

Ferroelectric and Piezoelectric Properties in the Presence of Compositionally Broken Inversion Symmetry

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Abstract. We extend our first-principles study of novel ferroelectric perovskite systems in which compositional inversion symmetry is broken [N. Sai, B. Meyer and D. Vanderbilt, Phys. Rev. Lett. 84, 5636 (2000)] by (i) focusing on the piezoelectric response of the triple-cell heterovalent system $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$, and (ii) studying the strength of the symmetry breaking in the double-cell system $(\text{Ba}, \text{Sr})(\text{Ti}-\delta, \text{Ti}+\delta)\text{O}_3$ with simultaneous *A*-site and *B*-site substitutions. We observe the enhanced piezoelectric response coefficient e_{33} when increasing the compositional parameter δ in the triple-cell system. This enhancement is quite drastic for the metastable minimum, but only modest for the stable minimum, corresponding respectively to the minority and majority wells of the ferroelectric double-well structure. In the double-cell system, we find that the increase in strength of symmetry breaking with the chemical or concentration perturbation is dominated by the term linear in δ , in contrast with the δ^3 dependence found in the triple-cell system. A symmetry-based justification of the dominance of the linear term is provided.

INTRODUCTION

Technologically important materials that display ultra-high piezoelectric response have recently been found in many alloy ferroelectrics or more complex solid-solution systems [1]. Numerous theoretical calculations have been carried out on perovskite oxides such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ or ferroelectric relaxors represented by $\text{Pb}(\text{Zr}, \text{Nb}, \text{Ti})\text{O}_3$ and $\text{Pb}(\text{Mg}, \text{Nb}, \text{Ti})\text{O}_3$ to investigate the origin of the large response [2–5]. It was shown that the ferroelectric and piezoelectric properties exhibit great sensitivity to composition [1,4]. This feature, together with the variety of crystal configurations, has provided this class of materials with an exceptional tuning ability for improving the efficiency of applications.

The potential, however, for designing new materials with tuning freedom has by no means been exhausted. Very recently, we have for the first time reported a theoretical study of ferroelectric systems with compositionally broken inversion symmetry [6]. To summarize briefly, we studied ferroelectric systems of the form

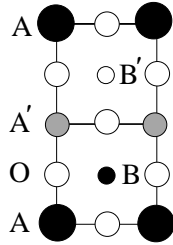


FIGURE 1. Side view of the $(A_{1/2}A'_{1/2})(B_{1/2}B'_{1/2})O_3$ structure. In our study, A and A' are Ba and Sr, and B and B' are either Sc and Nb or virtual Ti- δ and Ti+ δ atoms.

$(A_{1/3}A'_{1/3}A''_{1/3})BO_3$ and $A(B_{1/3}B'_{1/3}B''_{1/3})O_3$ with three different cations that alternate layer by layer along the stacking direction. Focusing on the breaking of the inversion symmetry along the ferroelectric direction, we found a great disparity between the effects of heterovalent substitutions, such as in $Ba(Sc_{1/3}Ti_{1/3}Nb_{1/3})O_3$, and isovalent substitutions, such as in $(Ba_{1/3}Sr_{1/3}Ca_{1/3})TiO_3$. The heterovalent symmetry-breaking perturbation is so strong as to completely suppress one of the minima in the ferroelectric double well, while isovalent substitution only weakly affects the ferroelectric behavior. In particular, the study has emphasized a triple-cell model system with cyclically alternating cations Ti, Ti- δ and Ti+ δ . Here δ is a continuous parameter, tunable between 0 and 1, that accounts for the nuclear charge difference between a true Ti atom and virtual atoms having slightly less or more nuclear charge. Surprisingly at first sight, the strength of the symmetry breaking in this system was found to scale as δ^3 .

It is generally expected that the piezoelectric response will increase for a system of lowered symmetry [7]. Therefore one might expect that it should be possible to enhance certain ferroelectric properties, such as the piezoelectric response, using the enormous freedom allowed for by the type and pattern of imposed compositional order. In the first part of the present paper, we describe previously unreported calculations of the piezoelectric response for the $Ba(Ti-\delta, Ti, Ti+\delta)O_3$ system.

In the second part of our paper, we study a double-unit-cell system denoted by $(A_{1/2}A'_{1/2})(B_{1/2}B'_{1/2})O_3$ as shown in Fig. 1. In contrast with the triple-cell system, inversion symmetry in the double-cell system is broken by simultaneous substitutions on the A - and B -sites. As before, the spontaneous polarization direction is assumed to lie along the tetragonal stacking direction. We will show that the strength of the symmetry breaking in the double-cell system has a quite different behavior compared to the triple-cell symmetry-breaking system.

METHOD

Total-energy calculations are based on the Vanderbilt ultrasoft pseudopotential [8] scheme within the local-density approximation. Details of the pseudopotentials can be found in Ref. [9]. A $4 \times 4 \times 2$ Monkhorst-Pack mesh [10] is used for sampling

the Brillouin zone in the self-consistent calculations and a 25-Ry plane-wave cutoff is used throughout. Our procedure for locating both local energy minima in the case of a distorted double-well potential has been reported previously in Ref. [6]. To study the piezoelectric response, the polarization P is calculated for each structure using the Berry-phase approach [11,12], with a $4 \times 4 \times 10$ k -point grid used for the k -space integration in the polarization calculations.

RESULTS

A Piezoelectric response of the triple-cell system

The lattice parameters for the Ba(Ti- δ ,Ti,Ti+ δ)O₃ system are chosen so that the volume is 1248.9au³ and $c/a = 3.036$. We have assumed the ferroelectric order parameter to lie only along the z -axis. In order to study quantitatively the symmetry breaking as a function of δ , we have tracked the ferroelectric ground state configurations at different δ by gradually increasing δ by small amounts. Each calculated relaxed structure at one value of δ is taken as the initial guess for the next structure, and the atomic coordinates are relaxed again. However, there exists a critical value of δ beyond which the secondary minimum vanishes and only one minimum remains locally stable.

The piezoelectric coefficients e_{ij} are defined as derivatives of the polarization with respect to strain at zero macroscopic electric field. Thus, in leading order, $P_i^\epsilon = P_i^s + e_{ij}\epsilon_j$, where P_i^s is the spontaneous polarization of the unstrained system along the i -th Cartesian direction, ϵ_j is the strain tensor, and e_{ij} is the piezoelectric tensor [2] in Voigt notation. It has been shown that the proper piezoelectric response is just related to the variation of the Berry phase with strain deformation [13]; we can therefore compute the proper response directly using

$$e_{ij} = \frac{e}{2\pi\Omega} \sum_{\alpha} \frac{d\phi_{\alpha}}{d\epsilon_j} R_{\alpha i} \quad (1)$$

where ϕ_{α} is the Berry phase in direction α , $R_{\alpha i}$ is the real-space lattice vector, and Ω is the volume. In our calculations, we focus on the principal element e_{33} and introduce several additional strains in the range $|\epsilon_3| \leq 0.01$ into the fully relaxed ground-state structure (reference state), and re-optimize the coordinates. We find that in order to obtain a good fit for every structure within the strain of this range, the variation of the polarization has to be fitted with at least a third-order polynomial in strain, where the linear coefficient gives the piezoelectric constant.

We also separately computed the clamped-ion piezoelectric response that involves only external strains at fixed coordinates. Its magnitude amounts to only 2-3% of the total piezoelectric response and it carries the opposite sign. Therefore, the total piezoelectric response is mainly due to the atomic sublattice displacements, or “internal strain,” similar to what has been found in the PT and PZT materials

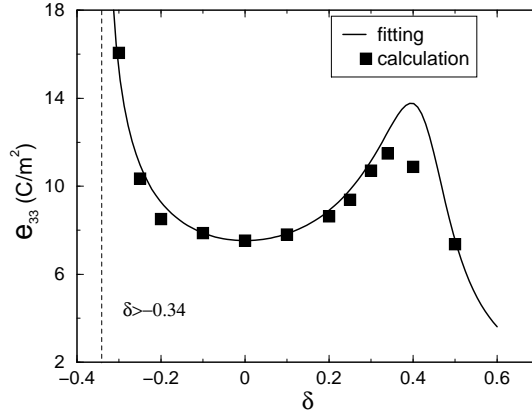


FIGURE 2. Calculated and fitted piezoelectric response e_{33} as a function of δ in the $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ system.

[2,3]. In the following, we report only the total piezoelectric response including both clamped-ion and internal-strain contributions.

The e_{33} piezoelectric response for both the principal (“majority”) and the secondary (“minority”) minima are plotted together as function of δ in Fig. 2 (solid squares). For $\delta=0$ the system is just BaTiO_3 in the tetragonal phase. We find that the polarization $P_s = 0.24\text{C}/\text{m}^2$ is very close to the experimental value of $0.27\text{C}/\text{m}^2$. e_{33} is found to be $7.5\text{C}/\text{m}^2$. For positive δ , we plot the piezoelectric response for the energetically-favored principal minimum. The e_{33} coefficient increases by a factor about 1.4 as it reaches a maximum at $\delta \sim 0.4$. Then the value starts to drop and becomes lower than that of BaTiO_3 at $\delta = 0$. The response is found to be significantly different for negative δ , corresponding to the secondary minimum; here e_{33} increases sharply for $\delta \leq -0.25$ and appears to diverge as δ approaches some critical value from above. The divergence is well fitted by a power law of the form $e_{33} \simeq A_0(\delta - \delta_c)^{-\gamma}$, where $\gamma = 0.31$, $A_0 = 5.58$, and the critical value δ_c equals -0.34 .

An intuitive explanation for the divergence of the piezoelectric response at δ_c is readily available. To produce a large piezoelectric response, the structure needs to have a nearly flat internal energy surface [14]. Thus, in ferroelectrics, the piezoelectric response tends to diverge at the paraelectric-to-ferroelectric phase transition [7]. When δ is tuned in the present system so that the secondary minimum is about to disappear, the saddle point approaches the secondary minimum, the barrier between them becomes very low, and the upward curvature at the secondary minimum is going to zero. Intuitively, this represents the kind of flat energy surface that can provide a large piezoelectric response.

Next, we show that a simple model that takes into account the macroscopic strain can illustrate quantitatively the behavior of the piezoelectric response within a range of δ corresponding to the physical structures. The total energy can be expanded in the ferroelectric soft-mode variable up to fourth order as

$$E = E_0 + E_1u + E_2u^2 + E_4u^4 \quad (2)$$

where the coefficients E_n are functions of δ , and the zero of u has been chosen to make the d^3E/du^3 term vanish. The leading δ -dependence of the E_1 coefficient is as $a_3\delta^3$, while E_2 and E_4 have a δ -dependence like $a_0 + a_2\delta^2$. This behavior follows from the symmetry, which allows simultaneous exchange of $u \leftrightarrow (-u)$ and $\delta \leftrightarrow (-\delta)$ without changing the total energy.

We write the free energy in terms of a single mode of the polarization P that couples to the macroscopic strain ϵ ,

$$F(P, \delta, \epsilon) = e_0(\delta) + e_1(\delta)P + e_2(\delta)P^2 + e_4(\delta)P^4 + c\epsilon P^2. \quad (3)$$

The equilibrium polarization $P_0(\delta)$ is given by $\partial F/\partial P = 0$, so that for $\epsilon \rightarrow 0$, the piezoelectric constant is

$$e_{33} = \frac{\partial P_0(\delta)}{\partial \epsilon} = \frac{2cP_0(\delta)}{2e_2(\delta) + 12e_4(\delta)P_0^2(\delta)}. \quad (4)$$

The interesting range of δ is when $P_0(\delta)$ is real. Within this range, we substitute the numerically computed coefficients $e_1(\delta)$, $e_2(\delta)$, and $e_4(\delta)$ into Eq. (4) and plot in Fig. 2 (smooth curve) the analytically fitted e_{33} versus δ for both the stable and the metastable minimum. We scale the constant c in Eq. (4) so that the fitted and the calculated e_{33} are equal at $\delta = 0$. Evidently, the two curves exhibit the same behavior. The data and the fit agree well within the δ range of ± 0.25 . Discrepancies in e_{33} , however, become more pronounced in the vicinity of the peak that appears at $\delta \approx 0.4$ in the calculations and $\delta = 0.4$ in the fit. The fitted peak is 20% higher than the calculated one.

We also use the above model in order to investigate what has caused the piezoelectric response to peak at $\delta = 0.4$. We calculate the curvature of the free-energy surface $\partial^2 F/\partial^2 P$ at the three stationary points (two minima and saddle point) and plot them in Fig. 3. At $\delta = 0$, the two minima have identical positive curvature. For the case of the metastable minimum, the curvature drops continuously as δ increases and vanishes at $\delta = -0.34$, which is consistent with the divergent piezoelectric response we find at this point. On the positive side of the plot, the curvature drops, forming a valley at $\delta = 0.4$, and then increases again. This result suggests that the behavior of the piezoelectric response can be explained by the nature of the δ -dependence of the curvature. Intuitively, one can say that increasing δ has two effects: a δ^2 tendency that makes e_2 less negative, and a δ^3 symmetry breaking. The first tendency makes both wells more shallow and soft, thus causing e_{33} to increase, as δ first deviates from zero with either sign. But then the δ^3 tendency establishes one of the wells as the principle well, and the e_{33} of this well is eventually suppressed as the growing positive e_2 term causes the remaining single well to deepen and harden with increasing δ .

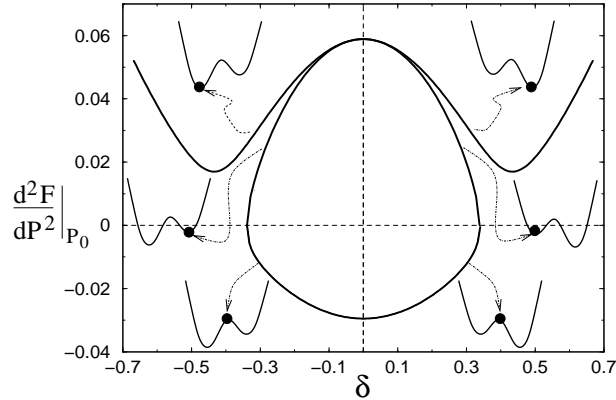


FIGURE 3. Second derivatives of the free-energy surface evaluated at the stationary points (minima or saddle points, as indicated by the sketches) according to the model of Eq. (3). (For $|\delta| > 0.34$ the secondary minimum and saddle point have disappeared.)

B Broken symmetry in the $(A_{1/2}A'_{1/2})(B_{1/2}B'_{1/2})O_3$ system

There are many possible layer sequences that can break the inversion symmetry along the growth direction of a mixed cubic perovskite. Here, we consider a layer sequence that accomplishes this with the minimum repeat period, only 10 atoms per primitive cell. Specifically, we study the $(A_{1/2}A'_{1/2})(B_{1/2}B'_{1/2})O_3$ system shown in Fig. 1, in which there are simultaneous alternating substitutions on both A and B sites.

It has been demonstrated in the case of the triple-cell system that heterovalent substitutions along the order-parameter direction have a much stronger effect on breaking the symmetry than isovalent substitutions. Hence, we first consider an “ A -iso- B -hetero” system $(Ba_{1/2}Sr_{1/2})(Sc_{1/2}Nb_{1/2})O_3$ in which the heterovalent perturbation occurs on the B site only. However, for this case we find that the symmetry breaking is already strong enough that there is only a single ferroelectric minimum, similar to what was found for the $Ba(Sc_{1/3}Ti_{1/3}Nb_{1/3})O_3$ triple-cell system [6]. Therefore, in order to understand how the system evolves from the unperturbed to the strongly-perturbed regime, we turn to the system $(Ba,Sr)(Ti+\delta, Ti-\delta)O_3$ where virtual atoms of type $Ti\pm\delta$ have been substituted on the B -sites, and increase δ gradually from 0 to 1.

The equilibrium volume is frozen to equal the sum of the volumes of $BaTiO_3$ and $SrTiO_3$ in their cubic structures [9]. We use $c/a = 1.012$, the same as for the $BaTiO_3$ 5-atom tetragonal cell. The previously-developed search strategy is applied to find the principal and secondary ferroelectric ground states for a series of broken-symmetry systems with δ increasing from system to system. The total energy as a function of the soft mode amplitude u is computed along the line direction that connects the two energy minima as shown in Fig. 4. When δ exceeds 0.3 the second minimum has already vanished, indicating a stronger symmetry breaking compared

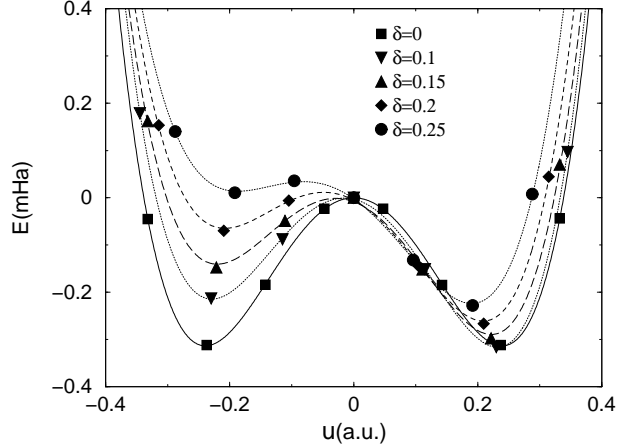


FIGURE 4. Total energy vs. soft-mode amplitude for different δ in the $(\text{Ba,Sr})(\text{Ti}+\delta, \text{Ti}-\delta)\text{O}_3$ system.

to the triple cell system. Hence, only the energy profiles concluding with $\delta = 0.25$ have been plotted.

Once again we analyze the results for the total energy as a function of the soft mode variable u via the polynomial expansion of Eq. (2). The δ -dependent coefficients E_1 , E_2 and E_4 are plotted as functions of δ in Fig. 5. For comparison, we have also plotted the corresponding coefficients for the $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ system in the same figure. The linear coefficient, which is a primary measure of the symmetry breaking (we name it the “symmetry breaking force”), clearly shows the leading dependence on δ to be linear in the double-cell system while it is as δ^3 in the triple-cell system. Indeed, a much stronger symmetry-breaking effect has been observed at very small δ in the present system. However, it is also indicated that further enhancement of the symmetry breaking with increasing δ will be much milder in this system than in the triple-cell system. The E_2 and E_4 coefficients show similar dependence on δ in the form of $a_1 + a_2\delta^2$ as in the triple-cell system. However, the intercept $E_2(\delta) = 0$ gives $\delta = 0.37$ and the critical value for the existence of a second energy minimum is only $\delta < 0.28$.

To compare the differences between the symmetry-breaking behavior in the two systems, it is instructive to consider the forces on the atoms while they sit at their ideal positions. We call this pattern of forces the “cubic force vector” \vec{f}_c . In general, \vec{f}_c can be expanded in powers of δ ,

$$\vec{f}_c = \vec{f}_c^{(0)} + \vec{f}_c^{(1)}\delta + \vec{f}_c^{(2)}\delta^2 + \vec{f}_c^{(3)}\delta^3 + \dots, \quad (5)$$

where $\vec{f}_c^{(0)}$ is the force vector at $\delta = 0$. Note that $\vec{f}_c^{(0)}$ is nonzero in this system, so that the unit vector $\hat{f}_c = \vec{f}_c/|\vec{f}_c|$ can be expanded as

$$\hat{f}_c = \hat{f}_c^{(1)} + a_2\hat{f}_c^{(2)}\delta + a_3\hat{f}_c^{(3)}\delta^2 + \dots. \quad (6)$$

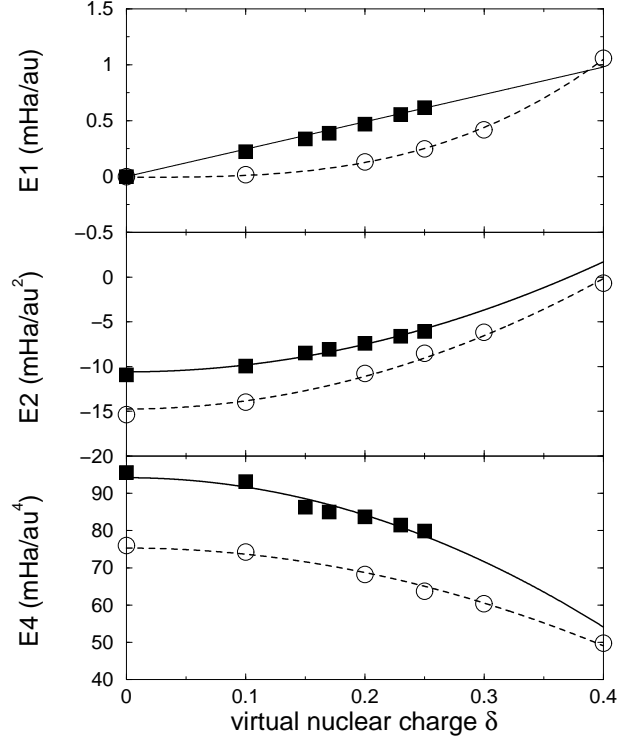


FIGURE 5. Total energy expansion coefficients in Eq. (2) as functions of δ for both the $(\text{Ba,Sr})(\text{Ti}+\delta, \text{Ti}-\delta)\text{O}_3$ system (solid squares) and $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ system (empty circles).

In Ref. [6], we identified the C_{3v} symmetry group with the $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ system. Note that C_{3v} is *not* the point-group symmetry; instead, it refers to the 6-element symmetry group of the $\delta=0$ system, generated by 2-fold mirror reflections along z and 3-fold translations along z . In this C_{3v} group, the ferroelectric mode unit vector $\hat{\xi}$ transforms according to irrep A_2 , while the perturbation pattern associated with δ belongs to irrep E . Thus, the coupling of the ferroelectric mode and the cubic force vector $\hat{\xi} \cdot \hat{f}_c$ can only have $\hat{\xi} \cdot \hat{f}_c^{(3)}\delta^2$ as the leading term because $\hat{f}_c^{(3)}$ is associated with the product of $E \times E \times E$ that contains the A_2 representation.

In contrast, the double cell system at $\delta = 0$ does not have symmetry with respect to a primitive translation, and so obeys the S_2 symmetry group generated by just the 2-fold mirror reflection along z . Both the ferroelectric mode vector and the perturbation of δ are odd in terms of the mirror operation, so that they both belong to the same irrep A_u . Therefore, a coupling of the form $\hat{\xi} \cdot \hat{f}_c^{(2)}\delta$ is still prohibited, but $\hat{\xi} \cdot \hat{f}_c^{(1)}$ does not have to vanish. Hence, the coupling between the ferroelectric mode and the symmetry-breaking cubic-force vector in the double-cell system is governed by both the terms in $\hat{\xi} \cdot (\hat{f}_c^{(1)} + a_3\hat{f}_c^{(3)}\delta^2)$.

To illustrate the above analysis, we show in Fig. 6 the coupling between $\hat{\xi}$ and \hat{f}_c . The angles are directly calculated from $\cos^{-1}(\hat{\xi} \cdot \hat{f}_c)$. In the bottom panel, the angle is shown for the $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ system. We observe that the angle decreases

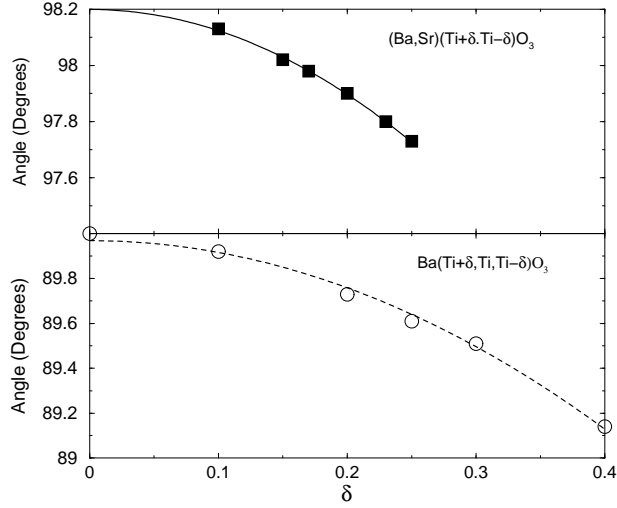


FIGURE 6. Angle between the ferroelectric mode vector $\hat{\xi}$ and the cubic force vector \hat{f}_c as a function of δ for the $(\text{Ba,Sr})(\text{Ti}+\delta, \text{Ti}-\delta)\text{O}_3$ (top panel) and $\text{Ba}(\text{Ti}+\delta, \text{Ti}, \text{Ti}-\delta)\text{O}_3$ (bottom panel) systems.

quadratically with increasing δ and intersects $\delta = 0$ at exactly 90° , in agreement with the predicted $\hat{\xi} \cdot \hat{f}_c^{(3)}\delta^2$ dependence. In the double-cell system shown in the upper panel, the angle has a similar quadratic dependence on δ , but the intercept is not at 90° but at 98.2° , illustrating that the $\hat{\xi} \cdot \hat{f}_c^{(1)}$ term does not vanish in the present system.

CONCLUSIONS

In summary, we studied the evolution of the piezoelectric response in the model ferroelectric system $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ with compositionally broken inversion symmetry. A divergence in the response is observed for the metastable energy minimum at the critical δ value where this secondary minimum is about to disappear. For the energetically favored minimum, the piezoelectric response is moderately enhanced and peaks in the vicinity of $\delta \sim 0.4$. A simple model based on a free-energy expansion in the zero macroscopic strain limit is used to describe the behavior of these responses. We also extended our studies to the double-cell system $(\text{Ba,Sr})(\text{Ti}+\delta, \text{Ti}-\delta)\text{O}_3$. We find that the strength of the symmetry breaking depends linearly on δ , providing a different picture from that of the triple-cell system studied previously.

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