

CHAPTER 10 CERAMIC MATERIALS

10.1 Define a ceramic material.

Ceramic materials are inorganic, nonmetallic materials that consist of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds.

10.2 What are some of the properties common to most ceramic materials?

While the properties of ceramic materials vary greatly, most ceramic materials are hard and brittle with low toughness and ductility but good electrical and thermal insulating properties. Also, ceramic materials typically have high melting temperatures and high chemical stability.

10.3 Distinguish between traditional and engineering ceramic materials and give examples of each.

Traditional ceramic materials are typically made from three components – clay, feldspar and silica – whereas engineering ceramics consist of pure or nearly pure compounds such as aluminum oxide (Al_2O_3), silicon carbide (SiC), and silicon nitride (Si_3N_4). Examples of traditional ceramics include bricks, tiles and electrical porcelain while applications of engineering ceramics include silicon carbide parts for high temperature gas turbine engine components, zirconium dioxide crucibles for melting superalloys, and high performance ball bearing and races made of titanium and carbon nitride.

10.4 Using Pauling's equation (Eq. 2.10), compare the percent covalent character of the following compounds: hafnium carbide, titanium carbide, tantalum carbide, boron carbide, and silicon carbide.

Recall that Pauling's equation gives the percent covalent character as:

$$\% \text{ covalent character} = e^{-0.25(X_A - X_B)^2} \times 100\%$$

Applying this equation, a table can be generated as follows.

Compound	Electronegativities		$(X_A - X_B)^2$	$-0.25(X_A - X_B)^2$	% Covalent Character
	X_A	X_B			
HfC	1.2	2.5	1.69	-0.4225	65.5
TiC	1.3	2.5	1.44	-0.360	69.8
TaC	1.4	2.5	1.21	-0.3025	73.9
BC	2.0	2.5	0.25	-0.0625	93.9
SiC	1.8	2.5	0.49	-0.1225	88.5

10.5 What two main factors affect the packing of ions in ionic solids?

The two main factors which affect the packing of ions in ionic solids are:

1. The relative size of the ions in the ionic solid, assuming the ions are hard spheres with definite radii;
2. The need to balance the electrostatic charges to maintain electrical neutrality within the ionic solid.

10.6 Define (a) coordination number and (b) critical radius ratio for the packing of ions in ionic solids.

(a) The coordination number is the number of anions that surround a central cation.

(b) The critical radius ratio is the ratio of the radius of the central cation to the radius of the surrounding anions.

10.7 Using Fig. 10.60, calculate the critical radius ratio for octahedral coordination.

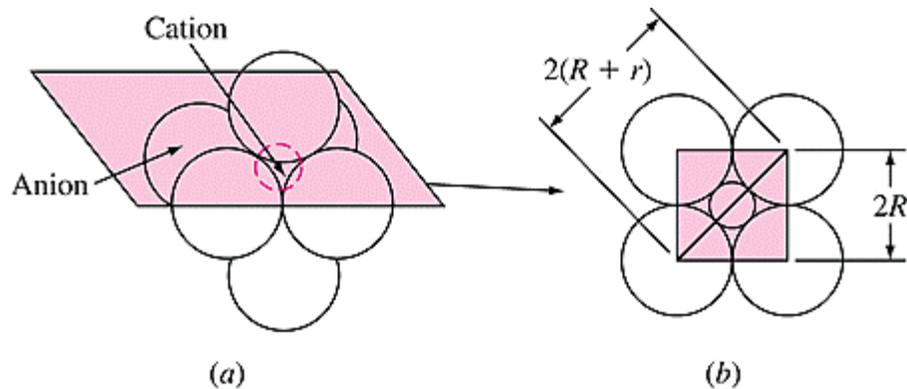


Figure 10.60 (a) Octahedral coordination of six anions (radii = R) around a central cation of radius r . (b) Horizontal section through center of (a).

From the triangle shown above in Fig. 10.60 (b),

$$\begin{aligned} [2(r + R)]^2 &= (2R)^2 + (2R)^2 \\ (r + R)^2 &= 2R^2 \\ r + R &= \sqrt{2}R \\ r &= \sqrt{2}R - R = 0.414R \\ \frac{r}{R} &= \mathbf{0.414} \end{aligned}$$

- 10.8 Predict the coordination number for (a) BaO and (b) LiF. Ionic radii are $\text{Ba}^{2+} = 0.143 \text{ nm}$, $\text{O}^{2-} = 0.132 \text{ nm}$, $\text{Li}^{+} = 0.078 \text{ nm}$, $\text{F}^{-} = 0.133 \text{ nm}$.

(a) Using Appendix II, the radius ratio for BaO is

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{r(\text{Ba}^{2+})}{R(\text{O}^{2-})} = \frac{0.143}{0.132} = 1.08$$

This ratio is greater than 0.732 and greater than 1.0. This is an unusual case in which the cation is larger than the anion because the elements respectively lie in Periods 6 and 2 of the periodic table. But if we invert this ratio to represent an anion surrounded by cations, we obtain 0.93. BaO should thus show cubic coordination (CN = 8). The solid is actually octahedral, CN = 6.

(b) Using Appendix II, the radius ratio for LiF is

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{r(\text{Li}^{+})}{R(\text{F}^{-})} = \frac{0.078}{0.133} = 0.59$$

This ratio is greater than 0.414 and less than 0.732, thus LiF should have an octahedron coordination number, CN = 6, and it does.

- 10.9 Calculate the density in grams per cubic centimeter of CsI, which has the CsCl structure. Ionic radii are $\text{Cs}^{+} = 0.165 \text{ nm}$ and $\text{I}^{-} = 0.220 \text{ nm}$.

For the CsCl structure, $\sqrt{3}a = 2(r + R)$. Thus, the lattice constant measures,

$$a = \frac{2}{\sqrt{3}} (0.165 \text{ nm} + 0.220 \text{ nm}) = 0.445 \text{ nm} = 4.45 \times 10^{-8} \text{ cm}$$

Since the unit cell of CsI contains one Cs^{+} and one I^{-} ion, its mass is

$$m_{\text{unit cell}} = \frac{(1\text{Cs}^{+} \times 132.9 \text{ g/mol}) + (1\text{I}^{-} \times 126.9 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 4.32 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.32 \times 10^{-22} \text{ g}}{(4.45 \times 10^{-8} \text{ cm})^3} = 4.90 \text{ g/cm}^3$$

- 10.10 Calculate the density in grams per cubic centimeter of CsBr, which has the CsCl structure. Ionic radii are $\text{Cs}^{+} = 0.165 \text{ nm}$ and $\text{Br}^{-} = 0.196 \text{ nm}$.

For the CsCl structure, $\sqrt{3}a = 2(r + R)$. Thus, the lattice constant is,

$$a = \frac{2}{\sqrt{3}} (0.165 \text{ nm} + 0.196 \text{ nm}) = 0.417 \text{ nm} = 4.17 \times 10^{-8} \text{ cm}$$

Since the unit cell of CsI contains one Cs^+ and one Br^- ion, its mass is

$$m_{\text{unit cell}} = \frac{(1\text{Cs}^+ \times 132.9 \text{ g/mol}) + (1\text{Br}^- \times 79.90 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 3.53 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{3.53 \times 10^{-22} \text{ g}}{(4.17 \times 10^{-8} \text{ cm})^3} = 4.87 \text{ g/cm}^3$$

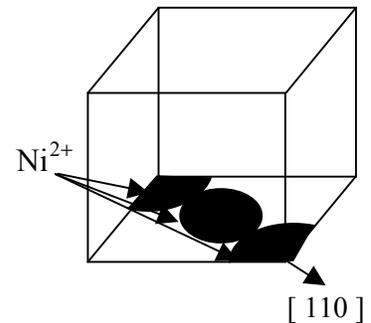
- 10.11 Calculate the linear densities in ions per nanometer in the $[110]$ and $[111]$ directions for (a) NiO and (b) CdO. Ionic radii are $\text{Ni}^{2+} = 0.078 \text{ nm}$, $\text{Cd}^{2+} = 0.103 \text{ nm}$, and $\text{O}^{2-} = 0.132 \text{ nm}$.

Since NiO and CdO have the NaCl crystal structure, $a = 2(r + R)$.

(a) For NiO in the $[110]$ direction,

$$a = 2(r_{\text{Ni}^{2+}} + R_{\text{O}^{2-}}) = 2(0.078 \text{ nm} + 0.132 \text{ nm}) = 0.420 \text{ nm}$$

$$\rho_L = \frac{2\text{Ni}^{2+}}{\sqrt{2}a} = \frac{2\text{Ni}^{2+}}{\sqrt{2}(0.420 \text{ nm})} = 3.37 \text{ Ni}^{2+}/\text{nm}$$



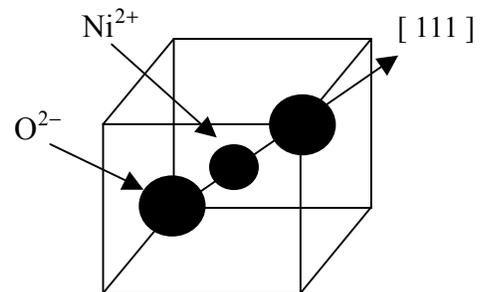
If we shift the origin from $(0, 0, 0)$ to $(0, \frac{1}{2}, 0)$, we obtain

$$\rho_L = \frac{2\text{O}^{2-}}{\sqrt{2}a} = \frac{2\text{O}^{2-}}{\sqrt{2}(0.420 \text{ nm})} = 3.37 \text{ O}^{2-}/\text{nm}$$

For the $[111]$ direction,

$$\rho_L = \frac{1\text{O}^{2-}}{\sqrt{3}a} = \frac{1\text{O}^{2-}}{\sqrt{3}(0.420 \text{ nm})} = 1.37 \text{ O}^{2-}/\text{nm}$$

$$\rho_L = \frac{1\text{Ni}^{2+}}{\sqrt{3}a} = \frac{1\text{Ni}^{2+}}{\sqrt{3}(0.420 \text{ nm})} = 1.37 \text{ Ni}^{2+}/\text{nm}$$



(b) For CdO in the [110] direction,

$$a = 2(r_{\text{Cd}^{2+}} + R_{\text{O}^{2-}}) = 2(0.103 \text{ nm} + 0.132 \text{ nm}) = 0.470 \text{ nm}$$

$$\rho_L = \frac{2\text{Cd}^{2+}}{\sqrt{2}a} = \frac{2\text{Cd}^{2+}}{\sqrt{2}(0.470 \text{ nm})} = \mathbf{3.01 \text{ Cd}^{2+}/\text{nm}}$$

Moving the origin from (0, 0, 0) to (0, 1/2, 0),

$$\rho_L = \frac{2\text{O}^{2-}}{\sqrt{2}a} = \frac{2\text{O}^{2-}}{\sqrt{2}(0.470 \text{ nm})} = \mathbf{3.01 \text{ O}^{2-}/\text{nm}}$$

For the [111] direction,

$$\rho_L = \frac{1\text{O}^{2-}}{\sqrt{3}a} = \frac{1\text{O}^{2-}}{\sqrt{3}(0.470 \text{ nm})} = \mathbf{1.23 \text{ O}^{2-}/\text{nm}}$$

$$\rho_L = \frac{1\text{Ni}^{2+}}{\sqrt{3}a} = \frac{1\text{Ni}^{2+}}{\sqrt{3}(0.470 \text{ nm})} = \mathbf{1.23 \text{ Ni}^{2+}/\text{nm}}$$

- 10.12 Calculate the planar densities in ions per square nanometer on the (111) and (110) planes for (a) CoO and (b) LiCl. Ionic radii are $\text{Co}^{2+} = 0.082 \text{ nm}$, $\text{O}^{2-} = 0.132 \text{ nm}$, $\text{Li}^{+} = 0.078 \text{ nm}$, and $\text{Cl}^{-} = 0.181 \text{ nm}$.

First recognize that both CoO and LiCl have the NaCl structure.

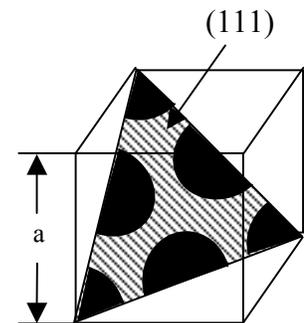
- (a) For CoO, if we consider the O^{2-} anions to be located at the FCC positions of a cubic unit cell, then the (111) plane contains the equivalent of two anions.

$$3 \times \frac{1}{6} \text{ anion} + 3 \times \frac{1}{2} \text{ anion} = 2 \text{ anions}$$

The lattice constant is $a = 2(r + R) = 2(0.082 \text{ nm} + 0.132 \text{ nm}) = 0.428 \text{ nm}$. The area of the (111) plane is,

$$A_{(111)} = \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)\left(\sqrt{\frac{3}{2}}a\right) = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.428 \text{ nm})^2 = 0.159 \text{ nm}^2$$

The planar density for the O^{2-} anions then becomes,



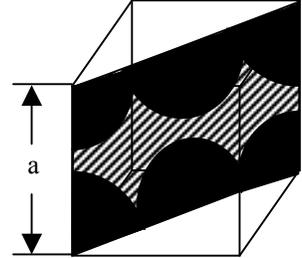
$$\rho_{\text{planar}} = \frac{2(\text{O}^{2-} \text{ ions})}{0.159 \text{ nm}^2} = \mathbf{12.6 \text{ O}^{2-} \text{ ions/nm}^2}$$

The planar density of the Co^{2+} cations is the same if we consider them to be located at the FCC lattice points of the unit cell. Consequently,

$$\rho_{\text{planar}}(\text{CoO}) = \mathbf{12.6 (\text{Co}^{2+} \text{ or } \text{O}^{2-}) \text{ ions/nm}^2}$$

For the (110) plane, we have two ions contained within the plane. The area of the plane is,

$$\begin{aligned} A_{(110)} &= \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)(a) = \frac{\sqrt{2}}{2}a^2 = \frac{\sqrt{2}}{2}(0.428 \text{ nm})^2 \\ &= 0.13 \text{ nm}^2 \end{aligned}$$



The (110) planar densities for CoO are,

$$\rho_{\text{planar}} = \frac{2(\text{O}^{2-} \text{ ions})}{0.13 \text{ nm}^2} = \mathbf{15.4 \text{ O}^{2-} \text{ ions/nm}^2}$$

$$\rho_{\text{planar}} = \frac{2(\text{Co}^{2+} \text{ ions})}{0.13 \text{ nm}^2} = \mathbf{15.4 \text{ Co}^{2+} \text{ ions/nm}^2}$$

(b) Similarly, for LiCl, the (111) planar densities are calculated as:

$$a = 2(r + R) = 2(0.078 \text{ nm} + 0.181 \text{ nm}) = 0.518 \text{ nm}$$

$$A_{(111)} = \frac{1}{2}bh = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.518 \text{ nm})^2 = 0.232 \text{ nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Cl}^- \text{ ions})}{0.232 \text{ nm}^2} = \mathbf{8.6 \text{ Cl}^- \text{ ions/nm}^2}$$

$$\rho_{\text{planar}} = \frac{2(\text{Li}^+ \text{ ions})}{0.232 \text{ nm}^2} = \mathbf{8.6 \text{ Li}^+ \text{ ions/nm}^2}$$

For the (110) plane,

$$A_{(110)} = \frac{1}{2}bh = \frac{\sqrt{2}}{2}a^2 = \frac{\sqrt{2}}{2}(0.518 \text{ nm})^2 = 0.19 \text{ nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Cl}^- \text{ ions})}{0.19 \text{ nm}^2} = \mathbf{10.5 \text{ Cl}^- \text{ ions/nm}^2}$$

$$\rho_{\text{planar}} = \frac{2(\text{Li}^+ \text{ ions})}{0.19 \text{ nm}^2} = \mathbf{10.5 \text{ Li}^+ \text{ ions/nm}^2}$$

- 10.13 Calculate the density in grams per cubic centimeter of (a) SrO and (b) VO. Ionic radii are $V^{2+} = 0.065$ nm, $Sr^{2+} = 0.127$ nm, and $O^{2-} = 0.132$ nm.

Both SrO and VO have the NaCl structure so $a = 2(r + R)$ and there are four anions and four cations per unit cell.

(a) For SrO,

$$a = 2(r + R) = 2(0.127 \text{ nm} + 0.132 \text{ nm}) = 0.518 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4Sr^{2+} \times 87.62 \text{ g/mol}) + (4O^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 6.89 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{6.89 \times 10^{-22} \text{ g}}{(5.18 \times 10^{-8} \text{ cm})^3} = \mathbf{4.96 \text{ g/cm}^3}$$

(b) For VO,

$$a = 2(r + R) = 2(0.065 \text{ nm} + 0.132 \text{ nm}) = 0.394 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4V^{2+} \times 50.94 \text{ g/mol}) + (4O^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 4.45 \times 10^{-22} \text{ g}$$

The density is thus,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.45 \times 10^{-22} \text{ g}}{(3.94 \times 10^{-8} \text{ cm})^3} = \mathbf{7.27 \text{ g/cm}^3}$$

- 10.14 Calculate the ionic packing factor for (a) MnO and (b) SrO. Ionic radii are $Mn^{2+} = 0.091$ nm, $Sr^{2+} = 0.127$ nm, and $O^{2-} = 0.132$ nm.

Both MnO and SrO have the NaCl structure. Thus there are four anions and four cations per unit cell and the ionic packing factor is calculated using the equation:

$$IPF = \frac{\text{Vol. of ions per unit cell}}{\text{Vol. of unit cell}} = \frac{4\left(\frac{4}{3}\pi r^3\right) + 4\left(\frac{4}{3}\pi R^3\right)}{a^3} = \frac{16/3\pi(r^3 + R^3)}{a^3}$$

(a) For MnO, $a = 2(0.091 \text{ nm} + 0.132 \text{ nm}) = 0.446 \text{ nm}$ and the IPF is

$$IPF = \frac{16/3\pi(r^3 + R^3)}{a^3} = \frac{16\pi[(0.091 \text{ nm})^3 + (0.132 \text{ nm})^3]}{3(0.446 \text{ nm})^3} = \mathbf{0.577}$$

(b) For SrO, $a = 2(0.127 \text{ nm} + 0.132 \text{ nm}) = 0.518 \text{ nm}$ and the IPF is

$$\text{IPF} = \frac{\frac{16}{3}\pi(r^3 + R^3)}{a^3} = \frac{16\pi[(0.127 \text{ nm})^3 + (0.132 \text{ nm})^3]}{3(0.518 \text{ nm})^3} = \mathbf{0.524}$$

10.15 ZnTe has the zinc blende crystal structure. Calculate the density of ZnTe. Ionic radii are $\text{Zn}^{2+} = 0.083 \text{ nm}$ and $\text{Te}^{2-} = 0.211 \text{ nm}$.

Since ZnTe has the zinc blende crystal structure (ZnS), there are four zinc ions and four tellurium ions per unit cell. Also, the lattice constant is calculated as $a = \frac{4}{\sqrt{3}}(r + R)$.

$$a = \frac{4}{\sqrt{3}}(r + R) = \frac{4}{\sqrt{3}}(0.083 \text{ nm} + 0.211 \text{ nm}) = 0.679 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{Zn}^{2+} \times 65.38 \text{ g/mol}) + (4\text{Te}^{2-} \times 127.6 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 1.28 \times 10^{-21} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{1.28 \times 10^{-21} \text{ g}}{(6.79 \times 10^{-8} \text{ cm})^3} = \mathbf{4.09 \text{ g/cm}^3}$$

10.16 BeO has the zinc blende crystal structure. Calculate the density of BeO. Ionic radii are $\text{Be}^{2+} = 0.034 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.

Since BeO has the zinc blende crystal structure, there are four zinc ions and four oxygen ions per unit cell. Also, the lattice constant is calculated as $a = \frac{4}{\sqrt{3}}(r + R)$.

$$a = \frac{4}{\sqrt{3}}(r + R) = \frac{4}{\sqrt{3}}(0.034 \text{ nm} + 0.132 \text{ nm}) = 0.383 \text{ nm}$$

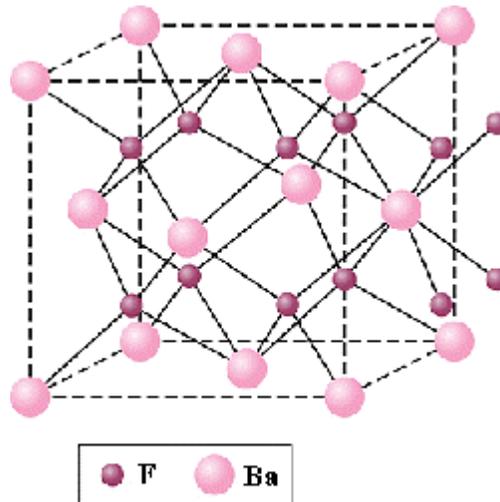
$$m_{\text{unit cell}} = \frac{(4\text{Be}^{2+} \times 9.012 \text{ g/mol}) + (4\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 1.66 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{1.66 \times 10^{-22} \text{ g}}{(3.83 \times 10^{-8} \text{ cm})^3} = \mathbf{2.95 \text{ g/cm}^3}$$

- 10.17 Draw the unit cell for BaF₂, which has the fluorite (CaF₂) crystal structure. If the Ba²⁺ ions occupy the FCC lattice sites, which sites do the F⁻ ions occupy?

The BaF₂ unit cell is shown below. With the Ba²⁺ ions occupying the FCC lattice sites, the F⁻ ions occupy the tetrahedral interstitial sites.



- 10.18 Calculate the density in grams per cubic centimeter of ZrO₂, which has the CaF₂ crystal structure. Ionic radii are Zn⁴⁺ = 0.087 nm and O²⁻ = 0.132 nm.

Since ZrO₂ has the CaF₂ crystal structure, there are four Zr⁴⁺ ions and eight O²⁻ ions per unit cell. Also, the lattice constant is calculated as $a = \frac{4}{\sqrt{3}}(r + R)$.

$$a = \frac{4}{\sqrt{3}}(r + R) = \frac{4}{\sqrt{3}}(0.087 \text{ nm} + 0.132 \text{ nm}) = 0.506 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{Zr}^{2+} \times 91.22 \text{ g/mol}) + (8\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 8.19 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{8.19 \times 10^{-22} \text{ g}}{(5.06 \times 10^{-8} \text{ cm})^3} = 6.32 \text{ g/cm}^3$$

- 10.19 What fraction of the octahedral interstitial sites is occupied in the CaF₂ structure?

All eight of the tetrahedral interstitial sites are occupied. However, none of the four octahedral interstitial sites are occupied; thus the fraction is *zero*.

- 10.20 Calculate the linear density in ions per nanometer in the [111] and [110] directions for CeO_2 , which has the fluorite structure. Ionic radii are $\text{Ce}^{4+} = 0.102 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.

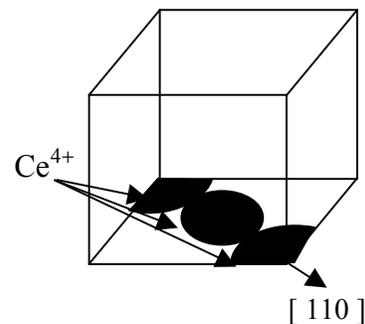
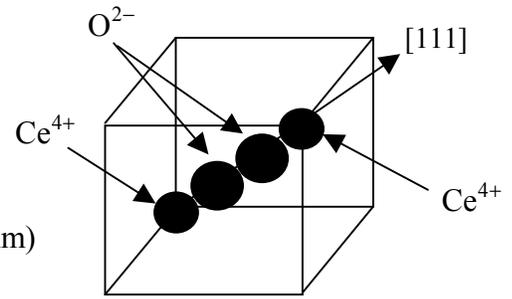
For CeO_2 in the [111] direction, there are two O^{2-} and one Ce^{4+} along the cube diagonal, which is $\sqrt{3}a$ in length.

$$a = \frac{4}{\sqrt{3}}(r_{\text{Ce}^{4+}} + R_{\text{O}^{2-}}) = \frac{4}{\sqrt{3}}(0.102 \text{ nm} + 0.132 \text{ nm}) = 0.540 \text{ nm}$$

$$\rho_L = \frac{1\text{Ce}^{4+} + 2\text{O}^{2-}}{\sqrt{3}a} = \frac{1\text{Ce}^{4+} + 2\text{O}^{2-}}{\sqrt{3}(0.540 \text{ nm})} = (1.07\text{Ce}^{4+} + 2.14\text{O}^{2-})/\text{nm}$$

For the [110] direction,

$$\rho_L = \frac{2\text{Ce}^{4+}}{\sqrt{2}a} = \frac{2\text{Ce}^{4+}}{\sqrt{2}(0.540 \text{ nm})} = 2.62 \text{ Ce}^{4+}/\text{nm}$$



- 10.21 Calculate the planar density in ions per square nanometer in the (111) and (110) planes of ThO_2 , which has the fluorite structure. Ionic radii are $\text{Th}^{4+} = 0.110 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.

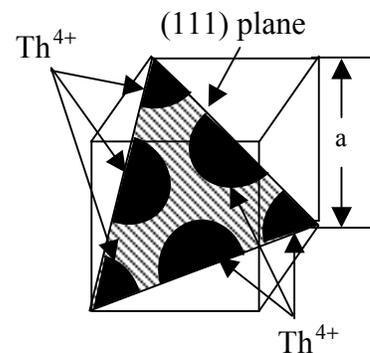
If we consider the Th^{4+} cations to be located at the FCC positions of a cubic unit cell, and the O^{2-} anions in the tetrahedral interstitial sites, then the (111) plane contains the equivalent of two cations.

$$3 \times \frac{1}{6} \text{ cation} + 3 \times \frac{1}{2} \text{ cation} = 2 \text{ cations}$$

The lattice constant is $a = \frac{4}{\sqrt{3}}(r_{\text{Th}^{4+}} + R_{\text{O}^{2-}}) = \frac{4}{\sqrt{3}}(0.110 \text{ nm} + 0.132 \text{ nm}) = 0.559 \text{ nm}$.

The area of the (111) plane is,

$$A_{(111)} = \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)\left(\frac{\sqrt{3}}{2}a\right) = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.559 \text{ nm})^2 = 0.270 \text{ nm}^2$$

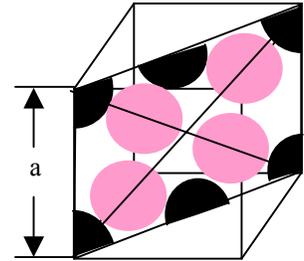


The planar density for the Th^{4+} cations on the (111) plane is thus,

$$\rho_{\text{planar}} = \frac{2(\text{Th}^{4+} \text{ ions})}{0.270 \text{ nm}^2} = \mathbf{7.4 \text{ Th}^{4+} \text{ ions/nm}^2}$$

For the (110) plane, we have two ions contained within the plane. The area of the plane is,

$$\begin{aligned} A_{(110)} &= \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)(a) = \frac{\sqrt{2}}{2}a^2 = \frac{\sqrt{2}}{2}(0.559 \text{ nm})^2 \\ &= 0.221 \text{ nm}^2 \end{aligned}$$



■ Th^{4+} ■ O^{2-}

The (110) planar densities for ThO are,

$$\rho_{\text{planar}} = \frac{4(\text{O}^{2-} \text{ ions})}{0.221 \text{ nm}^2} = 18.1 \text{ O}^{2-} \text{ ions/nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Th}^{4+} \text{ ions})}{0.221 \text{ nm}^2} = 9.1 \text{ Th}^{4+} \text{ ions/nm}^2$$

$$\rho_{\text{planar}}(\text{ThO}_2) = \mathbf{18.1 \text{ O}^{2-} \text{ or } 9.1 \text{ Th}^{4+} \text{ ions/nm}^2}$$

- 10.22 Calculate the ionic packing factor for SrF_2 , which has the fluorite structure. Ionic radii are $\text{Sr}^{2+} = 0.127 \text{ nm}$ and $\text{F}^- = 0.133 \text{ nm}$.

$$\text{IPF} = \frac{\text{Vol. of ions per unit cell}}{\text{Vol. of unit cell}} = \frac{(\frac{4}{3}\pi) \left[(4r_{\text{Sr}^{2+}}^3) + (8R_{\text{F}^-}^3) \right]}{a^3}$$

where $a = \frac{4}{\sqrt{3}}(0.127 \text{ nm} + 0.133 \text{ nm}) = 0.600 \text{ nm}$. Substituting,

$$\text{IPF} = \frac{4\pi \left[4(0.127 \text{ nm})^3 + 8(0.133 \text{ nm})^3 \right]}{3(0.600 \text{ nm})^3} = \mathbf{0.524}$$

- 10.23 What is the antifluorite structure? What ionic compounds have this structure? What fraction of the tetrahedral interstitial sites is occupied by cations?

The antifluorite structure consists of an FCC unit cell with anions occupying the FCC lattice points and cations occupying all eight tetrahedral sites. Thus the cation and anion positions of the fluorite structure are reversed. Examples of compounds having this

structure are Li_2O , Na_2O , K_2O , and Mg_2O . The fraction of the tetrahedral sites occupied by cations is one (1.0).

- 10.24 Why are only two-thirds of the octahedral interstitial sites filled by Al^{3+} ions when the oxygen ions occupy the HCP lattice sites in Al_2O_3 ?

When the oxygen ions occupy the HCP lattice sites in Al_2O_3 , only two-thirds of the octahedral interstitial sites are filled by Al^{3+} ions in order to maintain electrical neutrality. There can only be two Al^{3+} ions for every three O^{2-} ions.

- 10.25 Describe the perovskite structure. What fraction of the octahedral interstitial sites is occupied by the tetravalent cation?

The perovskite structure (CaTiO_3) consists of an FCC unit cell with Ca^{2+} cations in the corners, O^{2-} anions in the face centers, and a Ti^{4+} cation in the center octahedral interstitial site. The tetravalent cation Ti^{4+} fills one-fourth of the octahedral sites.

- 10.26 Calculate the ionic packing factor for CaTiO_3 , which has the perovskite structure. Ionic radii are $\text{Ca}^{2+} = 0.106$ nm, $\text{Ti}^{4+} = 0.064$ nm, and $\text{O}^{2-} = 0.132$ nm. Assume the lattice constant $a = 2(r_{\text{Ti}^{4+}} + r_{\text{O}^{2-}})$.

In the perovskite structure, there are a total of one calcium ion, one titanium ion, and three oxygen atoms. The ionic packing factor is therefore calculated as,

$$\text{IPF} = \frac{\text{Vol. of ions per unit cell}}{\text{Vol. of unit cell}} = \frac{(\frac{4}{3}\pi) \left[(r_{\text{Ca}^{2+}}^3) + (r_{\text{Ti}^{4+}}^3) + (3r_{\text{O}^{2-}}^3) \right]}{a^3}$$

where $a = 2(r_{\text{Ti}^{4+}} + r_{\text{O}^{2-}}) = 2(0.064 \text{ nm} + 0.132 \text{ nm}) = 0.392 \text{ nm}$. Substituting,

$$\text{IPF} = \frac{4\pi \left[(0.106 \text{ nm})^3 + (0.064 \text{ nm})^3 + 3(0.132 \text{ nm})^3 \right]}{3(0.392 \text{ nm})^3} = \mathbf{0.581}$$

- 10.27 Calculate the density in grams per cubic centimeter of SrSnO_3 , which has the perovskite structure. Ionic radii are $\text{Sr}^{2+} = 0.127$ nm, $\text{Sn}^{4+} = 0.074$ nm, and $\text{O}^{2-} = 0.132$ nm. Assume the lattice constant $a = 2(r_{\text{Sn}^{4+}} + r_{\text{O}^{2-}})$.

For $a = 2(r_{\text{Sn}^{4+}} + r_{\text{O}^{2-}}) = 2(0.074 \text{ nm} + 0.132 \text{ nm}) = 0.412 \text{ nm}$, and a unit cell mass of

$$m_{\text{unit cell}} = \frac{(1\text{Sr}^{2+} \times 87.62 \text{ g/mol}) + (1\text{Sn}^{4+} \times 118.7 \text{ g/mol}) + (3\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}}$$

$$= 4.22 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

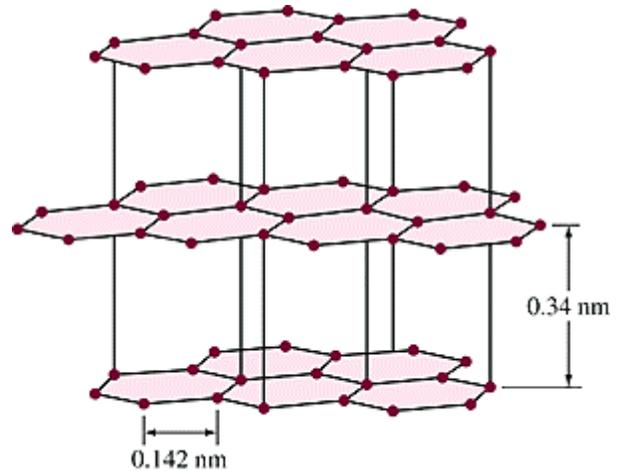
$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.22 \times 10^{-22} \text{ g}}{(4.12 \times 10^{-8} \text{ cm})^3} = \mathbf{6.03 \text{ g/cm}^3}$$

10.28 What is the spinel crystal structure?

The spinel structure has the general form AB_2O_4 where A represents a metal ion with a +2 valence and B is a metal cation with a +3 valence. The oxygen ions form an FCC lattice in which the A and B ions occupy the octahedral and tetrahedral interstitial sites.

10.29 Draw a section of the graphite structure. Why are the layers of graphite able to slide past each other easily.

The layers of graphite within the graphite structure can easily slide past each other because the bonds between the layers are weak secondary bonds, as compared to the strong covalent bonds between the carbon atoms constituting the layers.



10.30 Describe and illustrate the following silicate structures: (a) island, (b) chain, and (c) sheet.

- (a) Island silicate structures are formed when positive ions, such as Mg^{2+} and Fe^{2+} bond with oxygen anions of the SiO_4^{4-} tetrahedra.
- (b) Chain or ring structures are produced when two corners of each SiO_4^{4-} tetrahedron bond with the corners of two other tetrahedra. The result is the SiO_3^{2-} structure.
- (c) Sheet silicate structures form when three corners in the same plane of a silicate tetrahedron are bonded to the corners of three other silicate tetrahedra. The unit chemical formula of this structure is $\text{Si}_2\text{O}_5^{2-}$.

10.31 Describe the structure of a sheet of kaolinite.

A sheet of kaolinite consists of a negatively charged silicate sheet ($\text{Si}_2\text{O}_5^{2-}$) bonded to a positively charged sheet of $\text{Al}_2(\text{OH})_4^{2+}$. This composite sheet is comprised of small, flat hexagonal plates of parallel sheets bonded by weak secondary bonds.

10.32 Describe the bonding arrangement in the cristobalite (silica) network structure.

In the cristobalite silica structure, each silicon atom is bonded to four oxygen atoms and each oxygen atom forms part of two SiO_4^{4-} tetrahedra. The resulting network structure is a common crystalline phase of silica which exists at high temperatures of 1470 to 1710°C.

10.33 Describe the feldspar network structure.

In the feldspar silicate structural network, some of the Si^{4+} ions are replaced by Al^{3+} ions. The resulting negatively charged network is balanced by large cations of the alkali and alkaline earth elements, such as Na^+ , K^+ , and Ca^{2+} , which fit into the interstitial sites.

10.34 What are the basic steps in the processing of ceramic products by the agglomeration of particles?

The basic steps in the processing of ceramic products by the agglomeration are:

1. material preparation
2. forming or casting
3. thermal treatment by drying and firing to a high enough temperature for the particles to bond.

10.35 What types of ingredients are added to ceramic particles in preparing ceramic raw materials for processing?

Binders, lubricants and other additives are added to ceramic particles to achieve the desired set of ceramic properties.

10.36 Describe two methods for preparing ceramic raw materials for processing.

Ceramic raw materials are prepared by wet processing, dry processing or a combination of wet and dry processing. In wet processing, the additives are blended with water while in dry processing, the additives are ground dry with the raw materials.

10.37 Describe the dry-pressing method for producing such ceramic compounds as technical ceramic compounds and structural refractories. What are the advantages of dry-pressing ceramic materials?

In dry pressing, granular ceramic powder, in solution with small amounts of water and/or organic binder, is simultaneously compacted and shaped in a die. Subsequently, the parts are typically fired to achieve the desired microstructural properties such as strength. The advantages of dry-pressing ceramic materials are the ability to rapidly form a wide variety of shapes and the capability to achieve uniformity and close tolerances.

10.38 Describe the isostatic-pressing method for producing ceramic products.

In the isostatic process, the ceramic powder is loaded into a flexible airtight container that is inside a chamber of hydraulic fluid. Pressure is then applied to the fluid to compact the powder uniformly. The product, which possesses the shape of the container, is fired to attain the required microstructure and properties.

10.39 Describe the four stages in the manufacture of a spark plug insulator.

In manufacturing a spark plug insulator, four stages are completed: isostatic pressing, turning the blank, firing to fuse the powder, and glazing.

10.40 What are the advantages of hot-pressing ceramics materials?

The advantages of hot-pressing ceramics materials are producing improved mechanical properties and achieving high densities.

10.41 Describe the steps in the slip-casting process for ceramic products.

In the slip-casting process, five steps must be completed:

1. A powdered ceramic material and a liquid are prepared as a stable suspension called a slip.
2. The slip is poured into a porous mold which absorbs some of the slip liquid. The remaining slip forms a semihard layer on the mold surface.
3. For a drain casting process, excess slip is poured out of the cavity once a sufficient wall thickness has formed. For a solid casting process, casting is continued until the entire mold cavity is filled.
4. The material in the mold is allowed to dry to provide adequate strength for handling and the subsequent removal of the part from the mold.
5. Finally, the cast part is fired to attain the required microstructure and properties.

10.42 What is the difference between (a) drain and (b) solid slip casting?

Refer to step (3) in the solution to Problem 10.41.

10.43 What are the advantages of slip casting?

Advantages of slip casting include the ability to form parts with thin-walls and complex shapes and the low cost associated with creating developmental parts and short production runs.

- 10.44 What types of ceramic products are produced by extrusion? What are the advantages of this process? Limitations?

Extrusion is used to produce ceramic products which have a uniform cross-section (bricks and tiles) and which are hollow (sewer pipes). The advantages associated with this process include the ability to efficiently form a single long shape which is subsequently cut to the desired lengths and the ability to achieve close tolerances. However, the extrusion process is limited by the need to produce a constant cross-section and by the need to cool the extruded part by air-blast or water cooling.

- 10.45 What are the purposes of drying ceramic products before firing?

Ceramics are dried before firing in order to remove water and organic binders.

- 10.46 What is the sintering process? What occurs to the ceramic particles during sintering?

The sintering process is a thermal treatment which causes ceramic particles to bond together by solid-state diffusion. This diffusion process, driven by high temperatures, occurs between the contacting surfaces of the particles and allows them to chemically bond. As the process proceeds, the sintered particles increase in size until an equilibrium grain size is attained. The energy of the surfaces of these grain boundaries is lower than the surface energy associated with the original individual particles.

- 10.47 What is the vitrification process? In what type of ceramic materials does vitrification take place?

In the vitrification process, the glass phase of the ceramic liquefies and fills the material's pores during firing, and then solidifies during cooling to form a vitreous or glassy matrix that bonds the particles. This process takes place in ceramic materials containing a glass phase such as porcelain and structural clay.

- 10.48 What are the three basic components of traditional ceramics?

The three basic components of traditional ceramics are clay, silica (flint) and feldspar.

- 10.49 What is the approximate composition of kaolin clay?

The approximate composition of kaolin clay is 45.5 percent SiO_2 , 37.4 percent Al_2O_3 , 13.9 percent H_2O , 1.68 percent Fe_2O_3 , 1.30 percent TiO_2 , 0.03 percent MgO , 0.011 percent Na_2O , 0.004 percent CaO , and 0.005 percent K_2O .

- 10.50 What is the role of clay in traditional ceramics?

In traditional ceramics, clay constitutes the primary component of the ceramic and makes the material workable prior to firing.

10.51 What is flint? What role does it have in traditional ceramics?

Flint, also called quartz, is silica (SiO_2) and serves as the refractory component of traditional ceramics.

10.52 What is feldspar? What role does it have in traditional ceramics?

Feldspar is an aluminum silicate crystalline mineral containing potassium, sodium or calcium. Because feldspar turns into glass upon firing, it is often used in traditional ceramics to bond together the refractory components.

10.53 List some examples of whiteware ceramic products.

Examples of whiteware ceramic products are bone china, dental porcelain, electrical insulation ware, vitreous tile and vitreous sanitary ware.

10.54 Why is the term *triaxial* used to describe some whitewares?

The term triaxial refers to the fact that the whiteware is composed of three primary materials – clay, feldspar and flint.

10.55 Determine the composition of the ternary compound at point *y* in Fig. 10.32.

At point *y*, the ternary compound has the composition 27 percent leucite, 36 percent silica, and 37 percent mullite.

10.56 Why are triaxial porcelains not satisfactory for use at high frequencies?

Triaxial porcelains are not satisfactory insulators for high frequency applications because dielectric losses become too large.

10.57 What kinds of ions cause an increase in the conductivity of electrical porcelain?

Alkali ions cause an increase in the conductivity of electrical porcelain.

10.58 What is the composition of most technical ceramics?

Most technical ceramics are composed of pure compounds or nearly pure compounds of chiefly oxides, carbides and nitrides.

10.59 How are pure single-compound technical ceramic particles processed to produce a solid product? Give an example.

Technical ceramics are typically cold or hot-pressed and then subjected to a process, such as sintering or reaction bonding, so that bonding can occur. Examples of technical ceramic are silicon nitride, alumina, silicon carbide and zirconia.

- 10.60 What are three major applications for ceramic materials in the electrical-electronics industries?

Three major applications for ceramic materials in the electrical-electronics industries are electrical insulators, capacitors and semiconductors.

- 10.61 Define the terms *dielectric*, *capacitor*, and *capacitance*. What is the SI unit for capacitance? What units are commonly used for capacitance in the electronics industry?

A dielectric is an electrical insulator. A capacitor is a device that stores electrical charge while capacitance is a proportionality constant which quantifies the ratio of stored charge to applied voltage. The SI unit of capacitance is coulombs per volt (C/V) or the farad (F). In the electronics industry, the smaller units of picofarad and microfarad are typically used.

- 10.62 What is the dielectric constant of a dielectric material? What is the relationship among capacitance, dielectric constant, and the area and distance of separation between the plates of a capacitor?

The dielectric constant represents the ratio of the capacitances achieved when a capacitor's plates are separated by a dielectric as compared to a vacuum.

A capacitor's capacitance, dielectric constant, plate area, and plate separation distance are related as $C = \kappa\epsilon_0 A/d$.

- 10.63 What is the dielectric strength of a dielectric material? What units are used for dielectric strength? What is dielectric breakdown?

The dielectric strength is the maximum electric field that a dielectric material can maintain without experiencing an electrical breakdown. This type of breakdown, referred to as a dielectric breakdown, causes the passage of current to occur.

The units used to measure dielectric strength are volts per mil in the U.S. Customary System and kilovolts per millimeter in the SI system.

- 10.64 What is the dielectric loss angle and dielectric loss factor for a dielectric material? Why is a high dielectric loss factor undesirable?

The dielectric loss angle, δ , is the angle by which the current's lead of the voltage is reduced when a capacitor uses a real dielectric. An ideal or loss-free dielectric causes zero angular loss and the current leads the sinusoidal voltage by 90° .

The dielectric loss factor is a measure of the electric energy a capacitor dissipates as heat in an ac circuit.

- 10.65 A simple plate capacitor can store $7.0 \times 10^{-5} \text{ C}$ at a potential of 12,000 V. If a barium titanate dielectric material with $\kappa = 2100$ is used between the plates, which have an area of $5 \times 10^{-5} \text{ m}^2$, what must be the separation distance between the plates?

$$C = \frac{q}{V} = \frac{7.0 \times 10^{-5} \text{ C}}{12,000 \text{ V}} = 5.8\bar{3} \times 10^{-9} \text{ F}$$

$$d = \frac{A\epsilon_0\kappa}{C} = \frac{(5 \times 10^{-5} \text{ m}^2)(8.85 \times 10^{-12} \text{ F/m})(2100)}{5.8\bar{3} \times 10^{-9} \text{ F}} = 1.59 \times 10^{-4} \text{ m} = \mathbf{0.159 \text{ mm}}$$

- 10.66 A simple plate capacitor stores $6.5 \times 10^{-5} \text{ C}$ at a potential of 12,000 V. If the area of the plates is $3 \times 10^{-5} \text{ m}^2$ and the distance between the plates is 0.18 mm, what must be the dielectric constant of the material between the plates?

$$C = \frac{q}{V} = \frac{6.5 \times 10^{-5} \text{ C}}{12,000 \text{ V}} = 5.42 \times 10^{-9} \text{ F}$$

$$\kappa = \frac{Cd}{A\epsilon_0} = \frac{(5.42 \times 10^{-9} \text{ F})(1.8 \times 10^{-4} \text{ m})}{(3.0 \times 10^{-5} \text{ m}^2)(8.85 \times 10^{-12} \text{ F/m})} = \mathbf{3675}$$

- 10.67 What is the approximate composition of electrical porcelain? What is a major disadvantage of electrical porcelain as electrical insulative material?

Electrical porcelain has the approximate composition of 50 percent clay, 25 percent silica, and 25 percent feldspar.

A major disadvantage of electrical porcelain is that it has a high power-loss factor as compared to other electrical insulating materials.

- 10.68 What is the approximate composition of steatite? What desirable electrical properties does steatite have as an insulative material?

Steatite porcelains are composed of approximately 90 percent talc and 10 percent clay. As an electrical insulating material, steatites have the advantageous properties of low power-loss factors, low moisture absorption and good impact strength.

- 10.69 What is the composition of fosterite? Why is fosterite an excellent insulator material?

The chemical composition of fosterite is Mg_2SiO_4 . Fosterite is an excellent electrical insulator because it lacks alkali ions in a vitreous phase; consequently, it provides

higher resistivity and lower electrical losses with increasing temperature, as well as lower dielectric losses at high frequencies, than the steatite insulators.

10.70 Why is sintered alumina widely used as a substrate for electronic-device applications?

Sintered alumina is widely used as a substrate for electronic-device applications because of its low dielectric losses and smooth surface.

10.71 Why is BaTiO_3 used for high-value, small, flat-disk capacitors? How is the capacitance of BaTiO_3 capacitors varied? What are the four major stages in the manufacture of a flat-disk ceramic capacitor?

BaTiO_3 is used for high-value, small, flat-disk capacitors because its exceptionally high dielectric constant, 1200 to 1500, allows for very high capacitance. The capacitance of BaTiO_3 capacitors can be further increased through the addition of additives such as BaZrO_3 and CaTiO_3 .

The four major stages of flat-disk ceramic capacitors are: (1) firing the ceramic disk; (2) applying silver electrodes; (3) soldering leads; (4) applying dipped phenolic coating.

10.72 What is a thermistor? What is an NTC thermistor?

A thermistor is a thermally sensitive resistor which is made from a ceramic semiconductor and which is used for temperature measurement and control. An NTC or negative temperature coefficient thermistor is a thermistor whose resistance decreases with increasing temperature.

10.73 What materials are used to make NTC thermistors?

NTC thermistors are made from sintered oxides of Mn, Ni, Fe, Co, and Cu.

10.74 What is believed to be the mechanism for electrical conduction in Fe_3O_4 ?

In Fe_3O_4 , the mechanism responsible for electrical conduction is believed to be the random location of the Fe^{2+} and Fe^{3+} ions in the octahedral sites; the structure allows for electron transfer between the Fe^{2+} and Fe^{3+} ions while maintaining electrical neutrality of the compound.

10.75 How is the electrical conductivity of metal oxide semiconductors for thermistors changed?

The electrical conductivity of metal oxide semiconductors for thermistors can be varied in a controlled manner through solid solution addition of a metal oxide having a different conductivity but a similar structure.

- 10.76 What changes occurs in the unit cell of BaTiO_3 when it is cooled below 120°C ? What is this transformation temperature called?

When BaTiO_3 is cooled to 120°C , the central Ti^{4+} cation and the surrounding O^{2-} anions shift slightly in opposite directions and thereby create a small electric dipole moment. At the critical temperature of 120°C , the shifting is accompanied by a crystalline structural change from cubic to tetragonal. This transformation temperature is called the *Curie temperature*.

- 10.77 What are ferroelectric domains? How can they be lined toward one direction?

Ferroelectric domains are regions within a ferroelectric material in which the small electric dipoles of the unit cells are aligned in one direction. The orientation of domains can be lined in one direction by applying an electrical field as the material passes through its Curie temperature. For example, if a sample of BaTiO_3 is held at 120°C and an electric field is applied, the dipoles within individual domains will orient themselves toward the negative plate and produce a strong dipole moment per unit volume of the material.

- 10.78 Describe the piezoelectric effect for producing an electrical response with the application of pressure on a ferroelectric material. Do the same for producing a mechanical response by the application of an electrical force.

When compressive forces are applied across a sample of a ferroelectric material, the sample length is reduced, and consequently, the distance between dipoles is reduced. As a result, the overall dipole moment of the material is decreased, which in turn, changes the charge density at the sample ends and causes a voltage potential to develop.

Similarly, if an electrical field is applied across the sample, the resulting charge density alteration at the sample ends will cause dimensional changes in the direction of the applied field. The sample thus produces the mechanical response of physical elongation or shrinkage.

- 10.79 Describe several devices that utilize the piezoelectric effect.

Two examples of devices which convert mechanical forces into electrical responses are the piezoelectric compression accelerometer, which measures vibratory accelerations over a wide range of frequencies, and the phonograph cartridge, which detects electrical responses via a stylus vibrating in the record grooves. Examples of devices which convert electrical responses into mechanical output include the ultrasonic cleaning transducer, which agitates liquid via vibrations induced by ac power, and the underwater sound transducer, which transmits sound waves through transducer vibrations stimulated by the application of voltage.

- 10.80 What are the PZT piezoelectric materials? In what ways are they superior to BaTiO_3 piezoelectric materials?

The PZT piezoelectric materials are ceramics made from solid solutions of lead zirconate (PbZrO_3) and lead titanate (PbTiO_3). The PZT ceramics have a broader range of piezoelectric properties, including a higher Curie temperature, than BaTiO_3 .

- 10.81 What causes the lack of plasticity in crystalline ceramics?

The lack of plasticity in crystalline ceramics is attributed to their ionic and covalent chemical bonds. In covalent crystals and covalently bonded ceramics, atoms bond through the exchange of electron charge between pairs of electrons, in a specific and directional manner. Consequently, if the ceramic is sufficiently stressed, electron-pair bonds undergo irreparable separation, causing the material to experience brittle fracture.

- 10.82 Explain the plastic deformation mechanism for some single-crystal ionic solids such as NaCl and MgO . What is the preferred slip system?

For some single-crystal ionic solids, such as NaCl and MgO , compressive stresses at room temperature cause considerable plastic deformation prior to fracture because planes of oppositely charged ions can slip relative to each other. These slip planes, which maintain their attraction through coulombic forces, typically prefer the $\{110\}\langle 110\rangle$ slip system for NaCl -type structures.

- 10.83 What structural defects are the main cause of failure of polycrystalline ceramic materials?

Brittle fracture of polycrystalline ceramics is principally caused by one of four structural defects: cracks produced during surface finishing; voids; inclusions; and large grains produced during processing.

- 10.84 How do (a) porosity and (b) grain size affect the tensile strength of ceramic materials?

(a) Pores serve as a source for stress induced crack initiation/propagation and reduce the cross-sectional area available for load application. Consequently, as the porosity of a ceramic material increases, the material tensile strength decreases.

(b) For a porosity-free ceramic, the flaw size, and thus the strength, is solely a function of grain size; the finer the grain size, the smaller the flaws at grain boundaries and the greater the ceramic tensile strength.

- 10.85 A reaction-bonded silicon nitride ceramic has a strength of 250 MPa and a fracture toughness of $3.4 \text{ MPa} \cdot \sqrt{\text{m}}$. What is the largest-sized internal flaw that this material can support without fracturing? (Use $Y = 1$ in the fracture-toughness equation.)

$$a = \frac{1}{\pi} \left(\frac{K_{IC}}{Y\sigma_f} \right)^2 = \frac{1}{\pi} \left[\frac{3.4 \text{ MPa}\sqrt{\text{m}}}{(1)(250 \text{ MPa})} \right]^2 = 5.89 \times 10^{-5} \text{ m} = 58.9 \text{ }\mu\text{m}$$

Thus the largest internal flaw is $2a = 2(58.9 \text{ }\mu\text{m}) = \mathbf{117.8 \text{ }\mu\text{m}}$.

- 10.86 The maximum-sized internal flaw in a hot-pressed silicon carbide ceramic is $25 \text{ }\mu\text{m}$. If this material has a fracture toughness of $3.7 \text{ MPa}\sqrt{\text{m}}$, what is the maximum stress that this material can support? (Use $Y = \sqrt{\pi}$.)

$$\sigma_f = \frac{1}{\sqrt{\pi a}} \left(\frac{K_{IC}}{Y} \right) = \frac{1}{\sqrt{\pi(2.5 \times 10^{-5} \text{ m})}} \left(\frac{3.7 \text{ MPa}\sqrt{\text{m}}}{\sqrt{\pi}} \right) = \mathbf{236 \text{ MPa}}$$

- 10.87 A partially stabilized zirconia advanced ceramic has a strength of 352 MPa and a fracture toughness of $7.5 \text{ MPa}\sqrt{\text{m}}$. What is the largest-sized internal flaw (expressed in micrometers) that this material can support? (Use $Y = \sqrt{\pi}$.)

$$a = \frac{1}{\pi} \left(\frac{K_{IC}}{Y\sigma_f} \right)^2 = \frac{1}{\pi} \left[\frac{7.5 \text{ MPa}\sqrt{\text{m}}}{\sqrt{\pi}(352 \text{ MPa})} \right]^2 = \left[\frac{7.5 \text{ MPa}\sqrt{\text{m}}}{\pi(352 \text{ MPa})} \right]^2 = 4.60 \times 10^{-5} \text{ m} = 46.0 \text{ }\mu\text{m}$$

Thus the largest internal flaw is $2a = 2(46.0 \text{ }\mu\text{m}) = \mathbf{92.0 \text{ }\mu\text{m}}$.

- 10.88 A fully stabilized, cubic polycrystalline ZrO_2 sample has a fracture toughness of $K_{IC} = 3.8 \text{ MPa}\sqrt{\text{m}}$ when tested on a four-point bend test.
- (a) If the sample fails at a stress of 450 MPa , what is the size of the largest surface flaw? Assume $Y = \sqrt{\pi}$.
- (b) The same test is performed with a partially stabilized ZrO_2 specimen. This material is transformation-toughened and has a $K_{IC} = 12.5 \text{ MPa}\sqrt{\text{m}}$. If this material has the same flaw distribution as the fully stabilized sample, what stress must be applied to cause failure?

- (a) The largest edge or surface crack is equal to a :

$$a = \frac{1}{\pi} \left(\frac{K_{IC}}{Y\sigma_f} \right)^2 = \left[\frac{3.8 \text{ MPa}\sqrt{\text{m}}}{\pi(450 \text{ MPa})} \right]^2 = 7.23 \times 10^{-6} \text{ m} = \mathbf{7.23 \text{ }\mu\text{m}}$$

- (b) The stress which will cause failure is:

$$\sigma_f = \frac{1}{\sqrt{\pi a}} \left(\frac{K_{IC}}{\sqrt{\pi}} \right) = \frac{1}{\pi} \left(\frac{12.5 \text{ MPa}\sqrt{\text{m}}}{\sqrt{7.23 \times 10^{-6} \text{ m}}} \right) = \mathbf{1480 \text{ MPa}}$$

10.89 What are the two most important industrial abrasives?

The two most important industrial abrasives are fused alumina (Al_2O_3) and silicon carbide (SiC).

10.90 What are important properties for industrial abrasives?

Properties important to industrial abrasives include: porosity sufficient to allow air or liquid lubricant flow during grinding, cutting and polishing processes; good heat stability for withstanding high frictional heat generation; and high hardness for grinding and cutting processes.

10.91 Why do most ceramic materials have low thermal conductivities?

Most ceramic materials have low thermal conductivities because of their strong ionic-covalent bonding which restricts the motion of electrons required for both thermal and electrical conduction. Pure metals are excellent electron carriers and thus serve as important conductors of heat and electricity.

10.92 What are refractories? What are some of their applications?

Refractories are materials that have good heat resistance. They are used extensively by the metals, chemical, ceramic and glass industries for applications such as linings for various types of furnaces, kilns, ovens, incinerators and reactors.

10.93 What are the two main types of ceramic refractory materials?

The two main types of ceramic refractory materials are acidic refractories and basic refractories.

10.94 Give the composition and several applications for the following refractories:

(a) silica, (b) fireclay, and (c) high-alumina.

(a) Silica refractories contain 95 to 99 percent SiO_2 and are used for chemical reactor linings, glass tank parts, ceramic kilns and coke ovens.

(b) Fireclays are mixtures of plastic fireclay, flint (silica) clay, and clay grog which give a combined composition of approximately 51 to 54 percent SiO_2 and 37 to 42 percent Al_2O_3 . Their refractory applications include linings for cement, rotary, and lime kilns, linings for aluminum-melting and blast furnaces, and linings for incinerators.

(c) High-alumina refractories are composed of 45 to 99⁺ percent Al_2O_3 and 0 to 50 percent SiO_2 . These materials are used in boiler, phosphate, carbon black and spent-acid furnaces, coke kilns, glass-tank refiner walls, continuous-casting tundish linings, and coal gasification reactor linings.

- 10.95 What do most basic refractories consist of? What are some important properties of basic refractories? What is a main application for these materials?

Most basic refractories consist of magnesia (MgO), lime (CaO), and chrome ore (Cr₂O₃). Some of the important properties associated with these materials are high bulk densities, high melting temperatures, and good resistance to chemical corrosion by basic slags and oxides. Consequently, these refractories are used mainly for the linings of basic-oxygen steelmaking furnaces.

- 10.96 What is the high-temperature reusable-surface insulation that can withstand temperatures as high as 1260°C made of?

High-temperature reusable surface insulation (HRSI) is made of a silica-fiber compound and can withstand 1260°C (2300°F).

- 10.97 Define a glass.

While glass is a ceramic material – made from inorganic materials at high temperatures– it differs from other ceramics in that its constituents are heated to fusion and then cooled in the rigid state without crystallization. Thus glass is formally defined as *an organic product of fusion that has cooled to a rigid condition without crystallization*.

- 10.98 What are some of the properties of glasses that make them indispensable for many engineering designs?

Glasses are indispensable to many engineering designs because they possess a unique combination of special properties – transparency, hardness and sufficient strength at room temperature, and excellent corrosion resistance to most environments.

- 10.99 How is a glass distinguished from other ceramic materials?

Unlike all other ceramic materials, glass constituents are heated to fusion and then cooled in the rigid state without crystallization. As a consequence, glass has an amorphous structure rather than crystalline.

- 10.100 How does the specific volume versus temperature plot for a glass differ from that for a crystalline material when these materials are cooled from the liquid state?

The plot of specific volume versus temperature for a glass differs from that of a crystalline material in two ways. First, the glass does not experience a rapid decrease in specific volume at a temperature associated with a melting point; the glass cooling curve conveys a gradual decrease in specific volume throughout the cooling range. Second, the glass curve contains a marked decrease in slope at a glass transition temperature which other ceramics do not possess.

10.101 Define the glass transition temperature.

The glass transition temperature, T_g , is the temperature at which the two slopes of a glass specific volume versus temperature curve intersect. Physically, this temperature falls within the narrow temperature range in which a glass changes from a rubbery, soft plastic state to a rigid, brittle glassy state. Thus, the T_g represents the point at which the material behaves more like a solid than a liquid.

10.102 Name two glass-forming oxides. What are their fundamental subunits and their shape?

Silica (SiO_2) and boron oxide (B_2O_3) are two glass-forming oxides. Their fundamental subunits are respectively, the SiO_4^{4-} tetrahedron and the BO_3^{3-} flat triangle.

10.103 How does the silica network of a simple silica glass differ from crystalline (cristobalite) silica?

In a simple glass, the tetrahedra are joined corner to corner, forming a loose network. In contrast, a crystalline material, such as cristobalite, has Si-O tetrahedra joined corner to corner in a regular arrangement, producing a network having a long-range order.

10.104 How is it possible for BO_3^{3-} triangles to be converted to BO_4^{4-} tetrahedral and still maintain neutrality in some borosilicate glasses?

BO_3^{3-} triangles can be converted to BO_4^{4-} tetrahedra by adding alkali and alkaline earth oxides whose cations provide the necessary electroneutrality.

10.105 What are glass network modifiers? How do they affect the silica-glass network? Why are they added to silica glass?

Glass network modifiers are oxides that break up the glass network. Examples include Na_2O , K_2O , CaO , and MgO . These oxides affect the silica glass network by breaking the network at the tetrahedra points. As a result, the tetrahedra have oxygen atoms with an unshared electron while the oxide's metal cations remain as ions ionically bonded in the network interstices. Glass modifiers are added to silica glass to facilitate forming and working the glass by lowering its viscosity.

10.106 What are glass intermediate oxides? How do they affect the silica-glass network? Why are they added to silica glass?

Glass intermediate oxides are oxides that cannot form a glass network by themselves but can join an existing one. These oxides may act as modifiers of the structure as well as become a part of the network chain. In the latter case, they sometimes leave the network deficient in electrons and alkali cations must be added for electrical neutrality. The intermediate oxides are added to glass to obtain special properties. For example,

large amounts (60 percent) of lead oxide can be added to produce an ornamental glass of great brilliance.

10.107 What is fused silica glass? What are some of its advantages and disadvantages?

Fused silica glass is composed of 99.5 percent SiO_2 and is the most important single-component glass. Its advantageous properties include a high spectral transmission and the ability to withstand radiation without browning. However, it is expensive and difficult to melt and fabricate.

10.108 What is the basic composition of soda-lime glass? What are some of its advantages and disadvantages? What are some applications for soda-lime glass?

Soda-lime glass has a basic composition of 71 to 73 percent SiO_2 , 12 to 14 percent Na_2O , and 10 to 12 percent CaO . Advantages of soda-lime glass are its low cost and ease of forming due to a low softening point. Disadvantages include low heat resistance and chemical durability. Some of its applications are windows, containers, electric bulbs, and pressed and blown ware.

10.109 What is the purpose of (a) MgO and (b) Al_2O_3 additions to soda-lime glass?

(a) MgO is added to soda-lime glass in small quantities of 1 to 4 percent to prevent devitrification.

(b) Al_2O_3 is added in quantities of 0.5 to 1.5 percent to increase durability.

10.110 Define the following viscosity reference points for glasses: working, softening, annealing, and strain.

The *working point* is the temperature which corresponds to a viscosity of 10^4 poises and which represents the thermal state at which glass fabrication operations can be performed.

The *softening point* is the temperature which corresponds to a viscosity of 10^8 poises and which represents the thermal state at which glass will flow at an appreciable rate under its own weight.

The *annealing point* is the temperature which corresponds to a viscosity of 10^{13} poises and which represents the thermal state at which internal stresses can be relieved.

The *strain point* is the temperature which corresponds to a viscosity of $10^{14.5}$ poises and which represents the thermal state below which the glass is rigid and stress relaxation only occurs at a slow rate.

10.111 Distinguish between hard and soft glasses and long and short glasses.

A hard glass has a high softening point as compared to a soft glass. Long glasses have large temperature differences between their softening and strain points; they solidify more slowly than a short glass as the temperature decreases.

- 10.112 A soda-lime plate glass between 500°C (strain point) and 700°C (softening point) has viscosities between $10^{14.2}$ and $10^{7.5}$ P, respectively. Calculate a value for the activation energy in this temperature region.

First, convert the temperatures to absolute values:

$$\text{Strain point} = T_{stp} = 500^\circ\text{C} + 273 = 773 \text{ K}$$

$$\text{Softening point} = T_{sp} = 700^\circ\text{C} + 273 = 973 \text{ K}$$

Using Eq. 10.5, $\eta_{stp} = \eta_0 e^{Q/RT_{stp}}$ and $\eta_{sp} = \eta_0 e^{Q/RT_{sp}}$. Dividing these equations and substituting the temperature and viscosity data,

$$\frac{\eta_{stp}}{\eta_{sp}} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_{stp}} - \frac{1}{T_{sp}}\right)\right]$$

$$\frac{10^{14.2} \text{ P}}{10^{7.5} \text{ P}} = \exp\left[\frac{Q}{8.314 \text{ J/mol}\cdot\text{K}}\left(\frac{1}{723 \text{ K}} - \frac{1}{923 \text{ K}}\right)\right]$$

$$10^{6.7} = \exp\left[(3.605 \times 10^{-5})Q\right]$$

$$\ln 10^{6.7} = (3.605 \times 10^{-5})Q$$

$$Q = 4.28 \times 10^5 \text{ J/mol} = \mathbf{428 \text{ kJ/mol}}$$

- 10.113 A soda-lime glass has a viscosity of $10^{14.6}$ P at 560°C. What will be its viscosity at 675°C if the activation energy for viscous flow is 430 kJ/mol?

Let $\eta_1 = \eta_0 e^{Q/RT_1}$ and $\eta_2 = \eta_0 e^{Q/RT_2}$ where $T_1 = 833 \text{ K}$ and $T_2 = 948 \text{ K}$. Then,

$$\frac{\eta_1}{\eta_2} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\frac{10^{14.6} \text{ P}}{\eta_2} = \exp\left[\frac{430 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}}\left(\frac{1}{833 \text{ K}} - \frac{1}{948 \text{ K}}\right)\right]$$

$$\frac{10^{14.6} \text{ P}}{\eta_2} = \exp(7.532) = 1866.6$$

$$\eta_2 = 2.133 \times 10^{11} \text{ P} = \mathbf{10^{11.329} \text{ P} \approx 10^{11.33} \text{ P}}$$

- 10.114 A soda-lime glass has a viscosity of $10^{14.3}$ P at 570°C . At what temperature will its viscosity be $10^{9.9}$ P if the activation energy for the process is 430 kJ/mol?

Let $\eta_1 = \eta_0 e^{Q/RT_1}$ and $\eta_2 = \eta_0 e^{Q/RT_2}$ where $T_1 = 843$ K. Then,

$$\frac{\eta_1}{\eta_2} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\frac{10^{14.3} \text{ P}}{10^{9.9} \text{ P}} = \exp\left[\frac{430 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}}\left(\frac{1}{843 \text{ K}} - \frac{1}{T_2}\right)\right]$$

$$\ln 10^{4.4} = \left[51,720\left(\frac{1}{843 \text{ K}} - \frac{1}{T_2}\right)\right]$$

$$T_2 = (0.0011862 - 0.0001959)^{-1} = \mathbf{1009.7 \text{ K} = 736.7^\circ\text{C}}$$

- 10.115 A borosilicate glass between 600°C (annealing point) and 800°C (softening point) has viscosities of $10^{12.5}$ P and $10^{7.4}$ P, respectively. Calculate a value for the activation energy for viscous flow in this region, assuming the equation $\eta = \eta_0 e^{Q/RT}$ is valid.

$$\frac{\eta_{ap}}{\eta_{sp}} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_{ap}} - \frac{1}{T_{sp}}\right)\right]$$

$$\frac{10^{12.5} \text{ P}}{10^{7.4} \text{ P}} = \exp\left[\frac{Q}{8.314 \text{ J/mol} \cdot \text{K}}\left(\frac{1}{873 \text{ K}} - \frac{1}{1073 \text{ K}}\right)\right]$$

$$10^{5.1} = \exp\left[(2.568 \times 10^{-5})Q\right]$$

$$\ln 10^{5.1} = (2.568 \times 10^{-5})Q$$

$$Q = 4.573 \times 10^5 \text{ J/mol} = \mathbf{457.3 \text{ kJ/mol}}$$

- 10.116 Describe the float-glass process for the production of flat-glass products. What is its major advantage?

In the float-glass process, a ribbon of glass flows out of a melting furnace and into a molten tin bath on which it floats. As the ribbon moves across the bath, it cools under a chemically controlled atmosphere to prevent oxidation. Once the glass surfaces are sufficiently hard, the sheet is removed from the float chamber and passed through alehr annealing furnace which removes residual stresses. The major advantage of this process over its predecessor, the rolling process, is that a very flat sheet of glass is produced which does not require costly grinding or polishing.

- 10.117 What is tempered glass? How is it produced? Why is tempered glass considerably stronger in tension than annealed glass? What are some applications for tempered glass?

Tempered glass is a high strength glass due to the compressive stresses developed on its surface during “tempering”. It is produced by heating the glass close to its softening temperature and then rapidly cooling the glass surface with air. Because the surfaces are rigid during the cooling of the glass interior, tensile stresses are developed in the interior while compressive stresses form at the surface. Tempered glass is stronger in tension than annealed glass because with tempered glass, the applied tensile stress must surpass the surface compressive stress before causing fracture. This glass is used in applications where safety is paramount, such as automobile windows and safety glass doors.

- 10.118 What is chemically strengthened glass? Why is chemically strengthened glass stronger in tension than annealed glass?

Chemically strengthened glass is a glass that has been given a chemical treatment to introduce large ions, and thus compressive stresses, into the glass surface. Like tempered glass, chemically strengthened glass is stronger in tension than annealed glass due to its residual surface stresses.