**Band-gap engineering via local environment in complex oxides**

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We examine band-structure engineering in extremely tetragonal ferroelectric perovskites ($ABO_3$) to make these materials suitable for photovoltaic applications. Using first-principles calculations, we study how $B$-site ordering, lattice strain, cation identity, and oxygen octahedral cage tilts affect the energies and the compositions of the valence and conduction bands. We find that extreme tetragonality makes the band gap highly sensitive to the $B$-cation ordering, with a layered $B$-site arrangement exhibiting a small band gap. It also leads to a strong sensitivity of the band gap to the oxygen octahedral tilting. These effects only occur for cations with filled $d$ states located near the valence-band maximum or empty $d$ states at the conduction-band minimum; this criterion is explained by crystal field theory. In addition to a smaller band gap, the layered $B$-site ordering has a strong impact on the carrier mobility. We find that the excited electron effective mass is similar to that found in Si and other classic semiconductors. Moreover, the hole effective mass is strongly anisotropic, indicating a two-dimensional hole gas in the layered $B$-cation ordering.

**I. INTRODUCTION**

Ferroelectric (FE) photovoltaic materials have recently attracted increasing attention for use in solar cell applications. The strong inversion symmetry breaking and spontaneous polarization $P$ of ferroelectrics separate charge carriers well,\(^{1,2}\) making them a promising class of photovoltaic materials.\(^{3-5}\) However, the poor matching of the band gap $E_g$ of most perovskite $ABO_3$ FE materials (3–4 eV) with the solar spectrum greatly reduces their solar energy conversion efficiency. In the last decades, great efforts have been made to understand electronic band structures\(^ {6-12}\) and to engineer a lower electronic band gap in oxide materials\(^ {13,14}\) using first-principles calculations. In this work, we use first-principles density-functional theory (DFT) calculations to explore how $B$-site ordering, lattice strain, cation identity, and oxygen octahedral cage tilts affect the electronic band gap in highly tetragonal ferroelectric perovskites. We find that local chemistry can be used to reduce the band gap by 1–2 eV and achieve the desired combination of low band gap, high polarization, and high electron mobility in FE perovskites.

**II. METHODOLOGY**

We studied the local environment and electronic structure of each oxide with DFT. We used the ABINIT program\(^ {15}\) to investigate $2 \times 2 \times 2$ 40-atom supercells, relaxing the internal ionic coordinates and lattice parameters. All atoms are represented by norm-conserving optimized\(^ {16}\) nonlocal\(^ {17}\) pseudopotentials generated using the OPIUM code\(^ {18}\) with a 60-Ry plane-wave cutoff. We used the generalized gradient approximation (GGA)\(^ {19}\) and a $2 \times 2 \times 2$ Monkhorst-Pack $k$-point sampling of the Brillouin zone.\(^ {20}\) We chose GGA in our study because we found that local-density approximation (LDA) predicts the rhombohedral structure to be lower in energy than the experimentally observed tetragonal ground state for Bi($Zn_{1/2}Ti_{1/2}$)O$_3$.\(^ {21}\) Although GGA is known to generally overestimate lattice parameters of ferroelectric perovskites,\(^ {22}\) the slight overestimation (5%–6%) of tetragonality compared with experiment still makes the GGA predictions reliable for Bi($Zn_{1/2}Ti_{1/2}$)O$_3$ (BZT). Orbital-projected densities of states (PDOS) are calculated with $8 \times 8 \times 8$ $k$-point meshes and Gaussian smearing. The plain DFT underestimates $E_g$ of semiconductors and insulators by 30%–50%.\(^ {23}\) For instance, PbTiO$_3$ (PTO) $E_g$ is underestimated by $\approx$1.5 eV. To address some of the shortcomings of DFT (concerning localized orbitals), the LDA+Hubbard $U$ (LDA+$U$) method was developed by using the on-site Coulomb interaction instead of the averaged Coulomb energy for localized $d$ and $f$ electrons.\(^ {24,25}\) Appropriate Hubbard $U$ values for Ti ($U = 9$ eV on 3d), Zn ($U = 8$ eV on 3d), W ($U = 9$ eV on 5d), and Mo ($U = 9$ eV on 4d) are estimated from the binary oxides (TiO$_2$, ZnO, WO$_3$, and MoO$_3$) and $ABO_3$ (PTO and BaTiO$_3$) whose experimental $E_g$ are well known. It should be noted that the presented results do not qualitatively change for reasonable variations of $U$. However, since LDA+$U$ has the shortcoming of predicting densities of states inaccurately, we only apply LDA+$U$ for correcting $E_g$ values. DFT is used for local structure relaxation and band dispersion analysis.

In cubic phase BZT, there are in total six possible $B$-cation arrangements in a 40-atom supercell. When the lattice symmetry becomes tetragonal, four of these arrangements have two different orientations relative to the (001) polar axis leading to a total of ten $B$-cation arrangements (Fig. 1). The 3:1 Zn-B$^+$ cation ratio leads to five possible arrangements for tetragonal phase 40-atom supercells of Bi($Zn_{3/4}W_{1/4}$)O$_3$ (BZW) and Bi($Zn_{3/4}Mo_{1/4}$)O$_3$ (BZM), as shown in Fig. 2.

**III. RESULTS**

We first focus our study on the newly synthesized BZT, as well as proposed materials BZW and BZM. BZT experimentally exhibits tetragonal symmetry,\(^ {26}\) while BZW and BZM relax into orthorhombic symmetry. These are environmentally friendly and exhibit extremely large tetragonality $c/a$ and $P$, either in the pure state\(^ {26}\) or in an alloy with PTO,\(^ {27,28}\) fulfilling the high polarization requirement.
All three oxides are insulators showing significant cation displacement and spontaneous polarization. Since A-site Bi\(^{3+}\) is small and very covalent, it usually moves off center by a large amount (≈1 Å). B-site Zn is known as a ferroelectrically active cation,\(^{29}\) showing large displacement. Because of the B-site and A-site displacement coupling,\(^{30}\) we observe large cation off-centering and large polarization for all three materials.

The local geometries and energetics of the relaxed BZW and BZM structures resemble BZT, as found in our previous study (Fig. 3).\(^{21}\) The general cation displacement trend is \(D_{\text{Bi}} > D_{\text{Zn}, \text{Ti}} > D_{\text{W}, \text{Mo}}\). With smaller \(D_{\text{Bi}}\) and averaged B-site Born effective charges in BZW and BZM, their polarization magnitude is about 20% smaller than that of BZT. BZW and BZM also show larger \(O_6\) octahedral rotations and non-(001) cation displacement components, due to their smaller tolerance factors of 0.934, compared with 0.949 for BZT.

For the three Bi-based materials, analysis of the ground-state wave functions shows that the valence band is mostly O 2\(p\) with some Zn 3\(d\). The conduction band is chiefly Bi 6\(p\) with some transition metal \(d\) and O 2\(p\). This is different from many previously studied ferroelectrics, where the valence-band maximum and conduction-band minimum usually consist of O 2\(p\), and the B-site transition metal \(d\) states (e.g., Ti 3\(d\) in PTO), respectively. In addition to the unusual presence of the A-site cation states at the conduction-band minimum, we find that the Zn 3\(d\) states are located at or just below the valence-band maximum.

The proximity and connectivity of Zn cations have a strong impact on the electronic structure (Table I). For all ten \(B\)-cation arrangements we study here, the \(E_g\) values are approximately 2.2 eV, except for supercell b. This structure exhibits a significantly lower band gap of 1.48 eV, and has alternating Zn and Ti \(B\)-cation layers stacked along the polar axis. Ju and Guo\(^{31}\) reported \(E_g\) lowering in this specific \(B\)-cation arrangement using a 20-atom supercell, but did not discuss or explain the origin of this effect. An even stronger difference (≈1 eV) between the arrangements containing all-Zn \(xy\) planes and the other arrangements is obtained for the BZM and BZW structures relaxed under the constraints of uniaxial polarization and suppressed \(O_6\) rotations (Table I, set I). We will refer to these as constrained structures in further discussion.

What is the reason for such strong \(E_g\) sensitivity to the \(B\)-cation arrangement? Figure 4 shows that while the conduction bands of arrangements a and b have similar energy and dispersion, the top valence bands of arrangement b rise...
by \( \approx 1 \) eV relative to arrangement a. The major atomic orbital components of the valence-band maximum are O 2\( p_x \) and O 2\( p_y \) for arrangement a; Zn 3\( d_{x^2-y^2} \), O 2\( p_x \), and O 2\( p_y \) for arrangement b. Additionally, in arrangement b, the O orbitals at the valence-band maximum come only from the O atoms in the all-Zn plane, and the higher energies of the Zn 3\( d_{x^2-y^2} \) orbitals lead to a decreased band gap (1.48 eV).

The significant Zn 3\( d_{x^2-y^2} \) character at the valence-band maximum can be explained in a crystal field theory framework. The filled Zn 3\( d \) states have a repulsive interaction with the O 2\( p \) states. The differences in shape and orientation of the five Zn 3\( d \) orbitals lead to a different strength of repulsion, breaking the Zn 3\( d \) degeneracy. In cubic perovskites, the transition metal B-sites are surrounded by six closest oxygen atoms in an octahedral environment, in which 3\( d_{x^2-y^2} \) and 3\( d_{z^2} \) are degenerate. By contrast, because of the high c/a ratio in BZT and significant B-cation off-centering displacement, every Zn atom is in a square pyramidal coordination with five nearest-neighbor oxygen atoms. The Zn 3\( d \) orbitals split, with 3\( d_{z^2} \) highest in energy, since it has the largest overlap with O 2\( p_x \) and O 2\( p_y \). Thus, the change from octahedral to square pyramidal geometry due to extreme tetragonality destabilizes the Zn 3\( d_{x^2-y^2} \) orbitals in BZT, which rise toward the valence-band maximum. This effect is present for both arrangements a and b. However, in arrangement b an additional crystal-field effect due to the presence of an all-Zn plane leads to a further destabilization of the Zn 3\( d_{x^2-y^2} \) orbital, as we discuss next.
The O atoms in an all-Zn$_{xy}$ plane are underbonded. In BZT, the average total valence of each O atom’s B-site neighbors is 6 (Zn$^{2+}$ + Ti$^{4+}$). This is the case for all the O atoms in arrangement a. When an O atom has two Zn neighbors, the total valence of its B-site neighbors is only 4. The B-O bonding is weaker than average, and the underbonded O valence must be compensated by the creation of shorter and stronger Bi-O bonds. This can be seen by comparing the Born effective charges and Bi-O bond lengths for the O atoms in arrangements a and b. The O $Z_{xx}$ element of the Born effective charge tensor is $-3.2$ for arrangement a but only $-2.1$ for the O atoms in the all-Zn plane in arrangement b. Similarly, the shortest Bi-O distance is 2.41 Å in arrangement a and 2.33 Å in arrangement b, indicating that a stronger Bi-O bond valence compensates for the depletion of density from the B-site Ti-O bonds. This can be seen by comparing the electron density distributions of the two arrangements, we see that the redistribution increases the repulsion between the O atoms in arrangement b. Comparing electron density distributions of the two arrangements, we see that there is a depletion of density from the B-site Ti-O bond is replaced by the Zn-O bond, and a build up of charge density in the Bi-O bonds closer to Zn (Figs. 5 and 6). Such an electron-density redistribution increases the repulsion between the O 2$p_z$, O 2$p_x$, and Zn 3$d_{x^2-y^2}$ orbitals. It destabilizes the Zn 3$d_{x^2-y^2}$ even more, raises its energy to the valence-band maximum, and decreases $E_g$, as observed in BZT arrangement b.

To explore the connection between the extreme tetragonality and the unusual cation arrangement sensitivity of $E_g$, we calculated the $E_g$ values for the tetragonal-symmetric BZT arrangements a and b at a range of lattice parameters (Table II).

![Table II](https://example.com/table2.png)

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contrast, neither the volume nor the individual lattice constants a and c are good predictors of $\Delta E_g^{a-b}$ (Table II). Reducing the c lattice parameter reduces the square pyramidal crystal-field splitting of the Zn orbitals, dropping the Zn $d_{x^2-y^2}$ states below the valence-band maximum and reducing $\Delta E_g^{a-b}$. Increasing a decreases the electrostatic repulsion between the O 2$p$ states and the filled Zn 3$d$ states, and $\Delta E_g^{a-b}$ is also reduced. These two effects are of approximately the same magnitude, such that a simultaneous increase of a and c leads to only slight changes in $\Delta E_g^{a-b}$. Thus a large c/a ratio is crucial for strong sensitivity of $E_g$ to the B-cation arrangement.

The energy ordering of the d orbitals is crucial for the band-gap engineering mechanism; we demonstrate this by studying substitution of different A and B cations. To isolate the effect of the cation identity, we use the equilibrium lattice constants from constrained BZT arrangements a and b. We first replace the Zn$^{2+}$ ions by Mg$^{2+}$. In Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ (BMT), the change in Mg/Ti ordering has almost no impact on $E_g$, since Mg 2$p$ orbitals are too far below the valence-band maximum. On the other hand, for Bi(Zn$_{1/2}$Zr$_{1/2}$)O$_3$ (BZZ), where Zr replaces Ti, the strong sensitivity of the $E_g$ to the cation arrangement is preserved, as seen from the data in Table II. To examine the impact of the changes in cation arrangement on $E_g$ for +3/+5 (B/B') A(B$_{1/2}$B$_{1/2}$)O$_3$ perovskites, we substitute Pb for Bi on the A site and Ga/Nb for Zn/Ti on the B site. Despite the proximity of Ga to Zn in the periodic table, our calculations show a small valence-band level change for Pb(Ga$_{1/2}$Nb$_{1/2}$)O$_3$ (PGN), because Ga 3$d$ orbitals are too low to reach the valence-band frontier and affect $E_g$. Similar results are found for Pb(Al$_{1/2}$Nb$_{1/2}$)O$_3$ (PAN) and Pb(Sc$_{1/2}$Nb$_{1/2}$)O$_3$ (PSN). In PAN, there are no d orbitals in the underbonded all-Al plane; in PSN, the Sc 3$d$ orbitals are too high in energy and are located above the conduction-band edge.

For PGN, PAN, and PSN at BZT lattice constants, the extreme tetragonality has a twofold impact on the conduction band. First, the conduction-band minimum is mainly composed of Pb 6$p$ orbitals, similar to the case of the three Bi-based materials we discussed earlier. Second, we find that the transition metal B-site d$^8$ states (Nb 4$d$) are shifted down by the change from the B-cation arrangement a to b. Nb 4$d$ states redistribute due to different B-cation orderings, however, but it does not alter the $E_g$ value since the conduction-band minimum is set by the energy of Pb 6$p$ orbitals. The crystal field theory framework is helpful for understanding the mechanism for Nb 4$d$ states shifting due to B-cation ordering. The higher than average bond order of the Nb-O bonds in the all-Nb plane leads to a decrease in Pb-O bonding for the O atoms bonded to two Nb cations. Such a charge transfer out of the Pb-O bonds and into the Nb-O bonds decreases the electrostatic repulsion between the electrons in the Pb-O bonds and the Nb d states. This shifts the Nb d states down in energy, especially Nb 4$d_{xy}$.

In order to engineer the combination of the valence and the conduction band by B-cation arrangement, we pick Pb(Zn$_{1/2}$Mo$_{1/2}$)O$_3$ (PZM) to study. The higher electronegativity of Mo$^{6+}$ (relative to Nb$^{5+}$) makes Mo 4$d$ located at the conduction-band minimum instead of Pb 6$p$, so that the change in the cation arrangement from a to b lowers the energy of the conduction band (Mo 4$d$) while raising the valence band level (Zn 3$d$). Our LDA+U calculations show that PZM...
The band gap of extremely tetragonal materials is highly sensitive to the tilting of the O6 octahedra. To determine the effect of the O6 tilt, we compare the $E_g$ values of fully relaxed and constrained supercells for BZT, BZW, and BZM. The effect of tilting is even more pronounced for BZW and BZM than for BZT. Here, the constrained structures without O6 rotations exhibit low $E_g$ values ($\approx 0.5–1.5$ eV) with extremely high $c/a$ and $P$. Between the arrangements containing all-Zn $xy$ planes and the other arrangements, the band-gap difference is around 1 eV. However, the $E_g$ values of fully relaxed BZW and BZM supercells vary around 2.2 eV (Table I, set II), with almost the same $E_g$ values for different $B$-cation arrangements.

A comparison of the band structures for the constrained and the fully relaxed geometries of BZW arrangement a′ (Figs. 2 and 7) shows that suppressing O6 rotations increases the bandwidth for both the valence band and the conduction band, decreasing $E_g$. Our results suggest that the $E_g$ can be significantly lowered by suppression of the O6 rotations, which is in agreement with the experimental observations on alkali tantalate materials LiTaO3, NaTaO3, and KTaO3. For these materials, distortions in the Ta-O-Ta bond angles ($37^\circ$, $17^\circ$, and $0^\circ$, respectively) track with the band gap (4.7, 4.0, and 3.6 eV, respectively).

In addition to the $E_g$ engineering via local chemistry, the extremely high tetragonality in Bi-based perovskites leads to unusual carrier mobility. For example, we find a strong dispersion at the conduction band in BZT arrangements a and b. The calculated electron effective mass tensors are 0.3–0.5me, for all three Cartesian directions. This is comparable to the effective mass for the classic semiconductors (Si, Ge, and GaAs), and much smaller than the electron effective mass usually found for the conduction band of perovskites [e.g., BaTiO3 longitudinal and transverse electron effective masses are 3–4me and 1.1–1.3me]. The effective mass is an important parameter predicting charge carrier mobility, and low carrier mobility is one of the obstacles for the use of ferroelectrics for efficient solar energy conversion. A low electron effective mass along the polarization direction in BZT therefore indicates significantly improved electron mobility over the current perovskite ferroelectrics.

Unlike the electron effective mass, the hole effective mass tensor in BZT displays strong anisotropy. For arrangement a, the longitudinal hole effective mass is 25.3me, and the transverse hole effective mass is 1.9me. The anisotropy is even stronger in arrangement b. While its transverse hole effective mass is 0.8me, the longitudinal hole effective mass is essentially infinity. The extremely large $\hat{z}$ direction hole effective masses are easily understood, since the large $c$ lattice parameter ($\approx 4.5$ Å, GGA) makes the structure almost two-dimensionally layered, such that all-Zn planes are isolated from their $\hat{z}$ direction neighbors. Hence the orbital overlap is significantly reduced. It impedes hole transfer along the polarization direction, forming a two-dimensional hole gas (2DHG). This has previously been found for a number of interfacial semiconductor systems.

### IV. Conclusion

In summary, our first-principles calculations suggest several key factors for band-structure engineering of highly tetragonal FE perovskites to make these materials suitable for visible sunlight absorption in solar energy applications. A combination of extreme tetragonality and all-Zn planes stacked perpendicular to the polar axis can significantly raise the energy of the valence band in $ABO_3$ perovskites, decreasing $E_g$ compared with other $B$-cation arrangements. Increased valence and conduction bandwidths are favored by smaller octahedral tilting. Lower conduction-band energies can be induced by incorporating $B$ cations with higher electronegativity. Design of extremely tetragonal materials with specially layered $B$ cations and suppressed oxygen octahedral rotation is a promising direction for the development of new low-$E_g$ highly polar FE semiconductors.

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36. The spin-orbit coupling effect does not change the results presented in the paper.