Inorganic Lecture Course  
Perovskite Materials  
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Lecture 3 (Ionic Bonding & Octahedral Tilting in Perovskites)

Questions

1. Consider the structure of the 3-layer Dion-Jacobson phase, CsBa$_2$Nb$_3$O$_{10}$, shown on the right. In addition to the barium and cesium atoms there are two different types of niobium (the niobium atoms in the outer layers, Nb1, and the niobium atoms in the inner layer), and four different oxygen atoms. The chemical environments of the oxygen atoms are not all equivalent.
   - O$_3$ and O$_4$ have two Nb neighbors and four Ba neighbors as they would in the ideal perovskite structure.
   - O$_2$ also has two Nb neighbors, but only two Ba neighbors.
   - O$_1$ has one Nb neighbor and four Cs neighbors.
   (a) Carry out a Pauling bond valence analysis assuming a symmetric environment (all bond valences equal) around the cations. What are the valences of the Cs–O, Ba–O and Nb–O bonds?
   (b) Calculate bond valence sums for each of the oxygen atoms, O$_1$–O$_4$. Are the valence sums all equal to 2 as required by Pauling’s 2$^{nd}$ rule? If not which oxygens are overbonded and which are underbonded?
   (c) If we assume the Cs–O and Ba–O bonds retain their ideal valence, what values of the Nb1–O$_1$, Nb1–O$_2$, Nb1–O$_3$, Nb2–O$_3$ and Nb2–O$_4$ bond valences are needed so that each of the Nb and O atoms has the correct bond valence sum?
   (d) Given the R$_{ij}$ values of x.xx Å (Cs–O), x.xx Å (Ba–O), x.xx Å (Nb–O), determine the bond distances that correspond to the valences you determined in part (c).

2. MgSiO$_3$ is the arguably the perovskite that is of greatest interest to geologists because it is thought to be the predominant compound in the earth’s upper mantle. Given the R$_{ij}$ values of x.xx Å for Mg–O bonds and x.xx Å for Si–O bonds calculate the tolerance factor for MgSiO$_3$. Given this value would you expect perovskite to be the most stable structure at room temperature and pressure?

3. For the following combinations of crystal system and lattice centering (a Bravais lattice) what is the most likely space group for an ABX$_3$ perovskite?
   (a) Body centered orthorhombic: Imma or Immm?
   (b) Body centered tetragonal: I4/mmm or I4/mcm?