Chem 253A Problem Set 2
Due Thursday, March 17th
Descriptive crystal chemistry & Phase Diagrams

1. $SrTiO_3$ has the perovskite structure, a = 3.905 Å. Calculate (a) the Sr-O bond length, (b) the Ti-O length, (c) the density of $SrTiO_3$. What is the lattice type?

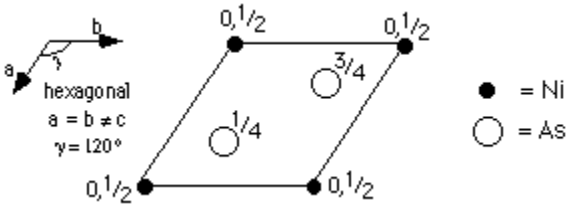
2. (a) Calculate the lower limiting cation-anion radius ratio for three-fold coordination and four-fold coordination (tetrahedral).
   (b) For B^{3+} (r = 0.20 Å) and O^{2-} (r = 1.40 Å), what coordination number would be predicted?

3. What structures might you expect the following compounds to adopt? Justify your responses.
   $SrCl_2$, ZnO, CoTe, MgO, Cs_2O.

4. (a) Explain how the "Radius Ratio Rules" may be used to rationalize or predict the structures of simple ionic solids.
   (b) At room temperature and atmospheric pressure all the alkali metal halides adopt the rock salt (NaCl) structure except cesium compounds CsCl, CsBr and CsI. Comment on this in the light of the following ionic radii:

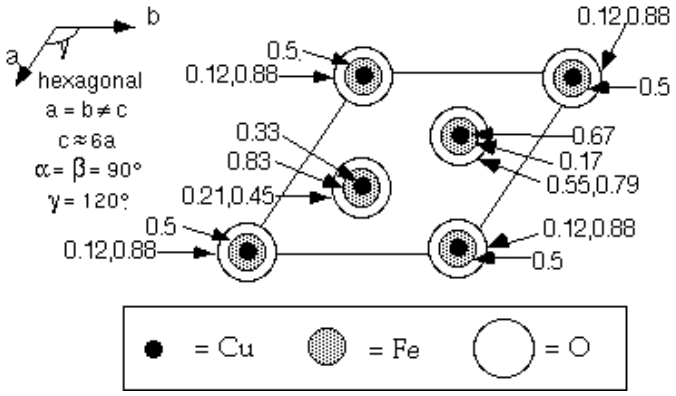
	Li^+	**Na^+**	**K^+**	**Rb^+**	**Cs^+**
r_M+/pm	60	95	133	149	169
	F^-	**Cl^-**	**Br^-**	**I^-**	
r_X-/pm	136	181	195	216	

5. The NiAs structure is shown in plan view below:



   (a) Identify the coordination numbers and geometries of Ni and As and show the coordination environment of each on a plan diagram.
   (b) If the structure is regarded as constructed of $NiAs_x$ polyhedra, describe how these polyhedra are linked together.

6. The *delafossite* structure of $CuFeO_2$ is shown in the plan view below:



(a) Draw a perspective sketch of the unit cell roughly to scale (note, $c = 6a$) and show the positions of the O and Cu ions. Hence identify the arrangement of O ions around Cu ions.
(b) Using the same approach as for NiAs, identify the arrangement of O ions around the Fe ion at (0,0,½). Show the coordination of O around Fe on a plan diagram.
(c) Describe how the $OCuFe_3$ tetrahedra are linked together in the *delafossite* structure.

7. Sketch the phase diagram for the system Al_2O_3-SiO_2 using the following information. Al_2O_3 and SiO_2 melt at 2060 and 1720 °C, respectively. One congruently melting compound, $Al_6Si_2O_{13}$, forms between Al_2O_3 and SiO_2 with a melting point of 1850 °C. Eutectics occurs at 5% Al_2O_3, 1595 °C, and ~ 67% Al_2O_3, 1840 °C.

8. Sketch a phase diagram for a system A-B that has the following features. Three binary compounds are present A_2B, AB and AB_2. Both A_2B and AB_2 melt congruently. AB melts incongruently to give A_2B and liquid. AB also has a lower limit of stability.

9. Construct a triangular grid for representing three-component phase diagrams. Let the three components be Na_2O, CaO and SiO_2. Mark on your triangle, using a mole% scale, the compositions of the following phases: Na_2SiO_3, $Na_2Si_2O_5$, $CaSiO_3$, Ca_2SiO_4, Na_2CaSiO_4, $Na_4CaSi_3O_9$, $Na_2CaSi_5O_{12}$.

10. Below are given the solidus and liquidus temperature for the Ge-Si system. Construct the phase diagram for this system and label each region:

Composition (wt%)	Solidus Temperature (°C)	Liquidus Temperature (°C)
0	938	938
10	1005	1147
20	1065	1226
30	1123	1278
40	1178	1315
50	1232	1346
60	1282	1367
70	1326	1385
80	1359	1397
90	1390	1408
100	1414	1414