

# Dielectric Permittivity and Pyroelectric Response of Compositionally Graded Ferroelectrics

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## ABSTRACT

A review of a thermodynamic model of polarization-graded ferroelectrics is presented. Using this formalism, the unusual dielectric and pyroelectric properties of compositionally graded ferroelectric films are analyzed. Results show that the “strength” of the grading can be chosen as a design parameter to achieve desirable dielectric and pyroelectric responses.

**Keywords:** Compositionally graded ferroelectrics; dielectric permittivity; pyroelectric

## INTRODUCTION

In recent years, compositionally graded ferroelectric thin films have gained considerable interest because of their unique behavior and properties. 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 with an attendant charge offset [1–3]. In addition to the polarization offset, graded ferroelectrics also possess a gigantic effective pyroelectric response [4, 5] and display little temperature dependence in the dielectric behavior [6]. While the former is associated with the aforementioned “built-in” potential, the latter stems from a gradient in transformation temperature that results in a diffuse phase transformation over a large temperature interval. The range where the dielectric permittivity and thus tunability is relatively constant can be adjusted via the degree of grading.

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In this article, we show from a detailed thermodynamic analysis that such effective pyroelectric coefficients are indeed the direct result of compositionally graded systems where the mean compositional Curie temperature corresponds to the temperature of maximum sensitivity of the material. We calculate near exact experimental results with no adjustable thermodynamic parameters. We employ the same theoretical formalism to explain the diffuse character of the ferroelectric-paraelectric phase transformation in compositionally graded ferroelectrics. The model used in this article is based on a generalized Landau-Ginzburg-Devonshire theory developed to analyze the polarization offset in graded ferroelectrics [7, 8]. This approach has been recently shown to be the continuum limit of transverse Ising models (TIM) [9, 10].

## THEORY

Consider a mono-domain, single-crystal, compositionally graded ferroelectric bar of length  $L$  sandwiched between two metallic electrodes. The easy axis of polarization is along the  $z$ -axis parallel to  $L$  such that  $P_1 = P_2 = 0$  and  $P_3 = P(z)$ . The ferroelectric is assumed to be homogeneous along the  $x$ - and  $y$ -directions, reducing the problem to only one dimension. The free energy per unit area can be expressed as [7, 8]:

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

where  $F_P(z)$ ,  $F_{Elastic}(z)$ , and  $F_{Electric}(z)$  are the energy contributions from the polarization, internal stresses, and the electric field, respectively. The first term  $F_P(z)$  is given by the Landau expansion in even powers of the polarization:

$$F_P(z) = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \frac{1}{2}A\left(\frac{dP}{dz}\right)^2, \quad (2)$$

accompanied by a Ginzburg gradient energy term. In relation (2),  $a$ ,  $b$ ,  $c$ , and  $A$  are the free energy expansion coefficients. The temperature dependence of the dielectric stiffness,  $a$ , is given by the Curie-Weiss law,  $a = (T - T_0)/\varepsilon_0 C$ ; where  $T_0$  and  $C$  are the Curie-Weiss temperature and constant, respectively, and  $\varepsilon_0$  is the permittivity of free space. The compositional inhomogeneity of the material system is reflected through the compositional dependence of the Landau coefficients. The Ginzburg coefficient  $A$  can be approximated as  $\delta^2 \cdot |a|$ , where  $\delta$  is a characteristic length along which the polarization varies.  $A$  is positive and thus the gradient term in the above relation acts as a restoring force that serves to damp out the spatial variations in  $P$ .

The second term of Eq. (1) is the elastic energy of the built-in, position-dependent stress field. This energy arises due the electrostrictive coupling between

the polarization and the self-strain and has two components: (i) the biaxial elastic energy due to the variation of the self-strain along  $L$ , and (ii) the energy associated with the bending of the ferroelectric due to the inhomogeneous elastic deformation. The elastic energy can be calculated from the conditions that both the average internal stress and the average momentum of the internal stress should be zero [11, 12]. A complete derivation of this elastic energy incorporating both sources was given elsewhere [8]. Accordingly:

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

where  $Q_{12}$  is the electrostrictive coefficient relating the strain in the  $x$ - $y$  plane to polarization  $P(z)$ ,  $\bar{C} = C_{11} + C_{12} - 2C_{12}^2/C_{11}$  is an effective elastic modulus,  $C_{ij}$  are the elastic moduli at constant polarization,  $\langle P \rangle$  is the average polarization:

$$\langle P \rangle = \frac{1}{L} \int_0^L P(z) \cdot dz, \quad (4)$$

and  $\kappa$  the radius of curvature resulting from the bending moment given by:

$$\kappa = \frac{24}{L^3} \int_0^L \left( z - \frac{L}{2} \right) \cdot Q_{12}[P^2(z) - \langle P \rangle^2] \cdot dz. \quad (5)$$

The last term in Eq. (1) represents the energy of the depolarization field  $E_D$  that arises from the inhomogeneous distribution of the polarization and an applied electric field  $E_A$  along the  $z$ -direction:

$$F_{Electric}(z) = -\frac{1}{2} E_D(z) \cdot P(z) - E_A \cdot P(z). \quad (6)$$

The depoling field is negligible if there exists a smooth compositional gradient across the ferroelectric; therefore, in the absence of an applied field, in which case  $F_{Electric}$  can be ignored.

The minimization of the free energy [Eq. (1)] with respect to the polarization yields the Euler-Lagrange equation:

$$A \frac{d^2 P}{dz^2} = \left\{ a + 4\bar{C} Q_{12} \left[ \left( z - \frac{L}{2} \right) \kappa - Q_{12} \langle P \rangle^2 \right] \right\} P + (b + 4\bar{C} Q_{12}^2) P^3 + c P^5. \quad (7)$$

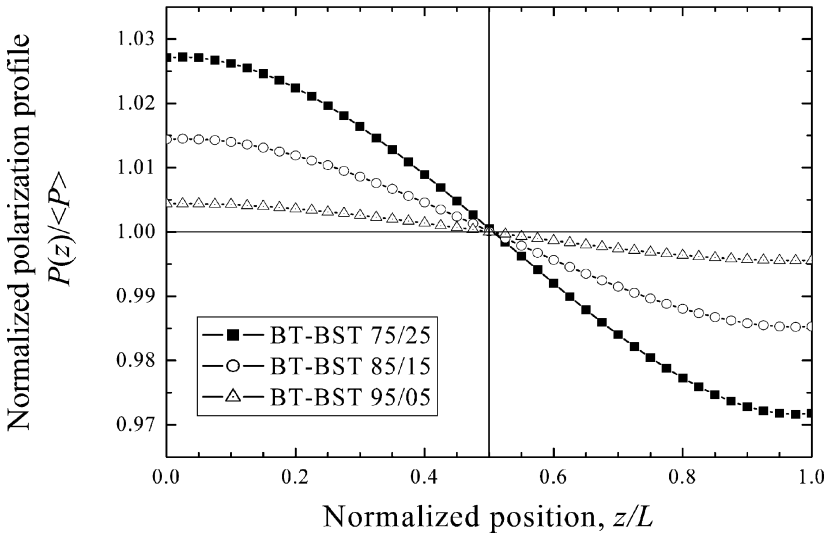
Equation (7) can be solved numerically to determine the polarization profile across the ferroelectric bar along the  $z$ -direction employing the boundary

conditions  $dP/dz = 0$  at  $z = 0$  and  $z = L$  which correspond to complete charge compensation at the ferroelectric/electrode interfaces.

## RESULTS AND DISCUSSION

For the analysis we have chosen compositionally graded  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST), mainly because there exists a great deal of information on the thermodynamic parameters and physical properties of  $\text{BaTiO}_3$  (BT) and  $\text{SrTiO}_3$  (ST). The coefficients  $a$ ,  $b$ ,  $c$ , and the elastic constants for BST are obtained by averaging the corresponding parameters of BT and ST [13]. The polarization profiles at room temperature ( $\text{RT} = 25^\circ\text{C}$ ) for three compositionally graded BST are plotted in Fig. 1. One of the end compositions is fixed at BT, and the other one is chosen to be BST 75/25, BST 85/15, and BST 95/05. Figure 1 shows that the polarization decreases monotonically across the thickness from the BT end towards the BST end. The polarization gradient diminishes close to the surfaces because of the charge compensation at the metallized ends. The slope of the polarization profile obviously depends on the “strength” of the gradient that can be characterized as the difference in the barium concentrations of the ends, a high difference yielding a steeper profile.

Compositionally graded ferroelectrics exhibit dispersed dielectric susceptibility as a function of temperature [4, 14, 15]. The broadness of dielectric susceptibility is inherently linked with the distribution of the phase transition



**Figure 1.** Normalized polarization profiles of BT-BST 75/25, BT-BST 85/15, and BT-BST 95/05 compositionally graded ferroelectric structures at  $\text{RT} = 25^\circ\text{C}$ .

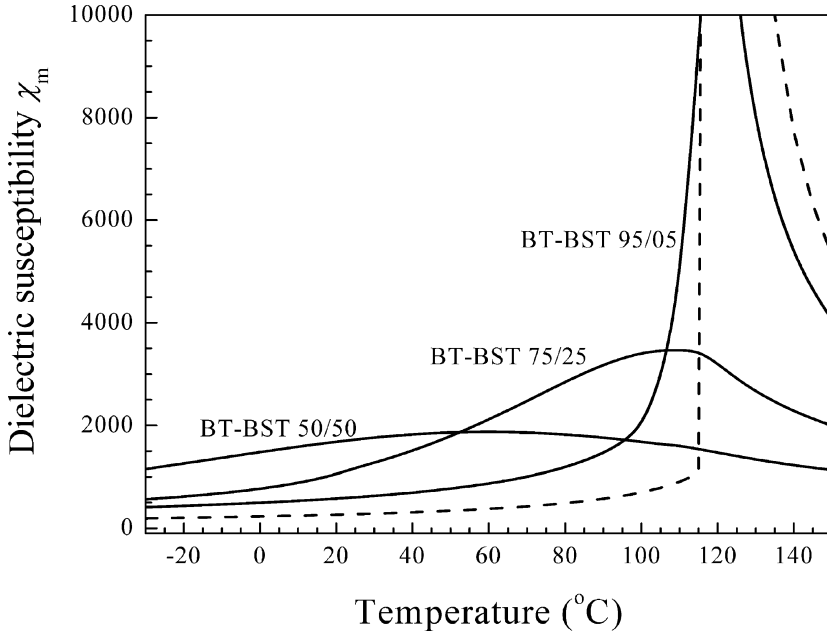
temperature resulting from the composition gradient across the ferroelectric. Calculating the polarization change  $\Delta P$  for  $E = 0$  and  $E \neq 0$ , respectively, we can obtain a position dependent dielectric susceptibility profile as:

$$\chi(z) = \frac{1}{\epsilon_0} \frac{\Delta P(z)}{E}, \quad (8)$$

and the (small-signal,  $E \rightarrow 0$ ) 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 2 shows  $\chi_m$  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 (shown as dashed line in Fig. 2), a dispersed dielectric susceptibility response with the temperature is predicted for compositionally 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.



**Figure 2.** Dielectric susceptibility  $\chi_m$  as a function of temperature for various compositionally graded  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  ferroelectric systems (solid line) and pure  $\text{BaTiO}_3$  (dashed line).

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. 2, the dielectric susceptibility is significantly flattened with respect to the temperature for BT-Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> graded ferroelectric compared to the homogenous BaTiO<sub>3</sub>, and it is less pronounced for the BT-Ba<sub>0.75</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> graded ferroelectrics. However, the broadening almost disappears for the BT-Ba<sub>0.95</sub>Sr<sub>0.05</sub>TiO<sub>3</sub> graded ferroelectrics, which possess the smallest gradient in our analysis. A steeper composition gradient can give rise to broader maximum of the dielectric susceptibility. The exact same feature has been reported experimentally in compositionally graded Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> ferroelectric thin films where a more pronounced broad plateau region of the permittivity with the variation of the temperature was observed for BT-Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> graded thin film compared to BT-Ba<sub>0.75</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> graded film [14].

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 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.

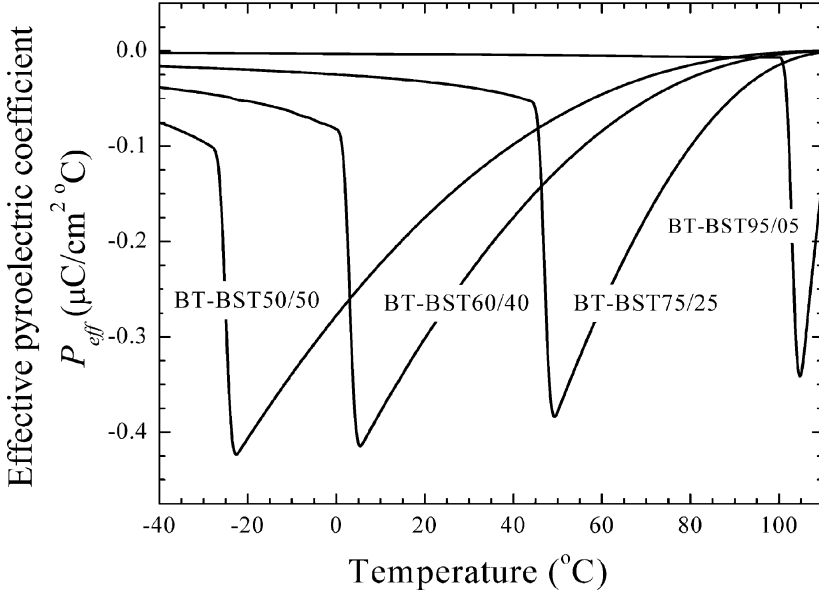
Using the polarization distribution of Fig. 1, a charge offset per unit area  $\Delta Q$  can be calculated based on the one-dimensional Poisson’s equation such that [16]:

$$\Delta Q = \frac{1}{L} \frac{C_Q}{C_F} \int_0^L z \cdot \left( \frac{dP(z)}{dz} \right) \cdot dz \quad (10)$$

where  $C_Q$  is the load capacitance in the Sawyer-Tower circuit and  $C_F$  is the capacitance of the graded ferroelectric. This charge offset translates to a displacement of the polarization vs. applied electric field hysteresis curve along the polarization axis. Experimental results show that this displacement is strongly temperature dependent [5, 17]. An effective pyroelectric coefficient can be defined as: [4]

$$p_{eff} = \frac{d(\Delta Q)}{dT} = \frac{1}{L} \frac{C_Q}{C_F} \frac{d}{dT} \int_0^L z \cdot \left( \frac{dP(z)}{dz} \right) dz. \quad (11)$$

In Fig. 3 we plot the temperature dependence of the charge offset and the effective pyroelectric coefficient for different compositionally graded BST. The ratio of  $C_Q/C_F$  typically ranges between 10–100 experimentally; for this analysis the ratio varies between 20 and 50, with  $C_Q = 0.2 \times 10^{-6}$  F and  $C_F$  calculated from the average dielectric permittivity as a function of the strength of the grading and the temperature. In our calculations,  $L$  was taken to be 1  $\mu\text{m}$ . For BT-BST 75/25, a maximum effective pyroelectric coefficient is found to occur  $\sim 50^\circ\text{C}$ , corresponding to the onset of the paraelectric phase at the BST 75/25



**Figure 3.** Effective pyroelectric coefficient as a function of temperature in different compositionally graded ferroelectrics: BT-BST 95/05; BT-BST 75/25; BT-BST 60/40; BT-BST 50/50.

end. This behavior is entirely consistent with both experimental observations [5, 17] and TIM analysis [9, 10]. We note that the effective pyroelectric response can be adjusted extrinsically by varying the ratio  $C_Q/C_F$  or the length  $L$  along which there is a systematic polarization variation.

The effect of the magnitude of the composition grading is also shown in Fig. 3. We fix the composition at one end of the ferroelectric and let the composition at the other end,  $x$ , vary between  $0.50 \leq x \leq 0.95$ . Thus,  $x$  can be considered as measure of the “strength” of the gradient. Figure 3 shows that the maximum pyroresponse is smaller for those materials with higher mean Curie temperatures due to a decrease in both the magnitude and temperature sensitivity of the built-in potential. A maximum pyroresponse is expected for BT-BST 67/33 at room temperature, since the transformation temperature for BST 67/33 is approximately room temperature. Gradients, defined by a barium composition fixed at one end less than 0.67 will result in a partial transformation of the film to its paraelectric state, thus yielding a lower pyroresponse. Pyroelectric coefficients on the order of  $0.1 \mu\text{C}/\text{cm}^2 \cdot ^\circ\text{C}$  are remarkable for thin film ferroelectrics, which often have values more typically in the range  $0.001$ – $0.01 \mu\text{C}/\text{cm}^2 \cdot ^\circ\text{C}$  [5, 17–19]. The theoretical results derived above, however, are consistent with experimental observations; the latter of which have yielded effective pyroelectric coefficients greater than  $1 \mu\text{C}/\text{cm}^2 \cdot ^\circ\text{C}$  [4, 5, 17].

## CONCLUSION

In this article, various compositionally graded BT-Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> ferroelectric systems are quantitatively analyzed via a theoretical model based on LGD formalism. Compositionally graded ferroelectrics were shown to exhibit broad maximum and dispersed susceptibility versus temperature as a result of the compositional gradient. A large effective pyroelectric coefficient, maximum value close to 0.4  $\mu\text{C}/\text{cm}^2\cdot^\circ\text{C}$ , was predicted.

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