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Effects of tricritical points and morphotropic phase boundaries on the piezoelectric properties of ferroelectrics

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The longitudinal piezoelectric coefficient d_{33}^{*} of a PZT-like ferroelectric is computed in the full composition-temperature parameter space using sets of parameters that control the position of the tricritical points and the degree of tilting of the morphotropic phase boundary separating the ferroelectric rhombohedral phase from the ferroelectric tetragonal phase. The system is modeled using a Ginzburg–Landau expansion of the free energy in terms of the electric polarization up to sixth order, including all the symmetry-allowed terms. We obtain two regions of the phase diagram with a large piezoelectric response. In the polar direction, d_{33}^{*} is large in the vicinity of the paraelectric to ferroelectric line of phase transitions, whereas in a nonpolar direction d_{33}^{*} is large in the vicinity of the morphotropic phase boundary. We find that a given degree of tilting of the morphotropic phase boundary can be obtained from free energies with different degrees of anisotropy, and therefore the titling and anisotropy are not directly related. On the other hand, the piezoelectric response is larger when the two tricritical points of the phase diagram are farther apart from each other than when they collapse onto a single tricritical point.

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I. INTRODUCTION

Since its development in the 1950s, Pb(Zr$_{1-c}$Ti$_c$)O$_3$ (PZT) has been the canonical piezoelectric material, with a large electromechanical coupling and piezoelectric response.[1–3] Despite these outstanding properties, there is significant interest in the development of new lead-free piezoelectrics because of concerns over the toxicity of lead.

Unfortunately, the piezoelectric response of lead-free materials is generally inferior to the performance of the PZT family.[4–6]

In the search for new materials to replace PZT, there is a need to establish the correspondence between characteristic features of the phase diagram and the piezoelectric performance. The piezoelectric response is usually a maximum in the vicinity of phase transitions because of the flattening of the free-energy profile facilitating polarization extension and/or polarization rotation.[7–11] While polarization extension is usually the dominant mechanism in phase transitions from a nonpolar to a polar phase, such as the paraelectric cubic to ferroelectric tetragonal in BaTiO$_3$, the polarization rotation mechanism is dominant in phase transitions between two polar phases with different crystal symmetries and different orientation directions of the polarization vector, such as the composition-driven rhombohedral-to-tetragonal phase transition in PZT.[12,13] These ideas have led to the suggestion of a phase diagram that takes advantage of both mechanisms simultaneously by introducing a polar phase between another polar phase of a different symmetry and a nonpolar phase in a narrow region of the temperature-composition parameter space.[13]

The large piezoelectric response in the lead-free solid solution, Ba(Ti$_{0.8}$Zr$_{0.2}$)O$_3$-(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT-BCT), recently reported by Liu and Ren,[14] has also been analyzed in terms of characteristic features of the phase diagram. More precisely, Liu and Ren associate the large piezoelectric response of BZT-BCT to the tricritical character of the triple point where the cubic paraelectric phase coexists with the ferroelectric rhombohedral and tetragonal phases.[14] It is argued that in the presence of a tricritical point a vertical morphotropic phase boundary (MPB) leads to an isotropic free energy along this boundary. Thus, a tilted MPB (as in BZT-BCT) in the presence of a tricritical point would correspond to a weakly anisotropic free energy that would lead to a large piezoelectric response by means of polarization rotation.

In this paper we will focus on the phase diagram of a PZT-like ferroelectric. PZT has been modeled by Haun *et al.*[15–20] using a Ginzburg–Landau–Devonshire sixth-order expansion of the free energy in terms of the polarization. The model is able to reproduce accurately the full temperature-composition phase diagram, but the composition dependence of the coefficients is so complex that the manipulation of the main properties of the phase diagram by means of changes in the model parameters becomes difficult. From the point of view of simplicity, Rossetti *et al.*[21] developed a similar model where the composition dependence of the parameters is at most linear. In this model, the expansion of the free energy is considered up to sixth order but the sixth-order term is assumed to be isotropic, that is, it does not depend on the direction of the polarization vector.

This gives rise to the phase diagram schematically shown in Fig. 1. The ferroelectric phase can be rhombohedral (F_R) or tetragonal (F_T), depending on the composition, and the paraelectric-to-ferroelectric phase transition can be first order or second order, defining two tricritical points with compositions c_R^{cr} and c_T^{cr}. The phase transition from the ferroelectric rhombohedral phase to the ferroelectric tetragonal phase, defining the MPB, is second order in this simplified model, contrary to experiment. This has a strong influence on the piezoelectric response.

To more faithfully describe the piezoelectric response in the vicinity of the MPB we generalize the model of Rossetti *et al.*[21]

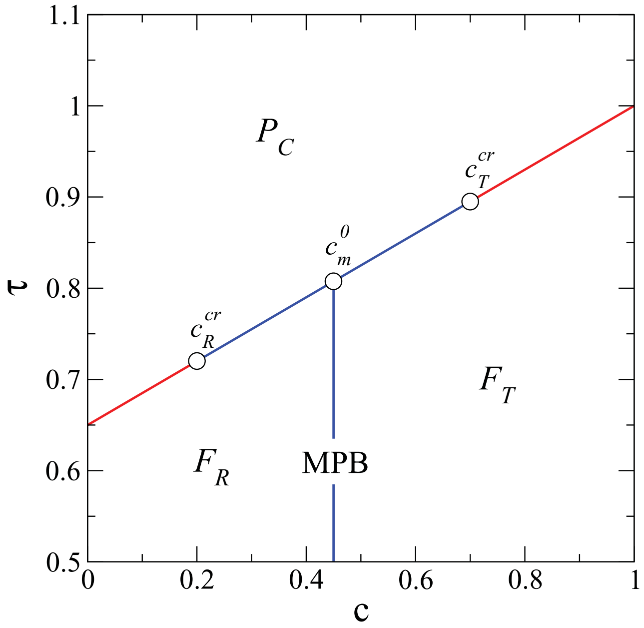

FIG. 1. (Color online) Schematic phase diagram of PZT that follows from the model of Ref. 21. Three phases are shown: ferroelectric rhombohedral (F_R), ferroelectric tetragonal (F_T), and paraelectric cubic (P_C). First- (second-) order phase transitions are shown in red (blue). The composition of the triple point is c_m^0, and the compositions of the tricritical points of the rhombohedral and tetragonal phases are c_R^{cr} and c_T^{cr}, respectively.

by including *anisotropic* sixth-order terms in the polarization. This is sufficient to obtain the proper first-order character of the rhombohedral-to-tetragonal phase transition at the MPB, and it keeps the complexity of the model to a minimum.

Our objective, with the aid of this model, is to investigate the effect of the degree of tilting of the MPB and the distance between the two tricritical points on the piezoelectric response in the full temperature-composition parameter space. One of our main findings is that the magnitude of the polarization is continuous across a vertical MPB and that discontinuities of this quantity are due to terms of order higher than six in the free-energy expansion or due to the tilting of the MPB. This suggests that, in the vicinity of a vertical MPB separating two nonpolar phases, flattening of the free energy with respect to polarization extension will not occur, and that polarization rotation is the dominant mechanism for the piezoelectric response.

The paper is organized as follows. After generalizing the model of Rossetti *et al.*,[21] we present in Sec. III the temperature-composition phase diagram and the piezoelectric response obtained with different sets of model parameters. In particular, we study the cases of a vertical MPB with a single and two tricritical points, and a tilted MPB with a single tricritical point. Finally, in Sec. IV we summarize and draw our conclusions.

II. MODEL

In this section we generalize the model of Rossetti *et al.*[21] by including the anisotropic sixth-order terms in the polarization. Using reduced units, the free-energy density is written as

$$\begin{aligned} f(c,\tau,\mathbf{n},p) = {} & \tfrac{1}{2}a_2(c)\,[\tau - \tau_C(c)]\,p^2 \\ & + \tfrac{1}{4}\big[a_4(c) - a_4'(c)\left(n_1^4 + n_2^4 + n_3^4\right)\big]p^4 \\ & + \tfrac{1}{6}\big[a_6(c) - a_6'(c)\left(n_1^6 + n_2^6 + n_3^6\right) \\ & - a_6''(c) n_1^2 n_2^2 n_3^2\big]p^6, \end{aligned} \tag{1}$$

where c is the molar fraction of PbTiO$_3$ (PT) in PZT, $\tau = T/T_C$ is the reduced temperature relative to the Curie temperature of PT, $\mathbf{n} = \{n_1,n_2,n_3\}$ is a unit vector in the direction of the polarization vector $\mathbf{P}$, and $p = P/P_s$ is its magnitude relative to the saturation polarization of PT. The free-energy density is made dimensionless by dividing each of the terms in Eq. (1) by the specific energy $u = k_B T_C/\Omega$, where k_B is Boltzmann's constant and Ω is the unit cell volume of PT.

Minimizing the free energy [Eq. (1)] with respect to the direction of the polarization vector (in polar coordinates) one can check that depending on the model parameters the result can be $\mathbf{n} = \{0,0,1\}$, $\mathbf{n} = \{\frac{1}{\sqrt{2}},\frac{1}{\sqrt{2}},0\}$ or $\mathbf{n} = \{\frac{1}{\sqrt{3}},\frac{1}{\sqrt{3}},\frac{1}{\sqrt{3}}\}$, which, because of polarization-strain coupling, gives rise to a tetragonal, orthorhombic, or rhombohedral crystal structure, respectively. For the model parameters and range of temperatures used in this paper, only the tetragonal and rhombohedral phases are stable. The tetragonal phase is stable for

$$a_4' + a_6' p^2 > 0, \tag{2}$$

and the rhombohedral phase is stable for

$$-a_4' - \tfrac{2}{3}a_6' p^2 + \tfrac{1}{9}a_6'' p^2 > 0, \tag{3}$$

where the equilibrium polarization is given by

$$p^2 = \frac{-\left[a_4 - a_4'\left(n_1^4 + n_2^4 + n_3^4\right)\right] \pm \sqrt{\left[a_4 - a_4'\left(n_1^4 + n_2^4 + n_3^4\right)\right]^2 - 4a_2\left(\tau - \tau_C\right)\left[a_6 - a_6'\left(n_1^6 + n_2^6 + n_3^6\right) - a_6'' n_1^2 n_2^2 n_3^2\right]}}{2\left[a_6 - a_6'\left(n_1^6 + n_2^6 + n_3^6\right) - a_6'' n_1^2 n_2^2 n_3^2\right]}. \tag{4}$$

Following Rossetti *et al.*[21] the coefficients $a_4(c)$ and $a_4'(c)$ are written as

$$\begin{aligned} a_4(c) &= b_4^0(c - c_0), \\ a_4'(c) &= b_4^0\xi\left(c - c_m^0\right), \end{aligned} \tag{5}$$

where b_4^0, c_0, ξ, and c_m^0 are parameters. We do not consider a temperature dependence of a_4' as it was already carried out in Ref. 21, and as this gives rise to unrealistically large negative values of this parameter at high temperatures, limiting the stability of the paraelectric phase to a finite temperature range.

We consider the case in which the paraelectric-to-ferroelectric phase transition at the triple point is second order. In this case, at this point the equilibrium polarization vanishes, and from Eqs. (2) and (3) we obtain that the location of the MPB is given by $a_4' = 0$. The parameter c_m^0 in Eqs. (5) thus corresponds to the composition of the triple point, and the corresponding temperature is given by $\tau_C(c_m^0)$.

The tricritical points are given by the condition,

$$a_4(c) - a_4'(c)\left(n_1^4 + n_2^4 + n_3^4\right) = 0, \tag{6}$$

which leads to,

$$\begin{aligned} c_R^{cr} &= \frac{c_0 - \frac{1}{3}\xi c_m^0}{1 - \frac{1}{3}\xi}, \\ c_T^{cr} &= \frac{c_0 - \xi c_m^0}{1 - \xi}. \end{aligned} \tag{7}$$

We now focus on the situation in which the two tricritical points overlap at the triple point and the MPB is vertical. At the triple point $a_4' = 0$; thus, in order that Eq. (6) be satisfied at this point, we need that $a_4(c_m^0) = 0$. In addition, if the MPB is vertical, $a_4(c)$ and $a_4'(c)$ should vanish at any point of the MPB, as they depend only on composition. The location of the MPB is determined by equating the free energies of the rhombohedral and tetragonal phases. In this case ($a_4 = a_4' = 0$) for the rhombohedral phase we have

$$f_R = \tfrac{1}{2}a_2(\tau - \tau_C)p_R^2 + \tfrac{1}{6}\left(a_6 - \tfrac{1}{9}a_6' - \tfrac{1}{27}a_6''\right)p_R^6, \tag{8}$$

with

$$p_R^2 = \sqrt{\frac{-a_2(\tau - \tau_C)}{a_6 - \frac{1}{9}a_6' - \frac{1}{27}a_6''}}, \tag{9}$$

and for the tetragonal phase,

$$f_T = \tfrac{1}{2}a_2(\tau - \tau_C)p_T^2 + \tfrac{1}{6}(a_6 - a_6')p_T^6, \tag{10}$$

with

$$p_T^2 = \sqrt{\frac{-a_2(\tau - \tau_C)}{a_6 - a_6'}}. \tag{11}$$

Equating Eqs. (8) and (10) we obtain

$$a_6'' = 24a_6'. \tag{12}$$

If Eq. (12) is satisfied, at the MPB the coefficient of the sixth-order term of the free energy is equal for the rhombohedral and the tetragonal phases [see Eqs. (8) and (10)]. Thus the magnitude of the polarization is also equal for both phases [see Eqs. (9) and (11)], and of course, by definition of phase transition the free energies are also equal. We also note that if there are two tricritical points ($c_R^{cr} \neq c_T^{cr}$), the condition given in Eq. (12) is sufficient to give rise to a vertical MPB, as at the triple point $a_4' = 0$, and thus the fourth-order term is isotropic.

In general the coefficients a_6' and a_6'' do not vanish, and therefore the free energy along a vertical MPB is anisotropic. This is in contrast with the result that Liu and Ren[14] obtained from a similar analysis of the sixth-order expansion of the free energy. The origin of this discrepancy is what is meant by the sixth-order coefficient being equal in the tetragonal and rhombohedral phases at the MPB. If the coefficient is equal it does not mean that it is independent of the direction of the polarization. We have seen this in equating Eqs. (8) and (10).

A notable consequence of the above analysis is that, for a vertical MPB, anisotropy arises from sixth- and higher-order terms of the free-energy expansion (the fourth-order term is isotropic, as $a_4' = 0$), and therefore the degree of anisotropy will be small, enhancing the piezoelectric response by means of the polarization rotation mechanism. On the other hand, we have obtained that the magnitude of the polarization is continuous across a vertical MPB. The discontinuity of this magnitude in PZT, where the MPB is almost vertical, is therefore small.[20]

Thus enhancement of the piezoelectric response that is due to a polarization extension in the vicinity of the MPB will be feasible only if the MPB is tilted, as in BZT-BCT. In fact, it has been suggested that in this material both polarization rotation due to the MPB and polarization extension due to the proximity of the cubic-tetragonal and cubic-rhombohedral phase transitions contribute to the exceptionally large piezoelectric response of this material.[13] In addition, if the change in the magnitude of the polarization at the MPB is large, the flattening of the free energy with respect to polarization extension may occur as a precursor to the tetragonal-to-rhombohedral phase transition without the need of the proximity to the paraelectric-to-ferroelectric transition.

We also note that, with the inclusion of the anisotropic sixth-order terms in the free energy, the rhombohedral-to-tetragonal phase transition at the MPB is first order, in agreement with experiment. Moreover, as the polarization vanishes at the triple point, the first-order character of the phase transition at the MPB decreases with increasing temperature, and it becomes continuous at the triple point, as observed experimentally[14] in BZT-BCT.

Analyzing the general expression of the free energy given in Eq. (1), we note that the term $a_6'(n_1^6 + n_2^6 + n_3^6)$ favors the stability of the tetragonal phase with respect to the rhombohedral phase, as it is larger for the tetragonal phase, whereas the term $a_6'' n_1^2 n_2^2 n_3^2$ favors the stability of the rhombohedral phase. When the relation given in Eq. (12) is satisfied, none of these structures is favored with respect to the other, as the summation of the two anisotropic sixth-order terms is equal for both structures, giving rise to the vertical MPB. Therefore a simple way of tilting the MPB toward the tetragonal phase (with the triple point fixed) is breaking this balance by increasing a_6'' or decreasing a_6', which increases the stability of the rhombohedral phase with respect to the tetragonal. On the other hand, the location of the tricritical points can be controlled by the parameters c_0 and ξ using Eq. (7).

The parameters and the data are given in reduced units, which are defined as the saturation polarization of PT at 298 K, $P_S = 0.75\ \mathrm{C/m^2}$, its Curie temperature $T_C = 748$ K, and the specific energy $u = 1.66 \times 10^8\ \mathrm{J/m^3}$. In these reduced units, the parameters, which are fixed throughout the paper, are

$$\begin{aligned} &\tau_C(c) = 0.35c + 0.65, \quad a_2(c) = 1.52c + 0.61, \\ &c_m^0 = 0.45, \quad b_4^0 = 3.00, \quad \xi = 1.50, \quad a_6 = 1.43. \end{aligned} \tag{13}$$

The parameters τ_C, a_2, c_m^0, and b_4^0 are directly taken from Ref. 21, whereas the parameter a_6 is taken from Ref. 15 as its average value from the composition $c = 0.1$ to $c = 1$. In the same way, the parameter a_6' is determined to be

$$a_6' = 0.42, \tag{14}$$

although its value will be varied in order to control the degree of tilting of the MPB. Finally, the parameter ξ is obtained from the assumption that $c_T^{cr} - c_m^0 = c_m^0 - c_R^{cr}$.

The piezoelectric response will be computed as the strain induced by an applied electric field. For a homogeneous polarization the strain is given by

$$\varepsilon_{ij} = p^2 q_{ijkl} n_k n_l, \tag{15}$$

where q_{ijkl} is the electrostrictive tensor. Using Voigt's notation, the three independent coefficients for cubic PZT are, in reduced units,[21]

$$q_{11} = 0.047, \qquad q_{12} = -0.017, \qquad q_{44} = 0.013. \tag{16}$$

We will focus on the longitudinal piezoelectric coefficient d_{33}^*, which can be computed in an arbitrary direction by applying a small electric field in this direction and measuring the corresponding longitudinal strain in the same direction.[7,8,12] This is done at each point of the $c - \tau$ parameter space in the [001] and the [111] directions. In the [001] direction the piezoelectric coefficient d_{33}^* is obtained as

$$d_{33}^{[001]} = \frac{\partial \varepsilon_{zz}}{\partial Ez}, \tag{17}$$

whereas in the [111] direction it is given by

$$d_{33}^{[111]} = \frac{1}{3}\frac{\partial[\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} + 2(\varepsilon_{yz} + \varepsilon_{xz} + \varepsilon_{xy})]}{\partial E}. \tag{18}$$

III. PHASE DIAGRAM AND PIEZOELECTRIC RESPONSE

In this section we present the temperature-composition phase diagram obtained with different sets of model parameters, and the piezoelectric coefficient d_{33}^* in the [001] and [111] directions of the different ferroelectric phases.

A. Vertical MPB with a single tricritical point

We start with a set of parameters which gives rise to a single tricritical point located at the triple point and a vertical MPB. For the parameter a_6' we choose the value given in Eq. (14). The parameter a_6'' is thus fixed to $a_6'' = 24a_6' = 10.08$. The existence of a single tricritical point imposes $c_0 = c_m^0 = 0.45$. The phase diagram and the piezoelectric response obtained with this set of parameters is shown in Fig. 2.

The piezoelectric coefficient d_{33}^* in the [001] direction [Fig. 2(a)] is especially large in two regions of the phase diagram. On the one hand, in the tetragonal phase it is large in the vicinity of the paraelectric-to-ferroelectric phase transition because of the flattening of the free energy with respect to polarization extension. On the other hand, in the rhombohedral phase the piezoelectric response is large near the MPB and especially as the triple point is approached. In the rhombohedral phase the polar direction is the [111] direction. Therefore, when the electric field is applied in the nonpolar [001] direction, in principle, both the polarization extension and the polarization rotation mechanisms may have a contribution to the piezoelectric response. Because of the difference in the orientation of the polarization between the tetragonal and rhombohedral phases, we expect a flattening of the free energy with respect to polarization rotation in the vicinity of the MPB. Moreover, as the magnitude of the polarization is continuous across the vertical MPB, such a flattening is not expected with respect to polarization extension. Thus, in the vicinity of the MPB, polarization rotation will be the dominant mechanism far from the triple point, whereas as the triple point is approached, flattening of the free energy with respect to polarization extension may occur because of the proximity of the paraelectric-to-ferroelectric transition, and thus both mechanisms would be operative.

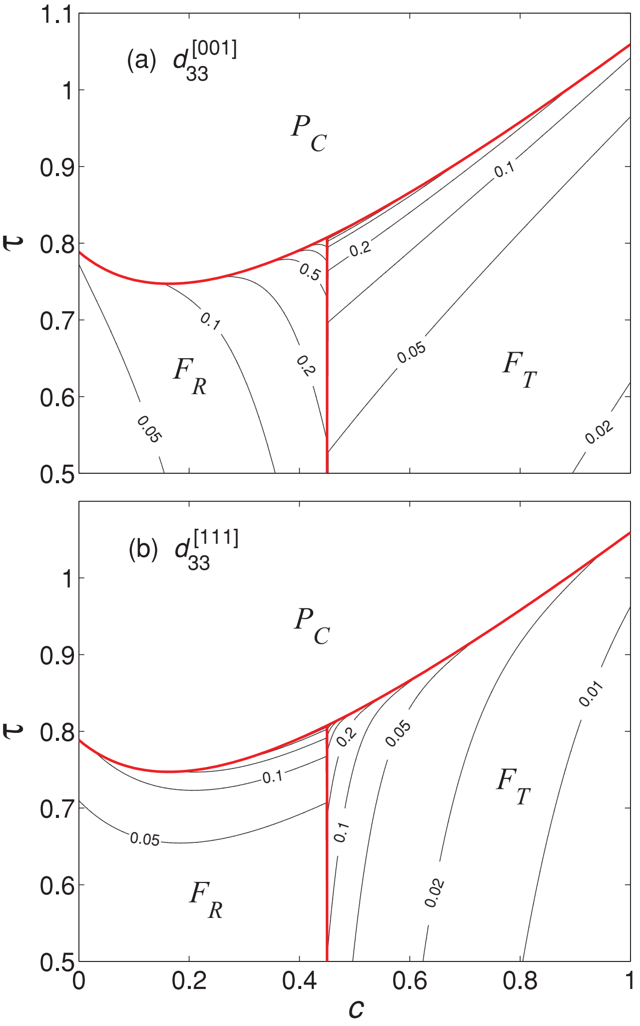

FIG. 2. (Color online) Contour map of the longitudinal piezoelectric coefficient d_{33}^* in the (a) [001] direction and the (b) [111] direction in the $c - \tau$ parameter space corresponding to the parameters $a_6' = 0.42$, $a_6'' = 24a_6' = 10.08$, and $c_0 = 0.45$, which give rise to a vertical MPB and a single tricritical point located at the triple point. The phase transitions (indicated in red) are first order in the whole phase diagram.

When the electric field is applied in the [111] direction [Fig. 2(b)], this corresponds to the polar direction in the rhombohedral phase and to a nonpolar direction in the tetragonal phase. Similarly, in this case we obtain a large piezoelectric response in the vicinity of the paraelectric-to-ferroelectric transition in the rhombohedral phase and in the vicinity of the MPB, but especially near the triple point in the tetragonal phase.

We note that when the electric field is applied in the nonpolar direction the piezoelectric response in the vicinity of the MPB is large but finite. This is in contrast with the result expected for an isotropic free energy, which is the divergence of the piezoelectric response at the MPB due to polarization rotation in the absence of an energy barrier.

B. Tilted MPB with a single tricritical point

In this subsection we study the effect of tilting the MPB. To this end, we first decrease the parameter a_6', which is set to zero, while the other parameters remain unchanged. This clearly decreases the degree of anisotropy of the free energy. As the anisotropic term $a_6'(n_1^6 + n_2^6 + n_3^6)$ stabilizes the tetragonal phase with respect to the rhombohedral phase, we expect that the suppression of this term will mainly affect the piezoelectric response of the tetragonal phase, particularly when the electric field is applied in the [111] direction, which induces the transition to the rhombohedral phase. The results obtained with these parameters are shown in Fig. 3. We note that the MPB is now slightly tilted toward the tetragonal phase, that is, it has a negative slope. As the parameters that determine the position of the tricritical points have not been changed, as before, a single tricritical point is located at the triple point. As expected, the longitudinal piezoelectric response of the tetragonal phase when the electric field is applied in the [111] direction is enhanced. The piezoelectric coefficient $d_{33}^{[111]}$ in the rhombohedral phase, and the piezoelectric coefficient $d_{33}^{[001]}$ in both phases change very little.

A similar degree of tilting of the MPB can also be obtained by increasing the parameter a_6'' to $a_6'' = 18.4$ while keeping $a_6' = 0.42$. In this case we are increasing the anisotropy of the free energy.

The piezoelectric response corresponding to these parameters is shown in Fig. 4. As the term $a_6'' n_1^2 n_2^2 n_3^2$ stabilizes the rhombohedral phase with respect to the tetragonal phase, the main effect of its increase is to decrease the piezoelectric response of the rhombohedral phase when the electric field is applied in the [001] direction, which induces the transition to the tetragonal phase. Moreover, since this term vanishes in the tetragonal phase, the longitudinal piezoelectric response of this phase strictly remains unchanged with respect to the results shown in Fig. 2, in both the [001] and the [111] directions. From these results we conclude that the degree of tilting of the MPB is not directly related to the degree of anisotropy of the free energy.

We also note that a tilted MPB allows for a discontinuity in the magnitude of the polarization. However, we do not observe an enhancement of the piezoelectric response in the polar direction in the vicinity of the MPB. This indicates that the discontinuity of the magnitude of the polarization does not induce a flattening of the free energy with respect to polarization extension in this region of the phase diagram. In the Ginzburg–Landau–Devonshire model of Haun *et al.*[20] an increase of the dielectric susceptibility and piezoelectric coefficients in both the polar and nonpolar directions is observed as the composition $c = 0.5$ is approached. In this model, however, the Curie constant has a peak at this composition,[18] and this is sufficient to induce a strong composition dependence of these magnitudes in the vicinity of the MPB.

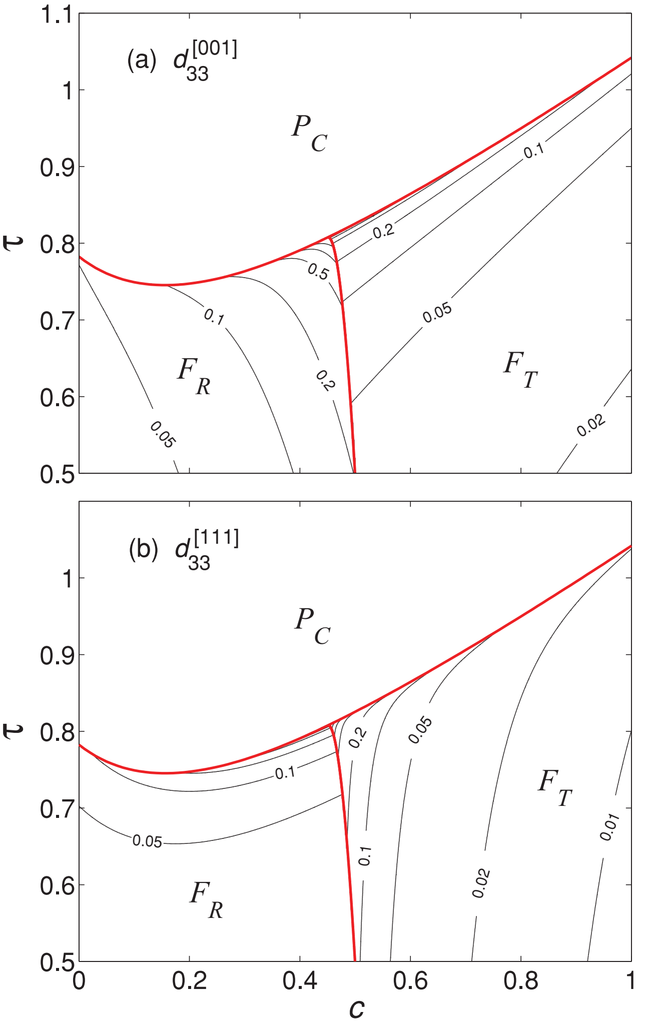

FIG. 3. (Color online) Contour map of the longitudinal piezoelectric coefficient d_{33}^* in(a) the [001] direction and (b) the [111] direction in the $c - \tau$ parameter space corresponding to the parameters $a_6' = 0$, $a_6'' = 10.08$, and $c_0 = 0.45$, which give rise to a slightly tilted MPB and a single tricritical point located at the triple point. The phase transitions (indicated in red) are first order in the whole phase diagram.

C. Vertical MPB with two tricritical points

In this subsection we analyze the effect of the degree of separation of the tricritical points on the piezoelectric response. To this end, the parameter c_0 is fixed to $c_0 = 0.325$ which together with $c_m^0 = 0.45$ and $\xi = 1.5$ gives rise to $c_R^{cr} = 0.2$ and $c_T^{cr} = 0.7$ [see Eq. (7)]. The parameters a_6' and a_6'' are fixed to $a_6' = 0.42$ and $a_6'' = 24a_6' = 10.08$, which give rise to the vertical MPB. The corresponding piezoelectric response is shown in Fig. 5. If we compare this result with the piezoelectric response obtained with a single tricritical point and the vertical

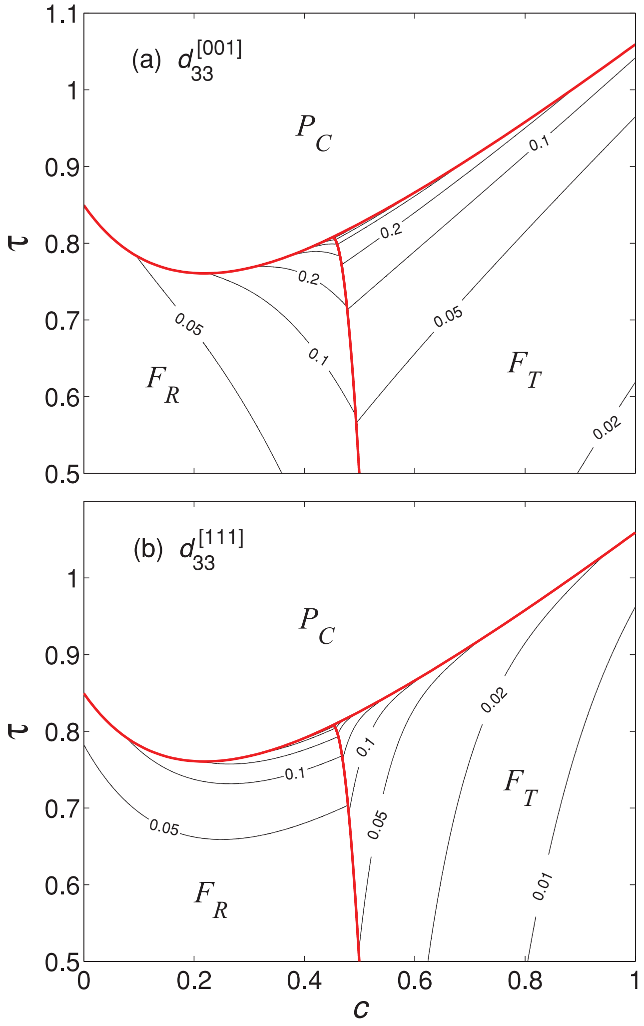

FIG. 4. (Color online) Contour map of the longitudinal piezoelectric coefficient d_{33}^* in (a) the [001] direction and (b) the [111] direction in the $c-\tau$ parameter space corresponding to the parameters $a_6' = 0.42$, $a_6'' = 18.4$, and $c_0 = 0.45$, which give rise to a slightly tilted MPB and a single tricritical point located at the triple point. The phase transitions (indicated in red) are first order in the whole phase diagram.

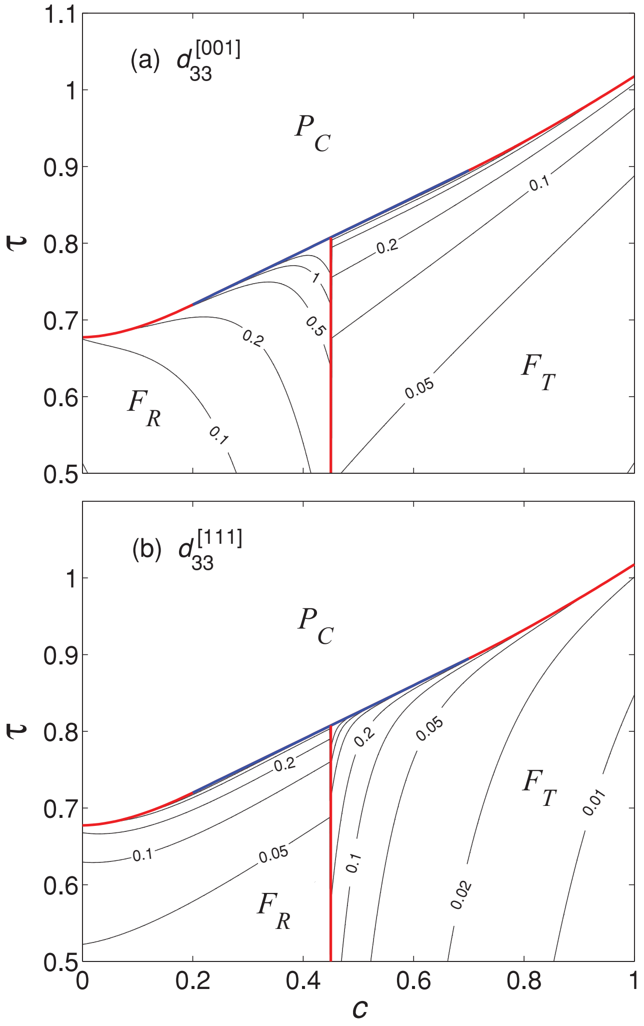

FIG. 5. (Color online) Contour map of the longitudinal piezoelectric coefficient d_{33}^* in (a) the [001] direction and (b) the [111] direction in the $c-\tau$ parameter space corresponding to the parameters $a_6' = 0.42$, $a_6'' = 10.08$, and $c_0 = 0.325$, which give rise to a vertical MPB and two tricritical points located at $c_R^{cr} = 0.2$ and $c_T^{cr} = 0.7$. First- (second-) order phase transitions are indicated in red (blue).

MPB (Fig. 2) we obtain that in the present case d_{33}^* is larger. The reason for this difference could be related to the fact that if the two tricritical points are separated the paraelectric-to-ferroelectric phase transition is second order in a large region of the phase diagram, and second order phase transitions give rise to larger response functions than first order phase transitions due to a bigger flattening of the free energy in their vicinity.

Experimental data available in the literature for the location of the tricritical points in PZT is somewhat contradictory. X-ray diffraction studies by Eremkin *et al.*[22] established the existence of two tricritical points $c_R^{cr} = 0.22$ and $c_T^{cr} = 0.55$. This is consistent with the results obtained from dielectric constant measurements by Noheda *et al.*,[23] which determined their location at $c_R^{cr} = 0.26$ and $c_T^{cr} = 0.51$.

Also, the theoretical work of Haun *et al.*[17] leads to two tricritical points $c_R^{cr} = 0.102$ and $c_T^{cr} = 0.717$. The tricritical point in the cubic-to-tetragonal line of phase transitions was also found in the calorimetric measurements of Rossetti *et al.*,[24] which estimated its location around $c_T^{cr} = 0.62$. This is in contrast with the x-ray diffraction[25] and dielectric and piezoelectric studies[26] of Mishra *et al.* in the vicinity of the MPB that obtained that the cubic-to-tetragonal phase transition is first order for all compositions, although the discontinuity of the phase transition decreases with decreasing Ti content and a tricritical point exists in the cubic-to-rhombohedral line of phase transitions.

Additionally, recent experiments on a number of systems (including PZT) appear to show that hysteresis always tends to become small at the triple point.[27] Thus it would appear that there is no strong experimental evidence for the location of the tricritical points.

According to the results presented here, the existence of dual tricritical points might help to enhance the piezoelectric response of PZT and be one of the reasons for the large values measured of d_{33}^*.

IV. SUMMARY AND CONCLUSIONS

In summary, we have developed a sixth-order Ginzburg–Landau model for PZT including all symmetry-allowed anisotropic terms in the free energy. The model is used to study the effects of the degree of tilting of the MPB and the separation between the two tricritical points on the longitudinal piezoelectric response in the $c - \tau$ parameter space. The analysis of the model leads to the conclusion that the magnitude of the polarization is continuous across a vertical MPB. Thus discontinuities of this quantity are due to terms of order higher than six in the free-energy expansion or due to the tilting of the MPB. This indicates that in the vicinity of a vertical MPB the free energy will not flatten with respect to polarization extension and that polarization rotation will be the dominant mechanism for the piezoelectric response.

Large values of the piezoelectric coefficient d_{33}^* are obtained in the vicinity of the paraelectric-to-ferroelectric phase transition in the polar direction and in the vicinity of the MPB in a nonpolar direction. The piezoelectric response is especially large in the vicinity of the triple point, where the free energy flattens with respect to both polarization extension and polarization rotation because of the proximity of the paraelectric-to-ferroelectric phase transition and the MPB, respectively. We have explicitly shown that the degree of tilting of the MPB is not directly related to the degree of anisotropy of the free energy and thus to the piezoelectric response. On the other hand the piezoelectric response is larger if the two tricritical points are farther apart from one another than if they overlap at the triple point of the $c - \tau$ phase diagram. The almost-vertical MPB of PZT is thus not sufficient to explain its large piezoelectric response.

The reason for the large piezoelectric response observed[14] in BZT-BCT remains an open question. On the one hand, the existence of a single tricritical point does not seem to enhance the piezoelectric response. On the other, the MPB of BZT-BCT is strongly tilted, which, following the sixth-order Ginzburg–Landau model used in this paper is indicative of free-energy anisotropy. Although the tilting of the MPB might allow for a discontinuity in the magnitude of the polarization, an enhancement of the piezoelectric response due to a flattening of the free energy with respect to polarization extension in the vicinity of a tilted MPB has not been observed in the present work.

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[1] G. Shirane and A. Takeda, J. Phys. Soc. Jpn. **7**, 5 (1952).
[2] G. Shirane, K. Suzuki, and A. Takeda, J. Phys. Soc. Jpn. **7**, 12 (1952).
[3] E. Sawaguchi, J. Phys. Soc. Jpn. **8**, 615 (1953).
[4] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Nature (London) **432**, 84 (2004).
[5] T. Takenaka and H. Nagata, J. Eur. Ceram. Soc. **25**, 2693 (2005).
[6] T. R. Shrout and S. J. Zhang, J. Electroceram. **19**, 111 (2007).
[7] D. Damjanovic, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **56**, 1574 (2009).
[8] M. Davis, M. Budimir, D. Damjanovic, and N. Setter, J. Appl. Phys. **101**, 054112 (2007).
[9] H. Fu and R. E. Cohen, Nature (London) **403**, 281 (2000).
[10] Z. Wu and R. E. Cohen, Phys. Rev. Lett. **95**, 037601 (2005).
[11] M. Budimir, D. Damjanovic, and N. Setter, Phys. Rev. B **73**, 174106 (2006).
[12] M. Budimir, D. Damjanovic, and N. Setter, J. Appl. Phys. **94**, 6753 (2003).
[13] D. Damjanovic, Appl. Phys. Lett. **97**, 062906 (2010).
[14] W. Liu and X. Ren, Phys. Rev. Lett. **103**, 257602 (2009).
[15] L. Q. Chen, Top. Appl. Phys. **105**, 363 (2007).
[16] M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics **99**, 13 (1989).
[17] M. J. Haun, E. Furman, H. A. McKinstry, and L. E. Cross, Ferroelectrics **99**, 27 (1989).
[18] M. J. Haun, Z. Q. Zhuang, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics **99**, 45 (1989).
[19] M. J. Haun, E. Furman, T. R. Halemane, and L. E. Cross, Ferroelectrics **99**, 55 (1989).
[20] M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics **99**, 63 (1989).
[21] G. A. Rossetti Jr., A. G. Khachaturyan, G. Akcay, and Y. Ni, J. Appl. Phys. **103**, 114113 (2008).
[22] V. V. Eremkin, V. G. Smotrakov, and E. G. Fesenko, Ferroelectrics **110**, 137 (1990).
[23] B. Noheda, N. Cereceda, T. Iglesias, G. Lifante, J. A. Gonzalo, H. T. Chen, and Y. L. Wang, Phys. Rev. B **51**, 16388 (1995).
[24] G. A. Rossetti Jr. and A. Navrotsky, J. Solid State Chem. **144**, 188 (1999).
[25] S. K. Mishra, A. P. Singh, and D. Pandey, Philos. Mag. B **76**, 213 (1997).
[26] S. K. Mishra and D. Pandey, Philos. Mag. B **76**, 227 (1997).
[27] X. Ren (private communication).