Set 3:

Theme: Connecting polyhedra. Factors that affect choice of structure type.

For description of structures, one can take basis in sphere packing or in connection of coordination polyhedras. We will first consider tetrahedra and octahedra as building blocks for isolated units and three-dimensional structures. Coordinationpolyhedra have got corners, edges, and faces that can be shared with adjoining polyhedra. Considerations of the distances involved shows which forms of connections that are undesirable due to repulsion between central atoms of the different polyhedra. The Principe for connections is often reflected in the chemical formula of the compound.

1.1. Consider the isolated units of connected octahedra in figure 1. What stoichiometry has the units (a) – (e)?

1.2. Al_2Cl_6, $Cr_2O_7^{2-}$, Mn_2O_7, SO_3 and CrO_3 are all constructed from tetrahedral units. Sketch the structure for the units/compounds and note how these are connected.

1.3. First consider an isolated octahedra, and then construct a continuously longer one-dimensional chain by letting the octahedra polymerize through shearing of two corners with neighboring octahedra. (Viz. edge sharing). What is the limiting value with respect to stoichiometry of such a connection of octahedra?

1.4. What type of connections of tetrahedra do you expect for the silicates (a) Ca_2SiO_4, (b) $KAlSiO_4$ (both Al and Si have tetrahedral surroundings of oxygen), (c) $Sc_2Si_2O_7$, (d) $MnSiO_3$ (e) $CaMgSi_2O_6$, (f) $CaAl_2(OH)_2(Si_2Al_2)O_{10}$?

1.5. The silicate minerals are classified according to their structural elements. Construct general formulas for silicate structures that are based on (a) groups of separate tetrahedras (single-, neosilicates), (b) tetrahedral dimmers (double-, sorosilicates), (c) ring formed structures (ring-, cyclosilicates), (d) monochains of tetrahedras (chain-, inosilicates), (e) two-dimensional network of tetrahedra that share three corners (layered-, fyllosilicates), (f) three-dimensional network of tetrahedra that share four corners (network-, tektosilikates).

1.6. How would you describe the CdI2-type structure from a basis of connection of polyhedra? (Hint: consider an AB-layer in projection on the ab-plane and draw the coordination polyhedra.)

Use the tables in West (1.8 p 37(NaCl), 1.9 p 38 (Zink blende), 1.10 p 38 (fluorite), 1.12 p 44 (würtsitt), 1.13 p 46 (NiAs) and 1.14 p 47 (CsCl)), which gives an overview on what compounds that crystallize with the NaCl-, NiAs-, CsCl-, and würtsite-type structures.

2.1. Discuss for which of these structural types you find compounds that typically represent respectively ionic, covalent, metallic or van der Waals bondings.

2.2. Why can NH_4Cl adopt the CsCl-type structure?

2.3. Discuss the difference in c/a ratio (spreading and deviation from ideal values) for würtsitt-, and NiAs-type phases.

3.1. What types of coordination are expected for BeO, CaO and BeO from the basis of relative size of anion and cation?
Be^{2+} r = 0.41 Å O^{2-} r = 1.24 Å

Ca^{2+} r = 1.14 Å
Ba^{2+} r = 1.50 Å

3.2. Consider an octahedra hole in a ccp anion structure. Calculate the ratio between the anion and a cation (in the octahedra hole) on the assumption that they can be described as spheres that is in contact with each other. Would it be beneficial if the cation was larger or smaller than the case that the ions are in touch? Do the same considerations for CN=8 and cubic as coordination polyhedra. (Hint: the anion spheres are in touch. Find the direction that the anion spheres and cation spheres are touching each other as pearls on a line.

3.3. Use the Sanderson's model to calculate partial charges for BaO. Use data from West.

3.4. For BeO the partial charge on oxygen of -0.36, for MgO -0.50, for CaO -0.56 and for SrO -0.60. How do you evaluate these variations on the basis of knowledge of trends in the periodic system?

3.5. LiF, MgO, ScN and TiC have all NaCl-type structure. Consider the degree of ionic vs. covalent character of the bonds in these compounds.

3.6. Sketch a Moser-Pearson diagram. Note where in the diagram that BeO, CaO, LiF and TiC occur. Note in the diagram where ionical bondigs dominate and where directional bonds dominate.

3.7. The monoxides of 3d-elements have as a rule normal NaCl-type structure. Explain why the structure for CuO is deformed. Compare this to the following structural data for CuO:
$a = 4.95, b = 3.41, c = 5.11$ Å $\beta = 99.5°$
Spacegroup $C2/c$ [C lattice has as equivalent points (0,0,0) and (1/2,1/2,0)]. Center of symmetry is present.
Cu in (1/4,1/4,0) and (3/4,1/4,1/2); O in (0,y,1/4) with y = 0.416.
Draw the structure in form of projection on the ac-plane. Calculate Cu-O distances. Draw the coordination polyhedra.

3.8. NiO has normal NaCl-type structure. For PtO (in same bigroup), the structure is deformed and Pt has almost plane quadratic surroundings of oxygen. Explain.

3.9. Give a possible reason to why the SnS structure deviates from the ideal NaCl-type structure.

Fig. 1.

(a) (b) (c) (d) (e)