PHYSICAL REVIEW B **79**, 174113 (2009)

Polarization coupling in ferroelectric multilayers

M. B. Okatan,[1] J. V. Mantese,[2] and S. P. Alpay[1,3,*]

[1]*Department of Chemical, Materials, and Biomolecular Engineering, Materials Science and Engineering Program, University of Connecticut, Storrs, Connecticut 06269, USA*

[2]*United Technologies Research Center, East Hartford, Connecticut 06108, USA*

[3]*Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA*

(Received 23 December 2008; revised manuscript received 12 March 2009; published 21 May 2009)

A thermodynamic model was developed to understand the role of charge compensation at the interlayer interfaces in compositionally graded monodomain ferroelectric multilayers. The polarization mismatch between the ferroelectric layers generates depoling fields with the polarization in each layer varying from its bulk uncoupled value as to adapt to the electrical boundary conditions. By treating the strength of the electrostatic field as a phenomenological parameter, it is shown that if there are localized charges to compensate for the polarization mismatch and relax the depolarization fields, ferroelectric layers behave independently of each other and exhibit a dielectric response that can be described as the sum of their corresponding intrinsic uncoupled dielectric properties. For perfectly insulating heterostructures with no localized charges, the depolarization field is minimized by lowering the polarization difference between layers, yielding a ferroelectric multilayer that behaves as if it were a single ferroelectric material. There exists an optimum value of coupling strength at which average polarization of the multilayer is maximized. Furthermore, ferroelectric multilayers may display a colossal dielectric response dependant upon the interlayer electrostatic interactions.

DOI: 10.1103/PhysRevB.79.174113 PACS number(s): 77.80.Bh, 77.22.Ej

I. INTRODUCTION

Unlike homogenous ferroelectrics (FEs), which are characterized by symmetric hysteresis loops with respect to the polarization and applied field axes, compositionally graded ferroelectric materials yield translations along the polarization axis with an attendant charge offset.[1–4] In addition, it has been found that polarization gradients can also be introduced via temperature and/or stress gradients.[5,6] A wide variety of ferroelectric systems including (Ba,Sr)TiO_3 (BST), (Ba,Sr)$Bi_4Ti_4O_{15}$, Pb(Zr,Ti)O_3, (Pb,Sr)TiO_3, (Pb,La)TiO_3, and (Pb,Ca)TiO_3 show polarization offsets with low leakage current when tested with symmetric voltage-current characteristics.[7–15] More recently, there have been significant advances in the deposition and characterization of bilayer and multilayer ferroelectrics which can be considered as the simplest building blocks of graded systems.[16–23] For example, ultrathin superlattice tricolor heterostructures composed of $BaTiO_3$ (BTO), $SrTiO_3$ (STO), and $CaTiO_3$ (CTO) layers display a clear polarization enhancement when compared to monolayer BTO films deposited under same conditions.[24] Asymmetric BTO, STO, and CTO superlattices grown by layer molecular-beam epitaxy show a large dielectric permittivity that depends on the stacking sequence of the superlattice.[25] Modulation of the thickness of the layers was experimentally shown to be an effective way to maintain a high remanent polarization in asymmetric superlattices of BTO and STO.[26] The paraelectric-ferroelectric phase transformation temperature of pseudomorphic (001) $KTaO_3/KNbO_3$ superlattices on (001) $KTaO_3$ substrate changes dramatically from 475 to 825 K when the superlattice periodicity is increased from 5.1 to 33.8 nm.[27] Recent experimental studies also show that there is a significant improvement in the dielectric tunability of ferroelectric superlattices and graded multilayer heterostructures.[28,29] Depending on the method of synthesis, it has been shown experimentally that high dielectric response in ferroelectric multilayers can be explained via a Maxwell-Wagner type of approach due to the presence of low-resistivity interfacial regions in BST 20/80-BST 80/20 superlattices.[30,31] However, Corbett *et al.*[32] also showed that for relaxor $0.2Pb(Zn_{1/3}Nb_{2/3})O_3-0.8BaTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ superlattices, the polarization behavior suggests a functional coupling between layers which might be related to the structural coupling behavior observed in $KTaO_3/KNbO_3$ superlattices.

Theoretically, the behavior of compositionally asymmetric ferroelectric multilayers has been described by a variety of approaches; including transverse Ising models (TIM),[33–36] first-principles simulations,[37–39] models based on basic electrostatic considerations,[40–42] and mechanistic approaches taking into account domain phenomena.[43] Tagantsev and Gerra[44] provided an extensive review of existing theoretical models for the description of interface-induced phenomena in ferroelectric thin films. In particular, thermodynamic models[33,35,45] have been successfully employed to explain the gigantic dielectric response and tunability in ferroelectric multilayer heterostructures.[46,47] Neaton and Rabe[48] utilized first-principles calculations that predict an enhancement in the polarization of BTO/STO heteroepitaxial bilayers. Very recently, it was shown via a first-principles analysis that the difference in "up" and "down" polarization states expected in asymmetric ferroelectric multilayers diminishes as the thickness of the constituting layers are increased.[49] Using thermodynamic models, Bratkovsky and Levanyuk[50,51] predicted the formation of electrical domains in multilayer films even if the polarization difference between layers is extremely small. Indeed, recent phase field simulations show that it is possible to form new domain patterns in simple ferroelectric-dielectric bilayers and in graded ferroelectric heterostructures.[52–54] We also note that the space charge effects have been studied in detail[55,56] where it is predicted that the ferroelectric transition is suppressed as space charge density increases. Similar studies in ferroelectric bilayers were also carried out recently by Misirlioglu *et al.*[57] wherein it was shown that space charges could contribute to the enhancement of the polarization.

These theoretical studies clearly illustrate that many of the novel properties of graded and multilayer ferroelectrics can be explained via electrostatic together with electromechanical interactions between layers that result from interlayer polarization differences. However, the "strength" of the interlayer coupling is strongly dependent on the concentration of interfacial defects which are invariably charged, having short-range local electrostatic fields. These defects can be generated in ferroelectric multilayers during synthesis and/or postprocessing steps; their formation may locally "relax" polarization difference and thus affect the commensurate bound charge concentration at the interlayer interfaces. While it is difficult to determine the exact defect structure and concentrations at the interfaces, as these depend on the specific synthesis/deposition conditions; the relaxation of the bound charges at multilayer interfaces and the commensurate variations in the internal electric field can be specified through a coupling strength parameter. In this paper, we present a theoretical analysis based on nonlinear thermodynamics coupled with basic electrostatic relations to understand the role of charge compensation at the interlayer interfaces. Our results show that the average polarization and the dielectric response of a multilayer ferroelectric with systematic variations in the composition may yield a colossal dielectric response, with an increase in more than two orders of magnitude in the dielectric permittivity.

II. THEORY

We consider a compositionally graded monodomain free-standing FE multilayer heterostructure consisting of n layers shown in Fig. 1(a). We assume that the multilayer is textured along the easy direction of polarization (z axis). These simplifications are employed so as to isolate the effect of the polarization mismatch between individual layers by avoiding strain-induced (epitaxial and thermal) polarization through electrostriction. The total (Gibbs) free energy density of such a multilayer structure consisting of n layers under short-circuit condition is

$$F_{\Sigma} = \sum_{i=1}^{n} \alpha_i \left(F_{0,i} + \frac{1}{2} a_i P_i^2 + \frac{1}{4} b_i P_i^4 + \frac{1}{6} c_i P_i^6 - E^{\text{ext}} P_i \right) - \frac{1}{2} \sum_{i=1}^{n} \alpha_i E_{D,i} P_i, \tag{1}$$

with

$$\sum_{i=1}^{n} \alpha_i E_{D,i} P_i = -\frac{\kappa}{\varepsilon_0} \sum_{i=1}^{n} \alpha_i (1-\alpha_i) P_i^2 + \frac{2\kappa}{\varepsilon_0} \sum_{i=1}^{n-1} \left[\alpha_i P_i \left(\sum_{j=i+1}^{n} \alpha_j P_j \right) \right]. \tag{2}$$

Here, α_i is the volume fraction of layer i, $F_{0,i}$ is the free energy density of the polarization-free paraelectric phase, and a_i, b_i, and c_i are the dielectric stiffness coefficients of layer i. The temperature dependence of the coefficient a_i is given by the Curie-Weiss law such that $a_i = (T - T_{C,i}) / \varepsilon_0 C_i$, where ε_0 is the permittivity of free space and $T_{C,i}$ and C_i are the Curie temperature and constant of layer i, respectively. E^{ext} is the externally applied electric field. $E_{D,i}$ is the depolarizing field in layer i that follows from the short-circuit boundary conditions; i.e., the potential drop along the multilayer must vanish along with the necessity of continuity of electric displacement field at the interfaces.[58,59] These result in

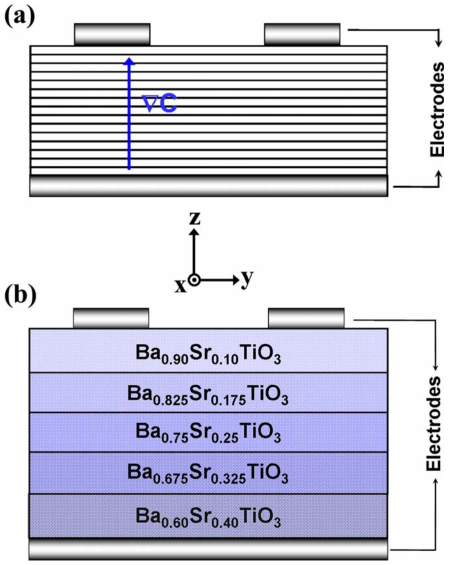

FIG. 1. (Color online) (a) A compositionally graded ferroelectric multilayer consisting of n layers; (b) a graded BST multilayer heterostructure consisting of BST 60/40–67.5/32.5–75/25–82.5/17.5–90/10 layers.

$$\sum_{i=1}^{n} \ell_i E_{D,i} = 0, \tag{3}$$

$$\kappa (P_i - P_{i+1}) + \varepsilon_0 (E_{D,i} - E_{D,i+1}) = 0, \quad i = 1,2, \ldots, (n-1), \tag{4}$$

where ℓ_i is the thickness of layer i. We assume that the individual layers that make up the graded ferroelectric heterostructure are thicker than the correlation length of ferroelectricity (typically $>1-10$ nm). The details of the thermodynamic formalism are provided in the Appendix.

In Eqs. (2)–(4), κ ($0 \leq \kappa \leq 1$) represents a scaling parameter that determines the strength of the internal depolarizing electric field between layers. $\kappa = 1$ corresponds to a defect-free, perfectly insulating interface and $\kappa = 0$ is a state where the polarization of each layer is perfectly screened from each other by interfacial localized charges. For our analysis, κ was taken to be same at each interlayer interface. The above set of relations yields the depolarizing field in each layer as

$$E_{D,i} = -\frac{\kappa}{\varepsilon_0}\left(P_i - \sum_{j=1}^{n} \alpha_j P_j\right), \tag{5}$$

where $\alpha_i = \ell_i / \Sigma_k^n \ell_k = \ell_i / L$. Inserting Eq. (5) into Eq. (1) and after arranging terms yield

$$F_\Sigma = \frac{1}{L}\sum_{i=1}^{n} \ell_i \left[F_{0,i} + \frac{1}{2}\left(a_i + \frac{\kappa}{\varepsilon_0}\right)P_i^2 + \frac{1}{4}b_i P_i^4 + \frac{1}{6}c_i P_i^6 - E^{\text{ext}} P_i\right] - \frac{\kappa}{2\varepsilon_0 L^2}\sum_{i=1}^{n} \ell_i P_i \sum_{j=1}^{n} \ell_j P_j. \tag{6}$$

In the limiting case corresponding to a continuously graded ferroelectric ($n \to \infty$), $P_i \equiv P(z)$, $a_i \equiv a(z)$, $b_i \equiv b(z)$, and $c_i \equiv c(z)$, the free energy density functional is given as

$$F = \frac{1}{L}\int_0^L \left[F_0 + \frac{1}{2}\left(a + \frac{\kappa}{\varepsilon_0}\right)P^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \frac{D}{2}\left(\frac{dP}{dz}\right)^2 - E^{\text{ext}} P\right]dz - \frac{\kappa}{2\varepsilon_0}\left(\frac{1}{L}\int_0^L P dz\right)^2, \tag{7}$$

where we have also included a Ginzburg gradient term D to take into account equilibrium fluctuations of polarization along the z axis. The equilibrium polarization profile can be obtained by minimizing the free energy functional with respect to P, which yields

$$D\frac{d^2P}{dz^2} = aP + bP^3 + cP^5 - E^{\text{ext}} + \frac{\kappa}{\varepsilon_0}\left(P - \frac{1}{L}\int_0^L P dz\right), \tag{8}$$

with boundary conditions given by

$$\left.\frac{dP}{dz}\right|_{z=0} = \left.\frac{dP}{dz}\right|_{z=L} = 0. \tag{9}$$

Equation (8) describes the role of κ such that $\kappa = 1$ corresponds to the classical Kretschmer-Binder[58] case of a perfectly insulating graded ferroelectric with no localized charges; i.e., overall polarization response is an intrinsic material property. For this condition the depolarizing field is at a maximum. On the other hand, for $\kappa = 0$, the graded heterostructure can be thought of as containing as many localized charges (or more) as there are bound charges that arise from the polarization gradient. For this configuration, the depolarizing field vanishes since the bound charges are compensated by localized charges in the ferroelectric material and the layers are completely decoupled. Such large concentrations of localized charges might result in an increase in the conductivity of the multilayer and would thus correspond to higher leakage currents.

For the case of a graded ferroelectric with distinct layers, the equilibrium state of polarization in the heterostructure is determined by simultaneously minimizing the total free energy density, F_Σ, with respect to polarization in each layer P_i, i.e., through the equations of state $\partial F_\Sigma / \partial P_i = 0$. This yields the following system of equations for $i = 1, 2, \ldots n$:

TABLE I. Materials and thermodynamic parameters of bulk $BaTiO_3$ and $SrTiO_3$. (T in °C) (Ref. 38).

	T_C (°C)	C (°C)	b (Nm^6/C^4)	c (Nm^{10}/C^6)
$BaTiO_3$	120	1.7×10^5	$1.44(T-175) \times 10^7$	3.96×10^{10}
$SrTiO_3$	−253	0.8×10^5	8.4×10^9	–

$$\alpha_i \left[a_i P_i + b_i P_i^3 + c_i P_i^5 + \frac{\kappa}{\varepsilon_0}\left(P_i - \sum_{j=1}^{n} \alpha_j P_j\right) - E^{\text{ext}}\right] = 0. \tag{10}$$

Using the equilibrium polarization of each layer i given by $\partial F_\Sigma / \partial P_i = 0$, the small-signal average dielectric constant of a multilayer can be determined from

$$\langle \varepsilon \rangle \cong \frac{1}{\varepsilon_0}\frac{d\langle P \rangle}{dE}, \tag{11}$$

where

$$\langle P \rangle = \sum_{i}^{n} \alpha_i P_i, \tag{12}$$

is the average polarization.

III. RESULTS AND DISCUSSION

For our analysis, we chose a multilayer BST heterostructure consisting of five layers having the same thickness and compositions $Ba_{0.6}Sr_{0.4}TiO_3$ (BST 60/40)-BST 67.5/32.5-BST 75/25-BST 82.5/17.5-BST 90/10, as shown in Fig. 1(b). We assume that for each layer the thermodynamic parameters such as the Curie temperature $T_{C,i}$ and constant C_i and dielectric stiffness coefficients b_i and c_i are linear functions of the composition and are thus determined by averaging corresponding values of $BaTiO_3$ and $SrTiO_3$ given in Table I.

The average polarization and corresponding average small-signal dielectric constant of multilayered BST heterostructure at room temperature are shown in Fig. 2 and 3, respectively, as a function of κ. It can be clearly seen in Fig. 2 that the polarization response of the BST multilayer consists of three regions: (i) for $10^{-2} \leq \kappa \leq 1$, the heterostructure does not possess an average spontaneous polarization, a region where the interlayer coupling is dominant, (ii) for $10^{-6} \leq \kappa \leq 10^{-2}$, there emerges a polarization in the ferroelectric heterostructure, and (iii) for $\kappa \leq 10^{-6}$, polarization stabilization. The reason for the origin of such different regimes can be understood by inspecting the polarization response of each layer shown in the inset of Fig. 2. In region (i), polarization is suppressed due to large Gibbs free energy increase necessary to induce polarization in the BST 60/40 and BST 67.5/32.5 layers which are paraelectric at room temperature. On the other hand, in regime (ii) the electrostatic energy due to polarization mismatch at each interlayer interface can be reduced by a decrease in Gibbs free energy

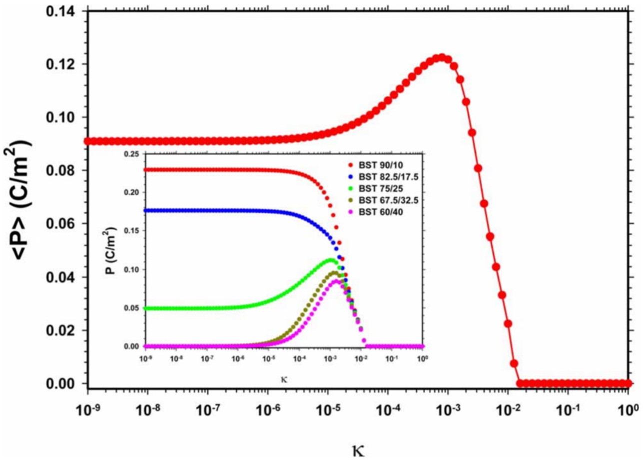

FIG. 2. (Color online) The variation in the average polarization and polarization of each layer (inset) with the coupling strength at room temperature for $E^{\text{ext}}=0$.

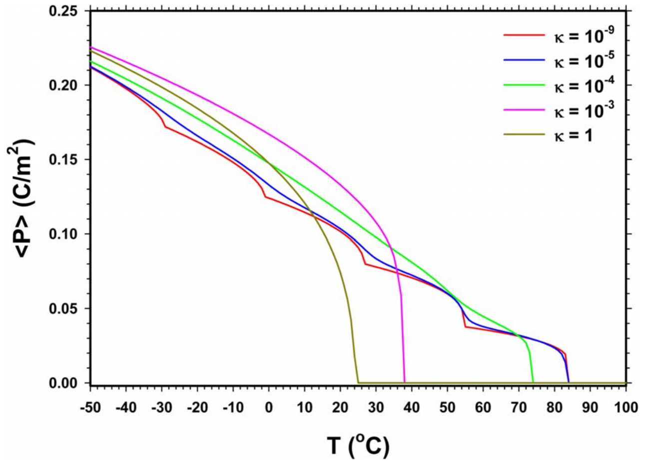

FIG. 4. (Color online) The temperature dependence of the average polarization of the BST multilayer shown in Fig. 1(b) at $E^{\text{ext}}=0$ calculated for various κ.

of the system due to charge compensation which leads to the emergence of an average spontaneous polarization. It should be noted that polarization first emerges for κ corresponding to $\approx 10^{-2}$, where the coupling in the BST heterostructure is strong enough to maintain polarization in each of the layers that make up the heterostructure in such a way that the polarizations in the individual layers are almost equal to each other whereas with a gradual softening in coupling strength (i.e., a decrease in κ), the difference between the polarization values of each layer increases. In this region, a maximum in the average polarization can be observed around $\kappa \approx 10^{-3}$. A further decrease in κ effectively causes each layer to act independently of each other. In region (iii), there is practically no coupling between layers such that each layer attains a polarization level corresponding to free-standing single crystal layers. For example, BST 60/40 and BST 67.5/32.5 are paraelectric whereas other layers exhibit ferroelectricity, as they would if these layers were free-standing single crystals. The average dielectric constant shows a peak at the emergence of the average polarization and a minimum at maximum average polarization. Compared to the decoupled condition ($\kappa \leq 10^{-6}$), the average dielectric constant exhibits an enhancement of one order of magnitude for strongly coupled layers with $10^{-2} \leq \kappa \leq 1$.

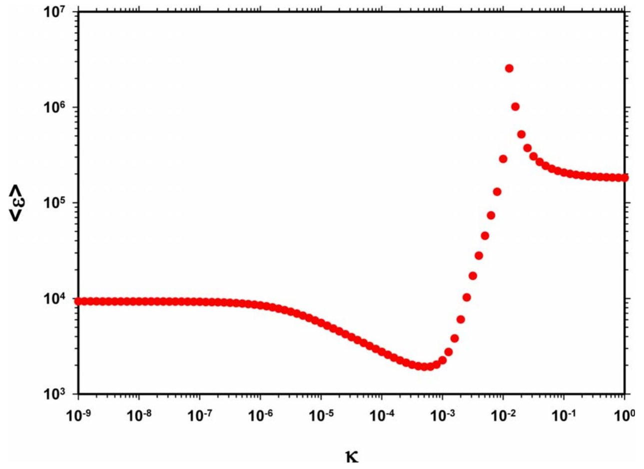

FIG. 3. (Color online) The room temperature average dielectric constant of the BST multilayer shown in Fig. 1(b) as a function of κ at $E^{\text{ext}}=0$.

The temperature dependence of the average polarization and the average dielectric constant are depicted in Figs. 4–6 for different κ. It is shown in Fig. 4 that at low values of κ such as 10^{-9}, the average polarization response of BST heterostructure exhibits cusps at certain temperatures, which correspond to Curie temperatures of each layer, due to absence of coupling in the heterostructure. We note that a similar trend has been predicted by Qu *et al.*[60] in BTO/PbTiO$_3$ superlattices where the interfacial coupling was treated as an adjustable parameter. As κ attains higher values these cusps tend to vanish. For visual clarification, in Fig. 5 we provide a three-dimensional plot of the variation in the average polarization as a function of temperature and κ. The cusps in the polarization curves as a function of κ reflect themselves as

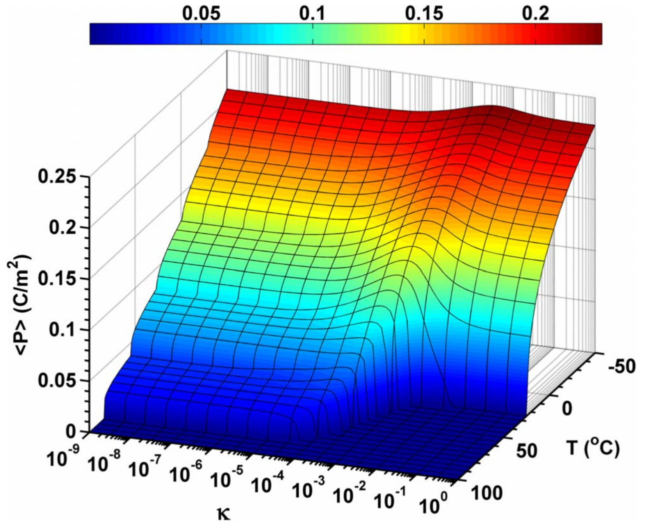

FIG. 5. (Color online) The temperature and κ dependence of the average polarization of the BST multilayer shown in Fig. 1(b) at $E^{\text{ext}}=0$.

peaks in the average dielectric constant shown in Fig. 6. These results indicate that it is possible to realize a large dielectric response depending on the interlayer electrostatic interactions.

If coupling strength is high enough such that $\kappa \geq 10^{-3}$, a smoothly varying average polarization profile as if the ferroelectric multilayer was a uniform ferroelectric material is obtained. For the case of $\kappa = 1$, the multilayered BST displays an overall response that can be thought of as a hypothetical homogeneous "bulk" ferroelectric material with dielectric stiffness coefficients equal to the weighted average of dielectric stiffness coefficients of the BST layers that it is made of, i.e., the system of equations given in Eq. (10) for $i = 1, 2, \ldots n$ can be represented as

$$\left.\begin{array}{l}
\alpha_1\left[a_1P_1 + b_1P_1^3 + c_1P_1^5 + \dfrac{\kappa}{\varepsilon_0}\left(P_1 - \sum_{j=1}^{n}\alpha_jP_j\right) - E^{\mathrm{ext}}\right] = 0 \\
\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\
\alpha_i\left[a_iP_i + b_iP_i^3 + c_iP_i^5 + \dfrac{\kappa}{\varepsilon_0}\left(P_i - \sum_{j=1}^{n}\alpha_jP_j\right) - E^{\mathrm{ext}}\right] = 0 \\
\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\
\alpha_n\left[a_nP_n + b_nP_n^3 + c_nP_n^5 + \dfrac{\kappa}{\varepsilon_0}\left(P_n - \sum_{j=1}^{n}\alpha_jP_j\right) - E^{\mathrm{ext}}\right] = 0
\end{array}\right\} \cong \langle a\rangle P_h + \langle b\rangle P_h^3 + \langle c\rangle P_h^5 - E^{\mathrm{ext}} = 0, \tag{13}$$

where P_h is the spontaneous polarization of this hypothetical homogeneous "bulk" ferroelectric material and

$$\langle a\rangle = \sum_{i=1}^{n}\alpha_i a_i,$$

$$\langle b\rangle = \sum_{i=1}^{n}\alpha_i b_i,$$

$$\langle c\rangle = \sum_{i=1}^{n}\alpha_i c_i. \tag{14}$$

Summing both sides of the equations given in Eq. (10) yields

$$\sum_{i=1}^{n}(\alpha_i a_i P_i + \alpha_i b_i P_i^3 + \alpha_i c_i P_i^5) - E^{\mathrm{ext}} = 0. \tag{15}$$

When $\kappa = 1$, the maximum difference between polarizations of the weakest layer (BST 60/40) and the strongest layer (BST 90/10) is on the order of 10^{-4} C/m^2. Therefore, in Eq. (15) the polarization of each layer P_i, to a good approximation, can be replaced with an average polarization $\langle P\rangle$ *or* with a constant polarization such as P_h in Eq. (13). Hence,

$$\sum_{i=1}^{n}(\alpha_i a_i P_i + \alpha_i b_i P_i^3 + \alpha_i c_i P_i^5) - E^{\mathrm{ext}} \cong \sum_{i=1}^{n}\alpha_i a_i\langle P\rangle + \sum_{i=1}^{n}\alpha_i b_i\langle P\rangle^3 + \sum_{i=1}^{n}\alpha_i c_i\langle P\rangle^5 - E^{\mathrm{ext}}. \tag{16}$$

The relation, Eq. (13), being identical within a margin of $(\langle P\rangle - P_h) \approx 10^{-4}$ C/m^2, is shown in Fig. 7 along with the polarization response of "bulk" BST 75/25 which is the average composition of the multilayered BST heterostructure considered here. It is also revealed in Fig. 7 that the overall response of the multilayered BST heterostructure is similar to but not exactly the same as its compositional average counterpart. In the case of a hypothetical homogeneous "bulk" ferroelectric material, Eqs. (8) and (13) are equivalent to each other, meaning that there will be no equilibrium polarization fluctuations such that

$$D\frac{d^2P}{dz^2} = 0, \tag{17}$$

and no depolarization field, i.e., polarization of hypothetical homogeneous "bulk" ferroelectric material is equal to its average polarization,

$$P = \frac{1}{L}\int_0^L P dz. \tag{18}$$

Thus,

$$aP + bP^3 + cP^5 - E^{\mathrm{ext}} = 0 = \langle a\rangle P_h + \langle b\rangle P_h^3 + \langle c\rangle P_h^5 - E^{\mathrm{ext}}. \tag{19}$$

It is worth noting that there is also a shift in the Curie temperature although the FE multilayer behaves as a single ferroelectric material. This shift is due to modification of the dielectric stiffness a_i in Eq. (1) by the electrostatic coupling terms given in Eq. (2).

The depolarizing field due to the polarization mismatch between layers in a multilayer ferroelectric heterostructure can also be minimized via the formation of ferroelectric domains. This possibility was not considered in this study. The internal fields that arise from the electrical boundary conditions in perfectly insulating multilayer heterostructures may

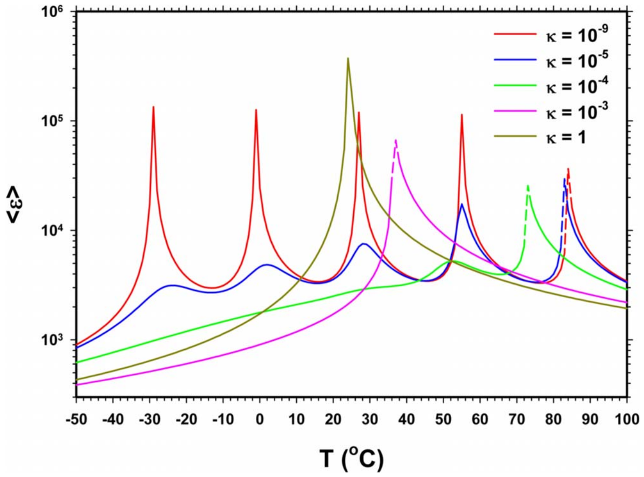

FIG. 6. (Color online) The variation in the average dielectric constant with temperature at different κ. Dashed curves show interpolations.

result in the formation of ferroelectric domain patterns as there are no free charge carriers for charge compensation at the interlayer interfaces. This has been predicted theoretically in ferroelectric and ferroelastic bilayers with a very slight change in the order parameter.[50] In a recent thermodynamic model for compositionally graded multilayer ferroelectrics in the limit of dense domain theory, Roytburd and Slutsker[43] showed that each layer will adopt a domain structure with systematic variations in the electrical domain fractions as a function of the composition, resulting in "wedge-like domains." The morphology of these domains is quite similar to the "zigzag" domain wall configurations in ferroelastic $Gd_2(MoO_4)_3$ and $Pb_3(PO_4)_2$.[61] Phase field simulations also provide interesting domain patterns that form in response to the depolarization fields emanating from the interlayer interfaces.[54] In a system where there are mobile charged defects, the domain morphology and the properties of multilayer ferroelectrics should also depend on the charge compensation at the interlayer interfaces. This becomes important in multilayer ferroelectric thin films where charged defects can be introduced rather easily during the synthesis. Therefore, one has to consider both mechanisms that lead to the relaxation of the internal electrostatic field simultaneously such that the overall dielectric response will be due to movement of ferroelectric domains (possibly with a wedge-domain morphology) whose fractions should also depend on the defect concentrations at the interlayer interfaces.

IV. CONCLUSION

We have developed a theoretical model based on nonlinear thermodynamics coupled with electrostatics to analyze the role of charge compensation at the interlayer interfaces in compositionally graded monodomain ferroelectric multilayers. It is shown that depending on the coupling strength, the dielectric properties of a compositionally graded free-standing ferroelectric multilayer may appear as if it was a single ferroelectric material if there are no localized charges or as a combination of dielectric responses of each layer independently if the bound charges due to polarization mismatch are neutralized by preexisting localized charges in the multilayer. We have also shown that the dielectric properties of such multilayers will depend greatly on the localized charge density, and it is possible to realize a large dielectric response depending on the interlayer electrostatic interactions.

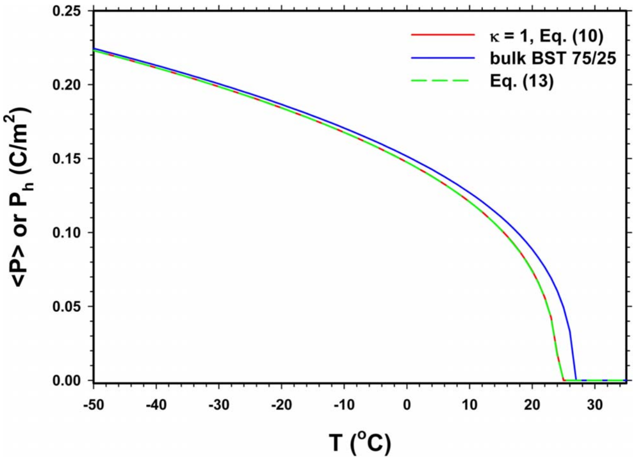

FIG. 7. (Color online) Verification of the equivalence between five-layered BST heterostructure [$\kappa=1$, Eq. (10)] and the corresponding hypothetical homogeneous bulk ferroelectric as defined via Eq. (13) at $E^{\mathrm{ext}}=0$. Polarization response of bulk BST 75/25 is included for comparison purposes.

ACKNOWLEDGMENTS

The work at UConn was supported by the U.S. Army Research Office through Grant No. W911NF-05-1-0528 and No. W911NF-08-C-0124. The authors also thank Alexander L. Roytburd (University of Maryland) for many useful discussions.

APPENDIX

The Landau-Ginzburg (LG)-type formulation of the free energy per unit volume, Φ, of a ferroelectric material due to the emergence of a spontaneous polarization P along the z axis (see Fig. 1) for a ferroelectric material exhibiting a phase transition from a high-temperature paraelectric cubic crystal structure to a low-temperature ferroelectric tetragonal crystal structure is given as

$$\Phi = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6. \tag{A1}$$

Here, F_0 is the free energy of the thermodynamic "reference state" being the high-temperature paraelectric cubic phase. Equation (A1) includes only even powers of the "order parameter" which is the polarization in accordance with the Neumann's principle and Landau theory of phase transformations.[62,63]

The interaction energy of the polarization with an externally applied electric field E^{ext} is given as

$$\Phi' = -E^{\text{ext}}P. \tag{A2}$$

On the other hand, the interaction energy of polarization with its own electric field, called the depolarizing electric field (E_D), is

$$\Phi'' = -\frac{1}{2}E_D P. \tag{A3}$$

Thus the total free energy per unit volume of a ferroelectric is given as

$$\tilde{\Phi} = \Phi + \Phi' + \Phi''. \tag{A4}$$

In a compositionally graded monodomain free-standing ferroelectric multilayer heterostructure consisting of n layers, the total free energy per unit volume F_Σ is given as the volumetric weighted sum of the free energies of contributing layers such that

$$F_\Sigma = \sum_{i=1}^{n} \alpha_i \tilde{\Phi}_i, \tag{A5a}$$

$$F_\Sigma = \sum_{i=1}^{n} \alpha_i \left(F_{0,i} + \frac{1}{2}a_i P_i^2 + \frac{1}{4}b_i P_i^4 + \frac{1}{6}c_i P_i^6 - E^{\text{ext}}P_i \right) - \frac{1}{2}\sum_{i=1}^{n} \alpha_i E_{D,i} P_i. \tag{A5b}$$

In an n-layered heterostructure, the electrical interaction of adjacent layers with each other has to be considered through Maxwell's equations at the interlayer interfaces; i.e., (i) the continuity of the component of the electric displacement field normal to the interface surface and (ii) the continuity of the component of the electric field parallel to the interface surface. In our case, as the electric field is normal to all interfaces, the latter condition is inherently satisfied. Therefore, as the electric displacement field is also normal to interlayer interfaces, we obtain from condition (i) at each interface of the multilayer

$$(P_i - P_{i+1}) + \varepsilon_0(E_{D,i} - E_{D,i+1}) = \sigma_{i,i+1}, \quad i = 1,2,\ldots,(n-1), \tag{A6}$$

$$\kappa(P_i - P_{i+1}) + \varepsilon_0(E_{D,i} - E_{D,i+1}) = 0, \quad i = 1,2,\ldots,(n-1), \tag{A7}$$

where $\sigma_{i,i+1}$ is the surface charge density of space charges at the interlayer interface between the i^{th} and $(i+1)^{\text{th}}$ layers and the dimensionless parameter, "coupling strength," at each interface is given as

$$\kappa = \left(1 - \frac{\sigma_{i,i+1}}{P_i - P_{i+1}} \right). \tag{A8}$$

Thus,

$$\sigma_{i,i+1} = (1-\kappa)(P_i - P_{i+1}), \quad i = 1,2,\ldots,(n-1). \tag{A9}$$

These relations must be satisfied along with the necessity that both electrodes *must* be held at the same potential[58] which can be expressed as

$$\sum_{i=1}^{n} \ell_i E_{D,i} = 0. \tag{A10}$$

The system of equations given by Eqs. (A7) and (A10) is solved as follows:

$$\begin{bmatrix} 1 & -1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & 1 & -1 & 0 & \cdots & 0 & 0 \\ 0 & 0 & 1 & -1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & & & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \ddots & -1 & 0 \\ 0 & 0 & 0 & 0 & \cdots & 1 & -1 \\ \ell_1 & \ell_2 & \ell_3 & \ell_4 & \cdots & \ell_{n-1} & \ell_n \end{bmatrix} \begin{vmatrix} E_{D,1} \\ E_{D,2} \\ E_{D,3} \\ \vdots \\ E_{D,n-2} \\ E_{D,n-1} \\ E_{D,n} \end{vmatrix} = -\frac{\kappa}{\varepsilon_0} \begin{vmatrix} P_1 - P_2 \\ P_2 - P_3 \\ P_3 - P_4 \\ \vdots \\ P_{n-2} - P_{n-1} \\ P_{n-1} - P_n \\ 0 \end{vmatrix}. \tag{A11}$$

The augmented matrix of Eq. (A11),

$$\left[\begin{array}{ccccccc|c} 1 & -1 & 0 & 0 & \cdots & 0 & 0 & -\kappa(P_1 - P_2)/\varepsilon_0 \\ 0 & 1 & -1 & 0 & \cdots & 0 & 0 & -\kappa(P_2 - P_3)/\varepsilon_0 \\ 0 & 0 & 1 & -1 & \cdots & 0 & 0 & -\kappa(P_3 - P_4)/\varepsilon_0 \\ \vdots & \vdots & \vdots & & & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \ddots & -1 & 0 & -\kappa(P_{n-2} - P_{n-1})/\varepsilon_0 \\ 0 & 0 & 0 & 0 & \cdots & 1 & -1 & -\kappa(P_{n-1} - P_n)/\varepsilon_0 \\ \ell_1 & \ell_2 & \ell_3 & \ell_4 & \cdots & \ell_{n-1} & \ell_n & 0 \end{array}\right], \tag{A12}$$

can be rewritten after a simple Gaussian elimination as

$$\left[\begin{array}{ccccccc|c}
1 & -1 & 0 & 0 & \cdots & 0 & 0 & -\kappa(P_1-P_2)/\varepsilon_0 \\
0 & 1 & -1 & 0 & \cdots & 0 & 0 & -\kappa(P_2-P_3)/\varepsilon_0 \\
0 & 0 & 1 & -1 & \cdots & 0 & 0 & -\kappa(P_3-P_4)/\varepsilon_0 \\
\vdots & \vdots & \vdots & & & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \ddots & -1 & 0 & -\kappa(P_{n-2}-P_{n-1})/\varepsilon_0 \\
0 & 0 & 0 & 0 & \cdots & 1 & -1 & -\kappa(P_{n-1}-P_n)/\varepsilon_0 \\
0 & 0 & 0 & 0 & \cdots & 0 & \displaystyle\sum_{i=1}^{n}\ell_i & \displaystyle\frac{\kappa}{\varepsilon_0}\left[\sum_{i=1}^{n-1}\left(\sum_{j=1}^{i}\ell_j\right)(P_i-P_{i+1})\right]
\end{array}\right]. \tag{A13}$$

The last summation term can be expressed as

$$\frac{\kappa}{\varepsilon_0}\left[\sum_{i=1}^{n-1}\left(\sum_{j=1}^{i}\ell_j\right)(P_i-P_{i+1})\right]=-\frac{\kappa}{\varepsilon_0}\left[\left(\sum_{j=1}^{n}\ell_j\right)P_n-\sum_{i=1}^{n}\ell_iP_i\right]. \tag{A14}$$

Now solving for $E_{D,n}$, one finds

$$\left(\sum_{i=1}^{n}\ell_i\right)E_{D,n}=-\frac{\kappa}{\varepsilon_0}\left[\left(\sum_{j=1}^{n}\ell_j\right)P_n-\sum_{i=1}^{n}\ell_iP_i\right], \tag{A15}$$

$$E_{D,n}=-\frac{\kappa}{\varepsilon_0}\left(P_n-\sum_{j=1}^{n}\alpha_jP_j\right). \tag{A16}$$

For clarification, it is worth mentioning that in Eq. (A16) the upper bound of summation "n" is independent of the index "n" given in the left-hand side of the equation. Through back substitution, it is straightforward to show that the solutions of the system of equations given in Eqs. (A7) and (A10) are

$$E_{D,i}=-\frac{\kappa}{\varepsilon_0}\left(P_i-\sum_{j=1}^{n}\alpha_jP_j\right),\quad i=1,2,\ldots,n. \tag{A17}$$

Inserting Eq. (A17) into expression $\Sigma_{i=1}^{n}\alpha_iE_{D,i}P_i$, the last term in Eq. (A5b) (without the factor $\frac{1}{2}$) and rearranging terms, one can easily derive Eq. (2) through the following steps:

$$\begin{aligned}
\sum_{i=1}^{n}\alpha_iE_{D,i}P_i&=\sum_{i=1}^{n}\alpha_i\left[-\frac{\kappa}{\varepsilon_0}\left(P_i-\sum_{j=1}^{n}\alpha_jP_j\right)\right]P_i\\
&=-\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{n}\alpha_iP_i\left(P_i-\alpha_iP_i-\sum_{\substack{j=1\\ j\neq i}}^{n}\alpha_jP_j\right)\\
&=-\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{n}\alpha_iP_i\left((1-\alpha_i)P_i-\sum_{\substack{j=1\\ j\neq i}}^{n}\alpha_jP_j\right)\\
&=-\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{n}\alpha_i(1-\alpha_i)P_i^2+\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{n}\alpha_iP_i\left(\sum_{\substack{j=1\\ j\neq i}}^{n}\alpha_jP_j\right).
\end{aligned} \tag{A18}$$

Expanding and reordering the terms of the second summation in Eq. (A18) yield

$$\begin{aligned}
\sum_{i=1}^{n}\alpha_i P_i\left(\sum_{\substack{j=1\\ j\neq i}}^{n}\alpha_j P_j\right) &= \alpha_1P_1\left(\alpha_2P_2+\alpha_3P_3+\alpha_4P_4+\ldots+\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad+\alpha_2P_2\left(\alpha_1P_1+\alpha_3P_3+\alpha_4P_4+\ldots+\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad+\alpha_3P_3\left(\alpha_1P_1+\alpha_2P_2+\alpha_4P_4+\ldots+\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad\vdots\\
&\quad+\alpha_{n-1}P_{n-1}\left(\alpha_1P_1+\alpha_2P_2+\alpha_4P_4+\ldots+\alpha_{n-2}P_{n-2}+\alpha_nP_n\right)\\
&\quad+\alpha_nP_n\left(\alpha_1P_1+\alpha_2P_2+\alpha_4P_4+\ldots+\alpha_{n-2}P_{n-2}+\alpha_{n-1}P_{n-1}\right)\\
&= 2\alpha_1P_1\left(\alpha_2P_2+\alpha_3P_3+\alpha_4P_4+\ldots+\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad+2\alpha_2P_2\left(\alpha_3P_3+\alpha_4P_4+\ldots+\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad+2\alpha_3P_3\left(\alpha_4P_4+\ldots+\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad\ddots\qquad\vdots\qquad\vdots\\
&\quad+2\alpha_{n-2}P_{n-2}\left(\alpha_{n-1}P_{n-1}+\alpha_nP_n\right)\\
&\quad+2\alpha_{n-1}P_{n-1}\left(\alpha_nP_n\right) = 2\sum_{i=1}^{n-1}\left[\alpha_iP_i\left(\sum_{j=i+1}^{n}\alpha_jP_j\right)\right]
\end{aligned}\tag{A19}$$

Thus,

$$\sum_{i=1}^{n}\alpha_iP_i\left(\sum_{\substack{j=1\\ j\neq i}}^{n}\alpha_jP_j\right)=2\sum_{i=1}^{n-1}\left[\alpha_iP_i\left(\sum_{j=i+1}^{n}\alpha_jP_j\right)\right].\tag{A20}$$

Inserting Eq. (A20) into Eq. (A18) results in Eq. (2);

$$\sum_{i=1}^{n}\alpha_iE_{D,i}P_i=-\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{n}\alpha_i(1-\alpha_i)P_i^2+\frac{2\kappa}{\varepsilon_0}\sum_{i=1}^{n-1}\left[\alpha_iP_i\left(\sum_{j=i+1}^{n}\alpha_jP_j\right)\right].\tag{A21}$$

As an example, we present the simplest case of a ferroelectric bilayer heterostructure ($n=2$). We define

$$F_i(P_i)=F_{0,i}+\frac{1}{2}a_iP_i^2+\frac{1}{4}b_iP_i^4+\frac{1}{6}c_iP_i^6-E^{\mathrm{ext}}P_i.\tag{A22}$$

From Eqs. (A5b), (A21), and (A22),

$$F_\Sigma=\sum_{i=1}^{2}\alpha_i(F_i(P_i))+\frac{1}{2}\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{2}\alpha_i(1-\alpha_i)P_i^2-\frac{\kappa}{\varepsilon_0}\sum_{i=1}^{1}\left[\alpha_iP_i\left(\sum_{j=i+1}^{2}\alpha_jP_j\right)\right]\tag{A23}$$

such that

$$F_\Sigma=\alpha_1F_1(P_1)+\alpha_2F_2(P_2)+\frac{1}{2}\frac{\kappa}{\varepsilon_0}(\alpha_1(1-\alpha_1)P_1^2+\alpha_2(1-\alpha_2)P_2^2)-\frac{\kappa}{\varepsilon_0}\alpha_1P_1\alpha_2P_2,\tag{A24}$$

$$F_\Sigma=\alpha_1F_1(P_1)+\alpha_2F_2(P_2)+\frac{1}{2}\frac{\kappa}{\varepsilon_0}\alpha_1\alpha_2(P_1^2-2P_1P_2+P_2^2),\tag{A25}$$

$$F_\Sigma=\alpha_1F_1(P_1)+(1-\alpha_1)F_2(P_2)+\frac{1}{2}\frac{\kappa}{\varepsilon_0}\alpha_1(1-\alpha_1)(P_1-P_2)^2,\tag{A26}$$

which is identical to Eq. (1) of Roytburd *et al.*[64] The internal fields in layers 1 and 2 are given as

$$E_{D,1}=-\frac{\kappa(1-\alpha_1)}{\varepsilon_0}(P_1-P_2),\tag{A27}$$

$$E_{D,2}=-\frac{\kappa(1-\alpha_2)}{\varepsilon_0}(P_2-P_1),\tag{A28}$$

respectively.

*Author to whom correspondence should be addressed; p.alpay@ims.uconn.edu

[1] N. W. Schubring, J. V. Mantese, A. L. Micheli, A. B. Catalan, and R. J. Lopez, Phys. Rev. Lett. **68**, 1778 (1992).
[2] M. Brazier, M. McElfresh, and S. Mansour, Appl. Phys. Lett. **74**, 299 (1999).
[3] D. Bao, N. Mizutani, X. Yao, and L. Zhang, Appl. Phys. Lett. **77**, 1203 (2000).
[4] D. Bao, N. Wakiya, K. Shinozaki, N. Mizutani, and X. Yao, J. Appl. Phys. **90**, 506 (2001).
[5] W. Fellberg, J. Mantese, N. Schubring, and A. Micheli, Appl. Phys. Lett. **78**, 524 (2001).
[6] J. V. Mantese, N. W. Schubring, A. L. Micheli, M. P. Thompson, R. Naik, G. W. Auner, I. B. Misirlioglu, and S. P. Alpay, Appl. Phys. Lett. **81**, 1068 (2002).
[7] X. Zhu, N. Chong, H. L.-W. Chan, C.-L. Choy, K.-H. Wong, Z. Liu, and N. Ming, Appl. Phys. Lett. **80**, 3376 (2002).
[8] S. G. Lu, X. H. Zhu, C. L. Mak, K. H. Wong, H. L. W. Chan, and C. L. Choy, Appl. Phys. Lett. **82**, 2877 (2003).
[9] S. Zhong, S. P. Alpay, M. W. Cole, E. Ngo, S. Hirsch, and J. D. Demaree, Appl. Phys. Lett. **90**, 092901 (2007).
[10] S.-J. Lee, S. E. Moon, H.-C. Ryu, M.-H. Kwak, Y.-T. Kim, and S.-K. Han, Appl. Phys. Lett. **82**, 2133 (2003).
[11] D. Bao, S. K. Lee, X. Zhu, M. Alexe, and D. Hesse, Appl. Phys. Lett. **86**, 082906 (2005).
[12] X. G. Tang, H. L. W. Chan, and A. L. Ding, Solid State Commun. **127**, 625 (2003).
[13] J. Sigman, P. G. Clem, and C. D. Nordquist, Appl. Phys. Lett. **89**, 132909 (2006).
[14] R. Nath, S. Zhong, S. P. Alpay, B. D. Huey, and M. W. Cole, Appl. Phys. Lett. **92**, 012916 (2008).
[15] I. Boerasu, L. Pintilie, and M. Kosec, Appl. Phys. Lett. **77**, 2231 (2000).
[16] J. Im, O. Auciello, P. K. Baumann, S. K. Streiffer, D. Y. Kaufman, and A. R. Krauss, Integr. Ferroelectr. **34**, 263 (2001).
[17] Y. Kim, R. A. Gerhardt, and A. Erbil, Phys. Rev. B **55**, 8766 (1997).
[18] P. K. Baumann, S. K. Streiffer, G. R. Bai, K. Ghosh, O. Auciello, C. Thompson, S. Stemmer, R. A. Rao, C. B. Eom, F. Xu, S. Trolier-mckinstry, D. J. Kim, J. P. Maria, and A. I. Kingon, Integr. Ferroelectr. **35**, 151 (2001).
[19] J. C. Jiang, X. Q. Pan, W. Tian, C. D. Theis, and D. G. Schlom, Appl. Phys. Lett. **74**, 2851 (1999).
[20] H. M. Christen, E. D. Specht, S. S. Silliman, and K. S. Harshavardhan, Phys. Rev. B **68**, 020101(R) (2003).
[21] J. Sigman, D. P. Norton, H. M. Christen, P. H. Fleming, and L. A. Boatner, Phys. Rev. Lett. **88**, 097601 (2002).
[22] K. P. Jayadevan and T. Y. Tseng, J. Mater. Sci.: Mater. Electron. **13**, 439 (2002).
[23] T. Tsurumi, T. Miyasou, Y. Ishibashi, and N. Ohashi, Jpn. J. Appl. Phys., Part 1 **37**, 5104 (1998).
[24] H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, Nature (London) **433**, 395 (2005).
[25] M. P. Warusawithana, E. V. Colla, J. N. Eckstein, and M. B. Weissman, Phys. Rev. Lett. **90**, 036802 (2003).
[26] T. Shimuta, O. Nakagawara, T. Makino, S. Arai, H. Tabata, and T. Kawai, J. Appl. Phys. **91**, 2290 (2002).
[27] E. D. Specht, H. M. Christen, D. P. Norton, and L. A. Boatner, Phys. Rev. Lett. **80**, 4317 (1998).
[28] J. Kim, Y. Kim, Y. S. Kim, J. Lee, L. Kim, and D. Jung, Appl. Phys. Lett. **80**, 3581 (2002).
[29] M. W. Cole, E. Ngo, S. Hirsch, M. B. Okatan, and S. P. Alpay, Appl. Phys. Lett. **92**, 072906 (2008).
[30] G. Catalan, D. O'Neill, R. M. Bowman, and J. M. Gregg, Appl. Phys. Lett. **77**, 3078 (2000).
[31] D. O'Neill, R. M. Bowman, and J. M. Gregg, Appl. Phys. Lett. **77**, 1520 (2000).
[32] M. H. Corbett, R. M. Bowman, J. M. Gregg, and D. T. Foord, Appl. Phys. Lett. **79**, 815 (2001).
[33] H.-X. Cao, Y.-H. Gao, Q. Jiang, and Z.-Y. Li, J. Appl. Phys. **96**, 1628 (2004).
[34] X. S. Wang, C. L. Wang, W. L. Zhong, and P. L. Zhang, Phys. Lett. A **285**, 212 (2001).
[35] H.-X. Cao and Z.-Y. Li, J. Phys.: Condens. Matter **15**, 6301 (2003).
[36] H.-X. Cao, V. C. Lo, and Z.-Y. Li, J. Appl. Phys. **98**, 114105 (2005).
[37] S. M. Nakhmanson, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **73**, 060101(R) (2006).
[38] S. M. Nakhmanson, K. M. Rabe, and V. David, Appl. Phys. Lett. **87**, 102906 (2005).
[39] N. Sai, B. Meyer, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5636 (2000).
[40] L. Pintilie, I. Boerasu, and M. J. M. Gomes, J. Appl. Phys. **93**, 9961 (2003).
[41] L. Bellaiche and D. Vanderbilt, Phys. Rev. Lett. **81**, 1318 (1998).
[42] M. B. Okatan, M. W. Cole, and S. P. Alpay, J. Appl. Phys. **104**, 104107 (2008).
[43] A. L. Roytburd and J. Slutsker, Appl. Phys. Lett. **89**, 042907 (2006).
[44] A. K. Tagantsev and G. Gerra, J. Appl. Phys. **100**, 051607 (2006).
[45] Z. G. Ban and S. P. Alpay, Appl. Phys. Lett. **82**, 3499 (2003).
[46] A. Erbil, Y. Kim, and R. A. Gerhardt, Phys. Rev. Lett. **77**, 1628 (1996).
[47] T. Tsurumi, T. Harigai, D. Tanaka, S.-M. Nam, H. Kakemoto, S. Wada, and K. Saito, Appl. Phys. Lett. **85**, 5016 (2004).
[48] J. B. Neaton and K. M. Rabe, Appl. Phys. Lett. **82**, 1586 (2003).
[49] X. Wu, M. Stengel, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. **101**, 087601 (2008).
[50] A. M. Bratkovsky and A. P. Levanyuk, Phys. Rev. B **66**, 184109 (2002).
[51] A. M. Bratkovsky and A. P. Levanyuk, Phys. Rev. Lett. **84**, 3177 (2000).
[52] Y. L. Li, S. Y. Hu, D. Tenne, A. Soukiassian, D. G. Schlom, X. X. Xi, K. J. Choi, C. B. Eom, A. Saxena, T. Lookman, Q. X. Jia, and L. Q. Chen, Appl. Phys. Lett. **91**, 112914 (2007).
[53] Y. L. Li, S. Y. Hu, D. Tenne, A. Soukiassian, D. G. Schlom, L. Q. Chen, X. X. Xi, K. J. Choi, C. B. Eom, A. Saxena, T. Lookman, and Q. X. Jia, Appl. Phys. Lett. **91**, 252904 (2007).
[54] A. Artemev, B. Geddes, J. Slutsker, and A. Roytburd, J. Appl. Phys. **103**, 074104 (2008).
[55] A. M. Bratkovsky and A. P. Levanyuk, Phys. Rev. B **61**, 15042 (2000).
[56] P. Zubko, D. J. Jung, and J. F. Scott, J. Appl. Phys. **100**, 114112 (2006).
[57] I. B. Misirlioglu, M. Alexe, L. Pintilie, and D. Hesse, Appl. Phys. Lett. **91**, 022911 (2007).
[58] R. Kretschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979).
[59] M. Dawber, C. Lichtensteiger, M. Cantoni, M. Veithen, P.

Ghosez, K. Johnston, K. M. Rabe, and J. M. Triscone, Phys. Rev. Lett. **95**, 177601 (2005).

[60] B. D. Qu, W. L. Zhong, and R. H. Prince, Phys. Rev. B **55**, 11218 (1997).

[61] R. B. Flippen and C. W. Haas, Solid State Commun. **13**, 1207 (1973).

[62] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1985), p. 20.

[63] D. ter Haar, *Collected Papers of L. D. Landau* (Pergamon, Oxford, 1965), p. 193.

[64] A. L. Roytburd, S. Zhong, and S. P. Alpay, Appl. Phys. Lett. **87**, 092902 (2005).