Compositional Inversion Symmetry Breaking in Ferroelectric Perovskites

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Ternary cubic perovskite compounds of the form $(A_{1/3}A'_{1/3}A''_{1/3})BO_3$ and $A(B_{1/3}B'_{1/3}B''_{1/3})O_3$, in which the differentiated cations form an alternating series of monolayers, are studied using first-principles methods. Such compounds are representative of a possible new class of materials in which ferroelectricity is perturbed by compositional breaking of inversion symmetry. For isovalent substitution on either sublattice, the ferroelectric double-well potential is found to persist, but becomes sufficiently asymmetric that minority domains may no longer survive. The strength of the symmetry breaking is enormously stronger for heterovalent substitution, so that the double-well behavior is completely destroyed. Possible means of tuning between these behaviors may allow for the optimization of resulting materials properties.

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In the last decade, the extensive use of first-principles theoretical methods to study ferroelectric perovskite oxides has led to a greatly expanded understanding of the ferroelectric and piezoelectric properties of this important class of materials. Theoretical investigations of electronic, dynamical, and structural properties have been shown to be in good accord with experimental observations for the simple ABO_3 perovskites [1]. Moreover, these studies provide microscopic insight into the ferroelectric instabilities, their relation to the long-range Coulomb interactions [2], and related questions about the origins of the piezoelectric response [3,4].

However, the materials of most interest for technological applications are generally not the simple ABO_3 perovskites, but *solid solutions* with stoichiometric substitutions of A or B metal atoms. Examples include PZT ($PbZr_{1-x}Ti_xO_3$), currently one of the most widely used ferroelectrics, and PZN ($PbZn_{1/3}Nb_{2/3}O_3$) and PMN ($PbMg_{1/3}Nb_{2/3}O_3$) and their solid solutions with $PbTiO_3$, which have recently been shown to have enormous piezoelectric response in single-crystal form [5]. In fact, this class of materials shows great promise for the development of *new materials* having improved dielectric and electromechanical properties. Not only is there an enormous space of chemical compositions to explore, but it may also be possible to optimize the desired material properties by tuning the degree and type of compositional order for the desired application [6,7].

In particular, Eckstein [8] has recently suggested that the artificial atomic-layer growth of *compositionally ordered structures that break inversion symmetry* might be especially exciting and fruitful in this regard. The resulting asymmetry of the ferroelectric double-well potential in such a material suggests the prospect of *qualitatively new behavior,* e.g., "self-poling" materials with tailored piezoelectric or dielectric properties.

In this Letter, we explore this exciting prospect by carrying out *ab-initio* theoretical calculations for several prospective model structures of this type. Specifically, we envision the artificial growth of materials of overall composition $(A_{1/3}A'_{1/3}A''_{1/3})BO_3$ or $A(B_{1/3}B'_{1/3}B''_{1/3})O_3$, in which the three different cations alternate layer-by-layer along the ferroelectric direction as illustrated in Figs. 1(a-b) for A-site and B-site modulation respectively. We will *assume* that such atomic-layer control will become possible [8], and investigate the energy landscapes and ferroelectric properties of the resulting materials. As will be shown below, we find that the asymmetry may easily be strong enough for self-poling to occur, even in the case of isovalent substitution. Moreover, we find a surprisingly strong variation of the strength of the symmetry breaking with the strength of the compositional perturbation, allowing for a very wide tunability of ferroelectric properties. Experimentally, such tunability might be exploited by growing alloy structures with a cyclic modulation of the concentration variable. We thus find very strong motivations for the development of such materials, and hope that our work will encourage experimental efforts directed toward their synthesis.

We adopt bulk $BaTiO_3$ as a prototypical parent compound and construct a series of model systems that allow us to test for the effects of A-site *vs.* B-site and isovalent *vs.* heterovalent substitution. Specifically, we consider $(Ba_{1/3}Sr_{1/3}Ca_{1/3})TiO_3$ as an example of an "A-iso" system (isovalent substitution on the A site), $Ba(Sc_{1/3}Ti_{1/3}Nb_{1/3})O_3$ as an example of a "B-hetero" system (heterovalent substitution on the B site), and $Ba(Ti_{1/3}Zr_{1/3}Hf_{1/3})O_3$ as an intermediate "B-iso" case. We construct 15-atom supercells by tripling the primitive unit cell along the z direction and cyclically alternating the identity of the A or B atom, as shown in Figs. 1(a-b). We assume that any ferroelectric order develops only along the z-direction, so that the material remains tetragonal, and only z displacements need be considered. (It may be possible to realize this situation by appropriate choice of lattice-mismatched substrate for

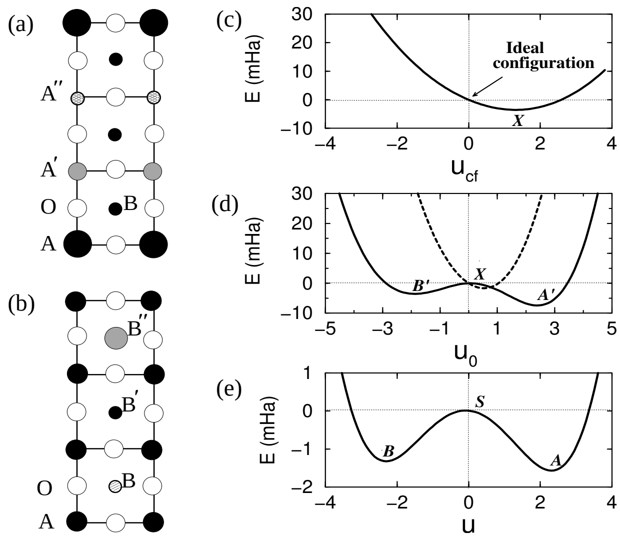

FIG. 1. Side views of (a) $(A_{1/3}A'_{1/3}A''_{1/3})BO_3$, and (b) $A(B_{1/3}B'_{1/3}B''_{1/3})O_3$ structures. Energy *vs.* displacement along (c) the cubic force direction, (d) the line $\mathbf{r} = \mathbf{r}_X + u_0\hat{\xi}_0$, and (e) the line connecting the minima A and B. Solid (dashed) curves are for A-iso (B-hetero) systems.

epitaxial growth, but it is not our purpose here to investigate this possibility.) We also assume perfect control of layer-by-layer composition, resulting in the ideal stacking of Figs. 1(a-b), and carry out our theoretical studies only at zero temperature. Much future work clearly remains to be done in relaxing these assumptions, but the study of simple prototypical systems is a natural first step.

The *ab-initio* calculations are carried out using the Vanderbilt ultra-soft pseudopotential scheme [9] in the local-density approximation. Details of the pseudopotentials can be found in Ref. [10]. Good k-point convergence is obtained using a (6,6,2) Monkhorst-Pack mesh, corresponding to the bulk (6,6,6) mesh [11], and a 25-Ry plane-wave cutoff is used throughout. Because experimental lattice constants a and c are not available for the ordered compounds of interest, the calculated theoretical equilibrium values were usually used. However, in some cases the c/a ratio was fixed and only the cell volume was optimized, as detailed below.

In the presence of the broken inversion symmetry, it is not always easy to locate both local energy minima corresponding to the two ferroelectric ground states. We have found that the following procedure is quite reliable for finding both minima, if they exist. First, we place the atoms at the ideal cubic coordinates and calculate the pattern of forces, thus defining a "cubic force direction" $\hat{\xi}_{\rm cf}$ in the 15-dimensional configuration space. We then use $\hat{\xi}_{\rm cf}$ as the search direction for a line minimization, and denote the minimum along this line $\mathbf{r} = u_{\rm cf}\,\hat{\xi}_{\rm cf}$ to be X, as shown in Fig. 1(c). Next, starting from X, we carry out a second line minimization along the line $\mathbf{r} = \mathbf{r}_X + u_0\,\hat{\xi}_0$, where $\hat{\xi}_0$ corresponds to the ferroelectric mode unit vector of bulk $BaTiO_3$. As shown in

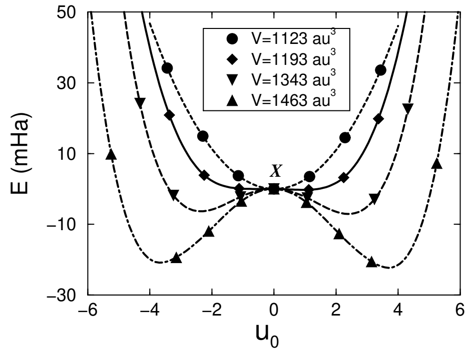

FIG. 2. Energy vs. displacement along the line $\mathbf{r} = \mathbf{r}_X + u_0\,\hat{\xi}_0$ in the A-iso system for several cell volumes.

Fig. 1(d), two scenarios can be identified. (i) If two minima A' and B' are found along this line, then we carry out a steepest-descent minimization from each, obtaining two distinct local minima A and B. Fig. 1(e) shows the perturbed double-well potential plotted along a line connecting points A and B (direction $\hat{\xi}$) in such a case. (ii) If only one minimum is found, as for the dashed line of Fig. 1(d), then the double-well potential has been destroyed, and a subsequent steepest-descent minimization identifies the unique minimum.

We first consider the application of this procedure to the A-iso system $(Ba_{1/3}Sr_{1/3}Ca_{1/3})TiO_3$. The relaxation from the ideal cubic structure to the point X illustrated in Fig. 1(c) is found to be dominated by ionic size effects: one sees a simple shift of the atoms toward smaller A-site cations and away from larger ones. Figure 1(d) then illustrates the minimization along $\mathbf{r} = \mathbf{r}_X + u_0\,\hat{\xi}_0$ for one particular fixed cell volume (1343 a.u.^{3}), indicating a modest asymmetry between minima A' and B'. However, since it is well established that the presence or absence of a ferroelectric instability depends strongly on cell volume in perovskites [10], we have repeated this step for a series of fixed atomic volumes in Fig. 2. (The curves in Fig. 2 could thus be roughly interpreted as corresponding to a series of related compounds having differing tendencies towards ferroelectric instability.) The results illustrate the typical evolution of the double-well potential with increased ferroelectric tendency, from a slightly asymmetric single-well minimum (V=1123 a.u.^{3}) to a slightly asymmetric double-well potential (V=1463 a.u.^{3}) [12]. It happens that the theoretical equilibrium volume V=1193 a.u.^{3} is a nearly borderline case; we find only a single minimum, but there are still two inflection points. In such a case, we modify the procedure of the previous paragraph by carrying out a steepest-descent minimization from each inflection point, and by doing so we succeed in finding the two distinct minima $\mathbf{r}_A$ and $\mathbf{r}_B$ in Fig. 1(e). For this case (V=1193 a.u.^{3}), we find a soft-mode amplitude of 0.3 a.u. and an average well depth (relative to the saddle point S) of 0.48 mHa per 5-atom cell, fairly close to the corresponding values of 0.25 a.u. and 0.43 mHa [10], respectively, for tetragonal bulk $BaTiO_3$.

The energy difference between the twin wells is modest, $\sim 15-20\%$ of the well depth.

Applying the same approach to the B-iso system $Ba(Ti_{1/3}Zr_{1/3}Hf_{1/3})O_3$, we observe very similar behavior: a strong volume-dependence of the ferroelectric tendency, and a modest inversion asymmetry for both single-well and double-well volumes. In this case, the structure does not develop a double-well potential until the volume is increased to 1468 a.u.^{3}, but the degree of asymmetry is similar as for the A-iso case. Thus, we conclude that the choice of A vs. B site for an isovalent chemical substitution does not strongly affect the strength of the asymmetry or the qualitative behavior of the system.

While the asymmetries may appear small in the case of isovalent substitution, they are large by one important measure. We define an "effective electric field" $\mathcal{E}_{\rm eff} = \Delta E/\Delta P_s$, where ΔE and ΔP_s denote the energy and polarization differences between the two local minima. If this quantity is larger than the coercive field of the material, it means that the thermodynamic preference for the energetically preferred minimum is strong enough to overcome the pinning of the domain walls and to spontaneously switch the material into a single-domain state. Using the Berry-phase approach [13] to calculate ΔP_s, we find $\mathcal{E}_{\rm eff}$=90 kV/cm at the equilibrium volume in the A-iso system. Since the typical coercive field of most perovskite ferroelectrics is closer to 15 kV/cm, we thus arrive at the important conclusion that the symmetry breaking may easily be strong enough to cause the material to self-pole, even in the case of isovalent substitution.

Turning now to the case of *heterovalent* chemical substitution, we find very different behavior in this case. Specifically, we consider the B-hetero system $Ba(Sc_{1/3}Ti_{1/3}Nb_{1/3})O_3$ in which the valence charges are +3, +4, and +5 on Sc, Ti, and Nb, respectively. Structural optimization results in a lattice constant of a = 7.60 a.u. and c/a = 3.023. The pattern of relaxation $\hat{\xi}_{\rm cf}$ leading to configuration X suggests that the electrostatic interaction is a dominant effect. Specifically, we observe bucklings of the AO and BO_2 planes that are consistent with a picture of static electric fields arising from the different B-atom valence charges.

Most importantly, for the heterovalent case we find *only a single minimum* when searching from X along $\hat{\xi}_0$, as shown by the dashed curve in Fig. 1(d). Various alternate search strategies failed to identify a second minimum; all trial structures were found to relax back to a unique structural ground state. The absence of the second minimum was not found to be sensitive to the cell volume, as was the case for isovalent substitutions. Thus, we find that the symmetry breaking is enormously stronger than for the isovalent case, and it is clear that resulting behavior is of a qualitatively different type.

In order to gain a better understanding of this behavior, and in particular to track the disappearance of the secondary minimum, we have developed a model system to study the effects of "turning on" the heterovalent symmetry-breaking perturbation gradually. We introduce a continuous variable δ, and construct artificial atoms with fractional nuclear charges that deviate by $\pm\delta$ from those of Ti (Z=22). Constructing a crystal out of a cyclic series of Ti$-\delta$, Ti, and Ti$+\delta$ atomic layers, we can continuously tune the system from ferroelectric $BaTiO_3$ (δ=0) to a full-fledged heterovalent system $Ba(Sc_{1/3}Ti_{1/3}V_{1/3})O_3$ (δ=1). The energies calculated along the $\hat{\xi}_0$ direction from X are plotted for a series of δ values in Fig. 3. As δ increases from 0 to 0.3, the asymmetry of the double well increases and the well depth decreases. At $\delta = 0.4$, the curve exhibits only a single energy minimum, signaling the transition from double-well to single-well behavior in response to the increasingly strong symmetry-breaking perturbation. To confirm the disappearance of the secondary minimum more directly, we also tracked its evolution as δ was "turned on" in a sequence of small steps, using the relaxed structure at one δ as a starting guess for the next. At $\delta = 0.34$, the minimum was confirmed to disappear, and subsequent relaxation led back to the principal (now global) minimum.

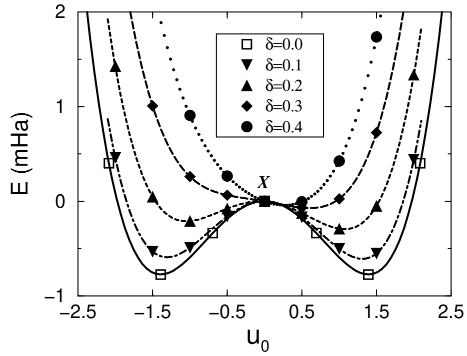

FIG. 3. Energy vs. displacement along the line $\mathbf{r} = \mathbf{r}_X + u_0\,\hat{\xi}_0$ in the B-hetero system with continuous δ.

To gain more insight into the structural relaxations, we have found it useful to introduce a measure of the "strength of the symmetry breaking." While it is tempting to choose a measure that is related to the energy difference between the two local minima, like the $\mathcal{E}_{\rm eff}$ introduced earlier, such a definition has the disadvantage of being ill-defined in the single-minimum case. Thus, we have adopted instead the following measure. For any curve such as that of Figs. 1(d-e), 2, or 3, we locate the point of minimum d^2E/du^2 (i.e., vanishing d^3E/du^3), and then define $F_{\rm sb}$ to be dE/du evaluated at that point. We refer to $F_{\rm sb}$ as the "symmetry-breaking force" since it measures the strength of the symmetry breaking and has units of force. It turns out to have a similar behavior as the well-depth difference in the double-well case, but has the advantage of remaining well-defined in the single-well case.

Calculations of $F_{\rm sb}$ in the A-iso and B-iso cases indicate that $F_{\rm sb}$ has only a modest and smooth dependence on cell volume even when passing through the transition from single-well to double-well behavior, confirming that the "strength of the symmetry breaking" is not the variable parameter in those cases. However, returning to the virtual-atom B-hetero system, we find that $F_{\rm sb}$ is an extremely sensitive function of δ, with numerical fits indicating a δ^3 dependence. It is not hard to see that $F_{\rm sb}$ must be an odd function of δ, but its cubic behavior may seem surprising at first sight. However, the vanishing of the linear term can be deduced from simple symmetry arguments. An intuitive form of the argument is to note that the symmetry-breaking perturbation, which is of the form $(+\delta,\ -\delta,\ 0)$ in successive layers, can be regarded as a superposition of two perturbations $(2\delta/3,\ -\delta/3,\ -\delta/3)$ and $(\delta/3,\ -2\delta/3,\ \delta/3)$ that *do not break* inversion symmetry. Thus, the principle of superposition prevents the occurrence of any symmetry-breaking response in linear order in δ, and in particular $F_{\rm sb}$ must vanish. (A more systematic analysis may be made by considering the C_{3v} symmetry group consisting of primitive translations along $\hat{z}$ and mirrors M_z. The ferroelectric mode vector and the perturbation δ are found to belong to the A_2 and E representations, repsectively, and thus cannot couple at linear order.)

Knowing the form of this extraordinarily strong cubic dependence of $F_{\rm sb}$ on δ, we can now understand the pronounced qualitative differences that were observed for the cases of isovalent and heterovalent substitution. We find that $F_{\rm sb}$ is about the same, $\sim$0.25 mHa/a.u., in the B-hetero system with $\delta = 0.25$ as in the A-iso system. Increasing δ from 0.25 to 0.4 increases $F_{\rm sb}$ by about a factor of four, enough to cause the transition to single-well behavior. A further increase of δ from 0.4 to 1.0 leads to a further increase of the symmetry-breaking force $F_{\rm sb}$ by a *factor of about 15*. Thus, in a fully-developed B-hetero system such as $\rm Ba(Sc_{1/3}Ti_{1/3}Nb_{1/3})O_3$, the strength of the symmetry breaking is more than an order of magnitude larger than needed to destroy the secondary minimum completely. It is hardly surprising, then, that we observed no secondary minimum in this case!

The enormous disparity between the behavior in the isovalent and heterovalent cases suggests that it may be of great interest to find a way of tuning the system continuously from one behavior to the other. One can imagine doing this by regarding δ not as a variable atomic number, but rather as representing a layer-by-layer composition variable. For example, one could conceive of the epitaxial growth of $\rm Ba(Sc_{1-y}Nb_y)O_3$ in an alternating sequence of layers with $y = 0.5(1+\delta)$, $y = 0.5$, and $y = 0.5(1-\delta)$. By the same symmetry arguments, the effective strength of the symmetry breaking must again scale as δ^3. Thus, by controlling the concentration variable δ, one can hope to tune the system over a very wide range of behavior.

One would clearly like to use this tunability to optimize the desired characteristics of the material, such as the piezoelectric response. It might naively be expected that increasing the strength of the inversion symmetry breaking will increase the piezoelectric response. (For example, if the parent material at δ=0 were *paraelectric*, then the piezoelectric response would be expected to scale as δ^3.) On the other hand, the materials that have the largest piezoelectric coefficients are typically ferroelectrics, and since a very strong symmetry breaking suppresses the ferroelectric behavior, it might be counterproductive to make δ too large. Clearly, further theoretical investigation is needed in order to clarify these issues.

Many other questions remain open and need to be resolved. For example, the conditions under which the polarization will remain oriented parallel to the growth direction, the behavior of the system as a function of temperature, and the properties of materials with simultaneous A-site and B-site substitution, are obvious candidates for further study. The thermodynamic behavior of these materials, which are technically pyroelectric but interpolate to a ferroelectric limit as $\delta \to 0$, are also deserving of investigation. In the meantime, we hope that our theoretical investigations will stimulate attempts at experimental growth and characterization of novel perovskites with compositionally broken inversion symmetry.

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