MATRL 100A: Structure and Properties I, Problem Set 5

This problem set is due in lecture on Wednesday, Nov 4th in hard copy. Write neatly, show your work clearly, and include units in all answers. While you are free to discuss this problem set with your classmates, the product that you turn in must be your own work. Do not copy or paraphrase each other’s work.

Chapter 12

1. Familiarize yourself with the procedure for finding the minimum cation-to-anion radius ratio for various coordination numbers.

Show that the minimum cation-to-anion radius ratio for a coordination number of 4 is 0.225.

2. On the basis of ionic charge and ionic radii given below (1), predict crystal structures for the following materials. Justify your selections.

(a) CsI
(b) NiO
(c) KI
(d) NiS

![Figure 1: Ionic radii for several cations and anions (for a coordination number of 6)](image)

3. Compute the atomic packing factor for the cesium chloride crystal structure in which $r_C/r_A = 0.732$.

4. The zinc blende crystal structure is one that may be generated from close-packed planes of anions.

   (a) Will the stacking sequence for this structure be FCC or HCP?
   (b) What is the coordination number of the cations?
   (c) Will cations fill tetrahedral or octahedral positions? Why?
   (d) What fraction of the positions will be occupied?

5. Magnesium oxide has the rock salt crystal structure and a density of 3.58 g/cm³.

   (a) Determine the unit cell edge length.
(b) How does this result compare with the edge length as determined from the radii in the Table (1), assuming that the Mg$^{2+}$ and O$^{2-}$ ions just touch each other along the edges?

6. Compute the theoretical density of diamond given that the C–C distance and bond angle are 0.154 nm and 109.5°, respectively. How does this value compare with the measured density?

7. Cadmium sulfide (CdS) has a cubic unit cell, and from x-ray diffraction data it is known that the cell edge length is 0.582 nm. If the measured density is 4.82 g/cm$^3$, how many Cd$^{2+}$ and S$^{2-}$ ions are there per unit cell?

8. For each of the following crystal structures, represent the indicated plane in the manner of Figure 2b, showing both anions and cations. Only the plane view is necessary.

   (a) (100) plane for the rock salt crystal structure
   (b) (110) plane for the cesium chloride crystal structure
   (c) (111) plane for the zinc blende crystal structure
   (d) (110) plane for the perovskite crystal structure

![Figure 2: (a) Reduced-sphere FCC unit cell with the (110) plane. (b) Atomic packing of an FCC (110) plane. Corresponding atom positions from (a) are indicated.](image)

9. In terms of bonding, explain why silicate materials have relatively low densities.

10. Would you expect Frenkel defects for anions to exist in ionic ceramics in relatively large concentrations? Why or why not?

11. Using the following data (3) that relate to the formation of Schottky defects in some oxide ceramic (having the chemical formula MO), determine the following:

   (a) The energy for defect formation (in eV)
   (b) The equilibrium number of Schottky defects per cubic meter at 1000°C
   (c) The identity of the oxide (i.e., what is the metal M?)

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$N_s$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>5.50</td>
<td>$9.21 \times 10^{19}$</td>
</tr>
<tr>
<td>1000</td>
<td>5.44</td>
<td>?</td>
</tr>
<tr>
<td>1250</td>
<td>5.37</td>
<td>$5.0 \times 10^{22}$</td>
</tr>
</tbody>
</table>

![Figure 3: Data for Problem 11](image)
12. (a) Suppose that Li₂O is added as an impurity to CaO. If the Li⁺ substitutes for Ca²⁺, what kind of vacancies would you expect to form? How many of these vacancies are created for every Li⁺ added?

(b) Suppose that CaCl₂ is added as an impurity to CaO. If the Cl⁻ substitutes for O²⁻, what kind of vacancies would you expect to form? How many of the vacancies are created for every Cl⁻ added?