Design of a low band gap oxide ferroelectric: \(\text{Bi}_6\text{Ti}_4\text{O}_{17}\)

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Abstract – A strategy for obtaining low band gap oxide ferroelectrics based on charge imbalance is described and illustrated by 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 \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) although 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 1.83\,eV for this material compared to \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\). Therefore, \(\text{Bi}_6\text{Ti}_4\text{O}_{17}\) is predicted to be a low band gap ferroelectric material.

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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 importance [1–5] have led to interest in materials with stronger 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 \(\text{BaTiO}_3\), \(\text{PbTiO}_3\) and \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\). Secondly, it readily forms oxides in two valence states, Ti\(^{4+}\) (e.g., \(\text{TiO}_2\) and \(\text{BaTiO}_3\)) and Ti\(^{3+}\) (e.g., \(\text{Ti}_2\text{O}_3\) and \(\text{LaTiO}_3\)). Finally, interfaces of \(\text{SrTiO}_3\) with \(\text{LaTiO}_3\) or \(\text{LaAlO}_3\) 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 \(\text{BaTiO}_3\) and the zero gap metal of the \(\text{LaAlO}_3/\text{SrTiO}_3\) 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 made ferroelectric.

\(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) is an interesting starting material from this point of view. It has a polarization of \(P \approx 50\,\mu\text{C/cm}^2\) 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 \(\text{BiTiO}_3\) and fluorite-like bismuth oxide blocks (see below) and can be grown in a 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 an 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 \(\text{Bi}_5\text{Ti}_3\text{FeO}_{15}\). Importantly, the polarization direction is almost perpendicular to the layer stacking direction in \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\). Here we exploit these facts to propose a new ferroelectric material based on \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) but with a lower band gap of \(\approx 1.8\,\text{eV}\), which is a much better value for exploiting the solar spectrum than typical oxide ferroelectric band gaps of 3\,eV or higher. The proposed material is based on an alternate layering with an extra perovskite layer and an extra compensating Bi-O fluorite layer, to yield a formula \(\text{Bi}_6\text{Ti}_4\text{O}_{17}\). This amounts to adding an extra perovskite layer to the perovskite block in \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\).
which adds positive charge to this block and compensating this by negative charge in an extra BiO$_2$ fluorite type layer.

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 Bi$_6$Ti$_4$O$_{17}$ and find a ferroelectric structure. The calculated polarization is smaller than Bi$_4$Ti$_3$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 [18–21]. Importantly, the application of this functional, which we denote TB-mBJ, to Bi$_4$Ti$_3$O$_{12}$ yields very close agreement with the measured experimental optical spectrum [12]. The calculated band gap of the new Bi$_6$Ti$_4$O$_{17}$ ferroelectric phase with the TB-mBJ functional is 1.83 eV.

As mentioned, we started with a full structural relaxation. This was done using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [22]. We used the VASP package [23,24] with projector augmented wave (PAW) pseudopotentials [25,26], for the initial structure relaxation. This 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 $4 \times 4 \times 1$ k-point mesh, where $c$ 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 Bi$_4$Ti$_3$O$_{12}$ with an additional perovskite BiTiO$_3$ block compensated by an additional fluorite BiO$_2$ layer. We then fully relaxed this structure for both the lattice parameters and internal coordinates allowing monoclinic Pb symmetry, which is the symmetry of Bi$_4$Ti$_3$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 $a = 5.479$ Å, $b = 5.510$ Å, $c = 25.278$ Å, $\alpha = 90.965^\circ$. The resulting unit cell volume is 763.4 Å$^3$. We then performed a further relaxation of the internal coordinates using the more precise all-electron general potential linearized augmented plane-wave (LAPW) method [27], with no imposed symmetry. These calculations were done with the WIEN2k code [28]. We used a well-converged LAPW basis with local orbitals to relax linearization errors and include semicore states [29]. The resulting structure is depicted in fig. 1 and the internal coordinates are given in table 1.

![Fig. 1: (Color online) Relaxed structure of Bi$_6$Ti$_4$O$_{17}$.](image)

Table 1: Internal coordinates of monoclinic Pb (No. 7, unique axis a) Bi$_6$Ti$_4$O$_{17}$. There are two formula units per cell, with all atoms occurring on general sites. The lattice parameters are $a = 5.479$ Å, $b = 5.510$ Å, $c = 25.278$ Å, $\alpha = 90.965^\circ$.

|   | x   | y   | z   |
|---|-----|-----|-----|
| Bi | 0.2481 | 0.0000 | 0.9997 |
| Bi | 0.2520 | 0.5045 | 0.1043 |
| Bi | 0.2254 | 0.5729 | 0.3143 |
| Bi | 0.2349 | 0.5433 | 0.4981 |
| Bi | 0.2199 | 0.4305 | 0.6830 |
| Bi | 0.2518 | 0.4947 | 0.8949 |
| Ti | 0.2607 | 0.0278 | 0.2315 |
| Ti | 0.2637 | 0.0051 | 0.4169 |
| Ti | 0.2616 | 0.0090 | 0.5796 |
| O  | 0.5005 | 0.2539 | 0.0596 |
| O  | 0.2678 | 0.0274 | 0.1648 |
| O  | 0.9989 | 0.2662 | 0.2535 |
| O  | 0.1801 | 0.9699 | 0.3439 |
| O  | 0.5499 | 0.1785 | 0.4108 |
| O  | 0.0356 | 0.2491 | 0.4356 |
| O  | 0.3276 | 0.9584 | 0.4976 |
| O  | 0.0302 | 0.2600 | 0.5606 |
| O  | 0.5383 | 0.1997 | 0.5847 |
| O  | 0.1779 | 0.0209 | 0.6529 |
| O  | 0.4939 | 0.2248 | 0.7409 |
| O  | 0.9985 | 0.2269 | 0.7424 |
| O  | 0.2673 | 0.9698 | 0.8320 |
| O  | 0.4996 | 0.2456 | 0.9392 |
| O  | 0.0002 | 0.2457 | 0.9392 |
Importantly, the structure does not relax to a higher symmetry non-polar group but stays essentially Pb.

The polarization was calculated using the Berry phase method [30] with the quantum espresso code [31]. The resulting polarization is in the monoclinic plane close to the b-axis as defined \((c = 5.510 \text{ Å})\), but rotated towards the long c-axis. The calculated polarization is \(19 \mu \text{C/cm}^2\) in the \(b-c\) plane, \(5.5^\circ\) away from \(b\). It comes mainly from Ti and the Bi off-centering in the perovskite blocks. Therefore the ferroelectricity can still exist in this charge imbalanced structure.

We used the relaxed structure, as above, as input to electronic structure calculations with the LAPW method. The calculations were performed relativistically, including spin-orbit, with a \(4 \times 4 \times 2\) k-point mesh for sampling the Brillouin zone. Parallel calculations were performed with the TB-mBJ functional and the standard PBE GGA.

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 \(E_g = 1.83 \text{eV}\) with this functional. For comparison, the PBE value is \(1.28 \text{eV}\). Therefore this material is predicted to be a low band gap oxide ferroelectric. Turning 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. This is of importance because, unlike d-d gaps, a charge transfer gap is generally associated with strong optical absorption above the band edge.

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

The reduced gap and polarization relative to Bi\(_4\)Ti\(_3\)O\(_{12}\) are related. As seen in 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.

![Fig. 3: (Color online) 1s core level positions of the O and Bi ions relative to the average core level position of the respective species as a function of the fractional position z along the c-axis as in table 1.](image)

Actually, it might seem that the net positive charge of perovskite blocks based on Bi\(^{3+}\)Ti\(^{4+}\)O\(_{12}^{-2}\) (net +1 per unit) means that one cannot add such a layer. 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. Importantly, stable Ti\(^{4+}\) oxides typically have band gaps of 3 eV or higher, while the present compound has a low band gap and while in itself it is an indication of chemical instability, prior results for metallic conduction at Ti interfaces with charge imbalance suggest that it may be possible to stabilize the present stacking even though it has a small band gap.

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. Figure 3 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 \(x = 0.75\). The deep 1s levels do not participate in bonding, and therefore their positions reflect the Coulomb potential. 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 greater than 1 eV, which is enough to explain the band gap reduction. Also, if the compound is synthesized, 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. 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 Bi$_3$Ti$_5$O$_{12}$, a sizable net polarization remains.

To our knowledge the proposed compound Bi$_6$Ti$_4$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 epitaxial constraints to impose strain on various layers in the Bi-Ti-O system. Once perfected it may become possible to grow alternate stackings, including the one proposed in a controlled way.

Even if it is not possible to grow the proposed material, it may be possible to grow other stacking sequences using charge imbalance to manipulate the band gap, starting with ferroelectrics such as PbTiO$_3$ or (Ba, Sr)TiO$_3$. For example, one could perhaps make superlattices consisting of PbTiO$_3$ with alternating substitutions of TiO$_2$ layers by, e.g., ScO$_2$ or AlO$_2$, which would have net negative charge, and PbO/BaO by BiO or LaO, which would have net positive charge; in this case the band gap remains.

The key result of the present study is that we show computationally by a specific example that it is possible to have charge imbalanced titanates that combine a low band gap with ferroelectricity.

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REFERENCES

[1] Choi T., Lee S., Choi Y. J., Kiryukhin V. and Cheong S. W., Science, 324 (2009) 66.
[2] Ichiki M., Furue H., Kobayashi T., Maeda R., Morikawa Y., Nakada T. and Nonaka K., Appl. Phys. Lett., 87 (2005) 222903.
[3] Pintilie L., Pintilie I. and Alexe M., J. Eur. Ceram. Soc., 19 (1999) 1473.
[4] Yang S. Y., Seidel J., Byrnes S. J., Shafer P., Yang C. H., Rossell M. D., Yu P., Chu Y. H., Scott J. F. and Ager J. W. et al., Nat. Nanotechnol., 5 (2010) 143.
[5] Huang H., Nat. Photon., 4 (2010) 134.
[6] Bennett J. W., Grinberg I. and Rappe A. M., J. Am. Chem. Soc., 130 (2008) 17409.
[7] Ortom A. and Hwang H. Y., Nature (London), 427 (2004) 423.
[8] Cummins S. E. and Cross L. E., Appl. Phys. Lett., 10 (1967) 14.
[9] Cummins S. E. and Cross L. E., J. Appl. Phys., 39 (1968) 2268.
[10] Sawaguchi E. and Cross L. E., Mater. Res. Bull., 5 (1970) 147.
[11] Oliveira R. C., Cavalcante L. S., Sczancoski J. C., Aguiar E. C., Espinosa J. W. M., Varela J. A., Pizani P. S. and Longo E., J. Alloys Compd., 478 (2009) 661.
[12] Singh D. J., Seo S. S. A. and Lee H. N., Phys. Rev. B, 82 (2010) 180103(R).
[13] Lee H. N., Hesse D., Zakharov N. and Gosele U., Science, 296 (2002) 2006.
[14] Armstrong R. A. and Newnham R. E., Mat. Res. Bull., 7 (1972) 1025.
[15] Snedden A., Lightfoot P., Dinges T. and Saiful Islam M., J. Solid State Chem., 177 (2004) 3660.
[16] Park B. H., Kang B. S., Bu S. D., Noi T. W., Lee J. and Jo W., Nature (London), 401 (1999) 682.
[17] Chon U., Jang H. M., Kim M. G. and Chang C. H., Phys. Rev. Lett., 89 (2002) 087601.
[18] Tran F. and Blaha P., Phys. Rev. Lett., 102 (2009) 226401.
[19] Singh D. J., Phys. Rev. B, 82 (2010) 155145.
[20] Singh D. J., Phys. Rev. B, 82 (2010) 205102.
[21] Kim Y. S., Marsman M., Kresse G., Tran F. and Blaha P., Phys. Rev. B, 82 (2010) 205212.
[22] Perdew J. P., Burke K. and Ernzerhof M., Phys. Rev. Lett., 77 (1996) 3865.
[23] Kresse G. and Hafner J., *Phys. Rev. B*, **47** (1993) R558.

[24] Kresse G. and Furthmüller J., *Phys. Rev. B*, **54** (1996) 11169.

[25] Blochl P. E., *Phys. Rev. B*, **50** (1994) 17953.

[26] Kresse G. and Joubert D., *Phys. Rev. B*, **59** (1999) 1758.

[27] Singh D. J. and Nordström L., *Planewaves Pseudopotentials and the LAPW Method*, 2nd edition (Springer Verlag, Berlin) 2006.

[28] Blaha P., Schwarz K., Madsen G., Kvasnicka D. and Luitz J., *WIEN2k. An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (K. Schwarz, Technische Universität Wien, Austria) 2001.

[29] Singh D., *Phys. Rev. B*, **43** (1991) 6388.

[30] Resta R., *Rev. Mod. Phys.*, **66** (1994) 899.

[31] Baroni S., Dal Corso A., de Gironcoli S., Gdanozzi P., Cavazzoni C., Ballabio G., Scandolo S., Chiarotti G., Focher P. and Pasquarello A. *et al.*, [http://www.quantum-espresso.org](http://www.quantum-espresso.org).