Polyoxoniobates: How Solution Chemistry Helps to Understand the Solid State

Keith A. Marek Final Seminar August 2, 2001

The fields of solid state chemistry,[1] polyoxoanion chemistry,[2] and coordination chemistry of early transition metal oxo compounds[3] have traditionally been viewed as separate, mutually exclusive areas. From a chemical perspective, however, the structure and bonding in these three seemingly different types of compounds is quite similar. The key feature that unifies the study of these three fields is the concept of metal oxygen d-p π bonding. For example, the same structural distortions that are observed in the vanadyl ion[4] also occur in perovskite compounds such as $BaTiO_3$[5] and $KNbO_3$.[6] Metal-oxygen bond distortions are also observed in polyoxometalate compounds such as $(\eta^5\text{-}C_5H_5)TiMo_5O_{18}{}^{3-}$.[7]

Compounds that possess the perovskite structure, such as $BaTiO_3$ and $KNbO_3$, exhibit ferroelectric behavior due to the metal-oxygen bond distortions that take place in the O—Ti—(O—Ti—)$_n$O—Ti—O chains in their structures at temperatures below the Curie point, T_C, which corresponds to a structural phase transition.[5] At temperatures near T_C, the direction of the metal-oxygen bond dipole can be easily switched, causing these compounds to exhibit high relative permittivities (dielectric constants) in this temperature region.[5] Lead zinc niobate, $Pb_3(ZnNb_2)O_9$ (PZN), belongs to a subset of ferroelectric materials known as relaxor ferroelectrics.[8] Structurally, PZN, like $BaTiO_3$ and $KNbO_3$, possesses the ABO_3 perovskite structure, with Pb atoms occupying the A sites and Zn and Nb atoms occupying the B sites. However, unlike barium titanate and potassium niobate, the phase transition in PZN occurs over a broad temperature range (90-240°C).[9] As a result, PZN exhibits a very high relative permittivity ($\varepsilon' > 30{,}000$) in this temperature range.[9] This diffuse phase transition can be attributed to the structural disorder that occurs in the B sites of the perovskite structure. Unlike $BaTiO_3$, which has essentially infinite titanium-oxygen chains, the PZN structure contains a broad distribution of niobium-oxygen chain lengths due to the presence of the Zn atoms on the B sublattice that interrupt the chains. Electron diffraction experiments[10] show that the Zn and Nb atoms in PZN are ordered on the B sublattice in a 1:1 NaCl-like fashion. This ordering cannot occur on the macroscopic scale, however, due to the overall 1:2 Zn:Nb stoichiometry. The relationship between the chemical ordering and the diffuse phase behavior exhibited by PZN is unknown.

In order to gain insight into the chemical ordering that takes place in PZN, the solution chemistry of polyoxoniobates was explored. The existing aqueous chemistry of Nb^V is dominated by the hexaniobate ion (Figure 1a) and its protonated forms which exist in solutions of pH 7 and higher.[2] Observation of other polyniobates has not been possible due to the formation of niobic acid, which occurs at lower solution pH. However, nonaqueous routes to polyoxoniobates are possible. Tetramethylammonium decaniobate $[N(CH_3)_4]_6Nb_{10}O_{28}$ was synthesized in 80% yield by reacting niobium ethoxide and tetramethylammonium hydroxide in wet ethanol. The decaniobate ion has a structure analogous to the decavanadate ion, shown in Figure 1b, and is stable in aqueous solution at pH 5.5. The decaniobate ion can be converted to the hexaniobate ion or its protonated forms by the addition of base, as observed by ^{17}O NMR spectroscopy.

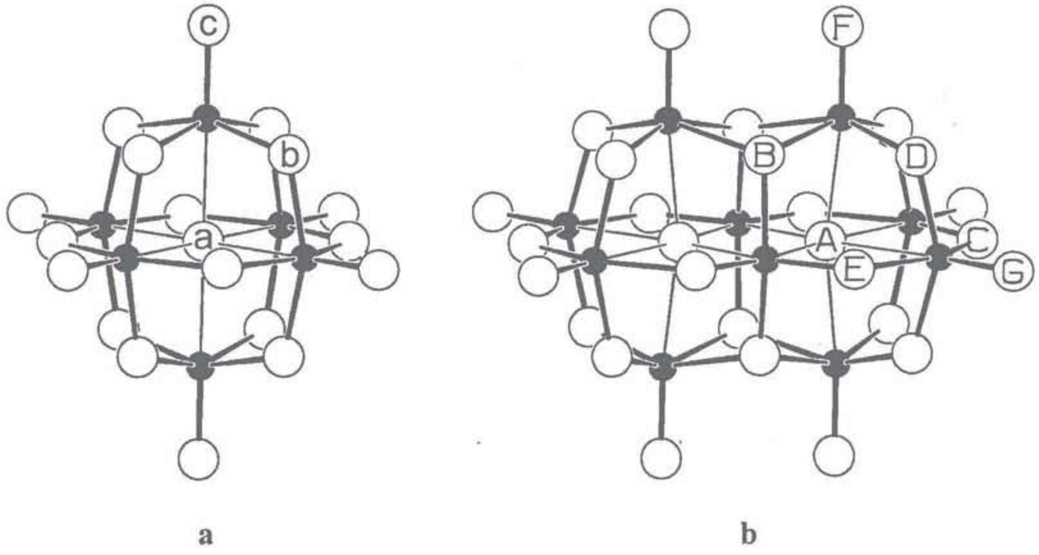

Figure 1

PZN can be thought of as a large $(Nb_2O_9^{8-})_n$ polyniobate with Pb^{2+} and Zn^{2+} cations. Doing so, however, imposes restrictions on the Nb and Zn B-site ordering. If every oxygen in the PZN structure is associated with the polyniobate, i.e. connected to at least one Nb atom, there can be no oxygen atoms between two Zn atoms. Considering this, a model for the chemical ordering in PZN was developed using a computer simulation. A 500×500×500 cubic array with random 1:2 Zn:Nb occupation was generated, and an algorithm was developed which rearranges this array to eliminate corner sharing ZnO_6 octahedra (i.e. eliminate O atoms which lie between two Zn atoms). This shuffling algorithm produces a structure with 1:1 NaCl-like Nb:Zn domains interspersed with clusters of polyniobate chains. This structure is consistent with the local NaCl-like ordering observed using electron diffraction.[10] In addition, a distribution of polyniobate chains is created which can be used to explain the diffuse phase behavior exhibited by PZN. A three-dimensional representation of these polyniobate chains is shown in Figure 2.

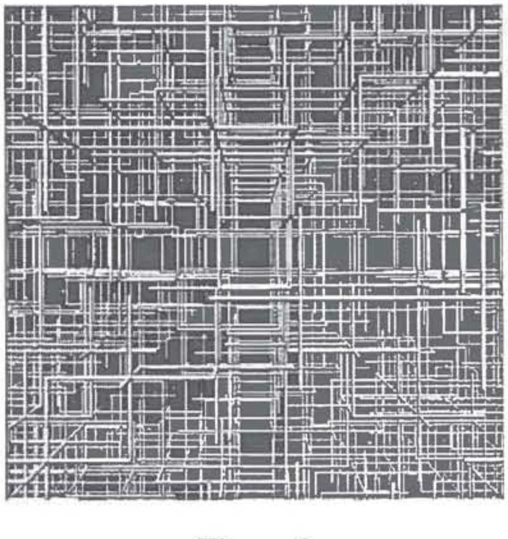

Figure 2

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