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Polar behavior of the double perovskites $\mathrm{Bi}M\mathrm{ZnNbO}_6$ (M=Pb and Sr) from density-functional calculations

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The polar behavior of double perovskite $\mathrm{BiPbZnNbO}_6$ and $\mathrm{BiSrZnNbO}_6$ was investigated using first-principles density-functional calculations within the local-density approximation. These materials have both A-site size disorder and ions with stereochemical activity. We found a strong ferroelectric distortion in both materials. The polarization of the Pb material is $>80\ \mu\mathrm{C/cm}^2$ along the rhombohedral direction and the Sr-based material is only slightly inferior. The high polarization results mainly from a large off-centering of Bi and the large Born effective charge of Nb, which yields a large contribution to the polarization although the Nb off-centers by a smaller amount. Neither of these materials favors a tetragonal state, and therefore solid solutions with PbTiO_3 may show morphotropic phase boundaries.

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I. INTRODUCTION

Perovskite ferroelectrics and relaxor ferroelectrics are widely used in applications including electromechanical transducers, actuators, passive electronic components, memory devices, and microwave technology. There is strong interest in obtaining improvements in materials performance, such as high polarization, high Curie temperature, improved electromechanical coupling, and lower loss. One approach is through the exploration of new materials. Besides this technological motivation, these materials have been the focus of considerable fundamental interest, particularly in unraveling the complex interplay between crystal chemistry and lattice distortions and in understanding the range of polar behaviors that can be produced by strain and chemical substitutions. Much has been learned over the past several years.

The lattice instabilities of perovskite oxides, $AB\mathrm{O}_3$ are often understood using the tolerance factor $t=(r_\mathrm{O}+r_A)/\sqrt{2}(r_\mathrm{O}+r_B)$, where r_O, r_A, and r_B are the ionic radii for the O, A-site, and B-site ions, respectively.[1–3] These materials are classed in two groups according to whether the tolerance factor is less than unity or not. Several $t>1$ ferroelectrics are known, including the prototypical materials, BaTiO_3 and KNbO_3. In these materials there is a tendency toward lattice distortions where the too-small B-site ion off-centers. This is strongly enhanced by covalency involving O $2p$ states and nominally unoccupied B-site d states. This then leads to enhanced Born effective charges and large longitudinal-optic-transverse-optic splittings.[4,5] In the majority of $t<1$ materials the $B\mathrm{O}_6$ octahedra are tilted and they are not ferroelectrics.[6] The exceptions are generally perovskites with lone-pair A sites such as Pb and Bi. In these cases, the ideal cubic perovskite structure is often unstable against octahedral tilting, but the ferroelectric instability, which is enhanced by the stereochemical activity of the A site, is stronger. In materials with $t<1$ but no stereochemically active A-site ion, there is often a substantial ferroelectric instability of the ideal cubic structure, but now the tilt instability is stronger, and so ferroelectricity does not occur.[7–9] However, according to first-principles calculations, if the octahedra are prevented from tilting by mixing large and small A-site ions they may become ferroelectrics.[10] There is experimental support for this. For example, ferroelectricity in the $(\mathrm{Ba,Ca})\mathrm{TiO}_3$ solid solution is strongly enhanced compared to what would be expected interpolating between the properties of the end-point compounds.[11] Importantly, this leads to new compositions that have high piezoelectric coefficients.[11,12]

Generally, high piezoelectric coefficients and electromechanical coupling are found near phase boundaries. In particular, the electromechanical coupling in perovskite piezoelectrics is associated with polarization rotation near morphotropic phase boundaries (MPBs).[13–15] These are generally boundaries between ferroelectric states differing in the direction of their ground-state polarization. Therefore one strategy for finding new piezoelectric compositions is to search for solid solutions with MPBs. A particular emphasis has been in solid solutions with PbTiO_3 (PT) as one end point, following the commonly used $\mathrm{Pb(Zr,Ti)O}_3$ (PZT) system and the $\mathrm{PbMg}_{1/3}\mathrm{Nb}_{2/3}\mathrm{O}_3$ (PMN)-PT and $\mathrm{PbZn}_{1/3}\mathrm{Nb}_{2/3}\mathrm{O}_3$ (PZN)-PT piezocrystal systems.[16] PT is tetragonal with a substantial tetragonality. There is considerable interest in finding materials that can be alloyed with PT and which have strong ferroelectricity with rhombohedral or related ground states to produce an MPB perhaps with high Curie temperature, high polarization, and high tetragonality on the tetragonal side of the MPB.

A development of potential importance is the realization that Bi-based perovskites can be very useful ferroelectrics, as exemplified by progress in BiFeO_3. In particular, the small ionic radius and stereochemical activity of Bi^{3+}, leads to large displacements in a low volume unit cell, and its high charge (3+ vs 2+ for Pb) and hybridization of Bi $6p$ states with O $2p$ states leads to a high Born charge.[17] It should be noted though that even in BiFeO_3, which is an excellent ferroelectric, there is a complex interplay of tilts and Bi off-centering.[18] Experimental work on the BiScO_3-PT solid solution shows an MPB with enhanced Curie temperature,[19] and there have been recent studies of several other Bi-based perovskites in solid solutions with PT.[20–24] One problem has been that while the small Bi ion tends to enhance tetragonality on the tetragonal side of the MPB, this same effect may prevent the occurrence of an MPB, leading to phase diagrams with only tetragonal phases.

Recently, an extremely large tetragonality ($c/a \sim 1.11$ and high Curie temperature T_C of ~ 700 °C at $x=0.6$ was reported for perovskite solution $(1-x)\mathrm{Bi}(\mathrm{Zn}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$-$(x)\mathrm{PbTiO}_3$.[25,26] This is reminiscent of the behavior of CdTiO_3-PT alloys, which also have highly enhanced tetragonality.[7,27,28] In perovskites the balance between tetragonal and rhombohedral states is generally controlled by a balance between the energy lowering due to tetragonal strain, which favors the tetragonal state, and the *B*-site off-centering, which favors a rhombohedral state[29] (note that with small *A*-site ions there is an additional stabilization of the tetragonal state because off-centerings along [001] directions are toward the most open face of the O cage around the *A* site; therefore, this direction is favored for the *A* site and this can be important if the displacement is very large[8]). The interplay of *A*-site and *B*-site off-centering, and the importance of the *B* site in determining the direction of the ferroelectric polarization suggests the exploration of alternate *B*-site ions in solid solutions with PT to obtain MPBs.[29,30]

Here, we present a study of the polar behavior of perovskite $(\mathrm{Bi,Pb})(\mathrm{Zn,Nb})\mathrm{O}_3$ and $(\mathrm{Bi,Sr})(\mathrm{Zn,Nb})\mathrm{O}_3$ using density-functional supercell calculations. The purpose is to explore the effect of combining the mechanisms discussed above in a perovskite that may be amenable to experimental synthesis. Specifically, the compositions explored have different size *A*-site cations (Pb and Bi), stereochemically active ions on the *A* site (particularly, Bi, though Pb may also contribute as discussed below), and ions with electronic structures that favor cross-gap hybridization and therefore ferroelectricity on the *B* site (Nb and Zn). One motivation for this study is to explore the use of *A*-site size disorder in combination with stereochemical activity to obtain *A*-site driven ferroelectricity. The ionic radii[2] of the *A*-site ions considered here are $r_{\mathrm{Pb}^{2+}}=1.63$ Å, $r_{\mathrm{Sr}^{2+}}=1.58$ Å, and $r_{\mathrm{Bi}^{3+}}=1.31$ Å. Thus, Bi^{3+} is significantly smaller than the other *A*-site ions and Pb and Sr have approximately the same size, but unlike Sr, Pb has stereochemical activity that can favor ferroelectricity, as in PbTiO_3.

Related to this there is an experimental report of the synthesis and some physical properties of perovskite $(\mathrm{Bi}_{0.5}\mathrm{Sr}_{0.5})(\mathrm{Mg}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$, $(\mathrm{Bi}_{0.5}\mathrm{Ba}_{0.5})(\mathrm{Mg}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$, $(\mathrm{Bi}_{0.5}\mathrm{Sr}_{0.5})(\mathrm{Zn}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$, $(\mathrm{Bi}_{0.5}\mathrm{Ba}_{0.5})(\mathrm{Zn}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$, and the solid solution of $(\mathrm{Bi}_{0.5}\mathrm{Ba}_{0.5})(\mathrm{Zn}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$ with PT and $(\mathrm{Bi}_{0.5}\mathrm{Sr}_{0.5})(\mathrm{Mg}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$ with SrTiO_3.[31,32] The compound $(\mathrm{Bi}_{0.5}\mathrm{Sr}_{0.5})(\mathrm{Mg}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3$ was reported to be ferroelectric based on the observation of a hysteresis loop below 103 K. All four compounds were reported to show phase transitions above room temperature and relatively high dielectric constants. They also show substantial microwave loss, which may indicate ferroelectricity.

II. APPROACH

The perovskite alloys were studied using supercell calculations within density-functional theory (DFT). The main results are for compositions $\mathrm{BiPbNbZnO}_6$ and $\mathrm{BiSrNbZnO}_6$. The large charge difference between Zn^{2+} and Nb^{5+} may be expected to lead to a strong ordering tendency on the *B* site. This is the case in the relaxor systems PZN and PMN, where a double perovskitelike structure occurs even though the Nb:Zn stoichiometry is not 1:1 (specifically, in PZN and PMN one double perovskite *B*-site sublattice is Nb and the other is 1/3 Nb and 2/3 Zn or Mg, which in turn may further order).[33–35] In the present case the stoichiometry is 1:1, which should further stabilize the ordering. Therefore we assume an ordering of the *B*-site lattice into a double perovskite structure. In contrast, there is no *a priori* reason to assume that the *A*-site lattice consisting of Pb and Bi is chemically ordered.

$\mathrm{BiPbZnNbO}_6$ (BPZN) and $\mathrm{BiSrZnNbO}_6$ (BSZN) have ferroelectrically active ions on both the *A* and *B* sites. On the *B* site both Zn^{2+} and Nb^{5+} favor ferroelectricity, as is evident from the stronger relaxor ferroelectricity of PZN relative to PMN and the ferroelectricity of KNbO_3. Likewise Bi^{3+} and Pb^{2+} are stereochemically active and favor ferroelectricity on the perovskite *A* site. However, both BPZN and BSZN are expected to be strongly *A*-site driven materials both based on ionic radius ($t<1$, and *A*-site size disorder) and lone-pair physics,[29] and as such a competition between octahedral tilts and polar off-centering may be expected similar to the $\mathrm{Pb(Zr,Ti)O}_3$ system, where tilts are active even at the MPB (Refs. 36 and 37). Therefore it is important that the supercells are constructed in a way that this competition can be included. The minimum size for this is $2\times2\times2$, or 40 atoms, since such a cell has an even number of units along the [001], [011], and [111] directions and therefore can accommodate the various Glazer tilt patterns.[38]

An additional constraint comes from the fact that with multiple *A*-site ions it is possible to choose cells that have polar space groups just because of the cation ordering and not because of lattice instability. This would not represent ferroelectricity but would rather simply be an artifact of the selected order. Therefore even though Bi and Pb are not expected to chemically order in the solid solutions, we consider them in a highly ordered state within our supercells. Here we select a rocksalt ordering of Pb and Bi on the *A* site. The cation ordering with this choice has symmetry $F\bar{4}3m$, which is nonpolar. Thus any polarization or off-centering is a consequence of lattice instability and not the choice of cation ordering, and furthermore, one may expect that a more disordered alloy would have a better frustration of the tilts and a stronger ferroelectric tendency.[10]

The DFT calculations were done using two methods. We used the general potential linearized augmented plane-wave (LAPW) method[39] for the structure relaxations. This is a full-potential all-electron method. We did the calculations using the local-density approximation (LDA) at a scalar relativistic level. Well-converged basis sets were employed with LAPW sphere radii of 2.3 bohr for Pb, Sr, and Bi, 1.90 bohr for Zn and Nb, and 1.55 bohr for O. We included local orbitals to relax linearization and to accurately treat semicore states.[40] The polarization and Born effective charges were calculated with an ultrasoft pseudopotential method as implemented in the QUANTUM ESPRESSO package,[41] using the relaxed struc-

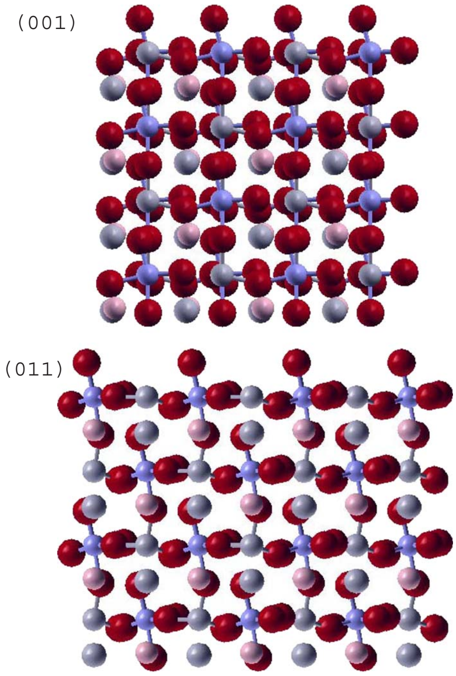

FIG. 1. (Color online) Structure of the 40 atom pseudocubic $BiPbZnNbO_6$ supercell after relaxation. The *B*-site O bonds are shown. The O ions are shown by (dark) red, Zn by (medium) gray, Nb by smaller (medium) blue, Pb by gray, and Bi by (smaller, light) pink spheres. For clarity eight $(2\times2\times2)$ supercells are shown. The top panel shows a view along (001) and the bottom shows a view along (011). Note that in addition to the cation off-centerings, there are noticeable octahedral tilts.

tures from the LAPW calculations. The results were converged with respect to the Brillouin-zone sampling, which was tested. The polarization was obtained using the Berry's phase method.

III. RESULTS

We started by assuming a pseudocubic structure, i.e., setting the lattice parameters of our 40 atom supercells to be orthogonal and equal. We then fully relaxed the internal coordinates of all atoms in the cell with no symmetry constraints. This was done as a function of the lattice parameter to obtain the equilibrium cell volumes for $BiPbZnNbO_6$ and $BiSrZnNbO_6$. This was done in the LDA using the LAPW method. The effective perovskite lattice parameters for the minimum energy were 3.99 Å, for $BiPbZnNbO_6$ and 3.97 Å, for $BiSrZnNbO_6$. As mentioned, $(Bi_{0.5}Sr_{0.5})(Zn_{0.5}Nb_{0.5})O_3$ was synthesized by Kosyachenko *et al.*[32] They reported a weakly tetragonal structure with lattice parameters $a=b=4.002$ and $c=4.015$ Å$(c/a=1.003)$ at 293 K. These values are ~0.9% larger than our calculated LDA lattice parameter. This size of underestimation is typical of LDA errors.

The structure of the 40 atom pseudocubic $BiPbZnNbO_6$ supercell at the LDA equilibrium volume is depicted in Fig. 1. As may be seen, there are large off-centerings of the Bi ions and also some octahedral tilting. Figure 2 shows the cation off-centerings in this cell for the different sites with respect to the centers of their O cages (the 12 nearest O ions for the *A* site and the 6 nearest for the *B* site). The largest off-centerings are of the Bi ions, consistent with Fig. 1, and what might be expected based on the small size and stereochemical activity of Bi^{3+}. These displacements are large (0.64 Å) and collinear along a [111] direction. Importantly, there are also large collinear displacements of the other cations. The Pb ions displace by ~0.39 Å, the Zn by ~0.27 Å, and the Nb by ~0.27 Å, all very close to [111]. This cooperative nature of the ferroelectricity, where all cations off-center significantly, is a characteristic of many good perovskite ferroelectrics including materials such as $KNbO_3$, $BaTiO_3$, and $PbTiO_3$.[29,42] These displacements would yield a point charge polarization based on nominal charges of 58 $\mu C/cm^2$ using nominal charges with the largest contributions coming from the Bi and Nb (note the +5 charge state of Nb). The actual polarization is higher (see below) because the nominal charges are enhanced due to covalency.

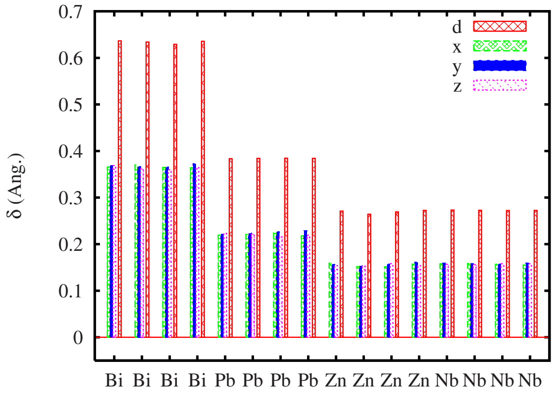

FIG. 2. (Color online) Cation off-centerings along the Cartesian directions with respect to their O cages for the various sites in LDA relaxed structure of the pseudocubic 40 atom supercell of $BiPbZnNbO_6$ at a lattice parameter of 3.99 Å. The total displacement magnitude of each ion is also given.

As is usual in perovskite ferroelectrics, we find that the ferroelectricity is enhanced as the volume is expanded and conversely under compression. However, over the volume range investigated (pseudocubic lattice parameter, $3.88\leq a\leq4.07$ Å), the material remains ferroelectric, with cation displacements along [111]. The average cation displacements as a function of *a* are given in Table I. The LDA typically underestimates lattice parameters, often by ~1–2 %, and as such the prediction of ferroelectricity in this material would seem to be robust against LDA volume errors.

We now discuss the electronic structure as it relates to ferroelectricity. The electronic density of states (DOS) and projections for the relaxed supercell are shown in Fig. 3. The calculated LDA band gap is 2.7 eV. This is almost certainly an underestimate due to the LDA band-gap error. Considering the sizable gap and the fact that all the ions are in chemically stable valence states it is likely that $BiPbZnNbO_6$ can be made as a good insulator at ambient temperature. This is an important consideration for a ferroelectric material to be used in applications. The stereochemical activity of Bi^{3+} and Pb^{2+} is associated with the lone-pair chemistry, which is usu-

TABLE I. Average displacements of the cations relative to their O cages in relaxed 40 atom $BiPbZnNbO_6$ cells as a function of pseudocubic lattice parameter, a.

a (Å)	δ_{Bi} (Å)	δ_{Pb} (Å)	δ_{Zn} (Å)	δ_{Nb} (Å)
3.88	0.50	0.28	0.20	0.22
3.92	0.54	0.31	0.23	0.24
3.98	0.62	0.38	0.26	0.27
3.99	0.64	0.39	0.27	0.27
4.03	0.69	0.44	0.30	0.30
4.07	0.75	0.50	0.35	0.32

ally discussed in terms of a high polarizability of the electrons in the occupied 6s orbitals of these ions. As shown, the Bi 6s states give rise to the DOS peak centered at −9.5 eV relative to the valence-band maximum (VBM), while the Pb 6s states are at −7.4 eV. The O 2p bands provide the DOS from −6 eV to the VBM, while the conduction bands are derived from unoccupied orbitals of metal character, primarily Nb 4d, Bi 6p, Pb 6p and at higher energies, Zn sp character. There is a modest hybridization between the Bi and Pb 6s states and the O 2p states as may be seen from the Bi and Pb s character at the top of the O 2p bands. However, this is a mixing of occupied states and as such does not signify chemical bonding. Instead, as has been noted previously for ferroelectric perovskites,[4,5] the important hybridization is between the O 2p states and unoccupied metal states, which favors ferroelectricity due to chemical bonding and leads to enhanced Born effective charges. The energy position of the Nb 4d states, which are dominant in the lower conduction bands from the conduction-band minimum (CBM) to ~1.2 eV above it is important because the low energy favors hybridization with O 2p states and ferroelectric off-centering, as was discussed in the case of PMN and $KNbO_3$ in relation to $KTaO_3$.[43,44] In the present case, there is a strong mixing of O 2p and Nb 4d states. This is evident from the Nb d character in the O 2p bands. The Bi 6p and Pb 6p states, which occur in the conduction bands from the CBM to ~4 eV above, also mix strongly with the O 2p bands. There is also cross-gap hybridization evident involving the Zn sp states, although this mixing is weaker perhaps because the Zn states occur further above the CBM. The values of the Born effective charges are enhanced by this cross-gap hybridization. The average values for Bi, Pb, Zn, and Nb are 4.4, 3.6, 2.9, and 5.8, respectively. The calculated polarization for the supercell is 85 $\mu C/cm^2$. This number was obtained using a Berry's phase calculation. The estimate of the polarization that is obtained by multiplying the Born charges and cation off-centerings in their O cages is 83 $\mu C/cm^2$ in close agreement with the Berry's phase calculation. For comparison the polarization of $BiFeO_3$ from DFT calculations is 90–100 $\mu C/cm^2$.[17]

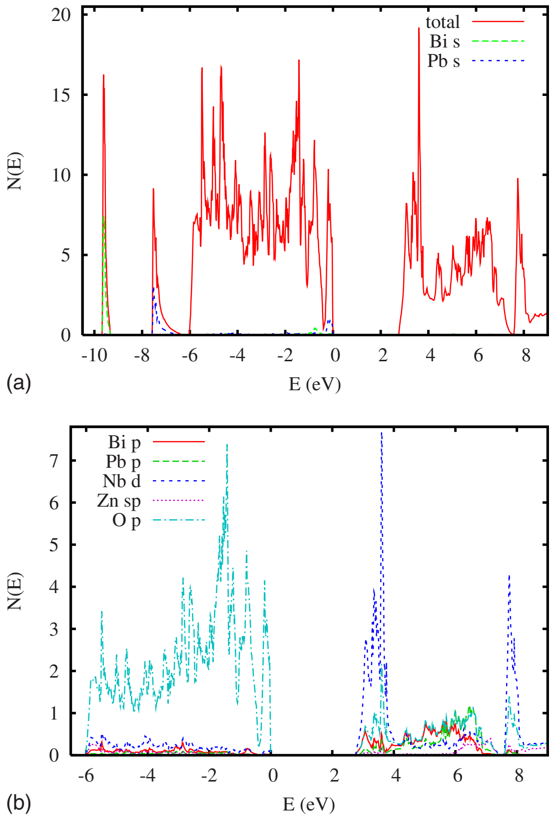

FIG. 3. (Color online) Electronic DOS of the pseudocubic relaxed $BiPbZnNbO_6$ supercell on a per formula unit basis. The top panel shows the total DOS and the Bi s and Pb s projections. The bottom panel shows Bi p, Pb p, Nb d, Zn sp, and O p projections. The projections are the integrals of components of the charge density with given angular character within the LAPW spheres. Note that for extended orbitals this gives an underestimate. The energy zero is set at the valence-band maximum.

The above discussion in terms of cross-gap hybridization due to interaction between O 2p states and extended, low-lying metal orbitals making up the conduction bands is different from a discussion in terms of a polarizable atomiclike s orbital. However, it should be emphasized that atomic character is not a uniquely defined quantity since it is basis set dependent (note that an expansion in terms of radial functions times spherical harmonics about a single site is a complete basis and so expansion about the different sites on a lattice is necessarily overcomplete). Furthermore, polarization of an s orbital implies a mixing in of some p character from unoccupied orbitals and in these perovskites this is 6p character that arises from conduction bands. The distinction between the two views is that in the lone-pair description the discussion is in terms of response to crystal potential similar to a conventional discussion of crystal field while in the cross-gap hybridization it is structure-dependent hybridization as in ligand field. Specifically, the first view focuses on the response of a single ion to its environment, while the latter view, which we emphasize here, emphasizes structure-dependent hybridization between metal and ligand states. This is analogous to the origin of crystal-field splittings in transition-metal oxide compounds, which arise primarily from hybridization with O 2p states and not the nonspherical crystal potential around the metal site.

As mentioned, high piezoelectric coupling in ferroelectric perovskites is generally found near an MPB, most commonly between a pseudocubic phase and a tetragonal phase, as in

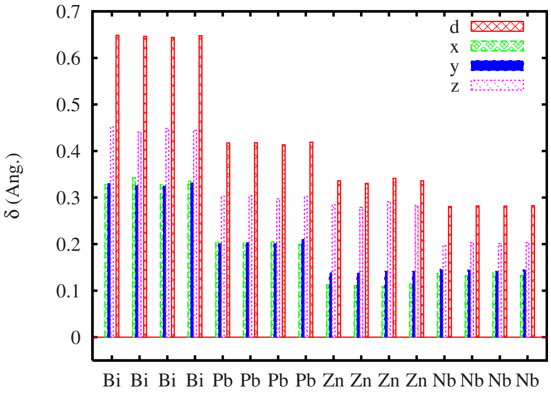

FIG. 4. (Color online) Cation off-centerings along the Cartesian directions with respect to their O cages for the various sites in LDA relaxed structure of the 40 atom supercell of $BiPbZnNbO_6$ at the same volume as in Fig. 2 but with an imposed c/a ratio of 1.0606. Note that despite the large tetragonal strain the cation displacements remain nearly collinear and do remain reasonably close to a [111] direction.

PZT. We did calculations as a function of imposed tetragonal strain for our supercell at a fixed volume equal to the equilibrium volume for the pseudocubic cell ($a=3.99$ Å). Over the range considered ($0.992<c/a<1.076$), the cation off-centerings stayed collinear and primarily along a [111] direction, and, in particular, at least up to the maximum strain considered, did not switch to an [001] average direction. As an example, cation off-centerings for $c/a=1.0606$ are shown in Fig. 4. The lowest energy is at $c/a\sim1.015$. However, near this minimum the cation displacements remain very close to a [111] direction. Instead it seems that the deviation of c/a from unity is due to the octahedral tilts and not strain coupling for the tetragonal ferroelectric state. Since the tilts are expected to be coupled to the *A*-site cation ordering, this may very well be an artifact of the specific ordering used in the necessarily small supercell studied here (note that the *A*-site cations would most likely be disordered in this material). In any case, $BiPbZnNbO_6$ is most likely pseudocubic with a rhombohedral ferroelectric state or weakly tetragonal. As such it may be of interest to investigate the $BiPbZnNbO_6$-$PbTiO_3$ solid solution to determine whether an MPB is present. We note that the tetragonality may be particularly sensitive to volume, as is the case in $PbTiO_3$, meaning that the LDA volume error may be particularly important for this, and also that errors due to the use of a small ordered supercell may be particularly important for this.

$BiPbZnNbO_6$ has two *A*-site ions with stereochemical activity. Bi shows large off-centerings while the Pb off-centerings are smaller, and furthermore Bi carries a higher charge. This raises the question of the role of Pb in the ferroelectricity. This question is also of interest because Pb is considered hazardous. This fact motivates searches for Pb-free replacements for the commonly used Pb-based ferroelectrics such as PZT. We performed calculations for 40 atom $BiSrZnNbO_6$ supercells similar to those discussed above for the Pb system. Some properties are compared with the Pb system in Table II. We found a slightly smaller equilibrium volume for the Sr system, corresponding to a pseudocubic $a=3.97$ Å. As shown in Fig. 5, the material is ferroelectric, with large collinear cation off-centerings along [111]. The calculated polarization is 79 $\mu C/cm^2$. These off-centerings are similar to those for the Pb system, except on the Sr site. This is also the case for calculations at the same volume. For a pseudocubic $a=3.98$ Å, the calculated off-centerings are 0.62 Å, 0.33 Å, 0.25 Å, and 0.25 Å, for Bi, Sr, Zn, and Nb, respectively, as compared with 0.62 Å, 0.38 Å, 0.26 Å, and 0.27 Å, for Bi, Pb, Zn, and Nb in the Pb compound at the same volume. This implies only slightly inferior ferroelectric properties for the Sr compound as compared to the Pb compound. The calculated average Born effective charges for $BiSrZnNbO_6$ are 4.4, 2.6, 2.8, and 5.8 for Bi, Sr, Zn, and Nb, respectively. These are very similar to $BiPbZnNbO_6$, except that the Sr Born charge is lower than that for Pb. Importantly, the LDA band gap of the Sr compound, $E_g=3.0$ eV, is slightly higher than that of the Pb compound. This large band gap combined with the stable valences of the

TABLE II. Comparison of properties of $BiPbZnNbO_6$ and $BiSrZnNbO_6$ cells as obtained from our LDA calculations. *a* denotes the pseudocubic lattice parameter, z^* are the average Born effective charges, δ are the average cation off-centerings with respect to the O cages, and *P* is the polarization.

	$BiPbZnNbO_6$	$BiSrZnNbO_6$
a(LDA)	3.99 Å	3.97 Å
δ(Bi)	0.64 Å	0.62 Å
z^*(Bi)	4.4	4.4
δ(Pb/Sr)	0.39 Å	0.33 Å
z^*(Pb/Sr)	3.6	2.6
δ(Zn)	0.27 Å	0.25 Å
z^*(Zn)	2.9	2.8
δ(Nb)	0.27 Å	0.25 Å
z^*(Nb)	5.8	5.8
P(111)	85 $\mu C/cm^2$	79 $\mu C/cm^2$

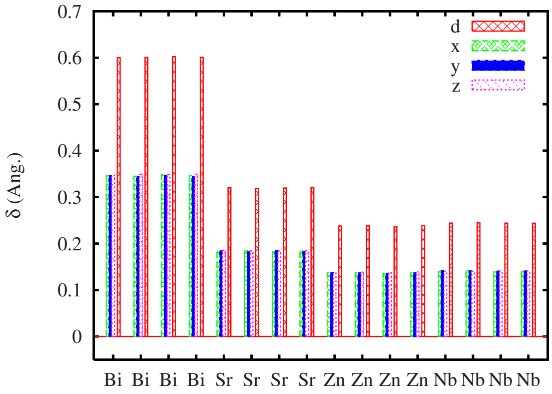

FIG. 5. (Color online) Cation off-centerings along the Cartesian directions with respect to their O cages for the various sites in LDA relaxed structure of the pseudocubic 40 atom supercell of $BiSrZnNbO_6$ at a lattice parameter of 3.97 Å. The total displacement magnitude of each ion is also given. Note the reduced off-centering of Sr relative to Pb (Fig. 2) in $BiPbZnNbO_6$ while the off-centerings of the other cations are similar.

various cations implies that highly insulating samples can be prepared. This may make $BiSrZnNbO_6$ a useful alternative Pb-free ferroelectric.

IV. SUMMARY AND DISCUSSION

Density-functional calculations for small supercells of double perovskite $BiPbZnNbO_6$ and $BiSrZnNbO_6$ indicate that these may be useful ferroelectric materials. They have high polarization due to the large displacement of Bi and the displacements of Nb combined with its high charge. They have substantial band gaps and stable chemistry consistent with synthesis of highly insulating samples. It will be of interest to measure properties experimentally and to investigate the solid solutions with $PbTiO_3$ to determine if a morphotropic phase boundary is present. Finally, we note that because these materials have mixtures of ions with different charges on both the A and B sites, they should have considerable chemical flexibility. While we considered $BiPbZnNbO_6$ in the double perovskite structure, $Bi_xPb_{1-x}Zn_{1/3+x/3}Nb_{2/3-x/3}O_3$ may exist over a large range of x. $BiPbZnNbO_6$ is the $x=0.5$ while $x=0$ is the known relaxor ferroelectric PZN. The $x=1$ perovskite $BiZn_{2/3}Nb_{1/3}O_3$ has not been reported, and instead the Bi_2O_3-ZnO-Nb_2O_5 system shows Nb-rich pyrochlore phases that presumably compete with the perovskite.[45] As such, it may be possible to synthesize the perovskite under pressure similar to other low tolerance factor Bi-based perovskites.[46,47] In any case, the chemical flexibility implies a tunability of properties that may be very helpful in obtaining useful ferroelectric properties including MPBs.

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