a*. The sample and an inert reference (usually alumina powder) are placed side by side in a furnace, and identical thermocouples are placed below each. The temperature of the furnace is then slowly ramped, and the difference in temperature $\Delta T = T_{\text{sample}} - T_{\text{ref}}$ is measured

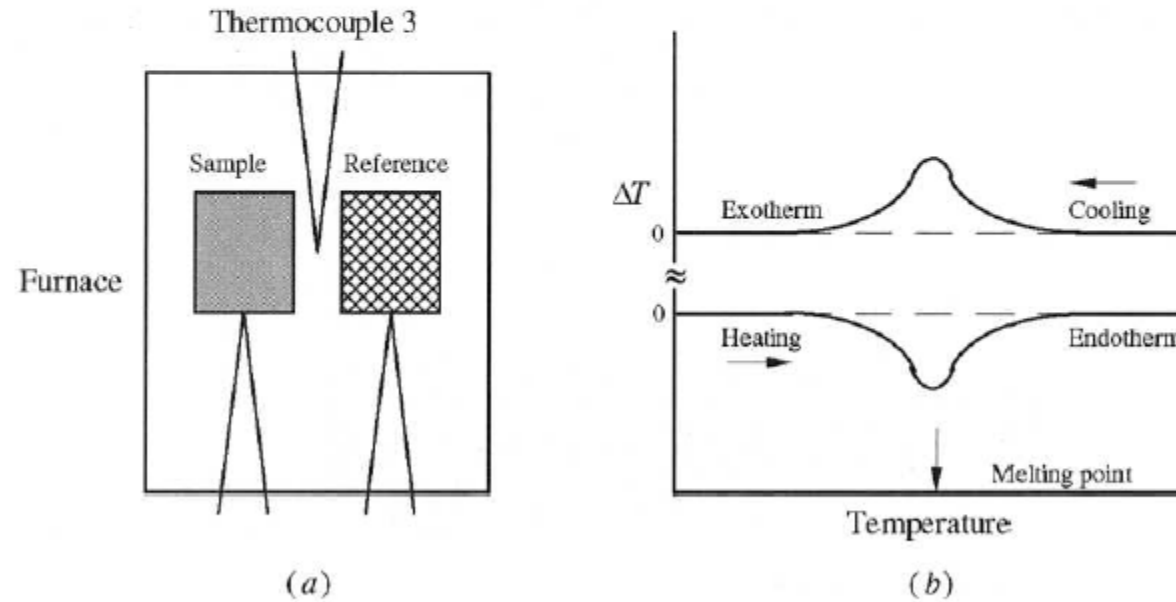
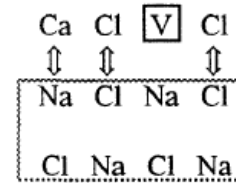
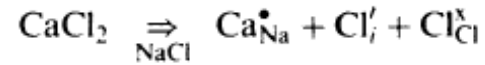
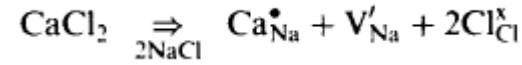
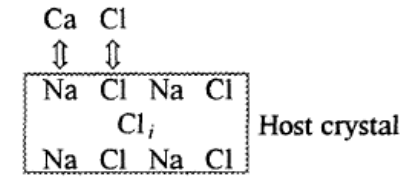


Figure 4.8 (a) Schematic of DTA setup. (b) Typical DTA traces upon heating (bottom curve) and cooling (top curve).

Kroger–Vink notation

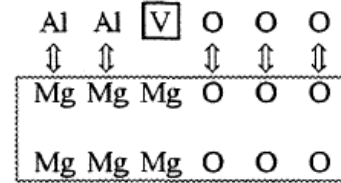


(a)

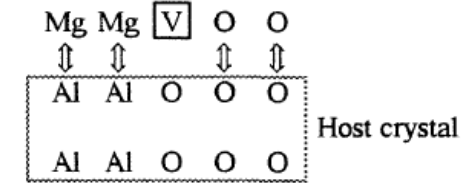


Host crystal

(b)



(c)



Host crystal

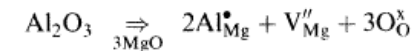
(d)

Figure 6.5 Bookkeeping technique for impurity incorporation reactions. (a) CaCl_2 in NaCl leaves a vacancy on cation sublattice. (b) An alternate reaction is for the extra Cl ion to go interstitial. This reaction is unlikely, however, given the large size of the Cl ion. (c) Al_2O_3 in MgO creates a vacancy on the cation sublattice. (d) MgO in Al_2O_3 creates a vacancy on the anion sublattice.

created does not change the *regular* site ratios of the host crystal (interstitial sites are not considered regular sites).

EXAMPLE 2

Doping MgO with Al_2O_3 (Fig. 6.5c):



EXAMPLE 3

Doping Al_2O_3 with MgO (Fig. 6.5d), one possible incorporation reaction is

