Ferroelectricity in the Dion-Jacobson CsBiNb$_2$O$_7$ from first principles

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We have studied ferroelectricity in Dion-Jacobson CsBiNb$_2$O$_7$ from first principles. Using group-theoretical analysis and first-principles density functional calculations of the total energy and phonons, we perform a systematic study of the energy surface around a paraelectric prototypic phase. Our results suggest that CsBiNb$_2$O$_7$ is a ferroelectric with a polarization of $P_s=40 \mu C \text{ cm}^{-2}$. We propose further experiments to clarify this point.

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The ABO$_3$ perovskites with their corner-sharing octahedra, display an amazing variety of physical properties by simply changing the A and B cations. In the rational design of new materials much effort has been directed towards manipulating the connectivity of perovskites by forming structures consisting of 2-d layers of perovskites separated by cation network. Homologous series of these layered perovskites 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 $[B_2O_2]_s[A'_{n-1}B_nO_{3n+1}]$ (where A=alkali metal, A’ alkali earth, and B transition metal) have been formed by a number of novel growth techniques including molecular beam epitaxy and soft chemistry techniques such as ion-exchange and intercalation reactions.

While ferroelectricity is ubiquitous in the ABO$_3$ perovskite titanates, niobates, and tantalates, the only layered perovskites to display a ferroelectric (FE) transition has been the Aurivillius compounds, while a predicted Ruddlesden-Popper FE has yet to be confirmed experimentally. Recently, Lightfoot and coworkers performed neutron diffraction on ceramic samples of the $n=2$ Dion-Jacobson compound CsBiNb$_2$O$_7$ and found that the room temperature structure crystallizes in the polar space group P2$_1$am. Nevertheless, from electrical measurements of the static dielectric constant, they concluded that CsBiNb$_2$O$_7$ does not display ferroelectricity.

In this letter we perform group theoretical analysis and first-principles calculations of the structural energetics and phonons of CsBiNb$_2$O$_7$. We show that the polar structure observed in Ref. 4 is a stable low-symmetry phase of CsBiNb$_2$O$_7$ for which we calculate a substantial polarization, $P_s\approx 40 \mu C \text{ cm}^{-2}$. Further we point out that the observed polar distortions from a non-polar reference structure are consistent with the criteria established by Abrahams for systems having a high probability of displaying a FE transition. All this strongly suggests that CsBiNb$_2$O$_7$ is a FE.

First-principles density-functional calculations using projector augmented-wave potentials were performed within the local density approximation (LDA) as implemented in the Vienna ab initio Simulation Package (VASP). The wavefunctions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. Integrals over the Brillouin zone were approximated by sums on a $6 \times 6 \times 2 \Gamma$-centered $k$-point mesh. Polarization was calculated using the modern theory of polarization implemented in VASP.

We approach the problem of identifying stable, low-symmetry phases of CsBiNb$_2$O$_7$ and possible ferroelectricity by investigating the lattice instabilities of a hypothetical reference structure. Reference structures of this type can be chosen by detecting a pseudosymmetry of the observed polar phase, that is by finding structures in a group-subgroup relation where the atomic distortions relating the two phases are relatively small. The simple tetragonal (paraelectric) space group P4/mmm, which the related compound, CsLaNb$_2$O$_7$ has been shown to form at room temperature, satisfies this requirement. While it is reasonable to assume that at a high temperature CsBiNb$_2$O$_7$ transforms to P4/mmm, we must emphasize that regardless of whether this transition occurs, P4/mmm is a good reference structure.

From x-ray and neutron powder diffraction, Ref. 4 showed that the unit cell of CsBiNb$_2$O$_7$ was orthorhombic at room temperature and in a $\sqrt{2}a_l \times \sqrt{2}a_l \times c_l$ relation to the simple tetragonal reference structure, systematic reflections being consistent with the non-polar space group Pmam and with the polar space group P2$_1$am. Subsequent Rietveld refinements gave a better fit to the P2$_1$am space group.

Both Pmam and P2$_1$am are subgroups of P4/mmm.

FIG. 1: Structure of ferroelectric CsBiNb$_2$O$_7$. 
Group-theoretic analysis shows that the zone-center $\Gamma_5$ phonons and the zone-boundary $M$-point phonons drive all relevant transitions.\cite{1,13} Performing phonon calculations at these selected points in the Brillouin zone and subsequently investigating the structural energetics around the reference structure facilitates a systematic method of determining possible low-symmetry structures. Specifically, as seen from Fig. 2, Pmam is related to P4/mmm by the freezing-in of a single $M_5$ zone-boundary phonon. On the other hand, a $\Gamma_5$ zone-center ferroelectric mode and a $M$-point zone-boundary mode are required to account for the symmetry change associated with P2$_1$am.

We performed full optimization of the lattice parameters and internal coordinates of CsBiNb$_2$O$_7$ in the tetragonal reference structure space group P4/mmm. Our calculated structural parameters are displayed in Table I where they are written in terms of the $\sqrt{2}a_{t} \times \sqrt{2}a_{t} \times c_{t}$ lattice vectors so as to readily compare with the P2$_1$am structure. Next we calculated the $\Gamma_5$ phonons by computing the relevant block of the dynamical matrix from finite differences of the Hellmann-Feynman forces. We found one unstable $\Gamma_5$ phonon with frequency $\omega = i$ 185 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 would lead directly to the C2mm space group without a doubling of the unit cell. Next we computed the $M_5^-$, $M_3^+$, 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 cm$^{-1}$ and $\omega_2 = i$ 70 cm$^{-1}$. The $M_5^-$ modes are antiferrodistortive, the character of which are Bi-O and Nb-O displacements for $\omega_1$ and $\omega_2$ respectively. The freezing-in of these $M_5^-$ modes leads to the paraelectric, doubled unit cell, Pmam space group. Finally, the $M_3^-$ and the $M_3^+$ phonons both consist only of oxygen motion in the Nb-O planes. The $M_3^+$ phonon is unstable ($\omega = i$ 190 cm$^{-1}$) leading to space group P4/mmbm 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/mmbm, and P2$_1$am are all possible due to the freezing-in of one or more unstable modes, as summarized in Fig. 2. 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, the results are as follows:

| Space Group | Irrep | $\Delta$ E/ f.u. |
|-------------|-------|-------------------|
| P4/mmbm     | $M_5^-$ | -400 meV |
| C2mm        | $\Gamma_5^-$ | -550 meV |
| Pmam        | $M_5^+$ | -350 meV |
| P2$_1$am    | $\Gamma_5^-$ and $M_3^+$ | -800 meV |
|             | or $\Gamma_5^-$ and $M_5^-$ | |

where it is clear that P2$_1$am, 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. 1. The results of the structural relaxations within the P2$_1$am space group are shown in Table I. We find lattice constants $\approx$1% smaller than those determined experimentally at 300 K, typical of LDA calculations. In Table II, we compare with the experimentally determined bond lengths. We find excellent agreement, within 1-2% except for the Bi-O$_3$ bonds which differ by 3-5%.

From phonon calculations, we have shown that lattice instabilities of a high symmetry reference structure of CsBiNb$_2$O$_7$ lead naturally to a P2$_1$am ground state. As we have stated the symmetry of this space group allows a ferroelectric polarization to develop along the a-axis. In fact, from Berry-phase calculations of the polarization we find that CsBiNb$_2$O$_7$ should have a polarization $P_s \approx 40 \mu C cm^{-2}$, which is about three times larger than the polarization of the $n=2$ Aurivillius compound SrBi$_2$Ta$_3$O$_9$ and comparable to that of the $n=3$ Bi$_3$Ti$_5$O$_{12}$.

In principle, a material is considered a ferroelectric if both 1) it displays a spontaneous polarization ($P_s$) and 2) if $P_s$ can be flipped in an electric field. This definition is reflected in an experimentally derived structural criteria for identifying possible ferroelectrics as 1) the largest $\Delta x > 0.1 \text{ Å}$ and 2) all $\Delta x < 1.0 \text{ Å}$, where $\Delta x$ can be though of as an atomic distortion along the polar

**TABLE I: Crystal structure of ferroelectric CsBiNb$_2$O$_7$, Space Group:** P2$_1$am, $a= 5.412 \text{ Å}, b= 5.343 \text{ Å}, c= 11.22 \text{ Å}$

| Atom | x | y | z | P4/mmm | x | y | z | P2$_1$am |
|------|---|---|---|--------|---|---|---|---------|
| Cs (2b) | 1/4 | 1/4 | 1/4 | 0.2536 | 0.2609 | 1/4 | |
| Bi (2a) | 1/4 | 1/4 | 1/4 | 0.2999 | 0.2652 | 0 |
| Nb (4c) | 1/4 | 1/4 | 0.2077 | 0.2414 | 0.7525 | 0.2077 | |
| O1 (2a) | 1/4 | 3/4 | 0 | 0.2065 | 0.6741 | 0 |
| O2 (4c) | 1/4 | 1/4 | 0.3617 | 0.2496 | 0.7842 | 0.3642 | |
| O3 (4c) | 0 | 0 | 0.1631 | 0.0174 | 0.0383 | 0.1551 | |
| O4 (4c) | 7/4 | 1/4 | 0.1631 | 0.4190 | 0.4380 | 0.1888 | |
Table II: Bond lengths (Å) of CsBiNb$_2$O$_7$. Space Group: P2$_1$ am, Exp.: a = 5.495Å, b = 5.423Å, c = 11.38Å. LDA: a = 5.412Å, b = 5.343Å, c = 11.22Å.

| Atoms  | Exp. Ref. | LDA   |
|--------|-----------|-------|
| Cs - O(2) | 3.038 | 2.968 |
| Nb - O(1) | 2.403 | 2.375 |
| Nb - O(2) | 1.755 | 1.764 |
| Nb - O(3) | 1.941 | 1.957 |
| Nb - O(4) | 1.973 | 1.948 |
| Bi - O(1) | 2.257 | 2.224 |
| Bi - O(3) | 2.707 | 2.614 |
| Bi - O(4) | 2.409 | 2.398 |

*Powder neutron diffraction, room temp.*

Axis from the centrosymmetric reference structure. In CsBiNb$_2$O$_7$, the largest atomic distortion relative to the oxygen framework is ∆x(Bi)≈0.5Å which clearly meets Abrahams’ structural criteria and suggests, independent of the first-principles results, that CsBiNb$_2$O$_7$ is a FE.

Experimentally, an indication of a ferroelectric transition is usually shown by the strong temperature dependence of the static dielectric constant around T$_c$, normally a Curie-Weiss behavior. At temperatures much lower than T$_c$, a strong temperature dependence of the dielectric constant is not expected, for example, the static dielectric constant of LiNbO$_3$ (T$_c$ = 1450 K) over the temperature range 0K-300K. The fact that the static dielectric constant of CsBiNb$_2$O$_7$ does not display a large temperature variation around room temperature does not preclude a ferroelectric transition at a higher temperature. Considering the FE-to-FE energy scale that we calculated, ∆E=400meV/f.u., T$_c$ is expected to be much higher than room temperature. This is consistent with other known ferroelectrics where the stereochemical activity of the Bi lone pair is the driving force towards ferroelectricity such as in BiFeO$_3$ and in SrBi$_2$Ta$_2$O$_9$. In fact, from an empirical expression that has proven quite successful in predicting T$_c$ of several new ferroelectrics, we find T$_c$ = $2 \times 10^4 (\Delta x)^2$ K = 810 K where ∆x is the largest metal atom (in this case Bi) displacement along the ferroelectric direction after a shift of origin so that ∆x(Cs)+∆x(Bi)+∆x(Nb)=0. We suggest that direct measurements of the polarization in CsBiNb$_2$O$_7$ be performed, such as E-P hysteresis loops, to reveal it’s ferroelectric nature since the actual T$_c$ may in fact be higher than the decomposition temperature of the material.

We have confirmed that the ground state of CsBiNb$_2$O$_7$ forms in the polar space group P2$_1$ am and expect a substantial polarization P$_z$ ≈ 40 μC cm$^{-2}$. The similarity of the computed lattice instabilities to the n=2 Aurivillius compounds is intriguing, the implications of which should be pursued further given the fundamental and technological interest in such materials. The Dion-Jacobson family of compounds may provide another avenue towards the design of new ferroelectrics and, given the propensity towards ion-exchange, multiferroics.

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1 D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, X. P. Pan, Mater. Sci. Eng. B 87, 282 (2001).
2 R. E. Schaak and T. E. Mallouk, Chem. Mater. 14, 1455 (2002).
3 C. J. Fennie and K. M. Rabe, Phys. Rev. B 71, 100102(R) (2005).
4 A. Snedden, K. S. Knight, and P. Lightfoot, J. Solid State Chem. 173, 309 (2003).
5 S. C. Abrahams, Acta Crystall. B 44, 585 (1988).
6 G. Kresse and J. Hafner, Phys. Rev. B 47, R558 (1993); G. Kresse and J. Furthmüller, ibid. 54, 11169 (1996).
7 P.E. Blöchl, Phys. Rev. B 50, 17953 (1994); G. Kresse and D. Joubert, ibid. 59, 1758 (1999).
8 R.D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, R1651 (1993).
9 By hypothetical reference we mean a CsBiNb$_2$O$_7$ structure that has yet to be observed experimentally.
10 K. M. Rabe, *Computer Simulation Studies in Condensed-Matter Physics XVI* 95, Eds. D. P. Landau, S. P. Lewis, and H. -B. Schüttrler, Springer-Verlag Berlin 2004.
11 J. M. Igartua, M. I. Aroyo, and J. M. Perez-Mato, Phys. Rev. B 54, 12744 (1996).
12 N. Kumada, N. Kinomura, and A. W. Sleight, Acta Crystallog. C 52, 1063 (1996).
13 H.T. Stokes and D. M. Hatch (2002). ISOTROPY http://stokes.byu.edu/isotropy.html
14 Bilbao Crystall. Server: http://www.cryst.ehu.es
15 R. Seshadri and N. A. Hill, Chem. Mater. 13, 2892 (2001).
16 C. J. Fennie and K. M. Rabe, unpublished.
17 J.M. Perez-Mato, M. Aroyo, A. García, P. Blaha, K. Schwarz, J. Schweifer, and K. Parlinski, Phys. Rev. B 70, 214111 (2004).
18 S. C. Abrahams, Acta Crystall. B 57, 485 (2001).
19 Shen Li, C. J. Fennie, and K. M. Rabe, in preparation.