

First principles investigation of $\text{Bi}_6\text{Ti}_4\text{O}_{17}$: oxide ferroelectricity with a low band gap

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We report first principles studies of the hypothetical compound $\text{Bi}_6\text{Ti}_4\text{O}_{17}$, which is an alternate stacking of the ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. We find that this compound is ferroelectric, similar to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ but with a reduced polarization. Importantly, calculations of the electronic structure with the recently developed functional of Tran and Blaha yield a much reduced band gap of 1.34 eV for this material. Therefore this material is predicted to be a low band gap oxide ferroelectric.

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Oxide ferroelectrics suitable for applications generally have band gaps of 3 eV or higher. However, observations of interesting photovoltaic effects that may be of practical importance¹⁻⁵ have led to interest in materials with higher light absorption and lower band gaps.⁶ In this regard, Ti is a particularly interesting element. First of all it occurs in a variety of well known useful ferroelectric materials, such as BaTiO_3 , PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Secondly, it readily forms oxides in two valence states, Ti^{4+} (e.g. TiO_2 and BaTiO_3) and Ti^{3+} (e.g. Ti_2O_3 and LaTiO_3). Finally, interfaces between LaAlO_3 and SrTiO_3 have been shown to be metallic with high mobility.⁷ This indicates that Ti in the oxide matrix represented by this interface is in a metallic state with valence intermediate between 3+ and 4+. Thus Ti^{4+} oxides with small band gaps intermediate between the large gaps of materials such as BaTiO_3 and the zero gap metal of the LaAlO_3 / SrTiO_3 interface could exist. In general the charge balance, in other words the ionic states, of atoms in solids are determined by the Ewald potential. The key questions are whether it is possible to use this in realizable layered structures to destabilize Ti^{4+} sufficiently to lower the band gap, without crossing over to Ti^{3+} or a metallic state, and if so, whether the resulting material can be ferroelectric.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is an interesting material from this point of view. It has a polarization of $P \sim 50 \mu\text{C}/\text{cm}^2$ at room temperature,⁸⁻¹⁰ and it has a moderately low absorption edge of 3 eV.^{11,12} It has a layered structure based on a stacking of perovskite BiTiO_3 and fluorite-like bismuth oxide blocks (see below) and can be grown in very high quality thin film form.¹³ The presence of separated oxide blocks in a material amenable to thin film growth allows more possibilities for chemical modification, while retaining the ferroelectric function.¹³⁻¹⁷ According to recent first principles calculations, the reduced band gap

in this material arises from a charge imbalance between the Bi-O and perovskite parts of the unit cell.¹² It is known that alternate layerings based on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can be grown in thin films. For example, Nakashima and co-workers recently reported synthesis and properties of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$. Here we exploit this to propose a new ferroelectric material based on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ but with a lower band gap of ~ 1.3 eV. This is a near ideal band gap for exploiting the solar spectrum. The material is based on an alternate layering with an extra perovskite layer and an extra compensating Bi-O fluorite layer, to yield a formula $\text{Bi}_6\text{Ti}_4\text{O}_{17}$. Importantly, Ti^{4+} contains no occupied d orbitals, and is non-magnetic. While this precludes any magnetic functionality, it does offer some advantages: the lack of magnetic moments is favorable for achieving reasonable mobility because there will not be strong magnetic scattering, and the band gap will be of charge transfer character and therefore associated with strong optical absorption in contrast to gaps of $d-d$ character.

We performed full density functional structural relaxations for this compound and find a ferroelectric structure. The calculated polarization is smaller than $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, but still sizable. We then did calculations of the electronic structure using the functional of Tran and Blaha,¹⁸ which is a modified Becke-Johnson form that includes the kinetic energy density and yields greatly improved band gaps for simple oxides and semiconductors.¹⁸⁻²⁰ Importantly, application of this functional, which we denote TB-mBJ, to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ yields very close agreement with the measured experimental optical spectrum.¹² The calculated band gap of the new $\text{Bi}_6\text{Ti}_4\text{O}_{17}$ ferroelectric phase with the TB-mBJ functional is 1.34 eV. This gap is indirect. The direct gap is ~ 0.2 eV higher.

As mentioned, we started with a full structural relaxation. This was done using the generalized gradient

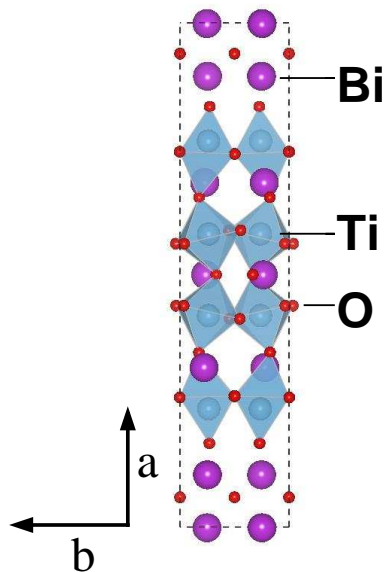


FIG. 1. (color online) Relaxed structure of $\text{Bi}_6\text{Ti}_4\text{O}_{17}$.

approximation (GGA) of Perdew, Burke and Ernzerhof (PBE).²¹ We used the VASP package^{22,23} with projector augmented wave (PAW) pseudopotentials.^{24,25} The structure relaxation was done in a scalar relativistic approximation with a plane-wave cutoff of 500 eV for the basis set and with a Brillouin zone sampling based on a $1 \times 4 \times 4$ \mathbf{k} -point mesh, where a is the long axis of the cell. Energy and force convergence was tested.

We started with an initial guess for the structure based on the layering of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with an additional perovskite BiTiO_3 block compensated by an additional fluoride BiO_2 layer. We then fully relaxed this structure for both the lattice parameters and internal coordinates allowing monoclinic Pc symmetry, which is the symmetry of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. This was continued until the stress tensor components were below 0.25 kBar and the atomic forces were below 0.01 eV/Å. The final structure had lattice parameters $a=25.289$ Å, $b=5.479$ Å, $c=5.510$ Å, and monoclinic angle $\beta=89.035^\circ$. The resulting unit cell volume is 763.4 Å³. The structure is depicted in Fig. 1 and the internal coordinates are given in Table I. Importantly, the structure does not relax to a higher symmetry non-polar group but stays essentially Pc .

The polarization was calculated using the Berry phase method.^{26–28} Within this approach the polarization in a periodic solid is defined modulo a polarization quantum, $e\mathbf{R}/V$, where e is the electronic charge, \mathbf{R} is a lattice vector, and V is the unit cell volume. We determined the branch (i.e. the number of quanta of polarization to be added) using the change from a reference structure, which we took to be the same structure with reversed atomic displacements. The resulting polarization is in the monoclinic plane close to the c -axis as defined ($c=5.510$ Å), but rotated towards the long

TABLE I. Internal coordinates of monoclinic Pc $\text{Bi}_6\text{Ti}_4\text{O}_{17}$. There are two formula units per cell, with all atoms occurring on general sites.

	x	y	z
Bi1	0.9985	0.2479	0.9999
Bi2	0.1035	0.2520	0.4921
Bi3	0.3162	0.2209	0.4426
Bi4	0.5003	0.2355	0.5496
Bi5	0.6833	0.2268	0.5777
Bi6	0.8940	0.2524	0.5060
Ti1	0.2343	0.2633	0.9772
Ti2	0.4192	0.2615	0.0138
Ti3	0.5812	0.2629	0.0097
Ti4	0.7654	0.2602	0.0358
O1	0.0590	0.5000	0.2445
O2	0.0590	0.9998	0.2447
O3	0.1663	0.2695	0.9786
O4	0.2594	0.4952	0.2319
O5	0.2570	0.9984	0.2345
O6	0.3461	0.1742	0.0309
O7	0.4129	0.5482	0.1979
O8	0.4387	0.0349	0.2711
O9	0.5007	0.3325	0.9655
O10	0.5884	0.5561	0.1800
O11	0.5619	0.0384	0.2603
O12	0.6539	0.1758	0.9773
O13	0.7398	0.5030	0.2814
O14	0.7441	0.9972	0.2735
O15	0.8335	0.2720	0.0356
O16	0.9389	0.5003	0.2555
O17	0.9388	0.0002	0.2554

a -axis. The calculated values are $P_{sa}=1.8\mu\text{C}/\text{cm}^2$, and $P_{sc}=12.5\mu\text{C}/\text{cm}^2$, along the a and c axes, respectively. The total polarization is $P=12.6\mu\text{C}/\text{cm}^2$. It comes from Ti and the Bi off-centering in the perovskite blocks.

We used the relaxed structure, as above, as input to electronic structure calculations with the general potential linearized augmented planewave (LAPW) method,²⁹ as implemented in the WIEN2k package.³⁰ We used a well converged LAPW basis with local orbitals to relax linearization errors and include semicore states.³¹ The LAPW sphere radii were 2.3 Bohr, 1.75 Bohr and 1.45 Bohr, for Bi, Ti and O, respectively. The calculations were performed relativistically, including spin-orbit, with a $2 \times 4 \times 4$ \mathbf{k} -point mesh for sampling the Brillouin zone. Parallel calculations were performed with the TB-mBJ functional and the standard PBE GGA. The LAPW forces with the PBE functional were small for the relaxed structure as obtained from from VASP.

The resulting electronic densities of states are shown in Fig. 2. While the TB-mBJ band gap is larger than that obtained with the standard PBE GGA, it is small compared to other oxide ferroelectric materials. We obtain a value $E_g=1.34$ eV with this functional. For comparison, the PBE value is 0.9 eV. Therefore this material is predicted to be a low band gap oxide ferroelectric. Turning

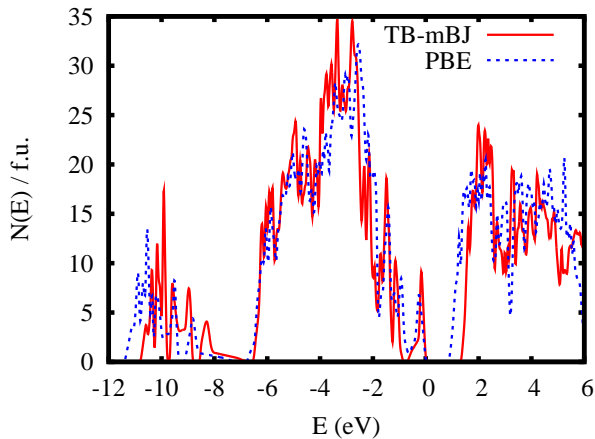


FIG. 2. (color online) Electronic density of states of $\text{Bi}_6\text{Ti}_4\text{O}_{17}$ as obtained with the PBE and TB-mBJ functionals based on the relaxed crystal structure. The states below ~ -7 eV are Bi 6s states, those from -7 eV to the valence band edge at 0 eV are the O 2p derived valence bands, and those above 0 eV are the conduction bands.

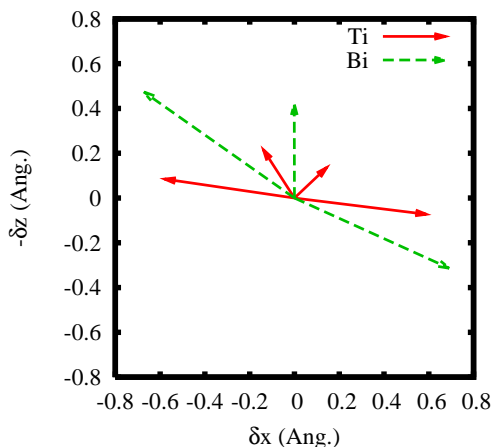


FIG. 3. (color online) Displacements in the monoclinic plane relative to their O cages of the Ti ions and the three Bi ions in the interior of the perovskite block (Bi3, Bi4, and Bi5 with the numbering of Table I). Note the the vertical axis is $-z$ to keep the table. x is along the a -axis and z is the perpendicular direction close to the c -axis. There are also displacements of the individual ions along b , but these cancel exactly and are not shown.

to the nature of the gap, the valence bands are comprised mainly of O 2p states, while the conduction bands are primarily from Bi 6p and Ti 3d states, although as in other ferroelectrics based on these elements, there is cross gap hybridization involving the O 2p orbitals and the nominally unoccupied Bi 6p and Ti 3d states. Thus the gap is of charge transfer character. While this is an expected result, it is of importance because, unlike $d-d$ gaps, a charge transfer gap is generally associated with strong optical absorption above the band edge.

The reduced gap and polarization relative to

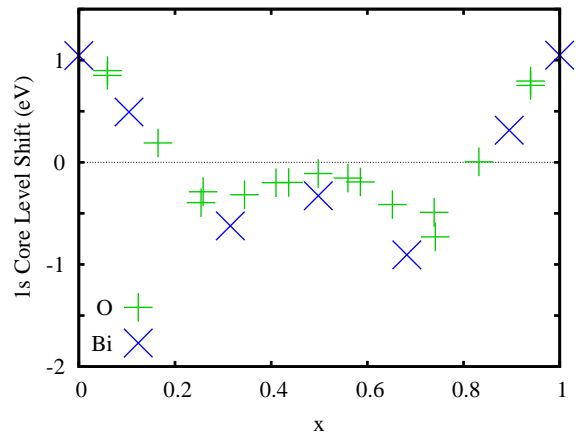


FIG. 4. (color online) 1s core level positions as a function of fractional position x along the a -axis as in Table I of the O and Bi ions relative to the average core level position of the respective species.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are related. Fig. 3 shows the displacements of the Ti and the three Bi ions in the interior of the perovskite block relative to the centers of their O cages in the x - z plane. As seen in this figure and also Fig. 1 there are large displacements relative to the O cages of the ions away from the center of the perovskite part of the unit cell especially for the Ti and Bi ions away on the outer planes of the perovskite block. This is a consequence of the fact that the perovskite layers have net positive charge, which is compensated by the Bi-O layers. Thus cations are pushed away from the center of the perovskite block towards the Bi-O block.

Actually, it may seem that the large positive charge of the perovskite blocks based on $\text{Bi}^{+3}\text{Ti}^{+4}\text{O}_3^{-2}$ (net +1 per unit) mean that they cannot exist. However, it should be emphasized that fully three dimensional perovskites based on Ti and trivalent ions, i.e. LaTiO_3 and YTiO_3 for example, do exist in nature. In these compounds Ti takes a trivalent +3 state. What we are really doing is driving the Ti in the direction of a +3 state. This is seen in the calculations in the form of indications that the compound is not a usual Ti^{4+} oxide. For example, the average Ti-O bond length is long -2.07 Å, reflecting what would amount to underbonding of Ti^{4+} , although it is short for Ti^{3+} . This is also evident in the Brown bond valence³² sums, which for Ti are close to the nominal value of 4.0 in stable ferroelectric materials such as $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$.³³ Both the inner and outer layer Ti are underbonded, with bond valence sums of 3.70 and 3.57, respectively. This is perhaps not surprising considering the excess of positive charge in the perovskite blocks, since nominal bond valences for the cations would then imply very strong overbonding of O. Importantly, stable Ti^{4+} oxides typically have band gaps of 3 eV or higher, while the present compound has a low band gap due to this imbalance.

The net positive charge in the perovskite layers is also

the origin of the reduced gap. The net positive charge pulls down the energies of the cation orbitals in this region reducing the gap. This effect can be clearly seen in the core level positions. Both Bi and O ions occur in both the perovskite and Bi-O parts of the unit cell. Fig. 4 shows the $1s$ core level positions of these ions as a function of the fractional coordinate along the a -axis relative to the average core level position of the respective ion. The perovskite part of the cell is approximately from $x=0.25$ to $x=0.75$. As may be seen, the core level is pulled to higher binding energy in the perovskite part of the cell, reflecting the positive charge in this region (electrons are negatively charged, so electronic states are pulled to higher binding energy by positive charge). The variation in the core level positions is almost 2 eV, which is enough to explain the band gap reduction. Also, if the compound is synthesized, the O $1s$ core level variations of this magnitude should be measurable.

Turning to the polarization, the local electric field induced cation displacement reflects a rotation of the polarizations of the individual perovskite layers to yield components along a that mostly cancel between the layers above and below the center (see Fig. 3). In other words the cations in the outermost layers of the perovskite blocks are pushed away from the center along

the a -axis, reducing the mainly c -axis net polarization. Nonetheless, while reduced relative to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, a sizable net polarization remains.

To our knowledge the proposed compound $\text{Bi}_6\text{Ti}_4\text{O}_{17}$ has not been reported. As such, a key question is how it could be made. It does not appear in existing phase diagrams, and we note that there are competing phases. The basic idea underlying this work is to exploit constraints imposed by layering, in this case charge imbalance. In a sense this is similar to past work using epitaxial constraints to impose strain on various layers in thin films to produce new ferroelectrics. By analogy the most likely route would seem to be based on thin film growth. In particular, as layer by layer growth of the Bi-Ti-O system is perfected it may become possible to grow alternate stackings, including the one proposed in a controlled way.

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