C. INFLUENCE OF MADELUNG ENERGY AND COVALENCY ON THE STRUCTURE OF $A^+B^{5+}O_3$ COMPOUNDS

Many oxides, fluorides and sulfides of formula ABX_3, where A and B are cations, crystallize in one of the hexagonal-perovskite polytypes. In the fluoro-perovskites (ABF_3) cation-cation Coulomb repulsive forces are small because the B cations have a relatively small (2^+) charge. Consequently the stability ranges for the polytypes are determined entirely by the ionic radii of the cations.

In the ABO_3 compounds, the stability ranges are not well defined by the ionic radii, since these ranges also depend significantly on the effective charges of the B cations. High-pressure synthesis techniques have been utilized to investigate the factors determining the structures of $A^+B^{5+}O_3$ compounds, for which no hexagonal polytypes have been reported.

The $A^{2+}B^{4+}O_3$ compound $BaTiO_3$ provides a clue to the behavior of the $A^+B^{5+}O_3$ compounds. The Goldschmidt tolerance factor[6] (t) is 1.06 for $BaTiO_3$. For such a high value of t, because of severe geometric hindrances, the cubic perovskite structure is geometrically less favorable than the hexagonal polytypes. Nevertheless, stoichiometric $BaTiO_3$ is cubic at high temperatures. Unlike the cubic form, the hexagonal structures involve face sharing of BO_6 octahedra, and the cation-cation repulsive forces are strongest across the shared faces. Apparently the effective charge on the Ti^{4+} ions in stoichiometric $BaTiO_3$ is sufficiently high that the loss of Madelung energy due to Ti^{4+}-Ti^{4+} repulsions makes the hexagonal forms less stable than the cubic. For oxygen-deficient $BaTiO_3$, however, the effective charge on the Ti^{4+} ions is reduced, and the hexagonal (6H) form is observed. The hexagonal (9R) polytype is formed by $BaRuO_3$, which has the same tolerance factor as $BaTiO_3$. In this case, the repulsive forces are reduced because Ru^{4+} ions have a much smaller effective charge than Ti^{4+} ions.

In a perovskite whose Goldschmidt factor is much greater than 1.0, there is considerable stretching of the B-O bond. By reducing the elastic restoring forces that would inhibit displacement of the B cation toward one or more near neighbor O ions, this stretching enhances any tendency for ferroelectric distortions. Thus $BaTiO_3$ (t = 1.06) is ferroelectric, but $SrTiO_3$ (t = 0.99) is not.

Since previous investigations had demonstrated that high pressures tend to stabilize the cubic perovskite phase, the synthesis of some new $A^+B^{5+}O_3$ compounds having large Goldschmidt factors was attempted. $RbNbO_3$ (t = 1.08) was synthesized at 65 kbar and 900°C. At atmospheric pressure and room temperature, this compound is an orthorhombic perovskite ($\underline{a}$ = 3.9965 Å, $\underline{b}$ = 5.8360 Å, $\underline{c}$ = 5.8698 Å), isostructural with the ferroelectric orthorhombic form of $BaTiO_3$. Once again ferroelectric distortions are associated with $t > 1$.

The compound $RbTaO_3$ (t = 1.08) was synthesized at 90 kbar and 900°C. It forms a cubic perovskite ($\underline{a}$ = 4.035 Å). Apparently the strong octahedral-site preference of the Ta^{5+} ion does not permit a ferroelectric distortion at room temperature, even for such a high value of t.

Synthesis of $RbNbO_3$ and $RbTaO_3$ shows that high-pressure stabilization of B^{5+} perovskites having very high Goldschmidt factors is possible. Heating these compounds, which are metastable at atmospheric pressure, results in their decomposition rather than transformation to a hexagonal structure. Therefore, it is certain that the $A^+B^{5+}O_3$ compounds do not have stable hexagonal polytypes, presumably because the high effective charge on the B^{5+} ions makes the cation-cation repulsion too strong.

To study the effect of covalency on ABO_3 structures, $A^+Sb^{5+}O_3$ compounds were also investigated, where the B cations have no outer d orbitals and there is strong Sb-O covalency. Regardless of tolerance factor, no $A^+Sb^{5+}O_3$ perovskite or perovskite polytype has been reported. Several high pressure syntheses were attempted, to see whether a perovskite structure involving 180° Sb^{5+}-O-Sb^{5+} bonds could be stabilized.

The compound $RbSbO_3$ (t = 1.085) was synthesized at 20 kbar and 1000°C. It has the Pn3 structure of cubic $KSbO_3$ (a = 9.6985 Å). The compound $TlSbO_3$ was also synthesized at elevated pressures; it exhibits a distorted form of the Pn3 structure. In this structure, pairs of SbO_6 octahedra share edges, and these pairs are linked at their corners to form a cubic network. The Sb-O-Sb bond angles are 90° and about 130°. Apparently this phase is more stable than the cubic perovskite structure, even though it requires placement of unscreened A^+ ions relatively close to each other within tunnels formed by this network.

It is concluded that 180° Sb^{5+}-O-Sb^{5+} bonds are unstable relative to 90° or 120° to 140° Sb^{5+}-O-Sb^{5+} bonds. This is presumably due to the stronger covalency that is possible if the oxygen ions do not use the same p orbital in the formation of two different Sb-O bonds.

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D. STRUCTURE OF $V_{0.95}Cr_{0.05}O_2$

The results of a structure refinement on a compound of nominal composition $V_{0.95}Cr_{0.05}O_2$ were recently reported.[7] In making this refinement, a face-centered orthorhombic cell[8] was used to index the diffraction pattern obtained by x-ray intensity measurements on a powdered sample.

An alternative, monoclinic structure for $V_{0.95}Cr_{0.05}O_2$ is suggested by the results of a recent structural investigation of $V_{0.976}Cr_{0.024}O_2$ by Marezio, et al.[9] On the basis of single crystal diffraction data they identify four crystallographically distinct phases as a function of temperature. The room-temperature modification (designated M2), with unit-cell parameters a = 9.0664 Å, b = 5.7970 Å, c = 4.5255 Å and β = 91.88°, is a monoclinic phase whose structure accounts for all the diffraction peaks observed in our powder pattern for $V_{0.95}Cr_{0.05}O_2$.

To study the possibility of deciding between the orthorhombic and monoclinic structures for $V_{0.95}Cr_{0.05}O_2$ by means of powder diffraction experiments, intensity calculations for this composition based on the two structures were compared. The calculated patterns differ significantly only in the character of the peak corresponding to a d-spacing of about 1.33 Å. For the monoclinic structure, the diffraction envelope in this region is composed of two peaks of approximately equal intensities, the 620 and 023. Their d-spacings of 1.3394 and 1.3376 Å, respectively, correspond to an angular separation of approximately 0.1° in 2Θ for copper radiation. For the orthorhombic structure, there is only a single peak, the 662, whose intensity is approximately equal to the sum of the two monoclinic peaks.

In an attempt to observe the splitting predicted by the monoclinic structure, the powder diffraction of $V_{0.95}Cr_{0.05}O_2$ near 70° was carefully re-measured, using CuKα radiation and a graphite crystal diffracted-beam monochromator. Figure III-3 reproduces a trace obtained in this region at a diffractometer speed of 1/8 °/min and chart speed of 1/2 inch/min. The $K\alpha_1$ and $K\alpha_2$ peaks are well resolved. The distance between these peaks, which are separated by about