

Magnitude of the intrinsic electrocaloric effect in ferroelectric perovskite thin films at high electric fields

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Monodomain contributions to the electrocaloric effect in mechanically free (bulk) and laterally clamped (thin film) BaTiO₃ are computed using a thermodynamic analysis. The authors show that the intrinsic electrocaloric coefficient at electric fields sufficient to destroy the discontinuous ferroelectric phase transition results in an adiabatic temperature change of 8 K that agrees closely with the giant value of 12 K recently observed experimentally for lead zirconate titanate thin films [A. S. Mischenko *et al.*, *Science* **311**, 1270 (2006)]. Perfect lateral clamping transforms the discontinuous transition into a continuous transition, which decreases the magnitude of the electrocaloric effect by 20% but reduces its sensitivity to temperature. © 2007 American Institute of Physics. [DOI: 10.1063/1.2750546]

The electrocaloric (EC) effect is a coupling between electrical and thermal properties of a dielectric solid wherein change in temperature occurs under adiabatic conditions in response to an applied electric field. The effect is analogous to the process of adiabatic demagnetization used to cool cryogenic systems to temperatures approaching absolute zero (see, e.g., Ref. 1). Because of their large temperature-dependent spontaneous electric polarization, the EC properties of ferroelectric crystals have attracted attention for use in solid-state cooling devices and in thermodielectric power converters since the 1960s.²⁻⁴ The magnitude of the EC effect that is observed experimentally depends both on the properties of the specific ferroelectric crystal and on the details of the measurement conditions. For the ferroelectric perovskites, the adiabatic temperature change (ΔT) measured on bulk or single crystal specimens has typically ranged from a few tenths of a degree to several Kelvins.⁴⁻⁶

Recently, however, recognizing that the EC effect that could be achieved in ferroelectric materials was primarily limited by the electric breakdown strength of the specimen, Mischenko *et al.*^{7,8} have investigated the EC properties of thin film (~300 nm) perovskite ferroelectrics under the application of high (~900 kV/cm) electric fields. In these high-field studies much larger effects than previously reported were found, with maximum values of $\Delta T=12$ K for PbZrO₃:PbTiO₃ (PZT) films⁶ and $\Delta T=5$ K for relaxor ferroelectric Pb(Mg_{1/3}Nb_{2/3})O₃:PbTiO₃ films.⁷ In this letter, we show directly by thermodynamic analysis that these giant EC effects as observed in thin film perovskites can be attributed to their intrinsic, monodomain thermodielectric properties when driven between sufficiently high electric fields and at temperatures near their ferroelectric Curie point. We further demonstrate that mechanical clamping in thin film structures does not result in a significant reduction of the EC response

but greatly reduces its dependence on temperature.

Here we compute the EC properties of mechanically free (bulk) and laterally clamped (thin film) BaTiO₃ as functions of temperature and electric field using a Landau-Devonshire thermodynamic formalism. The EC and pyroelectric properties of a dielectric material are converse effects governed by:

$$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E, \quad (1)$$

where S is the entropy, E the electric field, P the polarization, and T the absolute temperature. The application of E oriented parallel to the direction of polarization of absolute value P results in an adiabatic temperature change given by

$$dT(T,E) = -\frac{T}{C_E(T,E)} \left(\frac{\partial P(T,E)}{\partial T}\right)_E dE, \quad (2)$$

where $C_E(T,E)$ is the heat capacity per unit volume at constant electric field. For a bulk ferroelectric BaTiO₃ crystal, we write the free energy density of the unconstrained, stress-free monodomain state as

$$G_{\text{bulk}} = G_0(T) + \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 - EP, \quad (3)$$

where α_1 , α_{11} , and α_{111} are the Landau coefficients and $G_0(T)$ the energy of the paraelectric. The quadratic coefficient is given by the Curie-Weiss law, $\alpha_1(T) = (T - T_C)/(2C\epsilon_0)$, where T_C is the Curie temperature, C the Curie constant, and ϵ_0 the dielectric permittivity of vacuum.

For a thin film material deposited on a substrate the free energy is modified to take into account the clamping effect of the substrate and the internal stresses that may arise from lattice and thermal expansion mismatches. Considering the mechanical boundary conditions and the self-strain of the phase transformation, the free energy density of the thin film subject to perfect lateral clamping may be expressed by⁹

$$G_{\text{film}} = G_0 + \tilde{\alpha}_1 P^2 + \tilde{\alpha}_{11} P^4 + \alpha_{111} P^6 - EP + \tilde{G}_{\text{EL}}, \quad (4)$$

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$$\tilde{\alpha}_1 = \alpha_1 - 2u_m Q_{12} \tilde{C}, \quad (5)$$

$$\tilde{\alpha}_{11} = \alpha_{11} + Q_{12}^2 \tilde{C} \quad (6)$$

are the modified dielectric stiffness coefficients, $\tilde{G}_{\text{EL}} = u_m^2 \tilde{C}$ is the polarization-free strain energy, $\tilde{C} = C_{11} + C_{12} - 2C_{12}^2/C_{11}$, C_{ij} are the elastic constants at constant polarization, Q_{ij} are the cubic electrostrictive coefficients, and u_m is the in-plane misfit strain. All of the intrinsic material property coefficients entering into Eqs. (3)–(6) for BaTiO₃ (BT) were taken from Ref. 9. The phase transformation temperature varies linearly with the misfit strain through Eq. (5) while the two-dimensional clamping is described by Eq. (6). Depending on the magnitude of $Q_{12}^2 \tilde{C}$, lateral clamping alters the character of the discontinuous cubic to tetragonal phase transition independent of the misfit strain between the film and substrate.¹⁰

The value of the polarization and its dependence on temperature and applied field are given by the equilibrium condition, $\partial G_{\text{bulk}}/\partial P = 0$ or $\partial G_{\text{film}}/\partial P = 0$, and substitution of $P(T, E)$ into Eqs. (3) and (4) provides the corresponding equilibrium energies for the bulk and the thin film cases, respectively. The excess entropy S_E^{XS} and specific heat ΔC_E of the ferroelectric phase transition follow from,

$$S_E^{\text{XS}}(T, E) = -T \left(\frac{\partial G(P)}{\partial T} \right)_E, \quad (7)$$

$$\Delta C_E(T, E) = -T \left(\frac{\partial^2 G(P)}{\partial T^2} \right)_E, \quad (8)$$

where the absolute value of $C_E(T, E)$ is estimated by scaling the computed zero-field values of $\Delta C_E(T, E)$ to the lattice or “hard mode” contributions to the specific heat taken from experimentally measured data.¹¹

Following from Eq. (1), the way in which the magnitude of the electrocaloric effect varies subject to a change in electric field at constant temperature can be best appreciated by examining the behavior of the excess entropy. The application of the field E conjugate to the order parameter P destroys the ferroelectric phase transition and at a sufficiently large field $E = E^*$, the discontinuities at the temperature T_0 where the paraelectric and ferroelectric phases are in equilibrium will effectively disappear (Figure 1). On increasing the field from an initial value $E_a = 0$ to a nonzero field $E_b > E_a$, the maximum change in entropy will always occur at the temperature of the discontinuous zero-field ferroelectric phase transition $T = T_0$. Alternatively, if the field increase is made to take place starting from a much higher value that is sufficient to cause the discontinuities at T_0 to effectively disappear, e.g., $E_a = 50$ kV/cm $> E^*$, the maximum entropy change will always occur at the higher temperature $T = T^*$. On the other hand, when the field is increased from an intermediate nonzero value, e.g., $E_a = 10$ kV/cm $< E^*$, the maximum entropy change will occur at some different but intermediate temperatures $T_0 > T_i > T^*$. Consequently, it is clear that when the electric field is changed between two values E_a and E_b , both the magnitude of the electrocaloric effect and temperature at which it is maximized depend not only on the extent of the field change $\Delta E = E_b - E_a$ but also on the value of the initial field E_a .

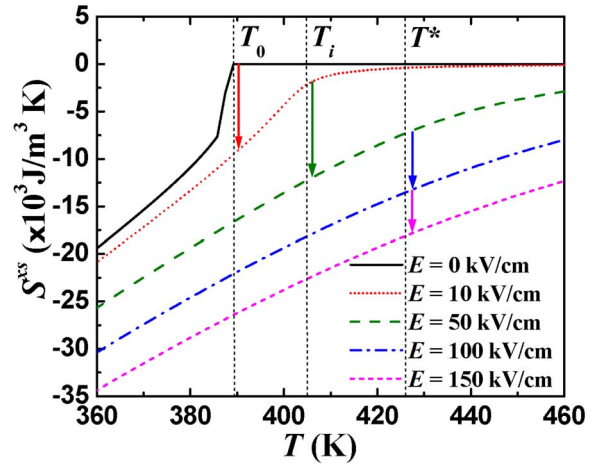


FIG. 1. (Color online) Excess entropy as a function of temperature at different electric fields for mechanically free (bulk) BaTiO₃. At $E=0$ there is a discontinuity at the paraelectric-ferroelectric transition and as E increases this discontinuity disappears. The vertical lines mark the temperatures where the maximum change in entropy occurs for an electric field change ($\Delta E = E_b - E_a$) having differing values of the initial applied field E_a and final field E_b as shown by the arrows (see text for details).

To compute the corresponding adiabatic temperature change $\Delta T = T_a - T_b$ we integrate Eq. (2) using as input values for $(\partial P(T, E)/\partial T)_E$ and $C_E(T, E)$ that follow from the Landau-Devonshire theory. The computed temperature variation of the polarization $P(T, E)$ and specific heat $C_E(T, E)$ for a bulk BT in the unconstrained and stress-free monodomain state as a function of applied field are shown in Figs. 2(a) and 2(b). In order to make a direct comparison with the recent experimental results recorded at high electric fields, we perform the integration for $\Delta E = 10, 50,$ and 100 kV/cm using an initial field $E_a = 50$ kV/cm $> E^*$. The results of the computations are shown in Fig. 3. Noting, as shown in Fig. 2(b), that the specific heat $C_E(T, E)$ is a weak function of field at $E > E^*$, we may use the data in Fig. 3 to evaluate the EC coefficient p at the temperature T_m where the adiabatic temperature change exhibits its maximum. Under these conditions we may write

$$p(T_m) \approx \left(\frac{C_E(T_m)}{T_m} \right) \frac{\Delta T(T_m)}{\Delta E}. \quad (9)$$

Substituting the values computed for BT at $E_a = 50$ kV/cm, $\Delta E = 100$ kV/cm with $C_E(T_m) = 3.05 \times 10^6$ J/K m³, $T_m = 415$ K, and $\Delta T(T_m) = 1.6$ K we find that the EC coefficient $p(T_m) = 1.2 \times 10^{-3}$ C/K m². An increase in the field change to a larger value $\Delta E = 480$ kV/cm would give $\Delta T(T_m) = 7.8$ K. Comparing this result to experimental data acquired at $E_a = 295$ kV/cm, $\Delta E = 480$ kV/cm reported for 350 nm PZT films⁷ near the discontinuous cubic to rhombohedral phase transition with $C_E(T_m) = 2.74 \times 10^6$ J/K m³, $T_m = 495$ K, and $\Delta T(T_m) = 12$ K, we find that $p(T_m) = 1.4 \times 10^{-3}$ C/K m². Hence we may conclude that the magnitude of intrinsic EC coefficient at electric fields sufficient to destroy the stress-free, discontinuous ferroelectric phase transition in BT is closely comparable to the giant value recently observed by experiment near the discontinuous ferroelectric transition in PZT.⁷

For thin film structures, the effect of clamping between the film and substrate must also be considered. Figure 2(c) and 2(d) show that perfect lateral clamping of BT transforms

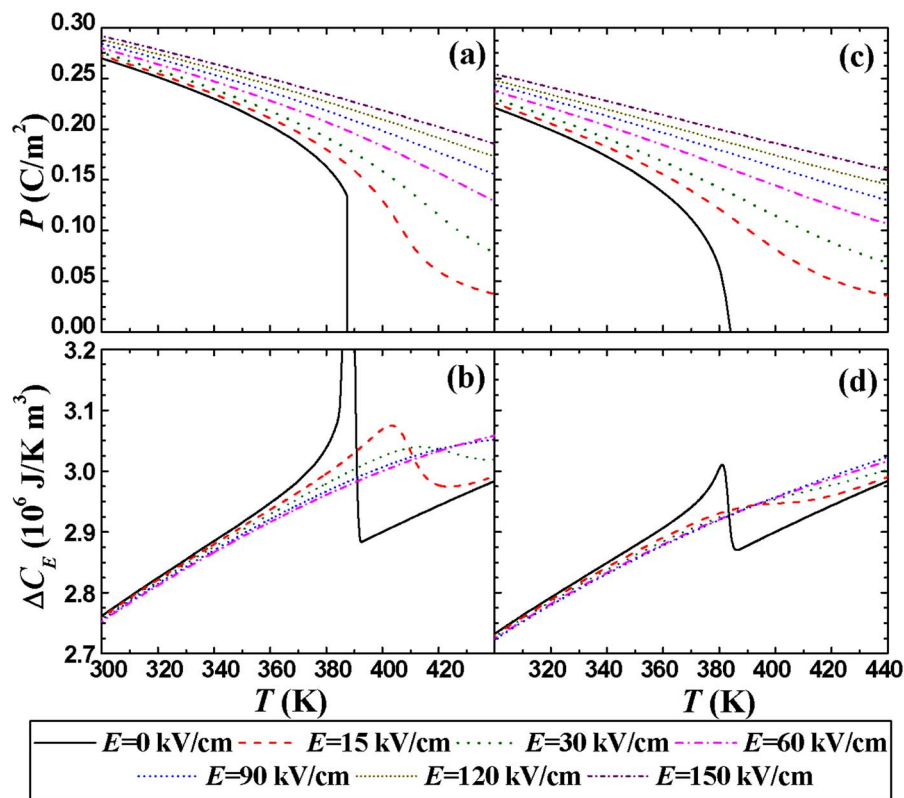


FIG. 2. (Color online) Plot of polarization vs temperature for (a) mechanically free, (c) clamped BaTiO₃ and plot of change in heat capacity with temperature for (b) mechanically free, (d) clamped BaTiO₃.

the discontinuous cubic to tetragonal transition occurring at T_0 into a continuous transition occurring at $T_C < T_0$ and this alteration of the phase transition order affects the temperature and field dependencies of $P(T, E)$ and $C_E(T, E)$. As seen in Fig. 3, this in turn results in a decrease in the adiabatic temperature change ΔT but greatly reduces its dependence on temperature. At $T_m = 390$ K it is found that electrocaloric coefficient of laterally clamped BT is $p(T_m) = 9.2 \times 10^{-4} \text{ C/K m}^2$, about 80% of the value observed for the bulk crystal. This finding has two immediate consequences. First, ferroelectric materials that exhibit continuous (or nearly so) phase transitions at their Curie temperatures may be expected to exhibit smaller EC effects than those with discontinuous phase transitions. Second, following

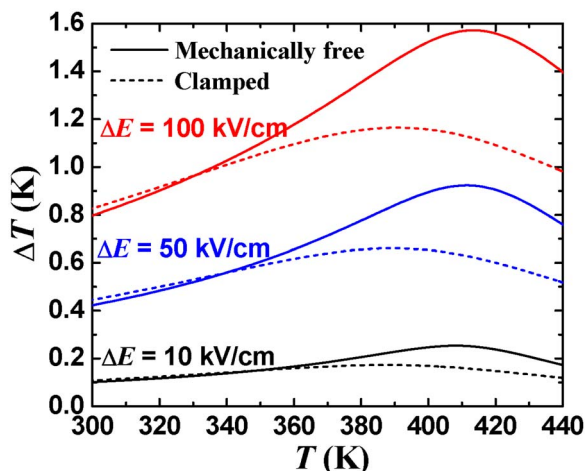


FIG. 3. (Color online) Adiabatic change of temperature (electrocaloric effect) as a function of working temperature for both mechanically free and clamped BaTiO₃ at various electric field changes ($\Delta E = E_b - E_a$), where E_a is 50 kV/cm.

from Eqs. (5) and (6), control of misfit strain in epitaxial ferroelectric thin films provides a means to vary both the magnitude and temperature dependencies of their EC properties.

In summary, we have shown that the giant adiabatic temperature change reported for PZT thin films at high electric fields, when unambiguously defined in terms of the corresponding EC coefficient, is in close agreement to that predicted by the thermodynamic theory for BT. This agreement implies that the giant electrocaloric effects as recently observed by experiment are intrinsic to the stress-free monodomain crystal. Lateral clamping causes a change in the order of the discontinuous ferroelectric phase transition, and reduces the magnitude of the electrocaloric effect, and reduces its dependence on temperature. Control of the misfit strain between film and substrate may therefore be used to adjust the electrocaloric properties of epitaxial thin film ferroelectrics.

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- ¹M.-H. Phan and S.-C. Yu, *J. Magn. Magn. Mater.* **308**, 325 (2007).
- ²J. D. Childress, *J. Appl. Phys.* **33**, 1793 (1962).
- ³E. Fatuzzo, H. Kiess, and R. Nitsche, *J. Appl. Phys.* **37**, 510 (1966).
- ⁴P. D. Thacher, *J. Appl. Phys.* **39**, 1996 (1968).
- ⁵G. Sebald, L. Seveyrat, D. Guyomar, L. Lebrun, B. Guiffard, and S. Pruvost, *J. Appl. Phys.* **100**, 124112 (2006).
- ⁶B. A. Tuttle and D. A. Payne, *Ferroelectrics* **37**, 603 (1981).
- ⁷A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, *Science* **311**, 1270 (2006).
- ⁸A. S. Mischenko, Q. Zhang, R. W. Whatmore, J. F. Scott, and N. D. Mathur, *Appl. Phys. Lett.* **89**, 242912 (2006).
- ⁹S. P. Alpay, I. B. Misirlioglu, A. Sharma, and Z.-G. Ban, *J. Appl. Phys.* **95**, 8118 (2004).
- ¹⁰N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).
- ¹¹F. Jona and G. Shirane, *Ferroelectric Crystals* (Dover, New York, 1962), p. 124.