

(Ba,K,La)ZrO₃ as a possible lead-free ferroelectric: Density functional calculations

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First-principles supercell calculations are used to investigate the lattice distortions in BaZrO₃ heavily codoped with K and La. We find that nonferroelectric BaZrO₃ can be made ferroelectric in this way. The ferroelectricity is the result of La off-centerings and can be understood using ionic size considerations. In particular, size disorder on the perovskite *A* site suppresses the tendency toward octahedral tilts with substitution of the small La ion. This results in *A*-site driven ferroelectricity.

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Ferroelectric, relaxor ferroelectric and piezoelectric oxides have been widely used in electronics and transducer applications for many decades.¹⁻³ By far the majority of ferroelectric and piezoelectric materials used in applications are based on the perovskite structure oxides, ABO₃, especially the Pb-based Pb(Zr, Ti)O₃ solid solution, which is often referred to as PZT. Nonetheless, there has been a strong interest in new ferroelectric materials over the last several years. This is motivated in part by environmental issues associated with the use of Pb and in part by several important discoveries. These include a high piezoelectric Pb-free textured ceramic based on (K, Na, Li)(Nb, Ta, Sb)O₃ perovskite⁴ and the fact that single-crystal piezoelectrics, which can be made from alloys of PbTiO₃ with several relaxors, but not PZT, single crystals of which are not available, offer order of magnitude improvements in piezoelectric performance.⁵⁻⁷

The lattice distortions of perovskite structure oxides, including those underlying ferroelectric behavior, have been extensively studied. The structural trends and occurrence of ferroelectricity are understood in terms of ionic size and covalency effects. The trends in ionic size are summarized by Goldschmidt tolerance factor,⁸⁻¹⁰ $t = (r_O + r_A) / \sqrt{2}(r_O + r_B)$, where r_O , r_A , and r_B are the ionic radii of O, *A* and *B* ions, respectively, as may be obtained from the table of Shannon.¹¹ $t > 1$ perovskites such as BaTiO₃ are often ferroelectric, while materials with $t \approx 1$ such as BaZrO₃ may be stable in the ideal full symmetry cubic structure, and $t < 1$ perovskites typically show distorted nonferroelectric structures with tilted BO₆ octahedra¹² as in, e.g., perovskite CaTiO₃. Exceptions are $t \leq 1$ materials containing Pb and Bi, such as PZT and BiFeO₃, where ferroelectricity occurs due to hybridization between Pb/Bi states and the O 2*p* states.¹³ First-principles calculations showed that covalency between *B*-site *d* states and O 2*p* states also plays a very important role in the ferroelectricity of materials like BaTiO₃.¹³ In any case, it is useful to classify perovskite ferroelectric materials as *A*-site or *B*-site driven. The latter are $t > 1$ materials such as BaTiO₃ and the former include the Bi and Pb containing

materials, which are the primary piezoelectric compositions. However, it has been shown using first-principles calculations that there are ways of designing *A*-site driven ferroelectrics without relying on the stereochemistry of Pb or Bi. In particular, in $t < 1$ perovskites the ideal cubic structure is unstable both against tilt modes and also against generally weaker but still substantial ferroelectric distortions.^{10,14} Moreover, the coherence length of tilt modes is often longer than that of *A*-site off-centering modes, with the implication that tilt modes can be preferentially suppressed by disorder.^{14,15} Ferroelectricity based on *A*-site size disorder in certain $t < 1$ perovskites, particularly (K, Li)NbO₃ and (La, Lu)₂NiMnO₆, has been found in first-principles calculations.^{16,17} This mechanism is not, however, universal.¹⁴ The purpose of this Brief Report is to show that this mechanism is also applicable in $t \approx 1$ perovskites, using BaZrO₃ as a starting point. In particular, we show that heavy codoping with K and La can be used to induce polar behavior in BaZrO₃. This behavior is dominated by La off-centering, as might be expected considering that K⁺ has a similar but slightly larger Shannon radius than Ba²⁺, while La³⁺ is significantly smaller.^{11,18} We note that BaZrO₃ occurs in the ideal cubic perovskite structure, with no tilts of the ZrO₆ octahedra, even at low temperature, as was verified by x-ray and neutron-diffraction studies down to $T = 2$ K (see Appendix).¹⁹ We also note that, although PbZrO₃ contains Pb and is the end point of the PZT system, pure PbZrO₃ has a nonferroelectric tilted ground state.

Ferroelectricity can be produced in BaZrO₃ by alloying with BaTiO₃. However, this increases the tolerance factor, and leads to *B*-site driven ferroelectricity, while the substitution considered here decreases the average tolerance factor, and results in *A*-site driven ferroelectricity.

The present results are based on density functional calculations within the local-density approximation (LDA) for 40-atom supercells at two different Ba concentrations. As mentioned, in perovskites octahedral tilting often competes with ferroelectricity. Therefore it is important to select supercells that allow both types of structural distortion in order to as-

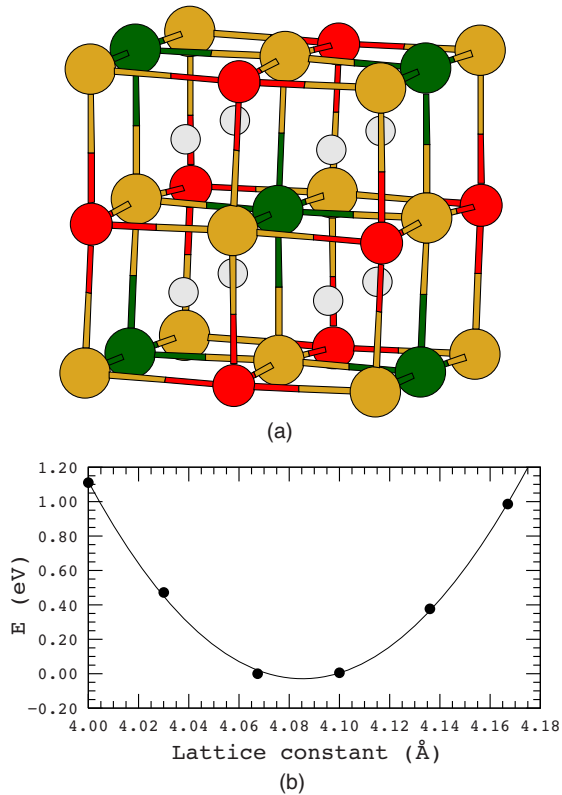


FIG. 1. (Color online) Cation ordering in the supercells used in our calculations: $(\text{Ba}_{1/2}\text{K}_{1/4}\text{La}_{1/4})\text{ZrO}_3$ (left) and $(\text{Ba}_{1/4}\text{K}_{3/8}\text{La}_{3/8})\text{ZrO}_3$ (right). The yellow, green, red, and gray circles represent the Ba, K, La and Zr atoms, respectively. The oxygen atoms are not shown. Note that the cation orderings do not induce a polar structure by themselves.

sess the tendency toward ferroelectricity. The particular $2 \times 2 \times 2$ 40-atom cells chosen are doubled along the 100, 110 and 111 directions and therefore allow arbitrary mixtures of rigid unit tilts including, in particular, the observed Glazer perovskite tilt patterns.¹² The structure relaxations were done using the general potential linearized augmented plane-wave (LAPW) method with local orbitals.^{20,21} We used a $2 \times 2 \times 2$ Monkhorst-Pack special \mathbf{k} -point mesh²² during the relaxations, and then tested the final structures by performing calculations of the forces with a $4 \times 4 \times 4$ mesh. We also tested the final structures by performing calculations with two very different Zr LAPW sphere radii.²³

As mentioned, the results given below are based on supercells, of composition $\text{Ba}_{1-x}\text{K}_{x/2}\text{La}_{x/2}\text{ZrO}_3$ with $x=1/2$ (25% La) and $x=3/4$ (37.5% La). The orderings of the A-site atoms were chosen to have as high symmetry as possible. This yields large separations between atoms of the same type, as shown in Fig. 1. Specifically, at $x=1/2$, Ba atoms were placed at (0,0,0), (1,1,0), (0,1,1) and (1,0,1), La atoms were at (0,0,1) and (0,1,0), and K atoms were at (1,0,0) and (1,1,1), all in units of the perovskite lattice parameter a . Without any atomic displacements this ordering yields a space group $P4/mmm$ (note that the primitive unit cell has 20 atoms, and a shifted origin). At $x=3/4$, Ba was placed at (0,0,0) and (1,1,1), La at (1,0,0), (0,1,0) and (0,0,1), and K at (0,1,1), (1,0,1) and (1,1,0). This yields space group $Pm\bar{3}m$.

The fact that without lattice distortions these supercells are centrosymmetric and therefore nonpolar is important because it means that any polar character found results from a spontaneous symmetry breaking due to off-centering of ions, and is not driven by some already polar ordering of the three types of A-site ions. This also means that ferroelectricity could be switchable.

The internal coordinates of the atoms in the supercells were fully relaxed with no symmetry constraints, while the lattice parameters were held fixed. Thus all atomic positions including the O positions were moved and in particular distortions of the O octahedra were allowed. The lattice parameters were determined as the value that minimizes that calculated total energy. This amounts to relaxing the volume but not allowing strains. This procedure has two sources of bias against ferroelectricity. First of all, the LDA almost invariably underestimates the volume of oxides—this favors tilt instabilities over ferroelectricity.^{24,25} Second, strain coupling, which is not considered here, generally favors ferroelectricity.^{26,27} In any case, the calculated lattice parameters were 4.105 Å and 4.085 Å, for $x=1/2$ and $x=3/4$, respectively. These values show a decreasing trend with K/La substitution for Ba, and are close to but smaller than the experimental lattice parameter of BaZrO_3 (4.192 Å).^{28,29} For comparison the calculated LDA lattice parameter of cubic BaTiO_3 is 4.153 Å. The decreasing trend with substitution is as may be expected from the fact that the average of the K^+ and La^{3+} ionic radii is smaller than the ionic radius of Ba^{2+} .^{11,18} However, the magnitude of the reduction is less than half of that which would be obtained by reducing the lattice parameter by twice the change in the average A-site Shannon radius. This is an indication that the substitution does in fact result in an increase in the volume available for A-site off-centering.

Our main results are summarized in Fig. 2 and Table I, which give the cation off-centerings with respect to the centers of their O cages. As may be seen, the largest off-centerings in both supercells are of the small La ions. At $x=1/2$ (25% La) the off-centerings of the two La ions are collinear with magnitude 0.229 Å, while at $x=3/4$ (37.5% La) they are significantly noncollinear, but with a larger average magnitude of 0.285 Å. One may note that these La displacements are comparable to the difference in ionic radii of Ba^{2+} and La^{3+} , which is 0.25 Å.

In both cells the result is a polar structure dominated by La off-centering. The average La off-centering lies between the [001] and [011] directions: close to [001] for the $x=3/4$ (37.5% La) supercell and at an intermediate angle for the $x=1/2$ supercell. In both cases the individual La off-centerings are at intermediate angles between [001] and [011] directions. Turning to the other cations, one may note significant but smaller off-centerings. Besides being smaller, these are also less collinear (with the exception of the two K ions at $x=3/4$). Further the off-centerings of the other A-site cations are not collinear with the average La displacements. However, in both cells the average Zr displacement is close to the same direction but much smaller in magnitude than the average La displacement. The angle between the average La and average Zr off-centerings is 12° and 11° for the $x=1/2$ and $x=3/4$ supercells, respectively. While we emphasize that

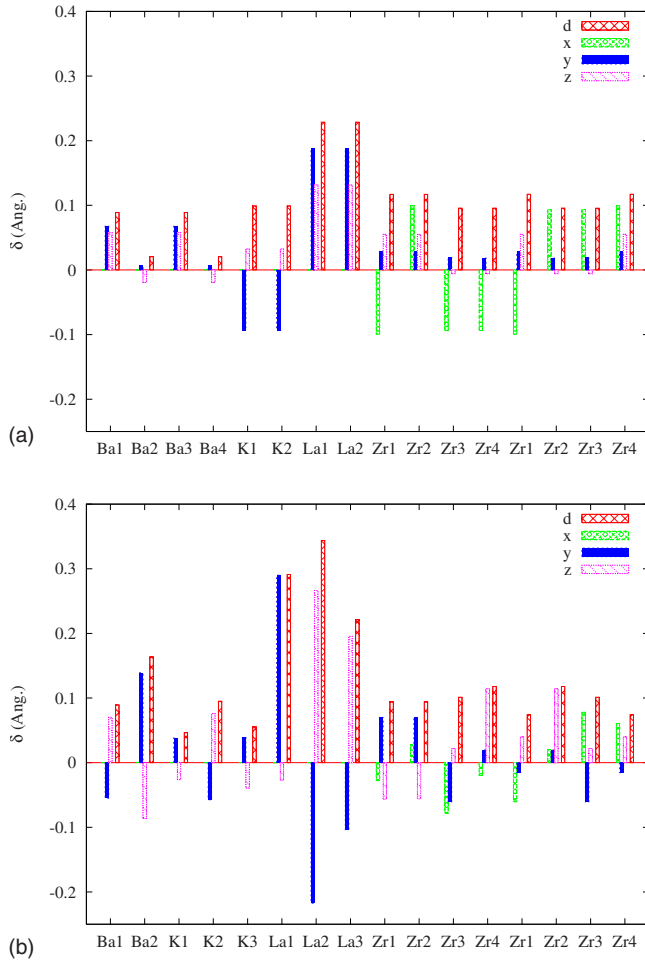


FIG. 2. (Color online) Bar charts showing the cation off-centerings with respect to their O cages for the relaxed structures of the $x=1/2$ (top) and $x=3/4$ (bottom) supercells. The bars show the three Cartesian directions as well as the magnitudes d of the displacements.

this is based on only two particular supercells, it does suggest that there is some cooperativity between La and Zr displacements. We note that the La displacements are sizable so

TABLE I. Off-centerings \mathbf{d} in \AA , for the various cations in the $x=1/2$ and $x=3/4$ supercells. $|\langle \mathbf{d} \rangle|$ denotes the magnitude of the average displacement of each atom type, while $\langle |\mathbf{d}| \rangle$ denotes the average magnitude of the off-centerings, which is necessarily larger. r is the ratio of these, which would be 0 for an antiferrodistortive ordering, and 1 for a ferroelectric ordering with perfectly collinear displacements.

		Ba	K	La	Zr
$x=1/2$	$ \langle \mathbf{d} \rangle $	0.042	0.099	0.229	0.034
	$\langle \mathbf{d} \rangle$	0.055	0.099	0.229	0.106
	r	0.77	1.00	1.00	0.32
$x=3/4$	$ \langle \mathbf{d} \rangle $	0.043	0.007	0.146	0.030
	$\langle \mathbf{d} \rangle$	0.126	0.066	0.285	0.097
	r	0.34	0.11	0.51	0.31

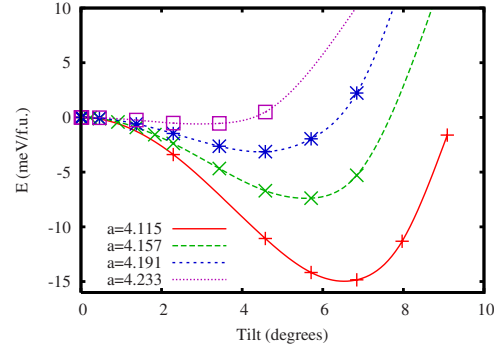


FIG. 3. (Color online) Energetics of the R -point tilt in pure BaZrO_3 at various lattice parameters a , given in \AA . The experimental low-temperature lattice parameter is 4.191 \AA . The energy zero is taken for each curve as the energy for zero tilt at that lattice parameter.

sizable polarization is expected. Considering La displacements $\sim 0.2 \text{ \AA}$, lattice parameter $\sim 4.1 \text{ \AA}$, A -site La fraction y , and nominal Born charge $Z^* = +3$, we estimate a polarization of $14y \mu\text{C}/\text{cm}^2$, which would be reduced by noncollinear displacements and enhanced by contributions from the Zr and other ions.

The relaxed structures of ordered high-symmetry supercells of BaZrO_3 heavily codoped with La and K show polar ground states, consistent with what might be expected based on previous results especially for $(\text{La}, \text{Lu})_2\text{MnNiO}_6$.¹⁷ This suggests that alloys would also be ferroelectric, since disorder is expected to be more effective in suppressing general tilts than ordered A -site patterns. In an actual alloy the local atomic structure would deviate considerably from that assumed in the simple supercells that we treated. Considering that there will be a strong interplay between the local atomic environment and the off-centerings, in particular from local electric fields associated with the different charge states of the various A -site ions, it may be that the polar character will manifest itself as relaxor ferroelectricity rather than ordinary ferroelectricity, and this may be composition dependent. In any case, what can be concluded from the present results is that $\text{Ba}_{1-x}\text{K}_{x/2}\text{La}_{x/2}\text{ZrO}_3$ is likely to be a polar material at least for $x \geq 1/2$. It will be of interest to synthesize this alloy and to measure its dielectric properties. The present case, which is based on the smaller size of La relative to Ba, is much less extreme in the degree of mismatch than the systems studied previously.^{16,17} While this results in smaller off-centerings of the small A -site ion, we do still find off-centerings. Importantly, the smaller mismatch means that this system can be expected to be more amenable to synthesis using conventional methods, consistent with the fact that there are a number of known perovskite solid solutions with mixtures of Ba and La on the A site.

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APPENDIX: GROUND-STATE STRUCTURE OF BaZrO₃

Several authors have reported that within density functional theory there is a tilt instability in BaZrO₃,^{9,19,30} while experiment shows that the material remains cubic. This discrepancy was discussed in terms of zero-point motion by Akbarzadeh and co-workers.¹⁹ We did LDA calculations of the energetics of the *R*-point tilt as a function of lattice parameter using a 10-atom cell with the tilt around an (001) axis. The result is shown in Fig. 3. At the experimental lattice parameter of 4.191 Å, we obtain a very shallow instability with a depth of 3 meV per formula unit and a tilt angle of ~4.4°, in good agreement with the results of Akbarzadeh and co-workers. The LDA lattice parameter is 4.157 Å, without allowing tilt and 4.152 Å, allowing tilt. We find a strong volume dependence, and as a result tilts are much

more stable at the LDA equilibrium volume, even though it corresponds to a linear compression of only ~1%. At the LDA volume the tilt instability amounts to 7.5 meV per formula unit at an angle of 6°. At both the LDA and experimental volumes the tilt mode is anharmonic with a strong upturn at higher angle, as is normal for a soft mode (it is the anharmonic term that yields a minimum). If one assumes that the most reliable LDA vibrational properties are obtained from calculations at the experimental volume, as in other ferroelectrics, the explanation that zero-point motion suppresses the tilt instability appears to be quite reasonable, while if the energy surface is closer to that at the LDA equilibrium volume another explanation may be needed. Inelastic neutron-scattering measurements on single crystals to determine the temperature dependence of the *R*₂₅ and other zone-boundary tilt modes should be helpful in resolving this.

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