First-principles investigation of the highly tetragonal ferroelectric material $Bi(Zn_{1/2}Ti_{1/2})O_3$

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First-principles calculations were performed to study the extremely tetragonal ferroelectric material $Bi(Zn_{1/2}Ti_{1/2})O_3$ (BZT). In agreement with experiment, we find that BZT displays extremely large cation displacements and tetragonality. Despite its high tetragonality and polarization, the local structure of the material exhibits a high degree of local disorder which is more typical of the solid solutions close to the morphotropic phase boundary. For the tetragonal phase of BZT, we show that a planar ordered (001) *B*-cation arrangement with the Zn and Ti stacking direction perpendicular to direction of *P* is the lowest in energy, in contrast with the (111) *B*-cation ordering usually found in perovskites. We attribute this unusual preference to the large cation displacements found in BZT, which raises the importance of *A*-*B* cation repulsive interactions, favoring separation of Zn and Ti cations.

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I. INTRODUCTION

Lead-free piezoelectric materials are attracting increased attention recently due to environmental concerns. Bi-based materials are considered as promising alternatives to Pb because of the similar $6s^2$ "stereochemically active lone pair" electron configuration. Bi^{3+} is likewise easily polarized, which promotes ferroelectric and piezoelectric properties. However, Bi-based materials are less stable than their Pb-based equivalents, and they are much less well studied. While numerous perovskite compounds based on Bi have been reported,[1–4] few form the perovskite structure under ambient conditions.[5,6] In order to find better alternatives to the widely used ceramic solid solution $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), many lead titanate ($PbTiO_3$, PT) solid solutions with morphotropic phase boundary (MPB) forming Bi-based additives have been studied.[7–13] Alloying with almost all Bi-based perovskites reduces the tetragonality of PT, but an unexpected enhancement of c/a was recently discovered in the $PbTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$ (PT-BZT) solution. The c/a ratio of the system systematically increases with the addition of BZT, reaching a value of 1.11 at the limit of substitution (≈50% BZT) under ambient pressure.[11]

The preparation of BZT in perovskite form at high pressure was also reported recently. It has an extremely high c/a ratio (1.211), and the refinement of x-ray diffraction data found large Bi (0.88 Å) and Zn/Ti (0.60 Å) displacements. This was ascribed to the pronounced influence of the $6s^2$ stereochemically active electron pair.[14,15] The refinement of x-ray diffraction data also found large thermal factors even at room temperature. This is likely due to structural disorder in the system, which cannot be fit exactly with a five-atom unit cell used in a standard Rietveld refinement. Because BZT is such a strongly polar material, its polarization could not be easily measured. Instead, using the refined coordinates and formal ionic charges, the polarization magnitude was estimated to be 1.03 C/m^2. Despite the large differences in both charge and size between the Zn and Ti cations, the electron diffraction did not give any evidence for long-range or short-range order of the *B* sites. This is in contrast to $Pb(Sc_{1/2}Nb_{1/2})O_3$ and other perovskites with similar charge and size differences that exhibit rocksalt (111) type *B*-cation ordering.[16] The high tetragonality of BZT is also interesting in light of its low tolerance factor ($t=0.95$). Typically, such a low tolerance factor leads to the appearance of large octahedral tilts and therefore an antiferroelectric phase, as seen in $PbZrO_3$ (PZ) (Ref. 17) and $Bi(Mg_{1/2}Ti_{1/2})O_3$ (BMT), the Mg analog of BZT.[18]

In this work, we use first-principles density functional theory (DFT) methodology to study properties of BZT that are not available from any current experiments. We evaluate the polarization of the material and study the local environment, resolving displacements of individual ions as well as tilts of the O_6 octahedra. We investigate the energetics of *B*-site cation ordering in BZT and find that they are qualitatively different from the previously studied ferroelectric perovskites. Due to its extreme tetragonality, the lowest-energy *B*-cation ordering is not rocksalt but rather a (001) ordering with the planar stacking direction orthogonal to the direction of polarization.

II. METHODOLOGY

The local *B*-site arrangements are studied using 40-atom supercells, which can be thought of as snapshots of small

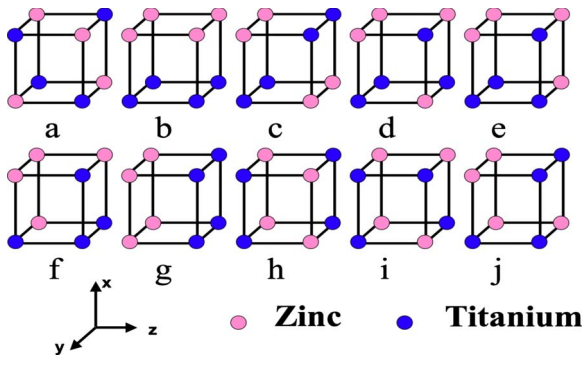

FIG. 1. (Color online) Ten *B*-cation arrangements for 40-atom tetragonal BZT supercells used in this work.

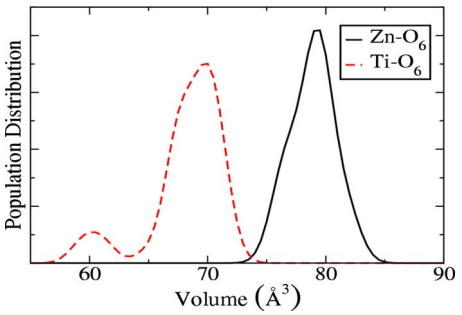

FIG. 2. (Color online) Octahedral volumes of Zn and Ti octahedra in BZT. The Zn cations always have larger octahedral cages than the Ti cations.

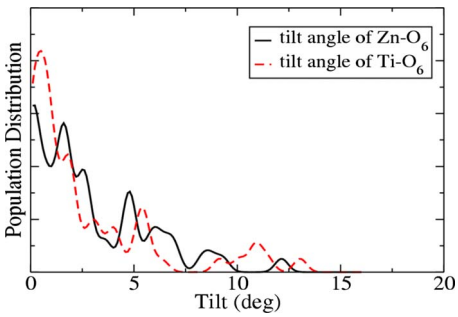

FIG. 3. (Color online) Distribution of octahedral tilts away from the Cartesian axes. The majority of BZT structures have widely distributed tilt angles.

regions of the real disordered solution. The ABINIT software package was used to relax the ionic positions and lattice constants.[19] All atoms are represented by norm-conserving optimized[20] designed nonlocal[21] pseudopotentials generated using the OPIUM code[22] with a plane-wave cutoff of 60 Ry. A generalized gradient approximation (GGA) (Ref. 23) and a $2\times2\times2$ Monkhorst-Pack sampling of the Brillouin zone[24] are used. Our calculations find both tetragonal and rhombohedral phase stable structures. GGA calculations find the experimentally observed tetragonal phase to be preferred, in contrast to the LDA calculations which find the opposite. Although GGA is known to generally overestimate lattice parameters of ferroelectric perovskites,[25,26] the slight overestimation of tetragonality compared with experiment (5%–6%) still makes the predictions reliable. For cubic lattice parameters, there are six possible arrangements of the Zn and Ti B cations in the $2\times2\times2$ supercell. For the tetragonal lattice parameters, four of these arrangements have two different orientations relative to the (100) polar axis leading to a total of ten unique B-cation arrangements studied in this work (Fig. 1).

III. RESULTS

A. Local structure

Since BZT is experimentally found to be tetragonal, we focus our analysis on the tetragonal ground states. First we analyze the size and the tilt angle of the O_6 cages from relaxed structures to characterize the distortions of the oxygen anions away from the perfect perovskite positions. For all relaxed supercells, the Zn-O_6 octahedra are larger than Ti-O_6 octahedra by $\approx$16%. As shown in Fig. 2, there is almost no overlap in the size distribution of the two types of octahedra. The difference in volumes is consistent with the ionic size difference of Zn and Ti cations (ionic radius of 0.740 Å for Zn and 0.605 Å for Ti). The peak at small volumes of the Ti-O_6 octahedra comes from structure (c) which differs from other structures in terms of c/a ratio and volume (as presented in Table I).

Examination of the octahedral tilt angles reveals a broad distribution (from $0°-15°$) (Fig. 3). A small tolerance factor means that the A-O sublattice prefers a smaller lattice constant than the B-O sublattice. Octahedral tilting preserves the large B-O cages, while decreasing the A-O distances, allowing both sublattices to achieve their preferences. While the majority of tilt angles are small and are comparable to the tilt angles found in tetragonal ferroelectric PZT,[27] a significant fraction of tilt angles are larger, similar to the ones found in antiferroelectric materials such as BMT and PZ. The large octahedral tilts mostly come from structure (c) and are expected from the tolerance factor analysis. The fact that most of the tilts are small shows that the tolerance factor argument is too simplistic to make correct ground-state crystal struc-

TABLE I. DFT energetics (eV/five-atom cell), tetragonality, spontaneous polarization (C/m^2), electrostatic ordering energy (eV/five-atom cell), and the relative distances of Bi to Zn/Ti cations (Å) are listed. The electrostatic energy is calculated using vacuum permittivity.

Supercell	DFT energy	c/a	P	Electrostatic	$R_{\text{Bi-Zn}}$	$R_{\text{Bi-Ti}}$
c	0.0827	1.077	0.815	−3.911	3.36	3.47
d	0.0759	1.266	1.368	−2.976	3.44	3.34
j	0.0463	1.275	1.375	−2.626	3.41	3.36
e	0.0442	1.276	1.381	−2.295	3.35	3.33
i	0.0439	1.284	1.386	−3.683	3.37	3.32
h	0.0408	1.280	1.354	−4.651	3.35	3.31
b	0.0398	1.274	1.405	0.644	3.39	3.34
a	0.0364	1.271	1.362	−5.100	3.43	3.28
f	0.0211	1.280	1.398	−1.942	3.35	3.45
g	0.0000	1.286	1.428	−1.611	3.42	3.48

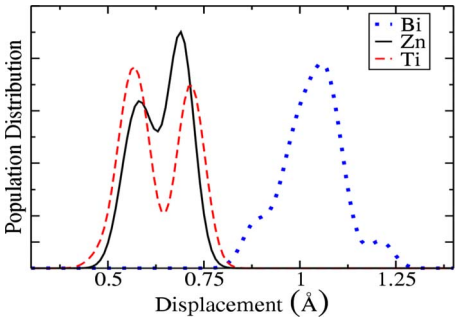

FIG. 4. (Color online) Distribution of cation displacements (Å) away from the oxygen cage centers.

ture predictions.[28] In highly tetragonal materials, the large *A*-cation off centering creates short *A*-O distances. Thus, the octahedral tilting is no longer the only possibility to achieve the preferences of both sublattices.

Relaxation of all ions yields large cation distortions. At the *A* site, Bi cations move by 1.0 ± 0.1 Å, creating three or four short Bi-O bonds and transforming the Bi-O_{12} cages into a Bi-O_4 square pyramid. The creation of shorter Bi-O bonds is necessary to satisfy the Bi valence of 3 since the Bi valence is only 2.84 in the ideal cubic perovskite structure. Off-center displacements are also favored by the long-range electrostatic interactions. At the *B* site, both Zn and Ti cations move off center by $0.6–0.7 \pm 0.1$ Å, creating short Zn-O and Ti-O bonds and making an important contribution to the overall polarization (Fig. 4).

We find that the directions of individual cation displacement are distributed in a cone of about 25° around the (100) overall polarization direction (Fig. 5). In agreement with previous results for the PZT solid solution,[27] the *A*-site displacement directions vary more than the *B*-site displacement directions. This is due to the influence of the *B*-cation arrangement on cation displacements which is stronger for the *A* site.[12] To avoid oxygen underbonding and overbonding, Bi cations tend to avoid the high-valence Ti and move toward the low-valence Zn. A simple illustration is provided by considering the Bi off-center distortions of structure (b). The Bi cations moving toward Zn cations move off center by about 1.21 Å along the (100) direction, while the Bi cations facing Ti cations move off center by about 0.79 Å along the (100) direction. The displacements of Bi cations facing the Zn cations are purely along (100), while the Bi cations facing Ti cations exhibit a significant (0.41 Å) displacement component in the *yz* plane.

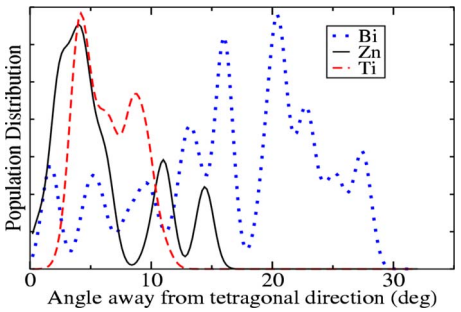

FIG. 5. (Color online) Angle distribution of cations away from the tetragonal direction.

The broad distributions found for cation displacement magnitude and direction account for the large thermal factors found by experimental Rietveld refinement. A thermal factor of 0.05 $Å^2$ found by Suchomel *et al.*[29] for the Bi cations is equivalent to a thermal vibration amplitude of about 0.1–0.22 Å. Such a large vibration is not reasonable at low temperature and is better explained by the variation in displacement magnitudes and directions of Bi cations found by our 0 K calculations. Experimental thermal factors for the Zn and Ti cations are about half those of the Bi cations, corresponding to the narrower distribution for Zn and Ti displacements in Fig. 4. Thus, while the c/a of BZT is much greater than that of PT, local structure shows a resemblance to the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ and PZT solid solutions of smaller c/a.

B. Strain and polarization

The total occupation of the *B* site by highly ferroelectrically active Zn and Ti cations and the coupling of *A*-site and *B*-site distortions allows extremely large cation displacements, stabilizing large polarization and strain. With the exception of supercell (c), we find that polarizations of all supercells are in the 1.35–1.43 C/m^2 range; c/a is in the 1.27–1.29 range (Table I). Thus, for the most part, the variation in *B*-cation ordering has only a minor impact on the polarization of the material. We found that our calculated polarization is significantly larger than the one estimated by Suchomel *et al.*[29] (1.03 C/m^2). The reason for this is that they used formal ionic charges which are smaller than the Born effective changes (Z^*). The 1.38 C/m^2 average polarization found for BZT is to our knowledge the largest known polarization for a stable ground state of a material.

The large polarization indicates that the Curie temperature (T_C) of BZT is also high, as T_C was found to be proportional to the square of the polarization for a variety of ferroelectrics. Using the proportionality constant between T_C and P^2 obtained from previous work (870 K m^4/C^2),[30] we can estimate the T_C of BZT as 1656 K, well above its decomposition temperature and higher than the 1400 K T_C of $LiNbO_3$, the highest known T_C in a perovskite-related ferroelectric to date.

C. Energetics of *B*-cation ordering

First-principles examination of the energetics of Zn/Ti ordering in BZT reveals unique features not found in other perovskites. Analysis of x-ray diffraction data carried out by Suchomel *et al.*[29] did not find any *B*-cation rocksalt ordering peaks for BZT. It is possible that in BZT the energy differences between the rocksalt ordering and other *B*-cation arrangements are small; thus, no ordering will be observed except for a very careful annealing protocol. This is to be expected as previous work showed that large off centering due to the stereochemically active lone pair reduces the preference for rocksalt in Pb-based perovskites as compared to Ba-based perovskites.[16,31] Alternatively, it is possible that unlike the case of Ba-based and Pb-based perovskites, *B*-cation

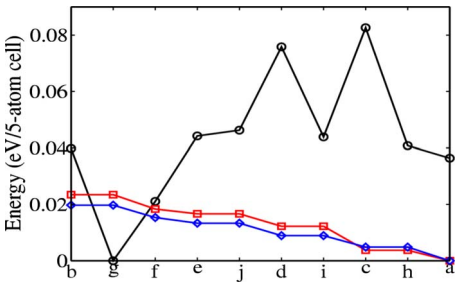

FIG. 6. (Color online) DFT energy differences from the lowest-energy *B*-cation arrangement shown for the relaxed tetragonal (black circles) and rhombohedral (red squares) structures. Also shown are the electrostatic energy differences for the relaxed cubic structures computed using formal ionic charges (blue diamonds). To facilitate comparison, the energy differences for the cubic structures are scaled down by a factor of 100.

ordering other than rocksalt is preferred for BZT. Our DFT calculations show that the latter is true, with two of the ten possible $2\times2\times2$ supercell *B*-cation arrangements lower in energy than the rocksalt ordering.

The energetics of the different *B*-cation arrangements are presented in Table I and Fig. 6. The lowest-energy 40-atom supercell exhibits a (001) ordering, with Zn and Ti planes alternating perpendicular to the tetragonal direction. This is in contrast with Ba-based and Pb-based perovskites where such an ordering is the highest in energy. We attribute the unusual preference for (001) ordering to the extreme tetragonality of BZT. Our finding implies that with a slow enough annealing schedule it should be possible to synthesize the (001) ordered BZT in the bulk. This is quite unusual, as until now planar (100) or (001) *B*-cation ordering has only been achieved in the bulk for the $La(Cu_{1/2}Sn_{1/2})O_3$ material.[32]

To verify that it is the extreme tetragonality of BZT that is causing the anomalous preference for the (001) ordering, we determine the energetics of rhombohedral BZT supercells (Fig. 6). Here, due to the absence of the tetragonal symmetry breaking, only six *B*-cation arrangements are possible in a $2\times2\times2$ supercell. We find that for rhombohedral BZT, the rocksalt *B*-cation ordering is the lowest in energy and the planar (001) ordering is the highest in energy, following the *B*-cation arrangement energy ranking seen previously in Ba-based and Pb-based perovskites. The energy ranking follows exactly the electrostatic energy differences for the cubic, undistorted BZT structures, as can be seen from Fig. 6. The energy difference between electrostatically favored (111) *B*-cation ordering and the less favored (001) ordering in Pb-based systems such as $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) (Ref. 16) is about four times larger than the energy difference in BZT. This is most likely due to the high covalency and the large off centering of the Bi cations. Burton and Cockayne[16] argued that the Pb 6*s*–O 2*p* hybridization enables bonding of Pb cations to the underbonded oxygen atoms, which reduces the energy cost of deviation from the (111) *B*-cation arrangement. Bi exhibits even greater covalency and hybridization than Pb so it is not surprising that the large Bi off-center distortions reduce the *B*-cation ordering energy differences more. Thus, in the rhombohedral phase, the cation distortions set the scale of the energy differences between the different *B*-cation orderings, while the electrostatics determines the energy ranking.

Electrostatic interactions are also important in tetragonal BZT, as shown by the comparison of the energies of the *B*-cation arrangements that are only different due to breaking of cubic symmetry by the tetragonal distortion. For example, for the case of (100) or (001) ordering where Zn and Ti cations are arranged in alternating planes [structures (b) and (g)], the DFT energy is higher for structure (b) with the tetragonal distortion parallel to the Zn/Ti sheet stacking direction and is lower for structure (g) with the tetragonal distortion perpendicular to the stacking direction. We consider the Zn cation as negative point charge and the Ti as positive charge (relative to the average formal charge of the *B* sites). On one hand, there are attractive electrostatic interactions between the Zn and Ti sheets. On the other hand, the electrostatic interactions within each sheet are repulsive. A tetragonal distortion parallel to the stacking direction leaves the repulsion unchanged and weakens the attractions. Conversely, a tetragonal distortion perpendicular to the stacking direction weakens the repulsions and leaves the attractions unchanged. This leads to a higher energy for structure (b) as compared to structure (g). Similar arguments are applicable for explaining the other energy splittings between structures (d) and (i), (e) and (j), and (c) and (h).

The inadequacy of the electrostatic model[33] to explain BZT *B*-cation ordering energetics suggests that there are important contributions other than electrostatics. Repulsion between the *A*-site and *B*-site cations, both of a direct and of through-oxygen kind, have been found to be important for compositional phase transitions in ferroelectrics.[34,35] These interactions are particularly important for materials where the large *A*-site displacements from high symmetry decrease the *A*-*B* cation distances, as is the case of BZT. We expect Bi-Ti repulsion to be more important due to the greater charge of the Ti cation, and we use the position of the first peak in the Bi-*B* cation partial pair-distribution function (PDF) as a rough measure of the strength of the Bi-*B* cation repulsion (Table I).

To reduce the Bi-Ti repulsion, Bi cations favor avoiding Ti and moving toward Zn. Such a preference can be best satisfied by the *B*-cation arrangements where Zn and Ti cations are grouped separately. This is opposite to the effect of the electrostatic interactions, which are favorable when Zn and Ti cations are interspersed. The (001) planar ordering of Zn and Ti easily allows the Bi cations to avoid Ti cations, raising the minimum Bi-Ti distance (3.48 Å) and lowering repulsive energy. Similarly, the highly grouped Zn and Ti cations in arrangement (f) lead to large Bi-Ti distances and low repulsion. For the rocksalt structure (a), the alternation of Zn and Ti cations makes it impossible to avoid Ti, giving rise to the shortest observed Bi-Ti distances (3.28 Å) and a high repulsive energy. For the (100) planar Zn and Ti orderings, the need to avoid Ti conflicts with the strong displacement along (100) that are required by the strain-polarization coupling. This makes the Bi-Ti distances shorter than in the (001) structure.

IV. CONCLUSION

We report a first-principles study of BZT. We demonstrate that this material has a number of unique properties, gener-

ated by its large c/a. Despite its macroscopic similarity with PT, BZT exhibits a disordered local structure similar to that of PZT. To the best of our knowledge, the polarization of 1.38 C/m^2 is the largest one reported for a bulk material (57% larger than P of PT). The relationship among c/a, P, and T_C allows us to predict a T_C of about 1600 K for BZT, larger than the 1460 K of the current highest T_C ferroelectric $LiNbO_3$. Finally, examination of the B-cation ordering energetics shows that the planar (001) stacking of Zn and Ti is the favored B-cation arrangement, unlike the rocksalt ordering typically favored in perovskite materials. We ascribe this anomalous effect to the greater importance of Bi-B cation repulsive interactions in BZT, driven by the large cation displacements in the material. A more general electrostatic model by Wu and Krakauer[36] included the effective charge on the A sites, depending on the local B-site configuration. In this approach, fitting to first-principles calculations is required, which might give interesting insights into the extent of Bi covalent bonding with O in different B-cation arrangements.

ACKNOWLEDGMENTS

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