

Hysteresis Offset and Dielectric Response of Compositionally Graded Ferroelectric Materials

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Ferroelectrics with a spatial variation in the polarization exhibit behavior and properties that are not routinely observed from homogenous bulk or thin film ferroelectrics. A systematic spatial variation in the polarization in a ferroelectric material can be achieved by variations in the composition of the material, impressing temperature gradients across the structure, or by imposing non-uniform external stress fields. In this article, a Landau-Ginzburg thermodynamic model is used to develop a methodology for analyzing compositionally graded ferroelectric materials. The composition gradient is shown to give rise to a corresponding polarization gradient. The misfit due to variations in the self-strain tends to flatten the polarization gradient and leads to the bending of the ferroelectric. The polarization gradients result in asymmetric hysteresis responses with “up” or “down” charge offsets which are strong functions of composition. Analysis shows that the compositional grading results in a broadening in the dielectric response as a function of temperature.

INTRODUCTION

Polarization-graded ferroelectrics are distinguished from homogenous ferroelectrics in that the electric dipole moment density varies with position in graded ferroelectrics [1]. This new class of ferroelectrics expands the applications and understanding of ferroelectric heterostructures and their related electric properties. As a result of the spatial variation of the polarization, polarization-graded ferroelectrics show unusual phenomena and properties that are not routinely observed for homogenous bulk ferroelectrics and their thin film counterparts. Unlike homogenous ferroelectrics, which are characterized by a symmetric hysteresis loop with respect to the polarization and applied field axes, graded ferroelectric devices display strikingly new

behavior, the most notable being a translation of the hysteresis loop along the polarization axis [2]. The shift in the hysteresis loops are attributed to a “built-in” potential, in analogy with the asymmetric current-voltage characteristics resulting from the “built-in” potential across chemically doped regions in semiconductor diode junctions [1, 3]. Due to the charge offset, a giant pseudo-pyroelectric response was reported in graded ferroelectrics [4, 5]. Other interesting properties for graded ferroelectrics include a diffuse phase transition accompanied with a broadening in the dielectric response with temperature [2, 6, 7]. Recently, Mantese and his co-workers expanded upon the concept of graded ferroelectrics and concluded that graded ferroelectric structures are capable of interchanging thermal/electric/mechanical energy, thereby creating completely novel devices based on graded ferroelectrics, such as transpacitor and other energy storage devices [1, 8–10].

It was shown experimentally that systematic variations in the polarization can be achieved in a number of ways including a variation in the composition of the material [11], setting up temperature gradients across a homogeneous ferroelectric bar [12], and by bending a homogeneous ferroelectric cantilever heterostructure [13]. Strukov *et al.* investigated the phase transitions and dielectric permittivity in triglycine sulfate (TGS) crystals in the presence of a temperature gradient [14, 15]. Their results show that spontaneous polarization as well as the dielectric permittivity are both function of the magnitude of the temperature gradients and the orientation of the temperature gradients with respect to the polarization. Pyroelectric properties of deuterated triglycine sulfate (DTGS) crystals subject to a stationary temperature gradient were also studied and a broadening of the maximum on the curve of pyroresponse vs. temperature was reported [16]. Experimental work has been carried out to study the hysteresis offset observed from temperature-graded bulk ferroelectrics. “Up” and “down” hysteresis offsets were experimentally observed when temperature gradients were imposed across a bulk $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ferroelectric material. Conversely, there was no hysteresis offset in the absence of a temperature gradient; thereby conclusively establishing the origin of the observed behavior as intrinsic to the polarization gradient [12].

Compositional grading is the most common way to introduce a polarization gradient in ferroelectric materials. In a study of the potassium tantalite niobate thin film with gradient in composition, Schubring *et al.* reported an unidirectional charge flow which results in a measurable hysteresis charge offset [2]. A smearing in the dielectric permittivity curves with respect to temperature has been found and a giant effective pyroelectric coefficient

has been observed. The hysteresis charge offset has been also observed in a variety of compositionally graded ferroelectric systems, including (Ba, Sr)TiO₃ [6, 11], Pb(Zr,Ti)O₃ [17–19], (Pb, La)TiO₃ [20], and (Pb, Ca)TiO₃ [21–23]. The presence of a polarization gradient has been demonstrated in homogenous (Pb,Sr)TiO₃ ferroelectric thin film by bending the ferroelectric heterostructure normal to the electrode surface [13]. It has been shown that external bending force can lead to a measurable asymmetric hysteresis charge offset, suggesting that the presence of a gradient in stress in a compositionally homogenous ferroelectric can give rise to polarization-graded structures with unconventional hysteresis behavior similar to graded ferroelectric devices (GFDs) and transcapitors [13].

However, while much is known experimentally concerning graded ferroelectric structures, theoretical descriptions and analysis of these or other transcapitive devices has been significantly lacking. Recently, we have developed a generalized Landau-Ginzburg formalism to analyze graded ferroelectrics as well as graded ferroic materials and devices in general [24]. A good agreement between theoretical calculations and experimental observation was found for temperature graded ferroelectrics [25]. In this article, we use a similar approach to analyze the compositionally graded ferroelectrics, which are the most studied graded ferroelectrics from an experimental point of view. We first provide a review of the Landau-Ginzburg theory for analyzing graded ferroelectrics. Then, the polarization profiles for compositionally graded ferroelectrics will be presented and the effect of the internal stresses due to the gradient in the self-strain will be highlighted. The charge offset and the dielectric properties of compositionally graded ferroelectrics will be subsequently addressed.

REVIEW OF LANDAU-GINZBURG MODEL FOR GRADED FERROELECTRICS

Consider a mono-domain ferroelectric of thickness L sandwiched between two metallic electrodes with the easy axis of polarization along the z -axis such that $P_1 = P_2 = 0$, $P_3 = P = f(z)$, as shown in Fig. 1.

A linear relationship between the barium concentration and the position along the z -direction is assumed, and the ferroelectric is homogeneous along the x - and y -directions, reducing the problem to only one dimension. Accordingly, the free energy per unit area can be expressed by [26]:

$$F(z) = \int_0^L [F_P(z) + F_{el}^i(z) + F_E(z)] dz \quad (1)$$

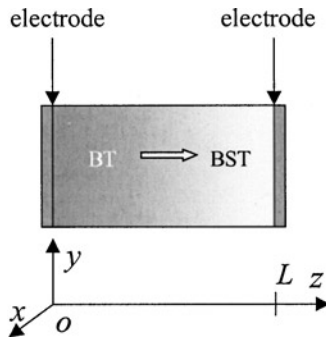


FIGURE 1 Schematic diagram showing a compositionally graded barium strontium titanate bar and the coordinate system used in the model (BT: BaTiO₃; BST: Ba_xSr_{1-x}TiO₃).

where $F_P(z)$, $F_{el}^i(z)$ and $F_E(z)$ are the energy contributions from polarization, stress and electric field respectively. The first term $F_P(z)$ can be expressed in the spirit of Landau as an expansion in terms of even powers of the polarization:

$$F_{pl}(z) = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 + \frac{1}{2}A \left(\frac{dP}{dz} \right)^2 \quad (2)$$

accompanied by a gradient energy term. In relation (2), α , β , γ , and A are the free energy expansion coefficients. The temperature dependence of the dielectric stiffness, α , is given by the Curie-Weiss law, $\alpha = (T - T_0)/\varepsilon_0 C$; where T_0 and C are the Curie-Weiss temperature and constant, respectively, and ε_0 is the permittivity of free space. The compositional inhomogeneity in the material system is reflected through the composition dependence of the Landau coefficients. Coefficient A can be approximated as $\delta^2 |\alpha|$, where δ is the characteristic length along which the polarization varies.

The second term of Eq. (1), $F_{el}^i(z)$, is the internal elastic energy due to the variation of the self-strain, i.e., $x^0(z) = Q_{12}[P^2(z) - \langle P \rangle^2]$, which is a result of the change of the lattice parameter within the compositionally graded unconstrained ferroelectric bar. It can be defined as [25]:

$$F_{el}^i(z) = \bar{C} \{ Q_{12}[P^2(z) - \langle P \rangle^2] + (z - L/2)\kappa \}^2 \quad (3)$$

where Q_{12} is the electrostrictive coefficient, $\bar{C} = C_{11} + C_{12} - 2C_{12}^2/C_{11}$ is an effective elastic constant, C_{ij} are the elastic moduli at constant

polarization, $\langle P \rangle$ is the average polarization and κ the radius of curvature resulting from the bending moment due to misfit between “layers” given by:

$$\kappa = 24/L^3 \int_0^L (z - L/2)x^0(z)dz \quad (4)$$

The last term $F_E(z)$ is Eq. (1) represents the energy contribution from the electric field and is given by:

$$F_E(z) = -\frac{1}{2}E^D P(z) - EP(z) \quad (5)$$

In Eq. (5), E is the external electric field along the z -direction and E^D is the depolarization field which we assume to be small due to the finite conductivity of the material as well as local compensation by defects such as oxygen vacancies in perovskite ferroelectrics.

The minimization of the free energy with respect to the polarization yields the Euler-Lagrange equation:

$$A \frac{d^2 P}{dz^2} = \{ \alpha + 4\bar{C} Q_{12} [(z - L/2)\kappa - Q_{12} \langle P \rangle^2] \} P + (\beta + 4\bar{C} Q_{12}^2) P^3 + \gamma P^5 - E \quad (6)$$

Equation (6) can be solved numerically to determine the polarization profile across the ferroelectric bar in the z -direction employing the boundary conditions $dP/dz = 0$ at $z = 0$ and $z = L$ which correspond to complete charge compensation at the ferroelectric/electrode interfaces. In our analysis, the coefficients α , β , γ , and the elastic constants for $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ are obtained by averaging the corresponding parameters of BaTiO_3 and SrTiO_3 [27].

POLARIZATION PROFILE

Figure 2 shows the normalized polarization profile for compositionally graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$. The end compositions are chosen to be $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ and BaTiO_3 , respectively. The solid line and the dashed line correspond to the polarization profiles with and without considering the internal elastic energy [i.e., $F_{el}^l(z)$ in Eq. (1)].

It can be seen from Fig. 2 that polarization decreases monotonically across the structure with a variation of the polarization along z -direction.

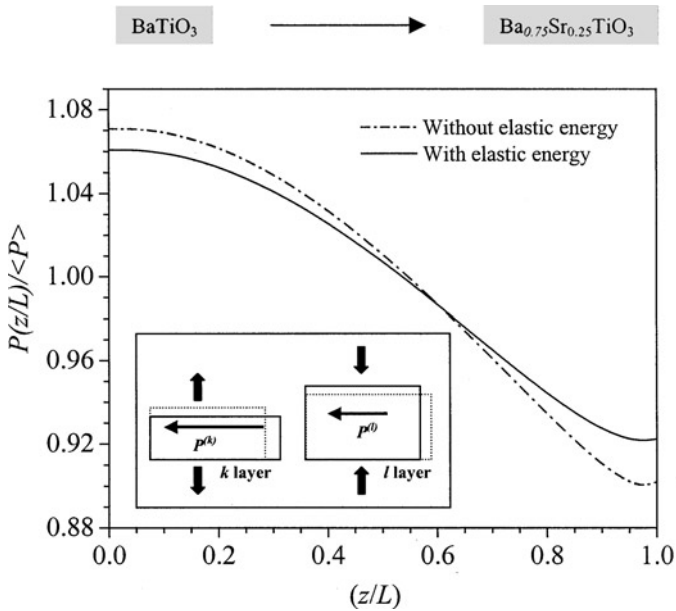


FIGURE 2 The normalized polarization profile for compositionally graded $\text{Ba}_3\text{Sr}_{1-x}\text{TiO}_3$ with and without considering the internal elastic energy due to self-strain gradient.

Apparently, the internal elastic energy further decreases the gradient and magnitude of the polarization profile. This effect is understandable through examination of the variation of the tetragonal lattice in two “layers” k and l with polarization greater or smaller than the average polarization, i.e., $P^{(k)}$ is greater than $\langle P \rangle$ and $P^{(l)}$ is smaller than $\langle P \rangle$, as shown in the inset of Fig. 2. Layer k and layer l are located at positions $z/L < 0.5$ and $z/L > 0.5$, respectively. The solid lines show the unconstrained tetragonal lattices of both layers. When these two “layers” are fitted together to be a part of a ferroelectric bar with average polarization $\langle P \rangle$, the in-plane lattice dimensions in layer k increases (tensile stresses) as indicated by the dashed lines, resulting in the decrease of the polarization in the z -direction. This is true for all the infinitesimally thin “layers” with initial polarization greater than the average polarization. Likewise, the in-plane dimensions in layer l (or any layer in a position $z/L > 0.5$) decreases due to in-plane compressive stresses resulting in an increase in the polarization in the z -direction. The overall result is that the polarization gradient tends to be smeared out by the internal elastic field.

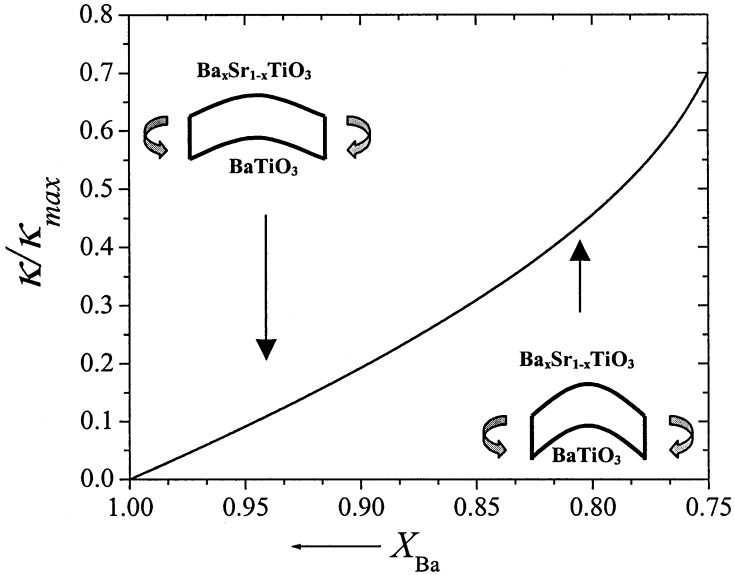


FIGURE 3 The normalized radius of curvature κ/κ_{max} as a function of barium concentration X_{Ba} on one end of the ferroelectric in compositionally graded $Ba_xSr_{1-x}TiO_3$. The insets schematically show the increasing bending of the ferroelectric bar when decreasing the barium concentration. The bending angles are highly exaggerated.

Another effect associated with the elastic field is the bending of the ferroelectric. Figure 3 plots the normalized radius of curvature κ/κ_{max} as a function of barium concentration on one end of the ferroelectric in a compositionally graded $Ba_xSr_{1-x}TiO_3$ (the other end has a fixed concentration corresponding to pure $BaTiO_3$). It can be seen that the radius of curvature increases in a steady fashion with decreasing barium concentration. This behavior is associated with the polarization gradient across the ferroelectric bar. Assuming there is no paraelectric region across the bar, the polarization gradient can be enhanced by decreasing the barium concentration on one end of the ferroelectric bar. The elastic field, therefore, increases in response to the variation of the polarization gradient. In accordance with Eq. (4), the radius of curvature increases with increasing elastic energy. Thus, the ferroelectric bar exhibits more bending as shown in the insets of Fig. 3.

ASYMMETRICAL CHARGE OFFSET AND DIELECTRIC PROPERTIES

The polarization profile then can be used to calculate the charge offset per unit area ΔQ based on the one-dimensional Poisson's Eq. [19]:

$$\Delta Q = \frac{k}{L} \int_0^L z \left(\frac{dP(z)}{dz} \right) dz \quad (7)$$

where k is the ratio of the capacitance of the graded ferroelectric C_F and the capacitance of a load capacitor C_Q [28]. In Fig. 4 we plot the charge offset $\Delta Q/\Delta Q_{\max}$ as a function of the barium concentration X_{Ba} on one end of the ferroelectric (the other end has a fixed concentration corresponding to pure BaTiO₃). ΔQ is defined as the magnitude of the shift of the origin of the $Q - E$ hysteresis loop, as schematically illustrated in the inset of Fig. 4. ΔQ_{\max} is the maximum charge offset. Figure 4 shows that the polarization gradient results in a charge offset and the magnitude of the charge offset strongly depends on the composition gradient. For compositionally homogenous materials ($X_{Ba} = 1$), there is no charge offset. ΔQ is not a monotonic function of the composition gradient. A maximum charge offset

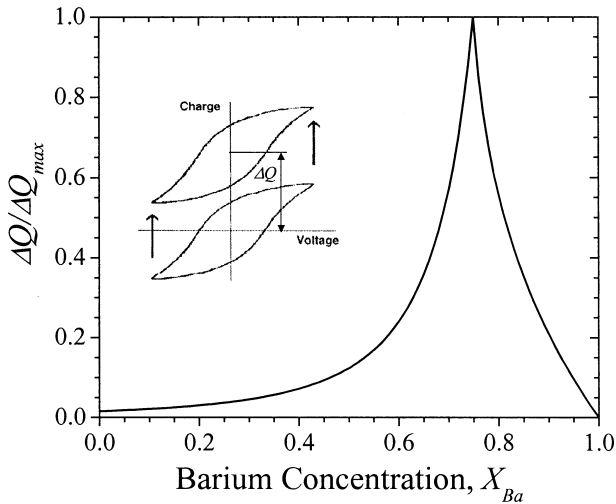


FIGURE 4 The calculated charge offset as a function of the minimum barium concentration X_{Ba} on one end of the ferroelectric (the other end has a fixed concentration corresponding to pure BaTiO₃).

may be obtained at a critical grading corresponding to the onset of paraelectric region with no spontaneous polarization in the ferroelectric bar.

Compositionally graded ferroelectrics exhibit dispersed dielectric susceptibility as a function of temperature [2, 6, 7]. The broadness of dielectric susceptibility is inherently linked with the distribution of the phase transition temperature resulting from the composition gradient across the ferroelectric. Calculating the polarization change ΔP for $E = 0$ and $E \neq 0$ respectively, we can obtain a position dependent dielectric susceptibility profile as:

$$\chi(z) = \frac{1}{\varepsilon_0} \frac{\Delta P(z)}{E} \quad (8)$$

and the mean susceptibility of the ferroelectric bar is given by:

$$\chi_m = \frac{L}{\int_0^L \{1/[\chi(z) + 1]\} dz} - 1 \quad (9)$$

Figure 5 shows χ_m as a function of temperature for various compositionally graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$. In contrast to a sharp peak of the dielectric susceptibility corresponding to the ferroelectric-paraelectric phase transformation at the Curie temperature for bulk homogenous ferroelectric, a typical dispersed dielectric susceptibility response with the temperature is predicted

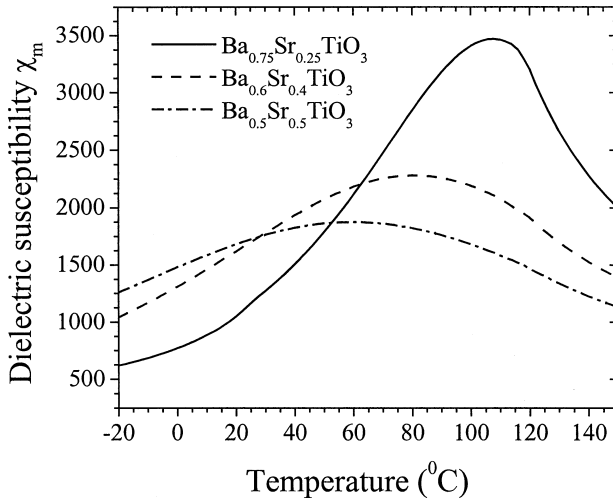


FIGURE 5 Dielectric susceptibility χ_m as a function of temperature for various compositionally graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ferroelectric systems.

for compositional graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ferroelectrics. The maximum in the susceptibility is broadened as a result of the compositional grading. It is not surprising that the extent of the broadening of the susceptibility displays a close relationship with the imposed composition gradient. As shown in Fig. 5, the dielectric susceptibility is significantly flattened with respect to the temperature for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ – BaTiO_3 graded ferroelectric. However, the broadening is less pronounced for a $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ – BaTiO_3 graded ferroelectric. A steeper composition gradient can give rise to broader maximum of the dielectric susceptibility. The exact same feature has been documented experimentally in compositionally graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ferroelectric thin films where more pronounced broad plateau region of the permittivity with the variation of the temperature was observed for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ – BaTiO_3 graded thin film compared to $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ – BaTiO_3 graded film [7].

Another important aspect of the theoretically calculated dielectric susceptibility is that the broad plateau of susceptibility is shifted towards lower temperatures with an increase in the compositional gradient, as indicated in Fig. 5. This is understandable because the “average” Curie temperature of the graded ferroelectric decreases with increasing compositional gradient. This result suggests that a high dielectric susceptibility with less temperature dependence at a desirable temperature can be achieved by appropriately tailoring the composition gradient.

CONCLUSION

In this article, a general thermodynamic model based on Landau-Ginzburg theory is used to analyze the compositionally graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$. We have shown that the internal elastic energy due to variation of the self-strain tends to flatten polarization gradient. As a result of the compositional inhomogeneity, compositional graded ferroelectrics exhibit a broad maximum or dispersed dielectric susceptibility versus temperature. Increasing the compositional gradient leads to the broader maximum of the dielectric susceptibility. This non-uniform polarization can also result in asymmetrical hysteresis with “up” or “down” charge offsets. Our analysis predicts a strong dependence of the charge offset on the polarization gradient.

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