Homework Assignment 1 (21 points total)

Review: Covering Sections 1-all, 2.3-8, 3.1-4, 4.1-3

Ceramic Structures and defects: Covering Sections 12.1-5

Solve Questions 12.4, 12.6, 12.14, 12.25 (a and d only), 12.26, 12.34

AND 4 Extra Questions (not extra credit, just extra beyond the book).

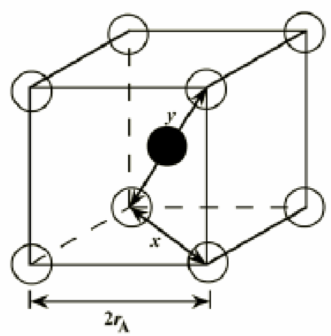
12.4: 3 points total

1 point for noticing one needs to work with the body center (this is 8 coordinated).

1 point for getting the distance of the body diagonal is sqrt(3).

1 point for the final answer. Students must show their work.

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

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

12.6: 3 points total

1 point for figuring out that CsCl structure (CN8) is what we want (i.e. 0.732<rc/ra<1)
1 point for Na as an answer.
1 point for Ca as another possible answer. NOTE: if students stated that Ca can't possibly work because it is a 2+ cation instead of 1+, that is acceptable and worth the point instead. Technically, though, we could use Ca as long as we didn't fill every Ca site (like in fluorite where every other site is empty).

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:

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

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

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

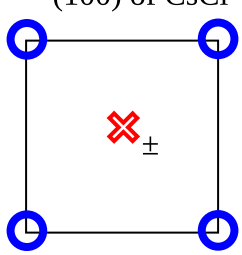
Thus, only sodium will form the CsCl crystal structure with fluorine.

12.14: Not graded (answer in the book)

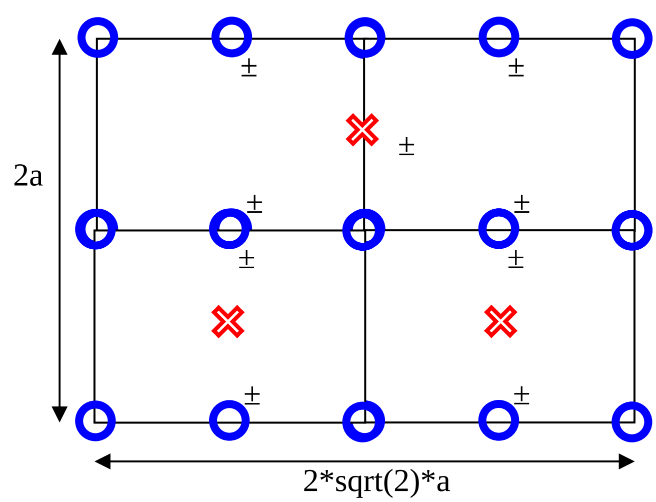
12.25 (a and d only): Not graded

What will the following planes look like:

(a) (100) of CsCl



(b) (110) of fluorite:



NOTE: similar to CsCl, but i) there is a 2x2 super-cell, and ii) the Ca cations (x's in the diagram) are only at the body center of every other cube.

12.26: 2 points total
2 points for any of the following. Each comment need not be present.

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.

Also, the glassy silicates have numerous defects and/or an amorphous character, causing a density that differs greatly from the theoretical density.

12.34 Not graded (answer in book, and similar to EQ4)

(a) For Ca^{2+} substituting for Li^+ in Li_2O, lithium vacancies would be created. For each Ca^{2+} substituting for Li^+, this adds one extra electron to the crystal. In order to maintain charge neutrality, there are several options.

i) One less electron should be added. For example, create a lithium vacancy, so that for every Ca^{2+} ion added, a single lithium vacancy is formed.

ii) Alternatively, use an anion that requires more electrons than usual per site. So, substitute an anion that needs 3 electrons on the O site (which normally needs 2 e-). For example, substitute a N, P, or As on the O site.

(b) For O^{2-} substituting for Cl^- in $CaCl_2$, an extra electron is taken so the crystal needs another electron to maintain charge balance. There are several options.

(i) Create a Chlorine (anion) vacancy, which means where we normally use up an electron, we won't, which is effectively the same as adding an electron.

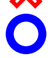
(ii) Use a substitutional cation that gives three electrons instead of 2 as Ca normally does. For example, substitute B or Al on the Ca site.

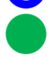
(iii) Use a singly charged interstitial cation. For example, place Li or Na in an interstitial site, giving an extra electron to the crysal.

Extra Question 1) Not graded, solved in class.

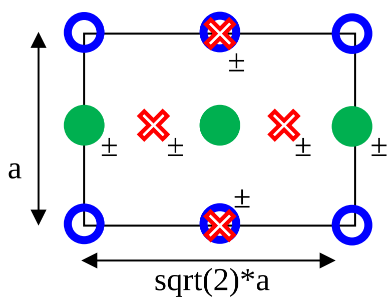
a) Draw a unit cell of a perovskite crystal.

 = oxygen

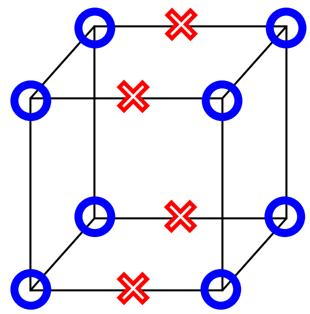
 = cation (usually smaller)

 = cation (usually larger)

b) Identify/draw the [110].



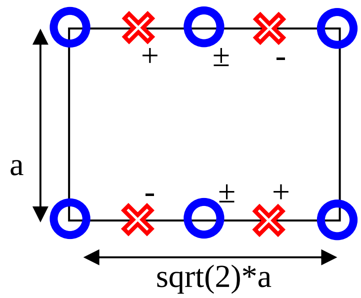
Extra Question 2) 5 points total (1 pt for a, and 3 pts. in b as follows: 1 pt for the rectangular shape and noting the a and sqrt(a) distances, 1 pt for the o's at the corners, 1 pt for including x's and o'x above and below the plane, and 1 pt for noticing that each x is only above OR below following an alternating pattern (not both above AND below for each site as with several class examples).



a) How many of each atom are there in the following crystal?

1 circle and 1 x of each per unit cell.

b) Draw the {110} for this crystal



Extra Question 3) 4 points total (1 pt for equation, 1 pt for getting N, 1 pt for getting the exponent (esp. noticing the C to K conversion), and 1 pt for the answer.

How many Frenkel defects will there be in a silver chloride crystal at 25 degrees Celsius if the energy for defect formation is 1.1 eV and the AgCl density is 5.5 g/cm^3 at this temperature?

Note: This is basically question 30, except at 25C instead of 350C.
You should use the following equation for the number of Frenkel defects at any given temperature. $N_{fr} = N \exp - Q_{fr}/(2kT)$

So N_{fr} = N * exp{ - 1.1 eV / [(2)(8.62 × 10-5 eV/K)(25 + 273 K)]}
(remember to add 273K since Boltzman's constant is in eV/Kelvin, not eV/Celsius)

=N * exp {-1.1 eV / (0.051375 eV/K)}
=N * exp {-21.4111}
=N * 5.027E-10

To determine N, we will use the given density and molecular formula (one Ag and one Cl each).

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

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

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

Finally, the full answer for the density of Frenkel defects will be:

N_{fr}=1.16E19 sites/m^3

That sounds like a lot, but compared to the number of lattice sites per volume this is very tiny indeed (just 1 in 10 billion).

Extra Question 4) 4 pts. total, 2 pts for each option. No pts given/taken for the stoichiometry part of the question.

If CaO is added to $CaCl_2$, what kinds of defects other than vacancies might form to compensate for the charge imbalance AND WHY?

a) IDENTIFY 2 options. NOTE: you may substitute any other atom you wish if you so choose, create any interstitials you like (but NOT anionic interstitials EVER), or use combined sets of defects.

b) How will each of your selections adjust the stoichiometry of the crystal?

We will assume that Ca will sit on a Ca site, so this does not create any defects.
The O will site on a Cl site, creating a charge imbalance that needs to be accommodated. The O requires 2 electrons, whereas the Cl needed just 1, so once the O is in the crystal we are missing an electron for charge balancing. Somehow, we need to either add an extra electron, or use one less electron. There are many options:

i) Create a Cl vacancy near the O on the Cl site. The Cl that should be at this vacancy site would have used up an electron—without it, that electron is available for the Oxygen that needs it. Stoichiometry is not maintained, as there are now not exactly twice as many Cl atoms as Ca atoms. Note that, while this answer would satisfy the charge imbalance, the question asks for defects OTHER THAN VACANCIES, so only ½ credit will be given if this is an answer.

ii) Substitute a group III cation for Ca somewhere. The third electron this cation can give to the crystal will be used for the Oxygen. Stoichiometry is maintained.

iii) Add an interstitial cation that provides one electron. For example, add a Li or Na interstitially, either of which would balance the charge by giving their electron to the crystal for the Oxygen to take. Stoichiometry is maintained.

iv) Add a doubly charged interstitial cation. But now there is an extra electron, so we need a corresponding defect to get rid of it. Maybe another O on a Cl site?

v) There are many other, more complicated possibilities. Interstitial anions are forbidden, so 1 negative point if this is an answer.