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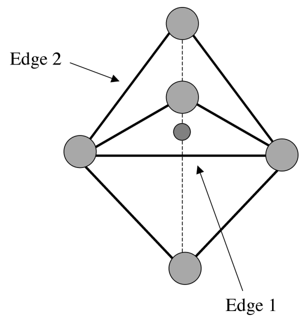
3.012 Fundamentals of Materials Science and Engineering – Fall 2003

Problem Set Two Solutions
Structure Graded Problems

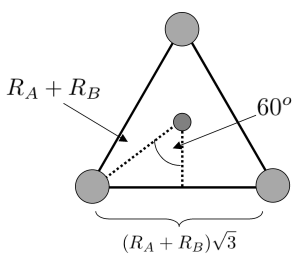
Problem 1



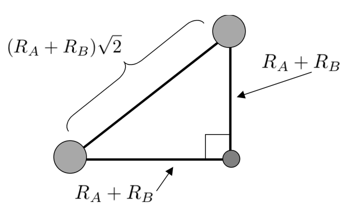
(a)

From looking at the structure as a whole it is difficult to determine if Edge 1 and Edge 2 are equal in length. Let's calculate the length of the two edges remembering that the anions (larger circles in the above figure) are in contact with the cation (small circle).

Edge 1



Edge 2



We now see that Edge 1 is actually longer than Edge 2.

(b)

The critical anion-anion separation is the edge where the anions would contact first. Thus, since Edge 2 is shorter, it is the critical anion-anion separation.

(c)

The permitted radius ratio can be found by finding the value of $\frac{R_A}{R_B}$ for which the two anions just touch. Using the figure above for Edge 2 we can see that this will happen when:

$$(R_A + R_B)\sqrt{2} = 2R_B$$

$$\left[\frac{R_A}{R_B} + 1\right]\sqrt{2} = 2$$

$$\frac{R_A}{R_B} = \frac{2}{\sqrt{2}} - 1$$

$$\frac{R_A}{R_B} = 0.414$$

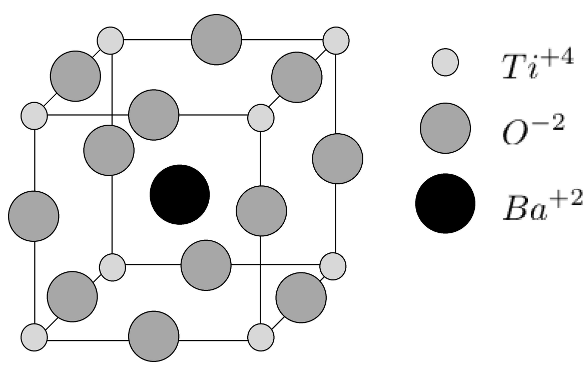
If we assume an AB compound, then the range of permitted radius ratios would be $0.414 \rightarrow 2.41$

(d)

If we look at the notes from the first lecture we see that for the same radius ratio we can have 6 fold coordination. Therefore, for ions with sizes within that range we can have 5 or 6-fold coordination. Since higher coordination is preferred, it is rare to see this kind of coordination.

Problem 2

A schematic of the structure might look something like this:



From this we get that the coordination of the Ti^{+4} and Ba^{+2} are:

$$CN_{Ti^{+4}} = 6$$

$$CN_{Ba^{+2}} = 12$$

(b)

Using the coordination information from part (a) we can find the bond strengths, S, for Ti and Ba:

$$S_{Ti} = \frac{4}{6} = \frac{2}{3}$$
$$S_{Ba} = \frac{2}{12} = \frac{1}{6}$$

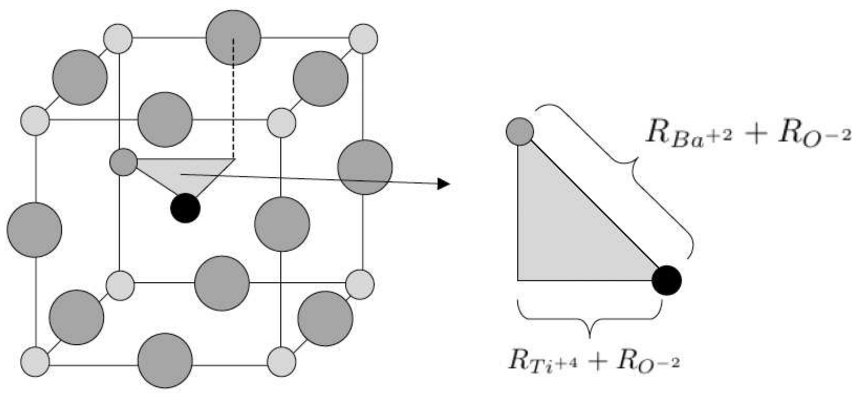
Now looking at the structure we see that each O^{-2} is surrounded by 4 Ba^{+2} and 2 Ti^{+4}.

$$\sum S = 4 * \frac{1}{6} + 2 * \frac{2}{3} = \frac{2}{3} + \frac{4}{3} = 2$$

Which is indeed the charge on the oxygen ion.

(c)

Using the ionic radii from Shannon-Prewitt we need to see if all the ions can touch given the geometry. Its helpful to select a portion of the structure that includes both radii. The figure below shows one such triangle that will be useful in making this determination:



We can select one of the sides of this isosceles triangle and then using the known ionic radii calculate the other side. We know:

$$R_{Ti^{+4}} + R_{O^{-2}} = 0.65 + 1.40 = 2.05\mathring{A}$$

Using the triangle above we can find a calculated value for the side $R_{Ba^{+2}} + R_{O^{-2}}$:

$$\sqrt{2.05^2 + 2.05^2} = 2.9\mathring{A}$$

If the Ba and O ions were indeed touching, that length <u>should</u> be:

$$R_{Ba^{+2}} + R_{O^{-2}} = 1.60 + 1.40 = 3.0$$

Therefore all the ions cannot be in contact in this structure.

(d)

Again using the triangle in the above figure we see that all the ions will be in contact when:

$$(R_{Ti^{+4}} + R_{O^{-2})}\sqrt{2} = R_{Ba^{+2}} + R_{O^{-2}}$$
$$R_{Ba^{+2}} - \sqrt{2}R_{Ti^{+4}} = R_{O^{-2}}(\sqrt{2} - 1) = 0.580$$