Theory of prospective tetrahedral ferroelectrics

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In this work we study, using first-principles methods, the energy vs. polarization relation of double perovskites $AA'BB'O_6$ where atoms in both A and B sites are arranged in rock-salt order. While rock-salt ordering is common on the B site in $A_2BB'O_6$ perovskite compounds, it is very rare on the A site in $AA'B_2O_6$ compounds where layered ordering is preferred instead. The high-symmetry structure for this class of compounds is the *tetrahedral* $F\bar{4}3m$ space group. If a ferroelectric instability occurs, the energy-vs.-polarization landscape $E(\mathbf{P})$ will tend to have minima for $\mathbf{P}$ along tetrahedral directions leading to a rhombohedral space group $R3m$, with two different values of spontaneous polarization and associated energy along opposite body diagonals; or along Cartesian directions, leading to space group $Imm2$. We search for polar *soft modes* at the Γ point of the high-symmetry $F\bar{4}3m$ structure and analyze the related eigenvectors to identify ferroelectric instabilities, which we find in $CaBaTiZrO_6$, $KCaZrNbO_6$ and $PbSnTiZrO_6$. We also find some zone-boundary octahedral-rotation instabilities, but do not pursue those here.

The calculations were performed using an *ab-initio* computer code package, ABINIT with norm-conserving pseudopotentials. $\mathbf{P}$ is calculated primarily using the Berry-phase approach.[1] The results of the first-principle calculations are modeled with a Landau-Devonshire expansion that is truncated at either 4th or 5th order in $\mathbf{P}$, and its predictions are found to agree favorably with our calculation. Recently, synthesis of $SrCaTiMnO_6$ in rock-salt order using layer-by-layer molecular-beam epitaxy on a (111) surface orientation has been reported.[2] Unfortunately our calculations on this system indicate no polarized structure.

[1] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).

[2] J.L Blok, G. Rijnders and D.H.A. Blank, private communication.