

Ab Initio Analysis of Ferroelectric and Magnetic Properties of Potentially Multiferroic Aurivillius Phases

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Multiferroic materials combining magnetic properties with electric polarization in the same phase, are promising for novel applications in electronic devices. [1] However, these combined properties are typically exhibited at low temperatures. Novel ways to integrate ferroelectricity with long-range magnetic order above room temperature are therefore of high relevance.

We focus on the Aurivillius family of naturally-layered perovskite-related materials, which combine well-established high temperature ferroelectric properties [2, 3] with a layered structure that allows for systematic introduction of various magnetic ions. The structure consists of m perovskite layers $(A_{m-1}B_mO_{3m+1})^{2-}$, stacked along the [001] direction, and separated by fluorite-like $(Bi_2O_2)^{2+}$ layers (see Figure 1a).

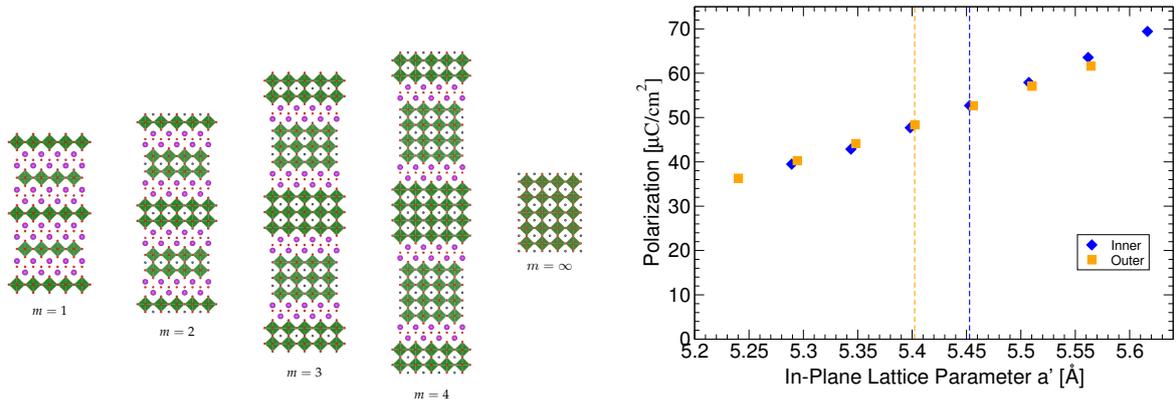
To exhibit robust multiferroic properties, the Aurivillius phases need to satisfy two criteria: i) maintain ferroelectricity despite the introduction of magnetic cations, and ii) form long-range magnetic order from magnetically dilute compositions. The simplest case that has been explored as potential multiferroic is $Bi_5FeTi_3O_{15}$. However, no well-established value exists for its spontaneous electric polarization, with reports varying from $3.5\mu C/cm^2$ to $\sim 30\mu C/cm^2$. [4, 5] Similarly, an antiferromagnetic Néel temperature of 80 K has been reported [6], in contradiction with other studies observing paramagnetic behavior with no magnetic long-range order even at very low temperatures. [4, 7–9]

To provide clarification as well as guideline for future studies, we first establish the intrinsic properties of $Bi_5FeTi_3O_{15}$ using first-principles electronic structure calculations and symmetry mode analysis. These results are then generalized to other Aurivillius phases. We also perform Monte Carlo simulations to assess the possibility of long-range magnetic order and estimate the corresponding ordering temperature.

For the case of $Bi_5FeTi_3O_{15}$, we find a slight preference of the Fe^{3+} cation to occupy the “inner” site within the perovskite-like layers, consistent with recent experimental observations. [10] This site-preference can be tuned by applying epitaxial strain and we observe a transition to an “outer”-site preference under strong in-plane tensile strain. The calculated value for the spontaneous electric polarization of $Bi_5FeTi_3O_{15}$ is $\sim 55\mu C/cm^2$, and can also be tuned by applying epitaxial strain (see Figure 1b). We obtain very strong antiferromagnetic coupling for Fe^{3+} in nearest-neighbor positions (~ 40 meV), but rather weak coupling (~ 1 -2 meV) at next-nearest neighbor distances and beyond, consistent with the Goodenough-Kanamori rules for superexchange.

To clarify whether magnetic long range order can occur in $Bi_5FeTi_3O_{15}$ and similar systems, despite the low concentration of magnetic cations and the short range of the magnetic superexchange interaction, we perform Monte Carlo simulations for an appropriately chosen Heisenberg model. We find that the critical temperature for magnetic long-range order depends crucially on the rather weak next-to-nearest neighbor coupling. On the other hand, the also very weak interlayer-coupling (i.e. across the fluorite layer) is less crucial as long as the coupling within the perovskite layers is sufficiently strong. We discuss possible strategies to obtain Aurivillius phases with high magnetic ordering temperatures.

Finally, in order to better understand the mechanism for ferroelectricity in $Bi_5FeTi_3O_{15}$ and other Aurivillius phases, we examine different 2-layered systems, based on the well-studied reference system $SrBi_2Ta_2O_9$ [11], where we systematically substitute the nominally “ferroelectrically-active” cations (Bi^{3+} and Ta^{5+}) by “non-ferroelectrically-active” cations (La^{3+} and Sb^{5+}). In total we consider 9 different compositions by also substituting Ta^{5+} with Nb^{5+} and Sr^{2+} with Ba^{2+} and Ca^{2+} . Strikingly, we find a spontaneous polarization of $\sim 15\mu C/cm^2$ even in the case of $SrLa_2Sb_2O_9$, with no nominally ferroelectrically-active cations. We discuss these results in light of the tri-linear coupling between soft and hard modes demonstrated for $SrBi_2Ta_2O_9$ [11] and the general concept of “hybrid improper ferroelectricity”. [12]



(a) The Aurivillius family of layered-perovskite related materials. m denotes the number of perovskite layers, recovering bulk at ∞ .

(b) Polarization as a function of bi-axial in-plane strain. “Outer” denotes Fe^{3+} as B-cation of a perovskite next to the (Bi_2O_2) layer, “Inner” denotes Fe^{3+} as B-cation of a perovskite surrounded by perovskites.

Figure 1: The Aurivillius family as robust ferroelectric materials.

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