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Effect of domain walls on the electrocaloric properties of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ thin films

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The electrocaloric properties of polydomain epitaxial $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ thin films are investigated using a Ginzburg-Landau-Devonshire thermodynamic model as a function of strain, temperature, and composition for $0.65 \leq x \leq 1$. Polarization transitions driven by epitaxial strain and extrinsic contributions from domain wall displacements are found to dramatically impact the electrocaloric response. Careful choice of epitaxial misfit strain and composition allows one to harness the intrinsic and extrinsic contributions to obtain large adiabatic temperature changes much below the Curie temperature of the material. © 2011 American Institute of Physics. [doi:10.1063/1.3614453]

Ferroelectric materials such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) have been the subject of intense study in the past decade due to their potential for use in a wide array of applications. One such application is solid state cooling with a ferroelectric material which is made possible via the electrocaloric effect which has attracted renewed interest since the observation of large electrocaloric effects in thin films of $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (Ref. 1) and $0.9\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$.² The electrocaloric effect refers to the change in temperature of a ferroelectric under adiabatic conditions in response to a change in the applied electric field. Since the spontaneous polarization in a ferroelectric is temperature dependent, an electric field that influences ferroelectric ordering can cause a change in temperature by raising or lowering the entropy associated with the order parameter. Although early studies focused on bulk or single crystal materials where large voltages (>500 V) were required to achieve temperature changes of 1-2K,³ recent studies of thin film ferroelectrics suggest that superior electrocaloric performance can be achieved by the application of small voltages and by taking advantage of enhanced breakdown strength in modern films.

As modern electronics trend towards smaller and smaller feature sizes, one major challenge will be effectively cooling these high performance materials. Ideally one would turn to low-power, fully integrated, high-performance cooling media. Modern electrocaloric thin films that can operate with relatively low applied voltages and require little power are exciting candidates for such applications. Such devices based on ferroelectrics would rely on thin films (typically >200 nm thick). Thus it is important to understand the electrocaloric response in such materials and to identify new pathways to improve their performance. Recently there has been increasing attention on ferroelectric thin film heterostructures in which the properties can be tuned through epitaxial strain, composition, temperature, electric field, and more.⁴ Theoretical studies have investigated the effects of strain^{5,6} and electric field^{7,8} on electrocaloric properties of monodomain ferroelectric films and suggest that tensile strained, Ti-rich PZT films should possess excellent electrocaloric properties.

Such monodomain states, however, are stable only in ultrathin films,^{9,10} and the thicker films that are technologically important possess a polydomain structure¹¹⁻¹³ with polarized domains separated by planar domain walls. It is known that the presence of domain walls can significantly affect the dielectric and piezoelectric properties.^{14,15} Thus, it is important to understand the effect of domain structures on the electrocaloric properties since the presence of large electric fields during this process can further enhance domain wall mobility. In this paper, we use a Ginzburg-Landau-Devonshire (GLD) theory of polydomain structures and extend it to finite electric fields to study the electrocaloric properties of Ti-rich PZT thin films as a function of electric field, temperature, composition, and epitaxial thin film strain.

We use the Gibbs free energy density (\tilde{F}) for a 001-oriented epitaxial ferroelectric thin film on a cubic paraelectric substrate to obtain the electrocaloric properties. In the crystallographic reference frame (x_1, x_2, x_3) of the paraelectric phase, \tilde{F} can be written in terms of the polarization P_i , electric fields E_i , and stresses σ_i as¹⁵

$$\begin{aligned} \tilde{F} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) \\ & + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_3^2P_1^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{112}\{P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)\} \\ & + \alpha_{123}P_1^2P_2^2P_3^2 + \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2) \\ & + s_{12}(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1) + \frac{1}{2}s_{44}(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) \\ & - \frac{1}{2}\epsilon_0(E_1^2 + E_2^2 + E_3^2) - E_1P_1 - E_2P_2 - E_3P_3. \end{aligned} \quad (1)$$

The primary stiffness coefficient (α_1) is given by the Curie-Weiss law as $\alpha_1 = \frac{T-T_c}{2\epsilon_0C}$; α_{ij} and α_{ijk} are the higher order stiffness coefficients, s_{ij} are the elements of the elastic compliance tensor at constant polarization, C is the Curie constant, and T_c is the ferroelectric Curie temperature. The phenomenological coefficients for the PZT system were obtained from Refs. 16 and 17. The free energy is supplemented by the relevant mechanical boundary conditions for the mono/polydomain phases¹⁵ and is minimized to obtain the

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equilibrium mono/polydomain structure as a function of misfit strain, composition, temperature, and electric field.

For Ti-rich PZT ($0.65 \leq x \leq 1$) thin films at 300 K and for the range of electric fields investigated here ($10 \text{ kV/cm} < E < 1000 \text{ kV/cm}$), the equilibrium domain structure can possess any of three different phases as a function of strain and composition: one monodomain (c phase) and two polydomain ($c/a/c/a$ and $a_1/a_2/a_1/a_2$) phases.¹⁴ The monodomain c phase is stable at compressive strains as in monodomain films.¹⁸ However, near zero strain, the r phase obtained in monodomain GLD models¹⁸ is replaced by the polydomain $c/a/c/a$ phase with 90° domain walls separating the various domains. At large tensile strains, the out-of-plane polarization vanishes, and the polydomain $a_1/a_2/a_1/a_2$ phase results at equilibrium. We note that within the composition range of interest ($0.65 \leq x \leq 1$) the PZT undergoes a proper ferroelectric transition from tetragonal to cubic phases at the T_c .

The electrocaloric and pyroelectric coefficients of a ferroelectric material are related by a Maxwell's relations as

$$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E. \quad (2)$$

The electrocaloric change in temperature upon application of an electric field can thus be calculated as⁵⁻⁸

$$\Delta T = -T \int_{E_a}^{E_b} \frac{1}{C_E(T, E)} \left(\frac{\partial P}{\partial T}\right)_E dE, \quad (3)$$

where $C_E(T, E)$ is the heat capacity per unit volume at constant electric field, $\left(\frac{\partial P}{\partial T}\right)_E$ is the pyroelectric coefficient of the ferroelectric, and $\Delta E = E_b - E_a$ ($E_a = 10 \text{ kV/cm}$ throughout this paper) is the range of the applied electric field. In the temperature range of interest (300-550 K), the absolute value of the heat capacity is approximately constant with composition for Ti-rich films at $2.7 \times 10^6 \text{ J/m}^3\text{K}$.⁸ Since the peak in the heat capacity associated with the polarization transition is $\sim 10\%$ of the background,^{1,8} we neglect the contribution of the polarization to the heat capacity in our calculations.

Among the three stable phases, the c phase and the $c/a/c/a$ phase possess a finite electrocaloric temperature change for applied fields along [001]. The $a_1/a_2/a_1/a_2$ phase has a vanishing electrocaloric response due to zero polarization in the same direction. In contrast to monodomain 1D GLD models which suggest an increasing electrocaloric performance with increasing tensile strain due to a reduced ferroelectric transition temperature, in a polydomain system the transition to an in-plane polarized state completely negates the effect of any electric field in the out-of-plane direction for films with large tensile strains. Thereby reducing the electric field induced temperature change to zero.

For the monodomain c phase, the electrocaloric coefficient is calculated from Eq. (2) as

$$\left(\frac{\partial S}{\partial E}\right)_T = \frac{-\alpha_0}{4P_3 \sqrt{(\alpha_{33}^*)^2 - 3\alpha_{111}\alpha_3^*}} \quad (4)$$

where $\alpha_{33}^* = \alpha_{11} + \frac{Q_{12}^2}{s_{11}+s_{12}}$, $\alpha_3^* = \alpha_1 - \frac{2S_m Q_{12}}{s_{11}+s_{12}}$, and S_m is the misfit strain. For the $c/a/c/a$ domain structure, the average out-of-plane polarization is $\langle P_3 \rangle = \phi' P_3'$, where ϕ' is the fraction of c domains. Thus, the electrocaloric coefficient can be calculated as $\left(\frac{\partial S}{\partial E}\right)_T = \phi' \frac{dP_3'}{dT} + P_3' \frac{d\phi'}{dT}$. The first term represents the *intrinsic* electrocaloric response due to a temperature dependent change in the magnitude of the polarization within the domains. Since the equilibrium c domain population ϕ' depends on temperature, we also have an *extrinsic* contribution¹⁹ to the primary electrocaloric coefficient as shown in the second term. The polydomain thermodynamic theory enables us to calculate the *intrinsic* and *extrinsic* contributions as a function of the applied electric field. For the $c/a/c/a$ phase, the equilibrium domain fraction ϕ' at finite electric fields is obtained as

$$\phi' = 1 - \frac{(s_{11} - s_{12})(S_m - Q_{12}P_3^2)}{s_{11}(Q_{11} - Q_{12})P_3^2} + \frac{E_3(s_{11}^2 - s_{12}^2)}{2s_{11}(Q_{11} - Q_{12})^2 P_3^3}, \quad (5)$$

where Q_{ij} are the electrostrictive coefficients. Thus, the extrinsic contribution to the electrocaloric effect can be calculated as $d\phi'/dT$. Using such a GLD model, we have investigated the adiabatic temperature change for a $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ film with $\Delta E = 100 \text{ kV/cm}$ (2 V drop across a 200 nm thick film) at 300K [Fig. 1]. As shown in the figure, when excluding the effect of domain walls, the *intrinsic* electrocaloric effect is maximized at mild compressive strains corresponding to the monodomain (c) to polydomain ($c/a/c/a$) transition. Including the effects of temperature and field on the motion of domain walls in the models shifts the maximum response to a critical tensile strain that corresponds to the disappearance of the out-of-plane polarization (i.e., the boundary between $c/a/c/a$ and $a_1/a_2/a_1/a_2$ phases). The motion of the domain walls alters the fraction of the 001-oriented domains in the $c/a/c/a$ phase and, in turn, the electrocaloric coefficient (Eq. (5)). Such extrinsic effects are observed to significantly alter the total electrocaloric response, and, in general, the extrinsic contribution adds to and subtracts from the intrinsic electrocaloric effect at mild tensile and compressive strains, respectively. The actual magnitude and sign of the extrinsic effect are a result of interplay between the strain and electric field dependent terms in Eq. (5).

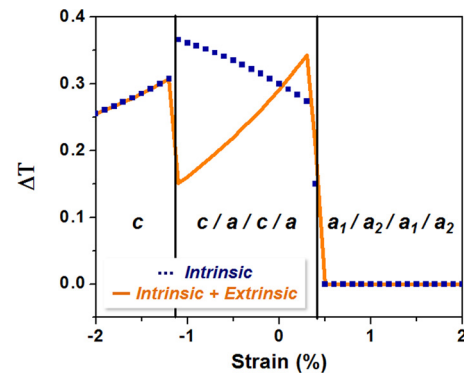


FIG. 1. (Color online) Dependence of the electrocaloric temperature change (ΔT) with epitaxial strain for $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films with $\Delta E = 100 \text{ kV/cm}$ at 300 K. The solid line indicates the total ΔT (intrinsic + extrinsic) while the dotted line shows ΔT assuming zero extrinsic contribution.

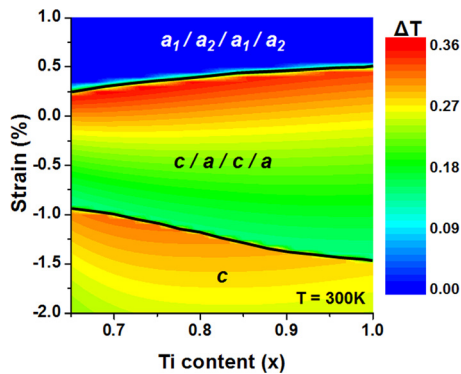


FIG. 2. (Color online) Electrocaloric temperature change as a function of strain and composition for the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ thin film system for $0.65 \leq x \leq 1.0$ at 300 K for the various equilibrium polydomain states with $\Delta E = 100$ kV/cm.

Upon a complete optimization of the electrocaloric response including the effect of the domain walls for $0.65 \leq x \leq 1$, a complete picture of the electrocaloric properties emerges [Fig. 2]. The electrocaloric temperature change is seen to be high along the two polarization phase transitions due to the large pyroelectric coefficients corresponding to these transitions. The maximum electrocaloric effect is obtained along the phase boundary between the $c/a/c/a$ and $a_1/a_2/a_1/a_2$ phases at small tensile strains. The maximum ΔT for $\Delta E = 100$ kV/cm at 300 K is $\Delta T = 0.36$ K at $x = 0.73$. With high electric fields corresponding to $\Delta E = 1000$ kV/cm (20 V drop across a 200 nm thick film), adiabatic temperature changes as large as $\Delta T = 2.9$ K can be obtained at 300 K in PZT films with $x = 0.73$ and $S_m = 0.3\%$. This can be further improved by moving slightly closer to the ferroelectric transition temperature of PZT. At a temperature of 500 K, a temperature change of ~ 6 K can be obtained in a $\text{PbZr}_{0.27}\text{Ti}_{0.73}\text{O}_3$ thin film at an applied field of ~ 1000 kV/cm [Fig. 3]. This temperature is still significantly less than the Curie temperature of this composition of PZT at this electric field; therefore, the ferroelectric breakdown strength should be high and such temperature changes feasible. Thus, large electrocaloric responses can be obtained at temperatures much below the Curie temperature by harnessing extrinsic contributions to the electrocaloric effect.

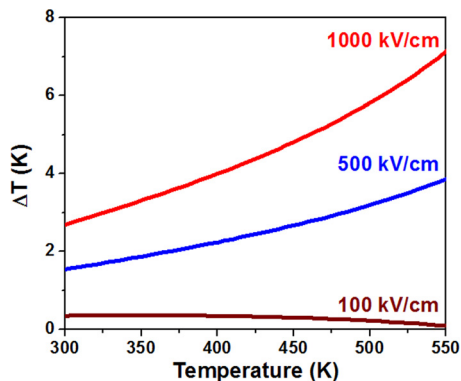


FIG. 3. (Color online) Dependence of the electrocaloric temperature change (ΔT) with temperature for $\text{PbZr}_{0.27}\text{Ti}_{0.73}\text{O}_3$ thin films with misfit strain ($S_m = 0.3\%$) and $E_a = 10$ kV/cm for various values of ΔE .

We note that these calculations assume that the domain walls are free to move without any energy barriers. In reality lattice imperfections or defects can pin domain walls, hinder their movement, and reduce the extrinsic contribution.^{20,21} The extrinsic contribution to electrocaloric response will be zero in the case of completely pinned domain walls, and our calculation, in effect, places an upper bound on the extrinsic contribution to the electrocaloric properties. Recent experimental results have demonstrated that while it is challenging to fabricate defect-free ferroelectric films, advances in thin film growth techniques can yield low defect density films, a few hundred nanometers in thickness, that exhibit significant extrinsic contributions to the dielectric response.²² In effect, this model shows the power of extrinsic contributions in enhancing electrocaloric response and provides further motivation to improve existing thin film growth processes.

Large electrocaloric effects have been observed in ferroelectric thin films, but operating such system in close proximity to the Curie temperature under the large applied electric fields necessary for such effects is technically difficult in films. Thus alternative routes to achieve high performance materials are needed. Recent work has demonstrated the importance of strain (due to thermal expansion mismatch between the film and substrate) to tune the temperature of maximum electrocaloric response in polycrystalline samples of various ferroelectric materials.²³ By adjusting the growth temperature, they show that the thermal stresses can be tuned to give large electrocaloric response near room temperature. Our study shows another pathway, in which by leveraging extrinsic factors such as domain wall displacement in ferroelectric thin films one can significantly alter the intrinsic response and obtain large electrocaloric responses in strain engineered epitaxial thin films at $T \ll T_c$. This should provide experimentalists with a new mechanism to engineer ferroelectric thin films with the excellent electrocaloric properties at any desired temperature.

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