http://aerostudents.com/files/materialsAndStructures/MaterialsScienceBookSolutions/CH12.pdf

CHAPTER 12

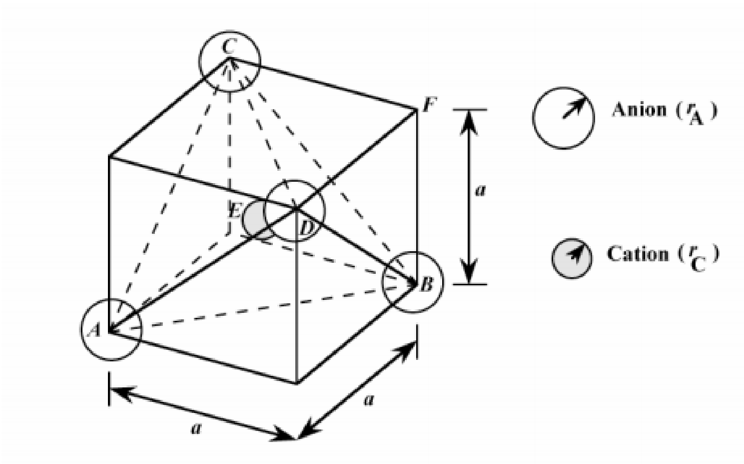
STRUCTURES AND PROPERTIES OF CERAMICS

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,

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

But

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

or

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

And

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

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,

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

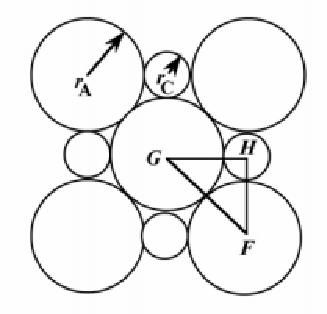
Solving for the r_C/r_A ratio leads to

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

TABLE 5.8 The range of radius ratios corresponding to different ion arrangements

r_+/r_- Values	Coordination number preferred	Name
0.732 to 0.999	8	Cubic
0.414 to 0.732	6	Octahedral
0.225 to 0.414	4	Tetrahedral

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

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

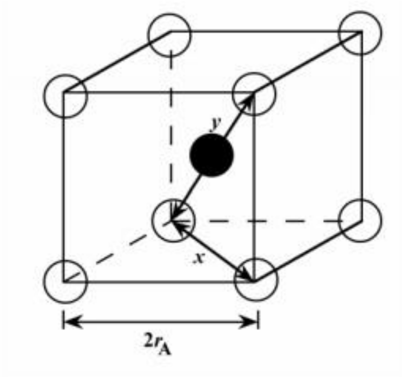
which leads to

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

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

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

Why does all theese problems say that we have found the minimum value for the cation anion ratio?

Table 5.8 below says that the cation anion ratio can have an interval of values.

From what I get it seems that if all the anions are in touch with eachother then the values 0,225, 0,414 and 0,732 have to be the possible cation anion ratios for the given arrangments? Can you show a mathematical relation that shows why the ratio can have an interal of values and not only the nmbers calculated in the proofs. And relate this mathematically to the derivation