

Ferroelectricity and multiferroicity in the Dion-Jacobson compounds $ABiNb_2O_7$, $A=Cs$, $(MnCl)$, from first principles

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While ferroelectricity in the perovskite oxides has long been the subject of intensive experimental and theoretical study, interest has recently grown in exploring the occurrence and mechanisms for ferroelectricity in other oxide structural families. This is motivated both by expanded opportunities for tuning polarization-related properties, including dielectric and piezoelectric coefficients, and by the search for new multiferroics¹ with stronger magnetic ordering and magnetoelectric coupling. Of particular interest are structures consisting of 2D perovskite layers separated by intergrowth layers of other metal oxides: homologous series of compounds such as the Dion-Jacobson $A[A'_{n-1}B_nO_{3n+1}]$, Ruddlesden-Popper $A_2[A'_{n-1}B_nO_{3n+1}]$, and Aurivillius $[Bi_2O_2][A'_{n-1}B_nO_{3n+1}]$ (A =alkali metal, A' alkaline earth, and B transition metal) compounds. In these layered structures, magnetic cations could be introduced into the intergrowth layers, leading to magnetic ordering and multiferroic behavior. For example, the Dion-Jacobson $n=2$ compound $CsLaNb_2O_7$, has been shown to easily undergo topochemical reactions where the Cs^{1+} intermediate layer is exchanged by a layer of $(TM^{2+}Cl^{1-})$ where TM =first row transition metal, e.g. Mn .^{2,3} However, of the layered perovskite compounds investigated so far, the only ferroelectrics experimentally realized are in the Aurivillius family, the best known examples being $SrBi_2Ta_2O_9$ and $Bi_4Ti_3O_{12}$, while a predicted Ruddlesden-Popper FE^4 has yet to be confirmed experimentally. Recently, Lightfoot and coworkers performed neutron diffraction on ceramic samples of the $n=2$ Dion-Jacobson compound $CsBiNb_2O_7$ and found that the room temperature structure crystallizes in the polar space group $P2_1am$.⁵ However, based on a low value of the static dielectric constant obtained from electrical measurements, Lightfoot et al. concluded that $CsBiNb_2O_7$ does not display ferroelectricity.

Here, we report our group theoretical analysis and first-principles calculations of the structural energetics and phonons to investigate the ground state structure and polarization of $CsBiNb_2O_7$. First-principles density-functional calculations using PAW potentials were performed within the LDA and LSDA+U as implemented in VASP. Polarization was calculated using the modern theory of polarization. As we discuss in more detail below, all evidence indicates that this material is a ferroelectric, with a high paraelectric-ferroelectric transition temperature consistent with the observation of a low static dielectric constant at room temperature. Further first-principles calculations are in progress to study the effect of substituting Bi for La in the known antiferromagnet $(MnCl)LaNb_2O_7$, in particular, whether the substitution will produce a ferroelectric instability in this magnetic system. Preliminary results suggest that the layered Dion-Jacobson systems are indeed attractive candidates for materials displaying multiferroic behavior.

We use a systematic approach to identify and compare candidate low-symmetry phases and possible ferroelectricity of $ABiNb_2O_7$, $A=Cs$ and $(MnCl)$ by investigating the lattice instabilities of the high-symmetry nonpolar $P4/mmm$ reference structure, which the related compounds, $ALaNb_2O_7$ have been shown to have at room temperature. We performed full optimization of the lattice parameters and internal coordinates of $ABiNb_2O_7$ in this tetragonal reference structure. By performing a group-theoretical analysis using the experiments on $CsBiNb_2O_7$ as a guide, we find that the zone-center Γ -phonons and the zone-boundary M -point phonons drive all relevant transi-

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tions. By performing phonon calculations at these selected points in the Brillouin zone, freezing in various unstable phonons, and optimizing the structural parameters in the resulting space groups, we can select the lowest energy structure as the predicted ground state.

In the case of CsBiNb₂O₇ we calculated the Γ_5^- phonons by computing the relevant block of the dynamical matrix from finite differences of the Hellmann-Feynman forces. We found one unstable Γ_5^- phonon with frequency $\omega = i 185 \text{ cm}^{-1}$. The character of the real-space eigendisplacement of this unstable mode consists mostly of Bi-ions moving against oxygen in Bi-O planes as would be expected due to the Bi 6s lone pair but also consists of a smaller amount of Nb-O displacements. The freezing-in of this ferroelectric mode leads directly to the C2mm space group without a doubling of the unit cell. Next, we computed the M_5^- , M_2^+ , and M_3^+ phonons at the $q=(1/2, 1/2, 0)$ point of the Brillouin zone. M_5^- has two unstable modes with frequencies $\omega_1 = i 210 \text{ cm}^{-1}$ and $\omega_2 = i 70 \text{ cm}^{-1}$. The M_5^- modes are antiferrodistortive, the character of which are Bi-O and Nb-O displacements for ω_1 and ω_2 respectively. The freezing-in of these M_5^- modes leads to the paraelectric Pmam space group with a doubled unit cell. Finally, the M_2^+ and the M_3^+ phonons both consist only of oxygen motion in the Nb-O planes. The M_2^+ phonon is unstable ($\omega = i 190 \text{ cm}^{-1}$) leading to space group P4/mbm while the M_3^+ phonon is stable. Based on the results of the phonon calculations, we see that transitions out of the P4/mmm reference structure to the space groups C2mm, Pmam, P4/mbm, and P2₁am are all possible due to the freezing-in of one or more unstable modes. To identify which phase is most energetically favorable and therefore most likely to be observed at low temperatures, we performed a series of structural relaxations within each of the above mentioned space groups. We relaxed all lattice parameters and internal coordinates, with results as follows: P4/mbm (M_2^+), -400 meV; C2mm (Γ_5^-), -550 meV; Pmam (M_5^+), -350 meV; P2₁am (Γ_5^- and M_2^+ or Γ_5^- and M_5^+), -800 meV. From this it is clear that P2₁am, being 800 meV lower than the tetragonal reference structure and 450 meV lower than Pmam, is the computed ground state, in full agreement with the Rietveld refinements of Ref. 5.

Using our computed structural parameters for the P2₁am phase of CsBiNb₂O₇ we calculate a substantial polarization, $P_s \approx 40 \mu\text{C}/\text{cm}^{-1}$. Further we point out that the observed polar distortions from an as yet hypothetical non-polar reference structure are consistent with the structural criteria established by Abrahams⁶ for systems having a high probability of displaying a FE transition, and application of the Abrahams formula for Tc gives an estimate of 810 K. This leads us to propose that CsBiNb₂O₇ is in fact a FE,⁷ and that the low static dielectric constant observed at room temperature results from the system being very far from the transition.

For the case of (MnCl)BiNb₂O₇, we follow a similar procedure as outlined above. Results of our ongoing investigation will be presented.

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