CHAPTER 12

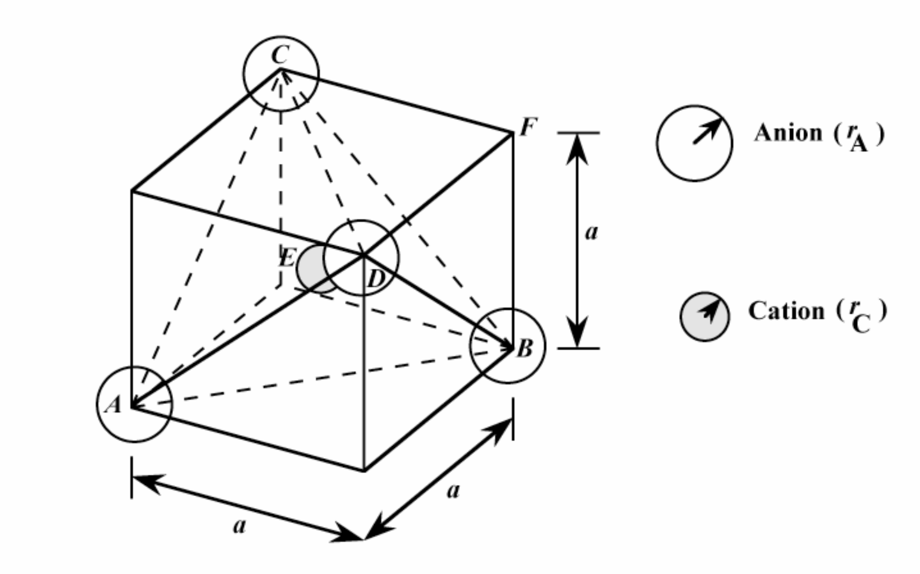
STRUCTURES AND PROPERTIES OF CERAMICS

PROBLEM SOLUTIONS

Crystal Structures

12.1 The two characteristics of component ions that determine the crystal structure of a ceramic compound are: 1) the magnitude of the electrical charge on each ion, and 2) the relative sizes of the cations and anions.

12.2 In this problem we are asked to show that the minimum cation-to-anion radius ratio for a coordination number of four is 0.225. If lines are drawn from the centers of the anions, then a tetrahedron is formed. The tetrahedron may be inscribed within a cube as shown below.



The spheres at the apexes of the tetrahedron are drawn at the corners of the cube, and designated as positions *A*, *B*, *C*, and *D*. (These are reduced in size for the sake of clarity.) The cation resides at the center of the cube, which is designated as point *E*. Let us now express the cation and anion radii in terms of the cube edge length, designated as *a*. The spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2r_{\mathrm{A}}$$

But

$$(\overline{AB})^2 = a^2 + a^2 = 2a^2$$

or

$$\overline{AB} = a\sqrt{2} = 2r_{\mathrm{A}}$$

And

$$a = \frac{2r_{\mathrm{A}}}{\sqrt{2}}$$

There will also be an anion located at the corner, point F (not drawn), and the cube diagonal $\overline{AEF}$ will be related to the ionic radii as

$$\overline{AEF} = 2(r_A + r_C)$$

(The line AEF has not been drawn to avoid confusion.) From the triangle ABF

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2$$

But,

$$\overline{FB} = a = \frac{2r_A}{\sqrt{2}}$$

and

$$\overline{AB} = 2r_A$$

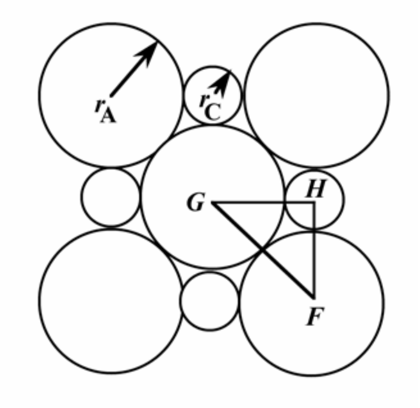
from above. Thus,

$$(2r_A)^2 + \left(\frac{2r_A}{\sqrt{2}}\right)^2 = \left[2(r_A + r_C)\right]^2$$

Solving for the r_C/r_A ratio leads to

$$\frac{r_C}{r_A} = \frac{\sqrt{6} - 2}{2} = 0.225$$

12.3 This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414 (using the rock salt crystal structure). Below is shown one of the faces of the rock salt crystal structure in which anions and cations just touch along the edges, and also the face diagonals.



From triangle *FGH*,

$$\overline{GF} = 2r_A$$

and

$$\overline{FH} = \overline{GH} = r_A + r_C$$

Since *FGH* is a right triangle

$$(\overline{GH})^2 + (\overline{FH})^2 = (\overline{FG})^2$$

or

$$(r_A + r_C)^2 + (r_A + r_C)^2 = (2r_A)^2$$

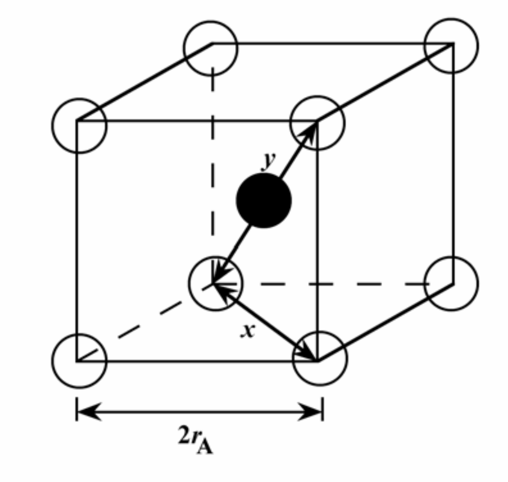
which leads to

$$r_A + r_C = \frac{2r_A}{\sqrt{2}}$$

Or, solving for r_C/r_A

$$\frac{r_C}{r_A} = \left(\frac{2}{\sqrt{2}} - 1\right) = 0.414$$

12.4 This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732. From the cubic unit cell shown below



the unit cell edge length is 2r_A, and from the base of the unit cell

$$x^2 = (2r_A)^2 + (2r_A)^2 = 8r_A^2$$

Or

$$x = 2r_A\sqrt{2}$$

Now from the triangle that involves *x*, *y*, and the unit cell edge

$$x^2 + (2r_A)^2 = y^2 = (2r_A + 2r_C)^2$$

$$(2r_A\sqrt{2})^2 + 4r_A^2 = (2r_A + 2r_C)^2$$

Which reduces to

$$2r_A(\sqrt{3} - 1) = 2r_C$$

Or

$$\frac{r_C}{r_A} = \sqrt{3} - 1 = 0.732$$

12.5 This problem calls for us to predict crystal structures for several ceramic materials on the basis of ionic charge and ionic radii.

(a) For CaO, using data from Table 12.3

$$\frac{r_{\text{Ca}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.100 \text{ nm}}{0.140 \text{ nm}} = 0.714$$

Now, from Table 12.2, the coordination number for each cation (Ca^{2+}) is six, and, using Table 12.4, the predicted crystal structure is sodium chloride.

(b) For MnS, using data from Table 12.3

$$\frac{r_{\text{Mn}^{2+}}}{r_{\text{S}^{2-}}} = \frac{0.067 \text{ nm}}{0.184 \text{ nm}} = 0.364$$

The coordination number is four (Table 12.2), and the predicted crystal structure is zinc blende (Table 12.4).

(c) For KBr, using data from Table 12.3

$$\frac{r_{\text{K}^{+}}}{r_{\text{Br}^{-}}} = \frac{0.138 \text{ nm}}{0.196 \text{ nm}} = 0.704$$

The coordination number is six (Table 12.2), and the predicted crystal structure is sodium chloride (Table 12.4).

(d) For CsBr, using data from Table 12.3

$$\frac{r_{\text{Cs}^{+}}}{r_{\text{Br}^{-}}} = \frac{0.170 \text{ nm}}{0.196 \text{ nm}} = 0.867$$

The coordination number is eight (Table 12.2), and the predicted crystal structure is cesium chloride (Table 12.4).

12.6 We are asked to cite the cations in Table 12.3 which would form fluorides having the cesium chloride crystal structure. First of all, the possibilities would include only the monovalent cations Cs^+, K^+, and Na^+. Furthermore, the coordination number for each cation must be 8, which means that $0.732 < r_C/r_A < 1.0$ (Table 12.2). From Table 12.3 the r_C/r_A ratios for these three cations and the F^- ion are as follows:

$$\frac{r_{Cs^+}}{r_{F^-}} = \frac{0.170 \text{ nm}}{0.133 \text{ nm}} = 1.28$$

$$\frac{r_{K^+}}{r_{F^-}} = \frac{0.138 \text{ nm}}{0.133 \text{ nm}} = 1.04$$

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{0.102 \text{ nm}}{0.133 \text{ nm}} = 0.77$$

Thus, only sodium will form the CsCl crystal structure with fluorine.

12.7 This problem asks that we compute the atomic packing factor for the rock salt crystal structure when $r_C/r_A = 0.414$. From Equation 3.2

$$\text{APF} = \frac{V_S}{V_C}$$

With regard to the sphere volume, V_S, there are four cation and four anion spheres per unit cell. Thus,

$$V_S = (4)\left(\frac{4}{3}\pi r_A^3\right) + (4)\left(\frac{4}{3}\pi r_C^3\right)$$

But, since $r_C/r_A = 0.414$

$$V_S = \frac{16}{3}\pi r_A^3\left[1 + (0.414)^3\right] = (17.94)\ r_A^3$$

Now, for $r_C/r_A = 0.414$ the corner anions in Table 12.2 just touch one another along the cubic unit cell edges such that

$$V_C = a^3 = \left[2\left(r_A + r_C\right)\right]^3$$

$$= \left[2\left(r_A + 0.414 r_A\right)\right]^3 = (22.62) r_A^3$$

Thus

$$\text{APF} = \frac{V_S}{V_C} = \frac{(17.94)\ r_A^3}{(22.62)\ r_A^3} = 0.79$$

12.8 This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions.

(a) The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 12.4).

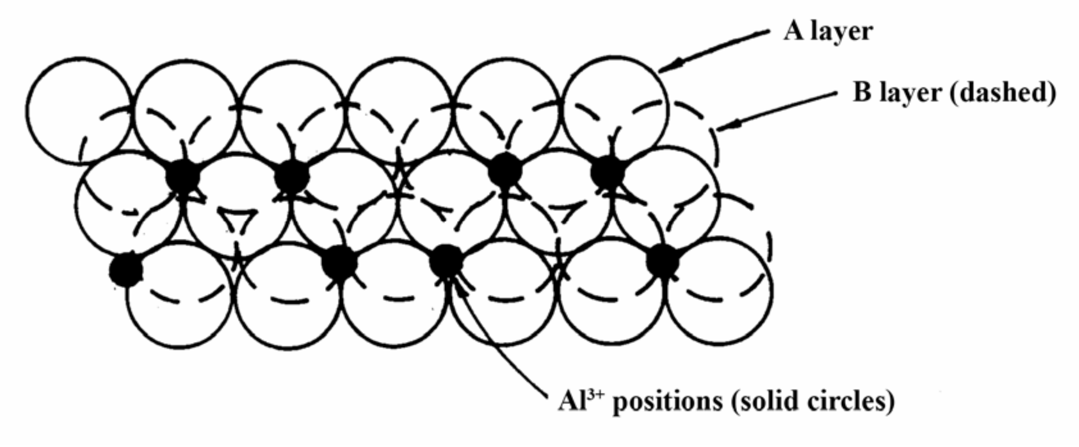
(b) The cations will fill tetrahedral positions since the coordination number for cations is four (Table 12.4).

(c) Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

12.9 This question is concerned with the corundum crystal structure in terms of close-packed planes of anions.

(a) For this crystal structure, two-thirds of the octahedral positions will be filled with Al^{3+} ions since there is one octahedral site per O^{2-} ion, and the ratio of Al^{3+} to O^{2-} ions is two-to-three.

(b) Two close-packed O^{2-} planes and the octahedral positions between these planes that will be filled with Al^{3+} ions are sketched below.



12.10 (a) This portion of the problem asks that we specify which type of interstitial site the Be^{2+} ions will occupy in BeO if the ionic radius of Be^{2+} is 0.035 nm and the O^{2-} ions form an HCP arrangement. Since, from Table 12.3, $r_{O^{2-}} = 0.140$ nm, then

$$\frac{r_{Be^{2+}}}{r_{O^{2-}}} = \frac{0.035\ \text{nm}}{0.140\ \text{nm}} = 0.250$$

Inasmuch as r_C/r_A is between 0.225 and 0.414, the coordination number for Be^{2+} is 4 (Table 12.2); therefore, tetrahedral interstitial positions are occupied.

(b) We are now asked what fraction of these available interstitial sites are occupied by Be^{2+} ions. Since there are two tetrahedral sites per O^{2-} ion, and the ratio of Be^{2+} to O^{2-} is 1:1, one-half of these sites are occupied with Be^{2+} ions.

12.11 (a) We are first of all asked to cite, for $FeTiO_3$, which type of interstitial site the Fe^{2+} ions will occupy. From Table 12.3, the cation-anion radius ratio is

$$\frac{r_{Fe^{2+}}}{r_{O^{2-}}} = \frac{0.077 \text{ nm}}{0.140 \text{ nm}} = 0.550$$

Since this ratio is between 0.414 and 0.732, the Fe^{2+} ions will occupy octahedral sites (Table 12.2).

(b) Similarly, for the Ti^{4+} ions

$$\frac{r_{Ti^{4+}}}{r_{O^{2-}}} = \frac{0.061 \text{ nm}}{0.140 \text{ nm}} = 0.436$$

Since this ratio is between 0.414 and 0.732, the Ti^{4+} ions will also occupy octahedral sites.

(c) Since both Fe^{2+} and Ti^{4+} ions occupy octahedral sites, no tetrahedral sites will be occupied.

(d) For every $FeTiO_3$ formula unit, there are three O^{2-} ions, and, therefore, three octahedral sites; since there is one ion each of Fe^{2+} and Ti^{4+}, two-thirds of these octahedral sites will be occupied.

12.12 First of all, open the “Molecular Definition Utility”; it may be found in either of “Metallic Crystal Structures and Crystallography” or “Ceramic Crystal Structures” modules.

In the “Step 1” window, it is necessary to define the atom types, colors for the spheres (atoms/ions), and specify atom/ion sizes. Let us enter “Pb” as the name for the lead ions (since “Pb” the symbol for lead), and “O” as the name for the oxygen ions. Next it is necessary to choose a color for each ion type from the selections that appear in the pull-down menu—for example, “LtBlue” (light blue) for Pb and LtRed (light red) for O. In the “Atom Size” window, it is necessary to enter an atom/ion size. In the instructions for this step, it is suggested that the atom/ion diameter in nanometers be used. From the table found inside the front cover of the textbook, the ionic radii for lead and oxygen are 0.120 nm and 0.140 nm, respectively, and, therefore, their ionic diameters are twice these values (i.e., 0.240 nm and 0.280 nm); therefore, we enter the values “0.240” and “0.280” for the two atom types. Now click on the “Register” button, followed by clicking on the “Go to Step 2” button.

In the “Step 2” window we specify positions for all of the ions within the unit cell; their point coordinates are specified in the problem statement. Now we must enter a name in the box provided for each of the ions in the unit cell. For example, for oxygen let us name the first ion “O1”. Its point coordinates are 000, and, therefore, we enter a “0” (zero) in each of the “x”, “y”, and “z” atom position boxes. Next, in the “Atom Type” pull-down menu we select “O”, the name we specified in Step 1. For the next oxygen ion, which has point coordinates of 100, let us name it “O2”; since it is located a distance of *a* units along the *x*-axis the value of “0.397” is entered in the “x” atom position box (since this is the value of *a* given in the problem statement); zeros are entered in each of the “y” and “z” position boxes. We next click on the “Register” button. This same procedure is repeated for all 10 the point coordinates for the oxygen ions, as well as the four coordinates for lead ions; these values are specified in the problem statement. For the oxygen ion having point coordinates of “111” respective values of “0.397”, “0.397”, and “0.502” are entered in the x, y, and z atom position boxes, since the unit cell edge length along the *y* and *z* axes are *a* (0.397) and *c* (0.502 nm), respectively. For fractional point coordinates, the appropriate *a* or *c* value is multiplied by the fraction. For example, for oxygen ions, the last point coordinate set in the left-hand column, $\frac{1}{2}\frac{1}{2}0$, the x, y, and z atom positions are $\frac{1}{2}(0.397) = 0.1985$, $\frac{1}{2}(0.397) = 0.1985$, and 0, respectively. The x, y, and z position entries for the 10 sets of point coordinates for the oxygen ions are as follows:

0, 0, and 0	0, 0, and 0.502
0.397, 0, and 0	0.397, 0, and 0.502
0, 0.397, and 0	0, 0.397, and 0.502
0.397, 0.397, and 0	0.397, 0.397, and 0.502
0.1985, 0.1985, and 0	0.1985, 0.1985, and 0.502

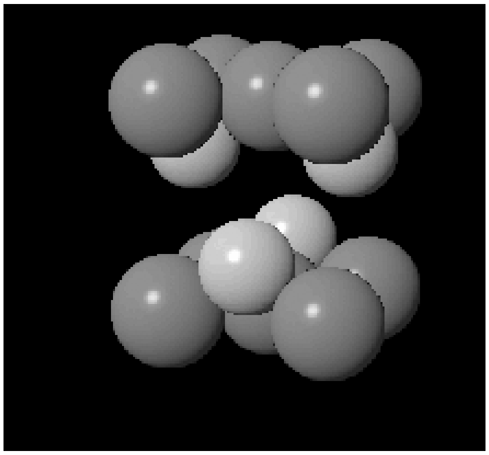
Likewise, for the lead ions, x, y, and z position entries for the four sets of points coordinates are the following:

0.1985, 0, and 0.383	0, 0.1985, and 0.1190
0.1985, 0.397, and 0.383	0.397, 0.1985, and 0.1190

In Step 3, we may specify which atoms are to be represented as being bonded to one another, and which type of bond(s) to use (single solid, single dashed, double, and triple are possibilities), or we may elect to not represent any bonds at all (in which case we click on the "Go to Step 4" button). If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds.

The window in Step 4 presents all the data that have been entered; you may review these data for accuracy. If any changes are required, it is necessary to close out all windows back to the one in which corrections are to be made, and then reenter data in succeeding windows. When you are fully satisfied with your data, click on the "Generate" button, and the image that you have defined will be displayed. The image may then be rotated by using mouse click-and-drag.

Your image should appear as follows:



Here the darker spheres represent oxygen ions, while lead ions are depicted by the lighter balls.

[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

12.13 We are asked to calculate the theoretical density of NiO. This density may be computed using Equation (12.1) as

$$\rho = \frac{n'(A_{\text{Ni}} + A_{\text{O}})}{V_C N_{\text{A}}}$$

Since the crystal structure is rock salt, $n' = 4$ formula units per unit cell. Using the ionic radii for Ni^{2+} and O^{2-} from Table 12.3, the unit cell volume is computed as follows:

$$V_C = a^3 = \left(2r_{\text{Ni}^{2+}} + 2r_{\text{O}^{2-}}\right)^3 = [2(0.069 \text{ nm}) + 2(0.140 \text{ nm})]^3$$

$$= 0.0730 \ \frac{\text{nm}^3}{\text{unit cell}} = 7.30 \times 10^{-23} \ \frac{\text{cm}^3}{\text{unit cell}}$$

Thus,

$$\rho = \frac{(4 \text{ formula units/unit cell})(58.69 \text{ g/mol} + 16.00 \text{ g/mol})}{\left(7.30 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)\left(6.023 \times 10^{23} \text{ formula units/mol}\right)}$$

$$= 6.79 \text{ g/cm}^3$$

12.14 (a) This part of the problem calls for us to determine the unit cell edge length for FeO. The density of FeO is 5.70 g/cm^3 and the crystal structure is rock salt. From Equation 12.1

$$\rho = \frac{n'(A_{\mathrm{Fe}} + A_{\mathrm{O}})}{V_C N_{\mathrm{A}}} = \frac{n'(A_{\mathrm{Fe}} + A_{\mathrm{O}})}{a^3 N_{\mathrm{A}}}$$

Or, solving for *a*

$$a = \left[\frac{n'(A_{\mathrm{Fe}} + A_{\mathrm{O}})}{\rho N_{\mathrm{A}}}\right]^{1/3}$$

$$= \left[\frac{(4 \text{ formula units/unit cell})(55.85 \text{ g/mol} + 16.00 \text{ g/mol})}{(5.70 \text{ g/cm}^3)(6.023 \times 10^{23} \text{ formula units/mol})}\right]^{1/3}$$

$$= 4.37 \times 10^{-8} \text{ cm} = 0.437 \text{ nm}$$

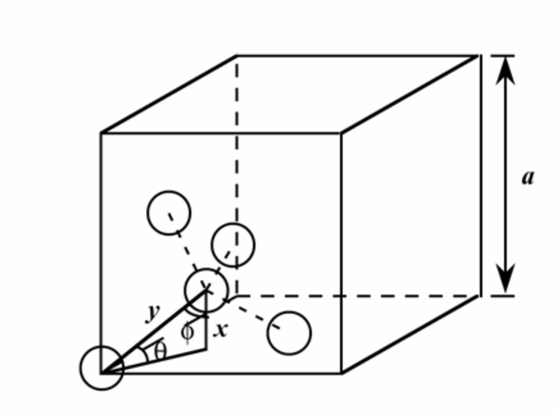
(b) The edge length is determined from the Fe^{2+} and O^{2-} radii for this portion of the problem. Now

$$a = 2r_{\mathrm{Fe}^{2+}} + 2r_{\mathrm{O}^{2-}}$$

From Table 12.3

$$a = 2(0.077 \text{ nm}) + 2(0.140 \text{ nm}) = 0.434 \text{ nm}$$

12.15 This problem asks that we compute the theoretical density of diamond given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell edge length from the given C—C distance. The drawing below shows the cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle or $\phi = 109.5°/2 = 54.75°$, which means that

$$\theta = 90° - 54.75° = 35.25°$$

since the triangle shown is a right triangle. Also, $y = 0.154$ nm, the carbon-carbon bond distance. Furthermore, $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta = (4)(0.154 \text{ nm})(\sin 35.25°) = 0.356 \text{ nm}$$

$$= 3.56 \times 10^{-8} \text{ cm}$$

The unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (3.56 \times 10^{-8} \text{ cm})^3 = 4.51 \times 10^{-23} \text{ cm}^3$$

We must now utilize a modified Equation 12.1 since there is only one atom type. There are 8 equivalent atoms per unit cell, and therefore

$$\rho = \frac{n' A_C}{V_C N_A}$$

$$= \frac{(8 \text{ atoms/unit cell})(12.01 \text{ g/g-atom})}{\left(4.51 \text{ x } 10^{-23} \text{ cm}^3\text{/unit cell}\right)\left(6.023 \text{ x } 10^{23} \text{ atoms/g-atom}\right)}$$

$$= 3.54 \text{ g/cm}^3$$

The measured density is 3.51 g/cm^3.

12.16 This problem asks that we compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell volume from the given Zn—S distance. From the previous problem, the unit cell volume V_C is just a^3, a being the unit cell edge length, and

$$V_C = (4y \sin \theta)^3 = [(4)(0.234 \text{ nm})(\sin 35.25°)]^3$$

$$= 0.1576 \text{ nm}^3 = 1.576 \times 10^{-22} \text{ cm}^3$$

Now we must utilize Equation 12.1 with $n' = 4$ formula units, and A_{Zn} and A_{S} being 65.39 and 32.06 g/mol, respectively. Thus

$$\rho = \frac{n'(A_{\text{Zn}} + A_{\text{S}})}{V_C N_{\text{A}}}$$

$$= \frac{(4 \text{ formula units/unit cell})(65.39 \text{ g/mol} + 32.06 \text{ g/mol})}{(1.576 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.023 \times 10^{23} \text{ formula units/mol})}$$

$$= 4.11 \text{ g/cm}^3$$

The measured value of the density is 4.10 g/cm^3.

12.17 We are asked to determine the number of Si^{4+} and O^{2-} ions per unit cell for a crystalline form of silica (SiO_2). For this material, a = 0.700 nm and ρ = 2.32 g/cm^3. Solving for n' from Equation 12.1, we get

$$n' = \frac{\rho V_C N_A}{A_{Si} + 2A_O} = \frac{\rho a^3 N_A}{A_{Si} + 2A_O}$$

$$= \frac{(2.32\,\text{g/cm}^3)(7.00 \text{ x } 10^{-8}\,\text{cm})^3 (6.023 \text{ x } 10^{23} \text{ formula units/mol})}{(28.09\,\text{g/mol} + 2[16.00]\,\text{g/mol})}$$

$$= 7.98 \text{ or almost } 8$$

Therefore, there are eight Si^{4+} and sixteen O^{2-} per unit cell.

12.18 (a) We are asked to compute the density of CsCl. Modifying the result of Problem 3.3, we get

$$a = \frac{2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}}{\sqrt{3}} = \frac{2(0.170\ \mathrm{nm}) + 2(0.181\ \mathrm{nm})}{\sqrt{3}}$$

$$= 0.405\ \mathrm{nm} = 4.05 \times 10^{-8}\ \mathrm{cm}$$

From Equation 12.1

$$\rho = \frac{n'(A_{\mathrm{Cs}} + A_{\mathrm{Cl}})}{V_C N_\mathrm{A}} = \frac{n'(A_{\mathrm{Cs}} + A_{\mathrm{Cl}})}{a^3 N_\mathrm{A}}$$

For the CsCl crystal structure, $n' = 1$ formula unit/unit cell, and thus

$$\rho = \frac{(1\ \text{formula unit/unit cell})(132.91\ \mathrm{g/mol} + 35.45\ \mathrm{g/mol})}{(4.05 \times 10^{-8}\ \mathrm{cm})^3/\text{unit cell}\,(6.023 \times 10^{23}\ \text{formula units/mol})}$$

$$= 4.20\ \mathrm{g/cm^3}$$

(b) This value of the density is greater than the measured density (3.99 $\mathrm{g/cm^3}$). The reason for this discrepancy is that the ionic radii in Table 12.3, used for this computation, were for a coordination number of six, when, in fact, the coordination number of both $\mathrm{Cs^+}$ and $\mathrm{Cl^-}$ is eight. The ionic radii should be slightly greater, leading to a larger V_C value, and a lower density.

12.19 This problem asks that we compute the density of CaF_2. A unit cell of the fluorite structure is shown in Figure 12.5. It may be seen that there are four CaF_2 units per unit cell (i.e., $n' = 4$ formula units/unit cell). Assume that for each of the eight small cubes in the unit cell

$$a = \frac{2r_{Ca^{2+}} + 2r_{F^-}}{\sqrt{3}}$$

and, from Table 12.3

$$a = \frac{2\,(0.100 \text{ nm}) + 2\,(0.133 \text{ nm})}{\sqrt{3}} = 0.269 \text{ nm} = 2.69 \text{ x } 10^{-8} \text{ cm}$$

The volume of the unit cell is just

$$V_C = (2a)^3 = \left[(2)\left(2.69 \text{ x } 10^{-3} \text{ cm}\right)\right]^3 = 1.56 \text{ x } 10^{-22} \text{ cm}^3$$

Thus, from Equation 12.1

$$\rho = \frac{n'(A_{Ca} + 2A_F)}{V_C N_A}$$

$$= \frac{(4 \text{ formula units/unit cell})\left[40.08 \text{ g/mol} + (2)(19.00 \text{ g/mol})\right]}{\left(1.56 \text{ x } 10^{-22} \text{ cm}^3\text{/unit cell}\right)\left(6.023 \text{ x } 10^{23} \text{ formula units/mol}\right)}$$

$$= 3.33 \text{ g/cm}^3$$

The measured density is 3.18 g/cm^3.

12.20 We are asked to specify possible crystal structures for an AX type of ceramic material given its density (2.10 g/cm^3), that the unit cell has cubic symmetry with edge length of 0.57 nm, and the atomic weights of the A and X elements (28.5 and 30.0 g/mol, respectively). Using Equation 12.1 and solving for n' yields

$$n' = \frac{\rho V_C N_\mathrm{A}}{\sum A_\mathrm{C} + \sum A_\mathrm{A}}$$

$$= \frac{(2.10\ \mathrm{g/cm^3})\left[(5.70 \times 10^{-8}\ \mathrm{cm})^3/\mathrm{unit\ cell}\right](6.023 \times 10^{23}\ \mathrm{formula\ units/mol})}{(30.0\ +\ 28.5)\ \mathrm{g/mol}}$$

$$= 4.00\ \mathrm{formula\ units/unit\ cell}$$

Of the three possible crystal structures, only sodium chloride and zinc blende have four formula units per unit cell, and therefore, are possibilities.

12.21 This problem asks us to compute the atomic packing factor for Fe_3O_4 given its density and unit cell edge length. It is first necessary to determine the number of formula units in the unit cell in order to calculate the sphere volume. Solving for *n'* from Equation 12.1 leads to

$$n' = \frac{\rho V_C N_A}{\sum A_C + \sum A_A}$$

$$= \frac{(5.24\ \text{g/cm}^3)\left[(8.39 \text{ x } 10^{-8}\ \text{cm})^3/\text{unit cell}\right](6.023 \text{ x } 10^{23}\ \text{formula units/mol})}{(3)(55.85\ \text{g/mol}) + (4)(16.00\ \text{g/mol})}$$

$$= 8.0\ \text{formula units/unit cell}$$

Thus, in each unit cell there are 8 Fe^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions. From Table 12.3, $r_{Fe^{2+}} = 0.077$ nm, $r_{Fe^{3+}} = 0.069$ nm, and $r_{O^{2-}} = 0.140$ nm. Thus, the total sphere volume in Equation 3.2 (which we denote as V_S), is just

$$V_S = (8)\left(\frac{4}{3}\pi\right)(7.7 \text{ x } 10^{-9}\text{cm})^3 + (16)\left(\frac{4}{3}\pi\right)(6.9 \text{ x } 10^{-9}\text{cm})^3$$

$$+ (32)\left(\frac{4}{3}\pi\right)(1.40 \text{ x } 10^{-8}\ \text{cm})^3$$

$$= 4.05 \text{ x } 10^{-22}\ \text{cm}^3$$

Now, the unit cell volume (V_C) is just

$$V_C = a^3 = (8.39 \text{ x } 10^{-8}\ \text{cm})^3 = 5.90 \text{ x } 10^{-22}\ \text{cm}^3$$

Finally, the atomic packing factor (APF) from Equation 3.2 is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{4.05 \text{ x } 10^{-22}\ \text{cm}^3}{5.90 \text{ x } 10^{-22}\ \text{cm}^3} = 0.686$$

12.22 This problem asks for us to calculate the atomic packing factor for aluminum oxide given values for the *a* and *c* lattice parameters, and the density. It first becomes necessary to determine the value of n' in Equation 12.1. This necessitates that we calculate the value of V_C, the unit cell volume. In Problem 3.6 it was shown that the area of the hexagonal base (AREA) is related to *a* as

$$\text{AREA} = 6\left(\frac{a}{2}\right)^2\sqrt{3} = 1.5a^2\sqrt{3}$$

$$= (1.5)\left(4.759 \text{ x } 10^{-8} \text{ cm}\right)^2\left(\sqrt{3}\right) = 5.88 \text{ x } 10^{-15} \text{ cm}^2$$

The unit cell volume now is just

$$V_C = (\text{AREA})(c) = \left(5.88 \text{ x } 10^{-15} \text{ cm}^2\right)\left(1.2989 \text{ x } 10^{-7} \text{ cm}\right)$$

$$= 7.64 \text{ x } 10^{-22} \text{ cm}^3$$

Now, solving for n' (Equation 12.1) yields

$$n' = \frac{\rho N_A V_C}{\sum A_C + \sum A_A}$$

$$= \frac{\left(3.99 \text{ g/cm}^3\right)\left(6.023 \text{ x } 10^{23} \text{ formula units/mol}\right)\left(7.64 \text{ x } 10^{-22} \text{ cm}^3\text{/unit cell}\right)}{(2)(26.98 \text{ g/mol}) + (3)(16.00\text{g/mol})}$$

$$= 18.0 \text{ formula units/unit cell}$$

Or, there are 18 Al_2O_3 units per unit cell, or 36 Al^{3+} ions and 54 O^{2-} ions. From Table 12.3, the radii of these two ion types are 0.053 and 0.140 nm, respectively. Thus, the total sphere volume in Equation 3.2 (which we denote as V_S), is just

$$V_S = (36)\left(\frac{4}{3}\pi\right)\left(5.3 \text{ x } 10^{-9}\text{cm}\right)^3 + (54)\left(\frac{4}{3}\pi\right)\left(1.4 \text{ x } 10^{-8}\text{cm}\right)^3$$

$$= 6.43 \text{ x } 10^{-22} \text{ cm}^3$$

Finally, the APF is just

$$\mathrm{APF} = \frac{V_S}{V_C} = \frac{6.43 \text{ x } 10^{-22} \text{ cm}^3}{7.64 \text{ x } 10^{-22} \text{ cm}^3} = 0.842$$

12.23 We are asked in this problem to compute the atomic packing factor for the diamond cubic crystal structure, given that the angle between adjacent bonds is 109.5°. The first thing that we must do is to determine the unit cell volume V_C in terms of the atomic radius r. From Problem 12.15 the following relationship was developed

$$a = 4y \sin \theta$$

in which $y = 2r$ and $\theta = 35.25°$. Furthermore, since the unit cell is cubic, $V_C = a^3$; therefore

$$V_C = (4y \sin \theta)^3 = [(4)(2r)(\sin 35.25°)]^3 = 98.43\, r^3$$

Now, it is necessary to determine the sphere volume in the unit cell, V_S, in terms of r. For this unit cell (Figure 12.15) there are 4 interior atoms, 6 face atoms, and 8 corner atoms. The entirety of the interior atoms, one-half of each face atom, and one-eighth of each corner atom belong to the unit cell. Therefore, there are 8 equivalent atoms per unit cell; hence

$$V_S = (8)\left(\frac{4}{3}\pi r^3\right) = 33.51\ r^3$$

Finally, the atomic packing factor is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{33.51\ r^3}{98.43\ r^3} = 0.340$$

12.24 We are asked in this problem to compute the atomic packing factor for the CsCl crystal structure. This requires that we take the ratio of the sphere volume within the unit cell and the total unit cell volume. From Figure 12.3 there is the equivalence of one Cs and one Cl ion per unit cell; the ionic radii of these two ions are 0.170 nm and 0.181 nm, respectively (Table 12.3). Thus, the sphere volume, V_S, is just

$$V_S = \frac{4}{3}(\pi)\left[(0.170 \text{ nm})^3 + (0.181 \text{ nm})^3\right] = 0.0454 \text{ nm}^3$$

For CsCl the unit cell edge length, a, in terms of the atomic radii is just

$$a = \frac{2r_{\text{Cs}^+} + 2r_{\text{Cl}^-}}{\sqrt{3}} = \frac{2(0.170 \text{ nm}) + 2(0.181 \text{ nm})}{\sqrt{3}}$$

$$= 0.405 \text{ nm}$$

Since $V_C = a^3$

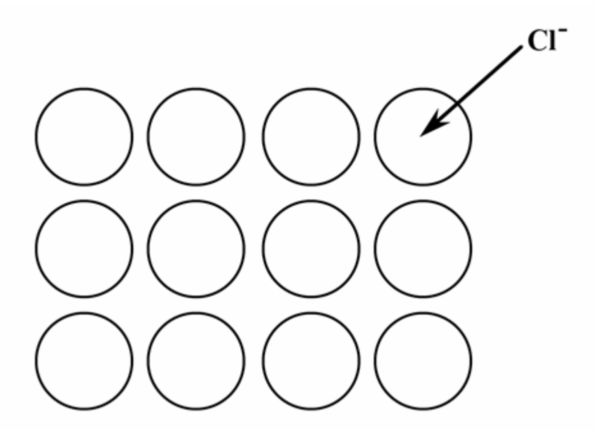
$$V_C = (0.405 \text{ nm})^3 = 0.0664 \text{ nm}^3$$

And, finally the atomic packing factor is just

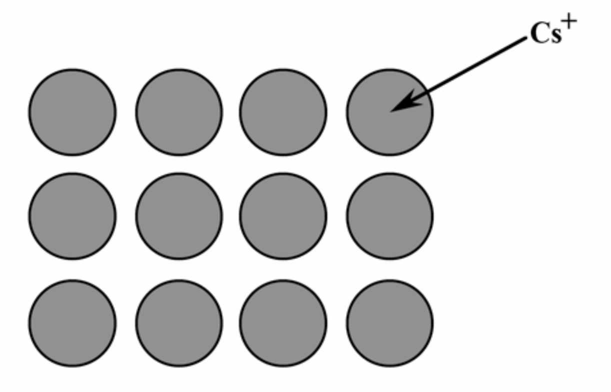
$$\text{APF} = \frac{V_S}{V_C} = \frac{0.0454 \text{ nm}^3}{0.0664 \text{ nm}^3} = 0.684$$

12.25 This problem asks that we represent specific crystallographic planes for various ceramic crystal structures.

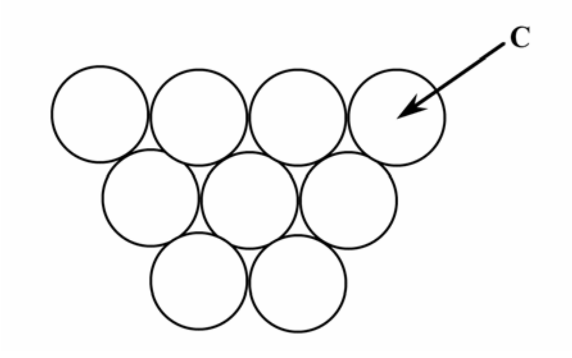
(a) A (100) plane for the cesium chloride crystal structure would appear as



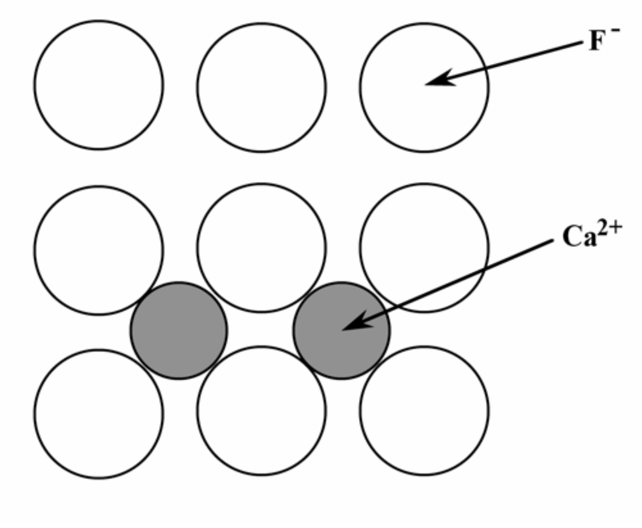
(b) A (200) plane for the cesium chloride crystal structure would appear as



(c) A (111) plane for the diamond cubic crystal structure would appear as



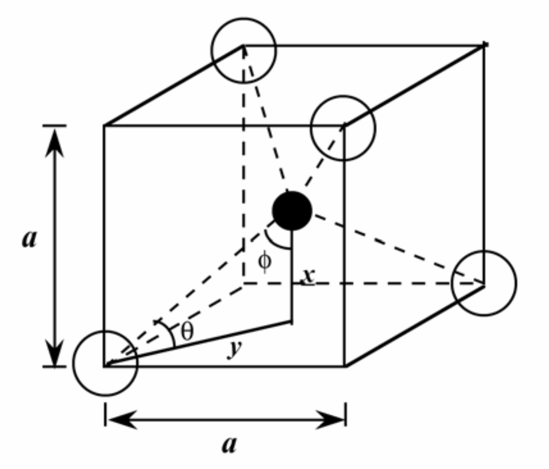
(d) A (110) plane for the fluorite crystal structure would appear as



Silicate Ceramics

12.26 The silicate materials have relatively low densities because the atomic bonds are primarily covalent in nature (Table 12.1), and, therefore, directional. This limits the packing efficiency of the atoms, and therefore, the magnitude of the density.

12.27 This problem asks for us to determine the angle between covalent bonds in the SiO_4^{4-} tetrahedron. Below is shown one such tetrahedron situated within a cube.



Now if we extend the base diagonal from one corner to the other, it is the case that

$$(2y)^2 = a^2 + a^2 = 2a^2$$

or

$$y = \frac{a\sqrt{2}}{2}$$

Furthermore, $x = a/2$, and

$$\tan\theta = \frac{x}{y} = \frac{a/2}{a\sqrt{2}/2} = \frac{1}{\sqrt{2}}$$

From which

$$\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35.26°$$

Now, solving for the angle ϕ

$$\phi = 180° - 90° - 35.26° = 54.74°$$

Finally, the bond angle is just 2ϕ, or $2\phi = (2)(54.74°) = 109.48°$.

Imperfections in Ceramics

12.28 Frenkel defects for anions would not exist in appreciable concentrations because the anion is quite large and is highly unlikely to exist as an interstitial.

12.29 We are asked in this problem to calculate the fraction of lattice sites that are Schottky defects for CsCl at its melting temperature (645°C), assuming that the energy for defect formation is 1.86 eV. In order to solve this problem it is necessary to use Equation 12.3 and solve for the N_s/N ratio. Rearrangement of this expression and substituting values for the several parameters leads to

$$\frac{N_s}{N} = \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \exp\left[-\frac{1.86 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(645 + 273 \text{ K})}\right]$$

$$= 7.87 \text{ x } 10^{-6}$$

12.30 This problem asks that we compute the number of Frenkel defects per cubic meter in silver chloride at 350°C. Solution of this problem is possible using Equation 12.2. However, we must first determine the value of N, the number of lattice sites per cubic meter, which is possible using a modified form of Equation 4.2; thus

$$N = \frac{N_A \rho}{A_{Ag} + A_{Cl}}$$

$$= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(5.50 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{107.87 \text{ g/mol} + 35.45 \text{ g/mol}}$$

$$= 2.31 \text{ x } 10^{28} \text{ lattice sites/m}^3$$

And, finally the value of N_{fr} is computed using Equation 12.2 as

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$

$$= (2.31 \times 10^{28} \text{ lattice sites/m}^3) \exp\left[-\frac{1.1 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(350 + 273 \text{ K})}\right]$$

$$= 8.24 \text{ x } 10^{23} \text{ defects/m}^3$$

12.31 This problem provides for some oxide ceramic, at temperatures of 750°C and 1500°C, values for density and the number of Schottky defects per cubic meter. The (a) portion of the problem asks that we compute the energy for defect formation. To begin, let us combine a modified form of Equation 4.2 and Equation 12.3 as

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \left(\frac{N_A \rho}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT}\right)$$

Inasmuch as this is a hypothetical oxide material, we don't know the atomic weight of metal M, nor the value of Q_s in the above equation. Therefore, let us write equations of the above form for two temperatures, T_1 and T_2. These are as follows:

$$N_{s1} = \left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right) \tag{12.S1a}$$

$$N_{s2} = \left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right) \tag{12.S1b}$$

Dividing the first of these equations by the second leads to

$$\frac{N_{s1}}{N_{s2}} = \frac{\left(\dfrac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\dfrac{Q_s}{2kT_1}\right)}{\left(\dfrac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\dfrac{Q_s}{2kT_2}\right)}$$

which, after some algebraic manipulation, reduces to the form

$$\frac{N_{s1}}{N_{s2}} = \frac{\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{12.S2}$$

Now, taking natural logarithms of both sides of this equation gives

$$\ln\left(\frac{N_{s1}}{N_{s2}}\right) = \ln\left(\frac{\rho_1}{\rho_2}\right) - \frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and solving for Q_s leads to the expression

$$Q_s = \frac{-2k\left[\ln\left(\frac{N_{s1}}{N_{s2}}\right) - \ln\left(\frac{\rho_1}{\rho_2}\right)\right]}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take T_1 = 750°C and T_2 = 1500°C, and we may compute the value of Q_s as

$$Q_s = \frac{-(2)(8.62 \times 10^{-5}\text{ eV/K})\left[\ln\left(\frac{5.7 \times 10^{9}\text{ m}^{-3}}{5.8 \times 10^{17}\text{ m}^{-3}}\right) - \ln\left(\frac{3.50\text{ g/cm}^3}{3.40\text{ g/cm}^3}\right)\right]}{\frac{1}{750 + 273\text{ K}} - \frac{1}{1500 + 273\text{ K}}}$$

$$= 7.70\text{ eV}$$

(b) It is now possible to solve for N_s at 1000°C using Equation 12.S2 above. This time let's take T_1 = 1000°C and T_2 = 750°C. Thus, solving for N_{s1}, substituting values provided in the problem statement and Q_s determined above yields

$$N_{s1} = \frac{N_{s2}\,\rho_1}{\rho_2}\exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$= \frac{(5.7 \times 10^{9}\text{ m}^{-3})(3.45\text{ g/cm}^3)}{3.50\text{ g/cm}^3}\exp\left[-\frac{7.70\text{ eV}}{(2)(8.62 \times 10^{-5}\text{ eV/K})}\left(\frac{1}{1000 + 273\text{ K}} - \frac{1}{750 + 273\text{ K}}\right)\right]$$

$$= 3.0 \text{ x } 10^{13}\text{ m}^{-3}$$

(c) And, finally, we want to determine the identity of metal M. This is possible by computing the atomic weight of M (A_M) from Equation 12.S1a. Rearrangement of this expression leads to

$$\left(\frac{N_A\rho_1}{A_M + A_O}\right) = N_{s1}\exp\left(\frac{Q_s}{2kT_1}\right)$$

And, after further algebraic manipulation

$$\left[\frac{N_A \rho_1}{N_{s1} \exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] = A_M + A_O$$

And, solving this expression for A_M gives

$$A_M = \left[\frac{N_A \rho_1}{N_{s1} \exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] - A_O$$

Now, assuming that T_1 = 750°C, the value of A_M is

$$A_M = \left\{\frac{(6.023 \times 10^{23} \text{ ions/mol})(3.50 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{(5.7 \times 10^9 \text{ ions/m}^3) \exp\left[\dfrac{7.7 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(750 + 273 \text{ K})}\right]}\right\} - 16.00 \text{ g/mol}$$

$$= 24.45 \text{ g/mol}$$

Upon consultation of the periodic table in Figure 2.6, the divalent metal (i.e., that forms M^{2+} ions) that has an atomic weight closest to 24.45 g/mol is magnesium. Thus, this metal oxide is MgO.

12.32 Stoichiometric means having exactly the ratio of anions to cations as specified by the chemical formula for the compound.

12.33 (a) For a $Cu^{2+}O^{2-}$ compound in which a small fraction of the copper ions exist as Cu^{+}, for each Cu^{+} formed there is one less positive charge introduced (or one more negative charge). In order to maintain charge neutrality, we must either add an additional positive charge or subtract a negative charge. This may be accomplished be either creating Cu^{2+} interstitials or O^{2-} vacancies.

(b) There will be two Cu^{+} ions required for each of these defects.

(c) The chemical formula for this nonstoichiometric material is $Cu_{1+x}O$ or CuO_{1-x}, where x is some small fraction.

12.34 (a) For Ca^{2+} substituting for Li^+ in Li_2O, lithium vacancies would be created. For each Ca^{2+} substituting for Li^+, one positive charge is added; in order to maintain charge neutrality, a single positive charge may be removed. Positive charges are eliminated by creating lithium vacancies, and for every Ca^{2+} ion added, a single lithium vacancy is formed.

(b) For O^{2-} substituting for Cl^- in $CaCl_2$, chlorine vacancies would be created. For each O^{2-} substituting for a Cl^-, one negative charge is added; negative charges are eliminated by creating chlorine vacancies. In order to maintain charge neutrality, one O^{2-} ion will lead to the formation of one chlorine vacancy.

Ceramic Phase Diagrams

12.35 There is only one eutectic for the portion of the ZrO_2-CaO system shown in Figure 12.26, which, upon cooling, is

$$\text{Liquid} \rightarrow \text{cubic } ZrO_2 + CaZrO_3$$

There are two eutectoids, which reactions are as follows:

$$\text{tetragonal} \rightarrow \text{monoclinic } ZrO_2 + \text{cubic } ZrO_2$$

$$\text{cubic} \rightarrow \text{monoclinic } ZrO_2 + CaZr_4O_9$$

12.36 (a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3-rich side of the spinel phase field (Figure 12.25) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg^{2+} vacancies as x, which means that $2x$ Al^{3+} ions have been added and $3x$ Mg^{2+} ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 + 2x)/2$; similarly the number of moles of MgO is $(50 - 3x)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 + 2x}{2}}{\dfrac{100 + 2x}{2} + (50 - 3x)}\right] \times 100$$

If we solve for x when the mol% of Al_2O_3 = 82, then x = 12.1. Thus, adding $2x$ or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

$$\% \text{ vacancies} = \frac{12.1}{100 + 50} \times 100 = 8.1\%$$

(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3. In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material which consists of 50 Mg^{2+} ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as y, which means that $2y$ Mg^{2+} ions have been added and $2y$ Al^{3+} ions have been removed. Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 - 2y)/2$; similarly the number of moles of MgO is $(50 + 2y)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% Al}_2\text{O}_3 = \left[\frac{\dfrac{100 - 2y}{2}}{\dfrac{100 - 2y}{2} + (50 + 2y)} \right] \times 100$$

If we solve for y when the mol% of Al_2O_3 = 39, then y = 7.91. Thus, 7.91 O^{2-} vacancies are produced in the original material that had 200 O^{2-} ions. Therefore, the percentage of vacancies is just

$$\% \text{ vacancies} = \frac{7.91}{200} \times 100 = 3.96\%$$

12.37 (a) The chemical formula for kaolinite clay may also be written as Al_2O_3–2SiO_2-2H_2O. Thus, if we remove the chemical water, the formula becomes Al_2O_3–2SiO_2. The formula weight for Al_2O_3 is just (2)(26.98 g/mol) + (3)(16.00 g/mol) = 101.96 g/mol; and for SiO_2 the formula weight is 28.09 g/mol + (2)(16.00 g/mol) = 60.09 g/mol. Thus, the composition of this product, in terms of the concentration of Al_2O_3, $C_{Al_2O_3}$, in weight percent is just

$$C_{Al_2O_3} = \frac{101.96 \text{ g/mol}}{101.96 \text{ g/mol} + (2)(60.09 \text{ g/mol})} \times 100 = 45.9 \text{ wt\%}$$

(b) The liquidus and solidus temperatures for this material as determined from the SiO_2–Al_2O_3 phase diagram, Figure 12.27, are 1825°C and 1587°C, respectively.

Brittle Fracture of Ceramics

12.38 (a) There may be significant scatter in the fracture strength for some given ceramic material because the fracture strength depends on the probability of the existence of a flaw that is capable of initiating a crack; this probability varies from specimen to specimen of the same material.

(b) The fracture strength increases with decreasing specimen size because as specimen size decreases, the probably of the existence of a flaw of that is capable of initiating a crack diminishes.

12.39 We are asked for the critical crack tip radius for a glass. From Equation 8.1

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Fracture will occur when σ_m reaches the fracture strength of the material, which is given as $E/10$; thus

$$\frac{E}{10} = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Or, solving for ρ_t

$$\rho_t = \frac{400\ a\sigma_0^2}{E^2}$$

From Table 12.5, E = 69 GPa, and thus,

$$\rho_t = \frac{(400)\left(1 \text{ x } 10^{-2} \text{ mm}\right)(70 \text{ MPa})^2}{\left(69 \text{ x } 10^3 \text{ MPa}\right)^2}$$

$$= 4.1 \text{ x } 10^{-6} \text{ mm} = 4.1 \text{ nm}$$

12.40 This problem asks that we compute the crack tip radius ratio before and after etching. Let

ρ_t = original crack tip radius, and

ρ_t' = etched crack tip radius

Also,

$$\sigma_f' = \sigma_f$$

$$a' = \frac{a}{2}$$

$$\sigma_0' = 4\sigma_0$$

Solving for $\frac{\rho_t'}{\rho_t}$ from the following

$$\sigma_f = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2} = \sigma_f' = 2\sigma_0'\left(\frac{a'}{\rho_t'}\right)^{1/2}$$

yields

$$\frac{\rho_t'}{\rho_t} = \left(\frac{\sigma_0'}{\sigma_0}\right)^2\left(\frac{a'}{a}\right) = \left(\frac{4\sigma_0}{\sigma_0}\right)^2\left(\frac{a/2}{a}\right) = 8$$

Stress-Strain Behavior

12.41 (a) For this portion of the problem we are asked to compute the flexural strength for a spinel specimen that is subjected to a three-point bending test. The flexural strength (Equation 12.7a) is just

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

for a rectangular cross-section. Using the values given in the problem statement,

$$\sigma_{fs} = \frac{(3)(350 \text{ N})\left(25 \text{ x } 10^{-3} \text{ m}\right)}{(2)\left(9.0 \text{ x } 10^{-3} \text{ m}\right)\left(3.8 \text{ x } 10^{-3} \text{ m}\right)^2} = 101 \text{ MPa} \quad (15{,}200 \text{ psi})$$

(b) We are now asked to compute the maximum deflection. From Table 12.5, the elastic modulus (*E*) for spinel is 260 GPa (38 x 10^6 psi). Also, the moment of inertia for a rectangular cross section (Figure 12.32) is just

$$I = \frac{bd^3}{12}$$

Thus,

$$\Delta y = \frac{FL^3}{48E\left(\dfrac{bd^3}{12}\right)} = \frac{FL^3}{4Ebd^3}$$

$$= \frac{(310 \text{ N})\left(25 \text{ x } 10^{-3} \text{ m}\right)^3}{(4)\left(260 \text{ x } 10^9 \text{ N/m}^2\right)\left(9.0 \text{ x } 10^{-3} \text{ m}\right)\left(3.8 \text{ x } 10^{-3} \text{ m}\right)^3}$$

$$= 9.4 \text{ x } 10^{-6} \text{ m} = 9.4 \text{ x } 10^{-3} \text{ mm} \; \left(3.9 \text{ x } 10^{-4} \text{ in.}\right)$$

12.42 We are asked to calculate the maximum radius of a circular specimen of MgO that is loaded using three-point bending. Solving for R from Equation 12.7b

$$R = \left[\frac{F_f L}{\sigma_{fs} \pi} \right]^{1/3}$$

which, when substituting the parameters stipulated in the problem statement, yields

$$R = \left[\frac{(5560 \text{ N})(45 \text{ x } 10^{-3} \text{ m})}{(105 \text{ x } 10^{6} \text{ N/m}^2)(\pi)} \right]^{1/3}$$

$$= 9.1 \text{ x } 10^{-3} \text{ m} = 9.1 \text{ mm} \ \ (0.36 \text{ in.})$$

12.43 For this problem, the load is given at which a circular specimen of aluminum oxide fractures when subjected to a three-point bending test; we are then are asked to determine the load at which a specimen of the same material having a square cross-section fractures. It is first necessary to compute the flexural strength of the aluminum oxide, Equation 12.7b, and then, using this value, we may calculate the value of F_f in Equation 12.7a. From Equation 12.7b

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

$$= \frac{(3000\ \text{N})(40\ \text{x}\ 10^{-3}\ \text{m})}{(\pi)(5.0\ \text{x}\ 10^{-3}\ \text{m})^3} = 306\ \text{x}\ 10^6\ \text{N/m}^2 = 306\ \text{MPa}\quad (42{,}970\ \text{psi})$$

Now, solving for F_f from Equation 12.7a, realizing that $b = d = 12$ mm, yields

$$F_f = \frac{2\sigma_{fs} d^3}{3L}$$

$$= \frac{(2)(306\ \text{x}\ 10^6\ \text{N/m}^2)(15\ \text{x}\ 10^{-3}\text{m})^3}{(3)(40\ \text{x}\ 10^{-3}\text{m})} = 17{,}200\ \text{N}\quad (3870\ \text{lb}_\text{f})$$

12.44 (a) This portion of the problem asks that we determine whether or not a cylindrical specimen of aluminum oxide having a flexural strength of 300 MPa (43,500 psi) and a radius of 5 mm will fracture when subjected to a load of 7500 N in a three-point bending test; the support point separation is given as 15 mm. Using Equation 12.7b we will calculate the value of σ; if this value is greater than σ_{fs} (300 MPa), then fracture is expected to occur. Employment of Equation 12.7b yields

$$\sigma = \frac{FL}{\pi R^3} = \frac{(7500 \ \text{N})(15 \ \text{x} \ 10^{-3} \ \text{m})}{(\pi)(5 \ \text{x} \ 10^{-3} \ \text{m})^3} = 286.5 \ \text{x} \ 10^6 \ \text{N/m}^2 = 286.5 \ \text{MPa} \quad (40{,}300 \ \text{psi})$$

Since this value is less than the given value of σ_{fs} (300 MPa), then fracture is not predicted.

(b) The certainty of this prediction is not 100% because there is always some variability in the flexural strength for ceramic materials, and since this value of σ is relatively close to σ_{fs} then there is some chance that fracture will occur.

Mechanisms of Plastic Deformation

12.45 Crystalline ceramics are harder yet more brittle than metals because they (ceramics) have fewer slip systems, and, therefore, dislocation motion is highly restricted.

Miscellaneous Mechanical Considerations

12.46 (a) This portion of the problem requests that we compute the modulus of elasticity for nonporous spinel given that E = 240 GPa for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0, using P = 0.05, which gives

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{240 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 265 \text{ GPa} \quad (38.6 \text{ x } 10^6 \text{ psi})$$

(b) Now we are asked to determine the value of E at P = 15 vol% (i.e., 0.15). Using Equation 12.9 we get

$$E = E_0(1 - 1.9P + 0.9P^2)$$

$$= (265 \text{ GPa})\left[1 - (1.9)(0.15) + (0.09)(0.15)^2\right] = 195 \text{ GPa} \quad (28.4 \text{ x } 10^6 \text{ psi})$$

12.47 (a) This portion of the problem requests that we compute the modulus of elasticity for nonporous TiC given that $E = 310$ GPa (45 x 10^6 psi) for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0, using $P = 0.05$, which gives

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{310 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 342 \text{ GPa} \quad (49.6 \text{ x } 10^6 \text{ psi})$$

(b) Now we are asked to compute the volume percent porosity at which the elastic modulus of TiC is 240 MPa (35 x 10^6 psi). Since from part (a), $E_0 = 342$ GPa, and using Equation 12.9 we get

$$\frac{E}{E_0} = \frac{240 \text{ MPa}}{342 \text{ MPa}} = 0.702 = 1 - 1.9P + 0.9P^2$$

Or

$$0.9P^2 - 1.9P + 0.298 = 0$$

Now, solving for the value of P using the quadratic equation solution yields

$$P = \frac{1.9 \pm \sqrt{(-1.9)^2 - (4)(0.9)(0.298)}}{(2)(0.9)}$$

The positive and negative roots are

$$P^+ = 1.94$$

$$P^- = 0.171$$

Obviously, only the negative root is physically meaningful, and therefore the value of the porosity to give the desired modulus of elasticity is 17.1 vol%.

12.48 (a) This part of the problem asks us to determine the flexural strength of nonporous MgO assuming that the value of n in Equation 12.10 is 3.75. Taking natural logarithms of both sides of Equation 12.10 yields

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

In Table 12.5 it is noted that for $P = 0.05$, $\sigma_{fs} = 105$ MPa. For the nonporous material $P = 0$ and, $\ln \sigma_0 = \ln \sigma_{fs}$. Solving for $\ln \sigma_0$ from the above equation and using these data gives

$$\ln \sigma_0 = \ln \sigma_{fs} + nP$$

$$= \ln (105 \text{ MPa}) + (3.75)(0.05) = 4.841$$

or $\sigma_0 = e^{4.841} = 127$ MPa (18,100 psi)

(b) Now we are asked to compute the volume percent porosity to yield a σ_{fs} of 74 MPa (10,700 psi). Taking the natural logarithm of Equation 12.10 and solving for P leads to

$$P = \frac{\ln \sigma_0 - \ln \sigma_{fs}}{n}$$

$$= \frac{\ln (127 \text{ MPa}) - \ln (74 \text{ MPa})}{3.75}$$

$$= 0.144 \text{ or } 14.4 \text{ vol\%}$$

12.49 (a) Given the flexural strengths at two different volume fraction porosities, we are asked to determine the flexural strength for a nonporous material. If the natural logarithm is taken of both sides of Equation 12.10, then

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

Using the data provided in the problem statement, two simultaneous equations may be written as

$$\ln (70 \text{ MPa}) = \ln \sigma_0 - (0.10)\, n$$

$$\ln (60 \text{ MPa}) = \ln \sigma_0 - (0.15)\, n$$

Solving for n and σ_0 leads to $n = 3.08$ and $\sigma_0 = 95.3$ MPa. For the nonporous material, $P = 0$, and, from Equation 12.10, $\sigma_0 = \sigma_{fs}$. Thus, σ_{fs} for $P = 0$ is 95.3 MPa.

(b) Now, we are asked for σ_{fs} at $P = 0.20$ for this same material. Utilizing Equation 12.10 yields

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

$$= (95.3 \text{ MPa}) \exp\left[-(3.08)(0.20)\right]$$

$$= 51.5 \text{ MPa}$$

DESIGN PROBLEMS

Crystal Structures

12.D1 This problem asks that we determine the concentration (in weight percent) of InAs that must be added to GaAs to yield a unit cell edge length of 0.5820 nm. The densities of GaAs and InAs were given in the problem statement as 5.316 and 5.668 g/cm^3, respectively. To begin, it is necessary to employ Equation 12.1, and solve for the unit cell volume, V_C, for the InAs-GaAs alloy as

$$V_C = \frac{n' A_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

where A_{ave} and ρ_{ave} are the atomic weight and density, respectively, of the InAs-GaAs alloy. Inasmuch as both of these materials have the zinc blende crystal structure, which has cubic symmetry, V_C is just the cube of the unit cell length, a. That is

$$V_C = a^3 = (0.5820 \text{ nm})^3$$

$$= \left(5.820 \text{ x } 10^{-8} \text{ cm}\right)^3 = 1.971 \text{ x } 10^{-22} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of indium arsenide, C_{InAs} using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{A_{\text{InAs}}} + \dfrac{\left(100 - C_{\text{InAs}}\right)}{A_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{189.74 \text{ g/mol}} + \dfrac{\left(100 - C_{\text{InAs}}\right)}{144.64 \text{ g/mol}}}$$

whereas for ρ_{ave}

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{\rho_{\text{InAs}}} + \dfrac{\left(100 - C_{\text{InAs}}\right)}{\rho_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}$$

Within the zinc blende unit cell there are four formula units, and thus, the value of n' in Equation 12.1 is 4; hence, this expression may be written in terms of the concentration of InAs in weight percent as follows:

$$V_C = 1.971 \text{ x } 10^{-22} \text{ cm}^3$$

$$= \frac{n' A_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(4\ \text{fu/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{189.74\ \text{g/mol}} + \dfrac{(100 - C_{\text{InAs}})}{144.64\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}\right](6.023 \text{ x } 10^{23}\ \text{fu/mol})}$$

And solving this expression for C_{InAs} leads to $C_{\text{InAs}} = 46.1$ wt%.

Stress-Strain Behavior

12.D2 This problem asks for us to determine which of the ceramic materials in Table 12.5, when fabricated into cylindrical specimens and stressed in three-point loading, will not fracture when a load of 445 N (100 lb_f) is applied, and also will not experience a center-point deflection of more than 0.021 mm (8.5×10^{-4} in.). The first of these criteria is met by those materials that have flexural strengths greater than the stress calculated using Equation 12.7b. According to this expression

$$\sigma_{fs} = \frac{FL}{\pi R^3}$$

$$= \frac{(445 \text{ N})(50.8 \times 10^{-3} \text{ m})}{(\pi)(3.8 \times 10^{-3} \text{ m})^3} = 131 \times 10^6 \text{ N/m}^2 = 131 \text{ MPa (18,900 psi)}$$

Of the materials in Table 12.5, the following have flexural strengths greater than this value: Si_3N_4, ZrO_2, SiC, Al_2O_3, glass-ceramic, mullite, and spinel.

For the second criterion we must solve for the magnitude of the modulus of elasticity, E, from the equation given in Problem 12.41 where the expression for the cross-sectional moment of inertia appears in Figure 12.32; that is, for a circular cross-section $I = \frac{\pi R^4}{4}$. Solving for E from these two expressions

$$E = \frac{FL^3}{12 \pi R^4 \Delta y}$$

$$= \frac{(445 \text{ N})(50.8 \times 10^{-3} \text{ m})^3}{(12)(\pi)(3.8 \times 10^{-3} \text{ m})^4 (0.021 \times 10^{-3} \text{ m})}$$

$$= 353 \times 10^9 \text{ N/m}^2 = 353 \text{ GPa } (49.3 \times 10^6 \text{ psi})$$

Of those materials that satisfy the first criterion, only Al_2O_3 has a modulus of elasticity greater than this value (Table 12.5), and, therefore, is a possible candidate.