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 \( E(P) \) will tend to have minima for \( P \) along tetrahedral directions leading to a rhombohedral space group \( R\bar{3}m \), with two different values of spontaneous polarization and associated energy along opposite body diagonals; or along Cartesian directions, leading to space group \( I\bar{mm}2 \). We search for polar soft modes at the \( \Gamma \) point of the high-symmetry \( F\bar{4}3m \) structure and analyze the related eigenvectors to identify ferroelectric instabilities, which we find in \( \text{CaBaTiZrO}_6 \), \( \text{KCaZrNbO}_6 \) and \( \text{PbSnTiZrO}_6 \). We also find some zone-boundary octahedral-rotation instabilities, but do not pursue those here.

The calculations were performed using an \textit{ab-initio} computer code package, ABINIT with norm-conserving pseudopotentials. \( P \) 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 \( P \), and its predictions are found to agree favorably with our calculation. Recently, synthesis of \( \text{SrCaTiMnO}_6 \) 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.
