

Effective pyroelectric response of compositionally graded ferroelectric materials

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A thermodynamic theory is used to determine the effective pyroelectric coefficients of polarization graded ferroelectrics, with values in excess of $0.1 \mu\text{C}/\text{cm}^2 \text{ } ^\circ\text{C}$ are predicted for various barium strontium titanate thin films. Maximum values closer to $0.4 \mu\text{C}/\text{cm}^2 \text{ } ^\circ\text{C}$ are obtained for a $1 \mu\text{m}$ thick material—compositionally graded between pure barium titanate and one that has barium to strontium in the ratio of 75:25. © 2005 American Institute of Physics.

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The dramatic reduction in obtainable fabrication line widths and unit cell dimensions, together with improved chip yields and reduced fabrication costs has resulted in a proliferation of low cost vision systems utilizing silicon based vision technology. Unfortunately, the sensitivity of silicon microarrays cannot be easily extended above $1 \mu\text{m}$ where night vision, chemical sensing, and thermal comfort systems often must operate. Thus, vision systems operating in this range often must rely upon expensive cryogenically cooled semiconductor-based technology or utilize high cost ferroelectric hybrid technologies which have resisted adaptation to mass production. Conversely, amorphous silicon and thermopile devices currently lack the sensitivity required for many of the applications described, yet offer cost effective means of production.

For many years, alternatives to the ferroelectric hybrid technology have been sought through the use of ferroelectric thin film technology, which has been so successfully employed in the commercialization of ferroelectric memory devices. However, despite much experimental work in this area, the large pyroelectric coefficients commonly observed in bulk ferroelectric materials have not been replicated in thin film form, with two exceptions—those materials being compositionally graded ferroelectric thin films formed from either potassium tantalum niobate,¹ and barium strontium titanate.^{2,3} In both instances effective pyroelectric coefficients comparable to bulk materials have been consistently observed, yet an explanation for their properties has been theoretically illusive.

In this letter, 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. The formalism employed in this letter is based on a general thermodynamic model developed to analyze the polarization offset in graded ferroelectrics.^{4,5} This approach has been verified to be the continuum limit of transverse Ising models (TIM).^{6,7}

Consider a monodomain, 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:^{4,5}

$$F(z) = \int_0^L [F_p(z) + F_{\text{elastic}}(z) + F_{\text{electric}}(z)] dz, \quad (1)$$

where $F_p(z)$, $F_{\text{elastic}}(z)$, and $F_{\text{electric}}(z)$ are the energy contributions from polarization, internal stresses, and the electric field, respectively. The first term $F_p(z)$ is given by the Landau expansion of the 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 Eq. (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, $a=(T-T_0)/\varepsilon_0C$; 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 of the material system is reflected through the composition dependence of the Landau coefficients. The Ginzburg coefficient A can be approximated as $\delta^2 \cdot |a|$, where δ 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

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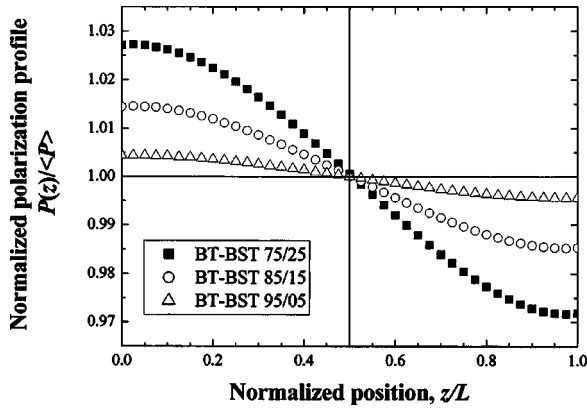


FIG. 1. Normalized polarization profiles of BT-BST 75/25, BT-BST 85/15, and BT-BST 95/5 compositionally graded ferroelectric structures at RT = 25 °C.

internal stress should be zero.^{8,9} A complete derivation of this elastic energy incorporating both sources was given elsewhere.⁵ Accordingly:

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

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 κ 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:

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

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

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

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

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.

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

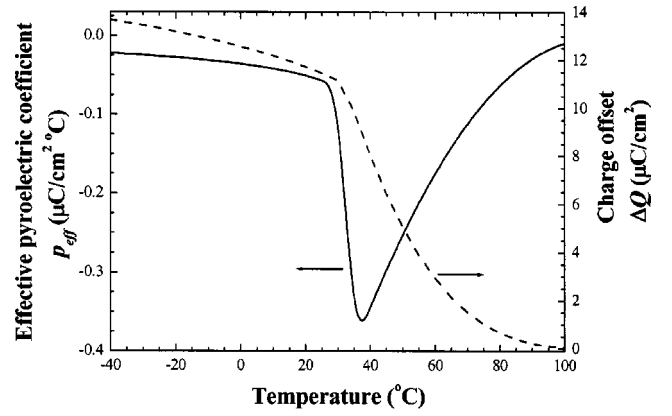


FIG. 2. Effective pyroelectric coefficient (solid line) and charge offset per unit area (dashed line) as a function of temperature in graded BT-BST 70/30.

of information on the thermodynamic parameters and physical properties of BaTiO_3 (BT) and 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.¹⁰ The polarization profiles at room temperature (RT = 25 °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 95/5. 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.

Using this polarization distribution of Fig. 1, a charge offset per unit area ΔQ can be calculated based on the one-dimensional Poisson’s equation such that:¹¹

$$\Delta Q = \frac{1}{L} \frac{C_Q}{C_F} \int_0^L z \cdot \left(\frac{dP(z)}{dz} \right) \cdot dz \quad (8)$$

where C_Q is the load capacitance in the Sawyer-Tower circuit and C_F is the capacitance of the graded ferroelectric.¹² This charge offset translates to a displacement of the polarization versus applied electric field hysteresis curve along the polarization axis. Experimental results show that this displacement is strongly temperature dependent.^{2,3} An effective pyroelectric coefficient can be defined as:¹

$$P_{\text{eff}} = \frac{d(\Delta Q)}{dT} = \frac{1}{L} \frac{C_Q}{C_F} \frac{d}{dT} \int_0^L z \cdot \left(\frac{dP(z)}{dz} \right) dz. \quad (9)$$

Figure 2 plotted the temperature dependence of the charge offset and the effective pyroelectric coefficient for compositionally graded BST. The end compositions are chosen to be BT and BST 70/30. The ratio of C_Q/C_F typically ranges between 10 and 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 $1 \mu\text{m}$. A maximum effective pyroelectric coefficient is found to occur ~ 35 °C, corresponding to the onset of the paraelectric phase at the BST 70/30 end. The charge offset decreases with temperature as a result of decreasing spontaneous polarization. This

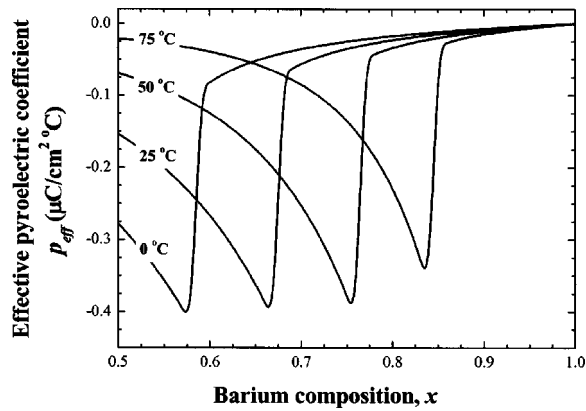


FIG. 3. Effective pyroelectric coefficient at different temperatures as a function of barium composition at one end of the graded ferroelectric with the composition of the other end fixed at BT.

behavior is entirely consistent with both experimental observations^{2,3} and TIM analysis.^{6,7} 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 shown in Fig. 3, where we plot the effective pyroelectric coefficient at different temperatures. Here, we fix the composition at one end of the ferroelectric and let the composition at the other end, x , vary between $0.5 \leq x \leq 1$. 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 $0.1 \mu\text{C}/\text{cm}^2 \text{ }^\circ\text{C}$ are remarkable for thin film ferroelectrics, which often have values more typically in the range $0.001\text{--}0.01 \mu\text{C}/\text{cm}^2 \text{ }^\circ\text{C}$.^{2,3,13,14} The theoretical results de-

rived above, however, are consistent with experimental observations; the latter of which have yielded effective pyroelectric coefficients greater than $1 \mu\text{C}/\text{cm}^2 \text{ }^\circ\text{C}$.¹⁻³ The detection scheme commonly used in the study of polarization-graded ferroelectrics offers the added benefits of lower device output impedance (and hence better signal energy transfer), and the potential to further improved signal to noise ratio by band limiting the input noise frequencies. The existence of a reliable/predictive model for graded ferroelectrics therefore greatly facilitates the design of infrared detectors that offer substantially higher levels of performance. Finally, the consistency of our predictions with experimental findings offer further credulity to the many other experimental findings pertaining to graded ferroelectrics; the latter of which have occasionally been argued as arising from contact effects.

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¹N. W. Schubring, J. V. Mantese, A. L. Micheli, A. B. Catalan, and R. J. Lopez, *Phys. Rev. Lett.* **68**, 1778 (1992).

²F. Jin, G. W. Auner, R. Naik, N. W. Schubring, J. V. Mantese, A. B. Catalan, and A. L. Micheli, *Appl. Phys. Lett.* **73**, 2838 (1998).

³M. S. Mohammed, G. W. Auner, R. Naik, J. V. Mantese, N. W. Schubring, A. L. Micheli, and A. B. Catalan, *J. Appl. Phys.* **84**, 3322 (1998).

⁴S. P. Alpay, Z.-G. Ban, and J. V. Mantese, *Appl. Phys. Lett.* **82**, 1269 (2003).

⁵Z.-G. Ban, S. P. Alpay, and J. V. Mantese, *Phys. Rev. B* **67**, 184104 (2003).

⁶H. X. Cao and Z. Y. Li, *J. Phys.: Condens. Matter* **15**, 6301 (2003).

⁷H. X. Cao, Y. H. Gao, Q. Jiang, and Z. Y. Li, *J. Appl. Phys.* **96**, 1628 (2004).

⁸A. Roytburd and J. Slutsker, *Acta Mater.* **50**, 1809 (2002).

⁹L. B. Freund, *J. Mech. Phys. Solids* **44**, 723 (1996).

¹⁰In SI units for $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, $a=1.12 \times 10^7(T-371 \cdot x+253)/(9 \cdot x+8)$, $b=(-11.96 \cdot x+8.4) \times 10^9$, $c=2.7 \times 10^{11}$, $C_{11}=(3.48-1.72 \cdot x) \times 10^{11}$, $C_{12}=(1-0.154 \cdot x) \times 10^{11}$, and $Q_{12}=-0.034$; data from Z.-G. Ban and S. P. Alpay, *J. Appl. Phys.* **91**, 9288 (2002).

¹¹Z. Chen, K. Arita, M. Lim, and C. A. P. Araujo, *Integr. Ferroelectr.* **24**, 181 (1999).

¹²C. B. Sawyer and C. H. Tower, *Phys. Rev.* **35**, 269 (1930).

¹³Z.-G. Ban and S. P. Alpay, *Appl. Phys. Lett.* **82**, 3499 (2003).

¹⁴A. Sharma, Z.-G. Ban, S. P. Alpay, and J. V. Mantese, *J. Appl. Phys.* **95**, 3618 (2004).