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The depolarizing field in ultrathin electrocalorics: an enemy or ally?

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Abstract

Ferroelectric thin films are considered among top candidates for room temperature electrocaloric materials as they exhibit excellent electric properties and allow application of record high electric fields. At the same time downsizing of ferroelectric electrocalorics brings about an unwanted but unavoidable depolarizing field that could critically alter or even destroy the films' electrocaloric properties. We use atomistic first-principles-based computational approach that does not rely on the use of Maxwell relations: (i) to reveal the critical role of the depolarizing field on the electrocaloric properties of ferroelectric ultrathin films; (ii) to demonstrate the contribution of nanodomains to the electrocaloric effect in such films; (iii) to revisit the potential limitations of the indirect approach to study electrocaloric effect in nanoscale ferroelectrics.

Electrocaloric effect (ECE) has received a lot of attention [1–8] following the discovery of giant ECE in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ thin films [1]. This effect is defined as a reversible change in temperature upon adiabatic application or removal of an electric field. The effect is very promising for near room temperature solid state refrigeration and integrated circuit cooling [3–5]. Ferroelectric (or generally polar) ultrathin films are particularly attractive for practical devices as they allow application of a much larger electric fields [1, 2]. At the same time scaling down polar materials brings about the undesirable but unavoidable companion - the depolarizing field. Such field appears in response to partial surface charge compensation and is known to have a dramatic effect on the electric properties and domain patterns in ferroelectric thin films [9–12]. In particular, it can alter the state of ferroelectric ultrathin films in two different ways. A weak depolarizing field (good surface charge compensation) reduces the film’s polarization while preserving the single domain state. A strong depolarizing field (poor surface charge compensation) causes the film to transition from a monodomain to a poly- or nanodomain state that eliminates the depolarizing field. Interestingly, despite the principal role it plays in the properties of ferroelectric thin films, the depolarizing field effect on the films electrocaloric response is largely unknown. In Ref.13 a phenomenological approach in combination with Maxwell relations was used to predict that the depolarizing field is detrimental to the electrocaloric properties of strained single domain BaTiO_3 films. The effect of (nano)domains on the electrocaloric properties was investigated in Ref.14 using Ginzburg-Landau-Devonshire thermodynamic model in combination with Maxwell relations. It was concluded that the domain wall motion could either enhance or reduce the ECE depending on the residual stress in the sample. In Ref.15 a phase-field approach was utilized to predict a large enhancement of ECE by means of domain engineering.

In the light of the recent studies one may wonder just how fruitful the downsizing of

ferroelectric electrocalorics really is. Will the detrimental influence of the depolarizing field destroy the gain in the ECE due to the application of much larger electric fields? Or could we actually take advantage of the depolarizing field by training nanodomains to enhance the ECE as proposed in Refs.[14, 15]? The latter possibility is particularly appealing but also controversial. Indeed, we learned to believe that the domain wall motion is irreversible and therefore its contribution to the ECE is expected to be detrimental. Do the recent findings mean that the nanodomain dynamics is fundamentally different from the dynamics of larger domains [16] and could contribute constructively to the ECE? Or could it be that the use of the indirect approach based on Maxwell relations to study ferroelectric *nano*structures should be revisited?

To address these questions we study the ECE in ferroelectric partially compensated ultrathin films using atomistic first-principles-based approach that does not require the use of Maxwell relations (direct approach). The aims of this study are: (i) to reveal the critical and multifold role of the depolarizing field in the electrocaloric properties of ferroelectric ultrathin films; (ii) to demonstrate the contribution of nanodomains to the ECE; (iii) to revisit the limitations of the indirect approach based on Maxwell relations to study the ECE in nanoscale ferroelectrics; (iv) to address the aforementioned controversies.

We simulate a 4.8 nm thick PbTiO_3 film grown on a SrTiO_3 substrate along [001] pseudocubic direction. The model resembles closely PbTiO_3 films synthesized experimentally [17–19]. PbTiO_3 bulk has been previously predicted to exhibit a giant intrinsic ECE of up to 35 K in the vicinity of its Curie temperature [20]. The film is modeled by a 12x12x12 supercell that is periodic along [100] and [010] pseudocubic directions, which are its in-plane directions. This supercell size was chosen to accommodate the equilibrium domain patterns [16]. Some representative results were cross-checked using 48x48x12 supercell. The total en-

ergy of this supercell is given by the effective Hamiltonian [21] with the parameters derived from first-principles [22]. This Hamiltonian correctly predicts a variety of structural and thermodynamical properties of PbTiO_3 which include the polarization, Curie point, tetragonality, and some others. The SrTiO_3 substrate is simulated by compressing the simulation supercell by -0.65% using the approach of Ref.23. The partial surface charge compensation due to (extrinsic) free carriers is modeled as proposed in Ref.[24]. Such technique correctly predicts domain patterns and electric response of partially compensated films [25, 26]. The quality of charge compensation is given in percentage of total surface charge screened, and is described by a parameter β . $\beta = 100\%$ and $\beta = 0\%$ correspond to a fully compensated and an uncompensated surface charge, respectively. Prior to ECE simulations the films were annealed from 1200 K to 5 K in steps of 5 K using the canonical Monte Carlo simulations. Thus equilibrated films were used in direct simulations of the ECE in the framework of adiabatic Monte Carlo approach proposed in Refs.27 and 28. Technically, the electric field directed along the growth direction was first applied and then removed very slowly at a rate of 50 V/m per one Monte Carlo sweep to ensure reversibility. The electrocaloric temperature was computed as a function of the applied field.

We begin by analyzing the equilibrated zero-field films that were obtained from the annealing simulations. In agreement with the previous studies [9, 29] we found that a good surface charge compensation ($\beta > 94\%$ in our case) results in formation of single domain structures with polarization pointing along the growth direction. The Curie point for such films decreases with decreasing β (see Fig.1). For well compensated films ($\beta > 95\%$) the Curie point exceeds its bulk value owing to the stabilizing role of the epitaxial compressive strain. In case of poor charge compensation ($\beta \leq 93\%$) we observe formation of nanostripe domains in agreement with earlier experimental [10, 19] and computational [23] studies.

Example of the nanostripe domain pattern is given in the inset to Fig.1. The width of the nanodomains is in excellent agreement with the experimental measurements for F_α phase [10]. For films with nanodomains the Curie temperature is smaller than in the bulk and decreases slightly with β . At the critical value of surface charge compensation ($\beta = 94\%$) we find a competition between the single domain and nanodomain states that leads to a coexistence of these states. For temperatures between 275 K and 580 K the nanodomain state has a slightly lower free energy. For all the other temperatures below the Curie point the monodomain state is energetically slightly more favorable.

Next we focus on the effect of partial charge compensation on the electrocaloric properties of PbTiO_3 films. Fig.2(a)-(c) shows the electrocaloric change in temperature as a function of the applied electric field for a few representative initial temperatures, T_0 , and screening parameter, β . The data for bulk unstrained PbTiO_3 are included for comparison. To aid in the interpretation of the electrocaloric data we also simulated the electric hysteresis (see panels (d)-(f)). These simulations were carried out using the effective Hamiltonian in the framework of classical Molecular Dynamics that incorporates temperature control and coupling with the electric field to model an isothermal application of an *ac* electric field. Note that our computational data are in qualitative agreement with the experimental measurements on the polydomain superlattices composed of ferroelectric PbTiO_3 and paraelectric SrTiO_3 [25]. For the highest reported T_0 of 600 K well compensated films ($\beta > 95\%$) exhibit a ferroelectric phase, while others exist in a paraelectric phase. The electrocaloric change in temperature, ΔT , responds strongly to the variation in charge compensation. However, the effect is highly nonlinear owing to the complex interplay between the direct influence of the depolarizing field and its indirect contribution through the change in T_C . In all cases we observe a suppressed ECE as compared to the effect in the unstrained bulk.

Fig.2 (b) and (e) shows similar data for a reduced temperature of 400 K. Here we find poorly compensated films ($\beta < 94\%$) in a nanodomain state. Interestingly, these films now exhibit a few notable features. First of all, their ΔT is no longer monotonic and demonstrates pronounced anomalies at the fields associated with domain restructuring including the transition between the nanodomain and single domain states. Secondly, the ECE in the nanodomain state itself is negligible. Thirdly (and surprisingly) we find that the electrocaloric change in temperature is fully reversible, despite the presence of the domain wall motion that is usually irreversible. The origin of such an unusual response can be traced to polarization vs electric field loops, or $P(E)$ loops, reported in Fig.2(e). Here we find that the field induced transition into a monodomain state for films with $\beta < 94\%$ is rather peculiar as it occurs with very little hysteretic losses. We attribute this finding to the unusual dynamics of nanodomains [16] and proximity to the transition temperature. More precisely, Ref.16 predicted that the effective mass of the nanodomain walls decreases with the film's thickness causing a transition into qualitatively different type of motion that could potentially be reversible. On the other hand, the proximity to the transition temperature is associated with shrinking of the hysteresis loop area that signals onset of reversible behavior.

As for the films with the critical charge compensation of 94%, at first they appear to have the best electrocaloric response even as compared to bulk. At the same time some of the electrocaloric ΔT is irrecoverable as evident from the finite value of ΔT upon removal of the electric field. This is the consequence of the substantial electric hysteresis present in the $P(E)$ curve in Fig.2(e). The reason why this film has the tendency for an improved electrocaloric performance will be discussed later.

Fig.2 (a) and (d) shows some representative data for the initial temperature of 200 K that is well below the Curie point. Here we find significantly lower ΔT . The nanodomain

films now exhibit a substantial electric hysteresis that leads to an irreversible heating of the simulated sample (see large ΔT after the electric field is removed). As a result the electrocaloric properties of poorly compensated films are almost entirely degraded. Interestingly, we find the largest response in films with a critical charge compensation of 94%. The response exceeds even the bulk values. To trace the origin of such an unexpected enhancement of the ECE we recall that such films exhibit a competition between and/or coexistence of the nanodomain and monodomain phases. The resulting frustration is likely to increase the entropy of the state and, therefore, to enhance the ECE. To test this hypothesis we turn to one of the Maxwell relations that predicts that the isothermal entropy change due to the electric field application is equal to the derivative of polarization with respect to temperature: $(\frac{\partial S}{\partial E})_T = (\frac{\partial P}{\partial T})_E$, where S , E , P , and T are the entropy, electric field, polarization, and temperature, respectively. The temperature evolution of the polarization for the film with critical charge compensation is given in Fig.3. The data were obtained from a depolarization of initially polarized supercell and correspond to zero electric field. Our computations predict a transition from a monodomain phase to a polydomain phase with nanobubbles [30] at 230 K, followed by a transition into a polydomain phase with nanostripes at 275 K, which finally transitions into a paraelectric phase at 580 K. Such sequence of phase transitions results in abrupt polarization changes in the temperature range of 230-275 K, and, in turn, leads to a large derivative $(\frac{\partial P}{\partial T})_E$. The Maxwell relation predicts that in this temperature range the isothermal entropy change (as well as the ECE) is also large. For comparison Fig.3 also gives data for the temperature evolution of polarization in bulk PbTiO_3 . In the temperature range of 230-275 K the polarization change in bulk is rather small, which explains the observed enhancement of ECE in a film with critical surface charge compensation. The finding of phase competition and resultant abrupt polarization changes also elucidates

the tendency of this film to exhibit large ECE in a nanodomain state at $T_0 = 400$ K (see panel (b) of Fig.2). It is important to note that in real samples point defects could critically influence both the phase competition and the mobility of nanodomains. As a result some variations in the temperature interval and charge compensation percentage associated with the enhanced ECE are expected.

To gain a further insight into the manifold effect of the partial charge compensation on the ECE in ferroelectric ultrathin films we plot the electrocaloric ΔT as a function of initial temperature in Fig.4. The data suggest that: (i) in single domain films and films above the Curie point the depolarizing field significantly reduces the ECE in agreement with the phenomenological result of Ref.13; (ii) films with nanodomains either exhibit a small ECE or lose their electrocaloric properties altogether to the irreversible nanodomain motion; (iii) in (monodomain) films where partial charge compensation creates frustration due to phase competition the ECE is enhanced (see data for $\beta = 94\%$ and T_0 below 250 K).

Our findings for the ultrathin films suggest revisiting the potential limitations of the indirect approach to study electrocaloric effect in nanoscale ferroelectrics. Ferroelectric nanostructures are prone to nanodomain formation whose motion is generally irreversible. Therefore, the use of indirect approach that implicitly assume reversibility to study such structures could be erroneous unless a special care is taken to ensure reversibility. Direct approaches to the ECE measurements [31] and simulations [27, 32] appear to be more suitable for studying ECE in ferroelectric nanostructures.

In summary, we used atomistic first-principles-based direct approach to study the effect of partial charge compensation on the ECE in epitaxial ultrathin ferroelectric films. Our computations predict that the residual depolarizing field could play a dual role in the electrocaloric properties of these films. In films where surface charge is compensated well enough

to allow for a monodomain state formation the depolarizing field causes a significant reduction of the electrocaloric change in temperature. In films where the depolarizing field led to the nanodomain formation the electrocaloric response is either substantially reduced or completely lost to the irreversible domain wall motion. In all these cases the depolarizing field has a negative effect on the electrocaloric properties. On the other hand, the depolarizing field is predicted to enhance the ECE response in ultrathin films when it creates a competition between the monodomain and nanodomain states. We believe that our findings provide a comprehensive view of the role of partial charge compensation in electrocaloric properties of ferroelectric ultrathin films and could potentially open up more ways to optimized cooling applications.

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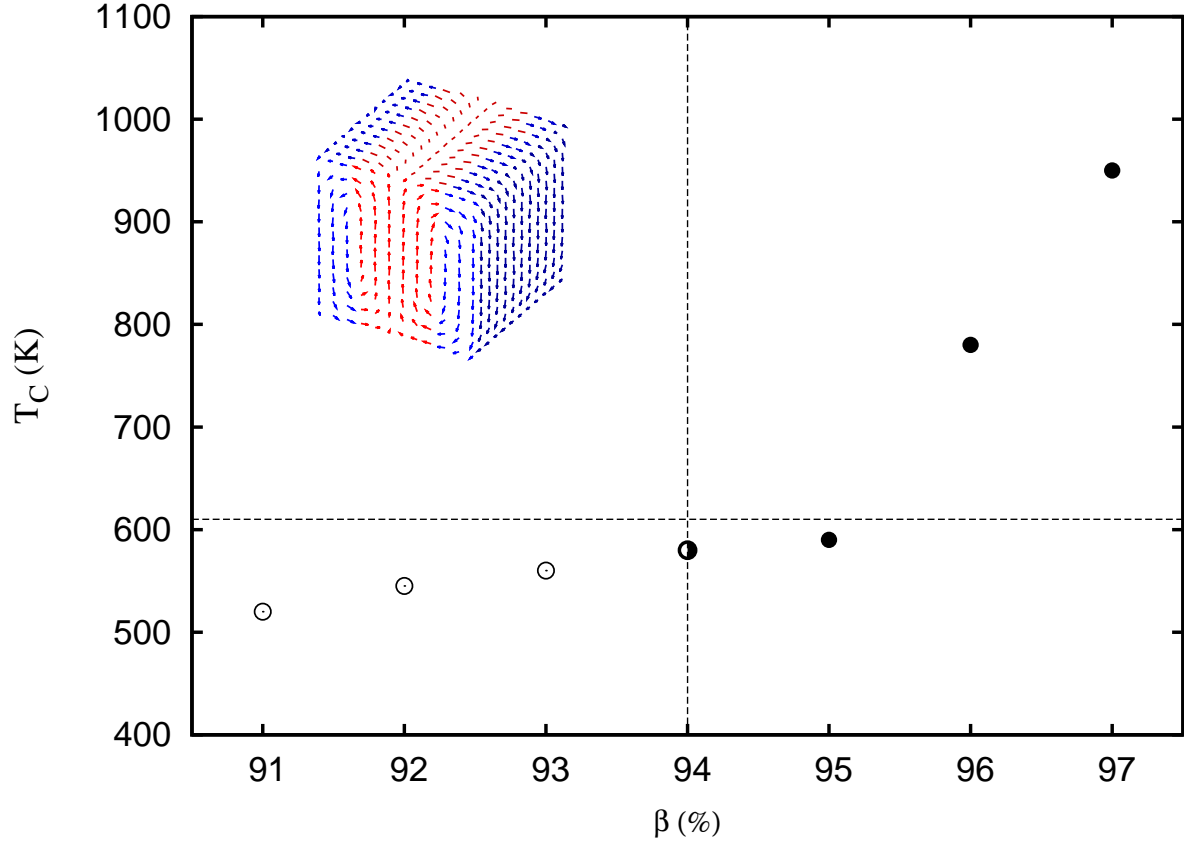


FIG. 1. (Color online). Dependence of the Curie temperature on the surface charge compensation, β . Filled (open) symbols indicate data for the films which undergo transition into a single domain (nanostripe domains) state. Half filled symbol indicate the data for the films with competing monodomain and nanodomain states. The horizontal line gives the computational Curie point for unstrained bulk PbTiO_3 . The vertical line shows the boundary between the monodomain and nanostripe domains phases. The inset gives a snapshot of a dipole pattern in the simulation supercell for a film with nanostripe domains. Red and blue color shows dipoles pointing “up” and “down”, respectively.

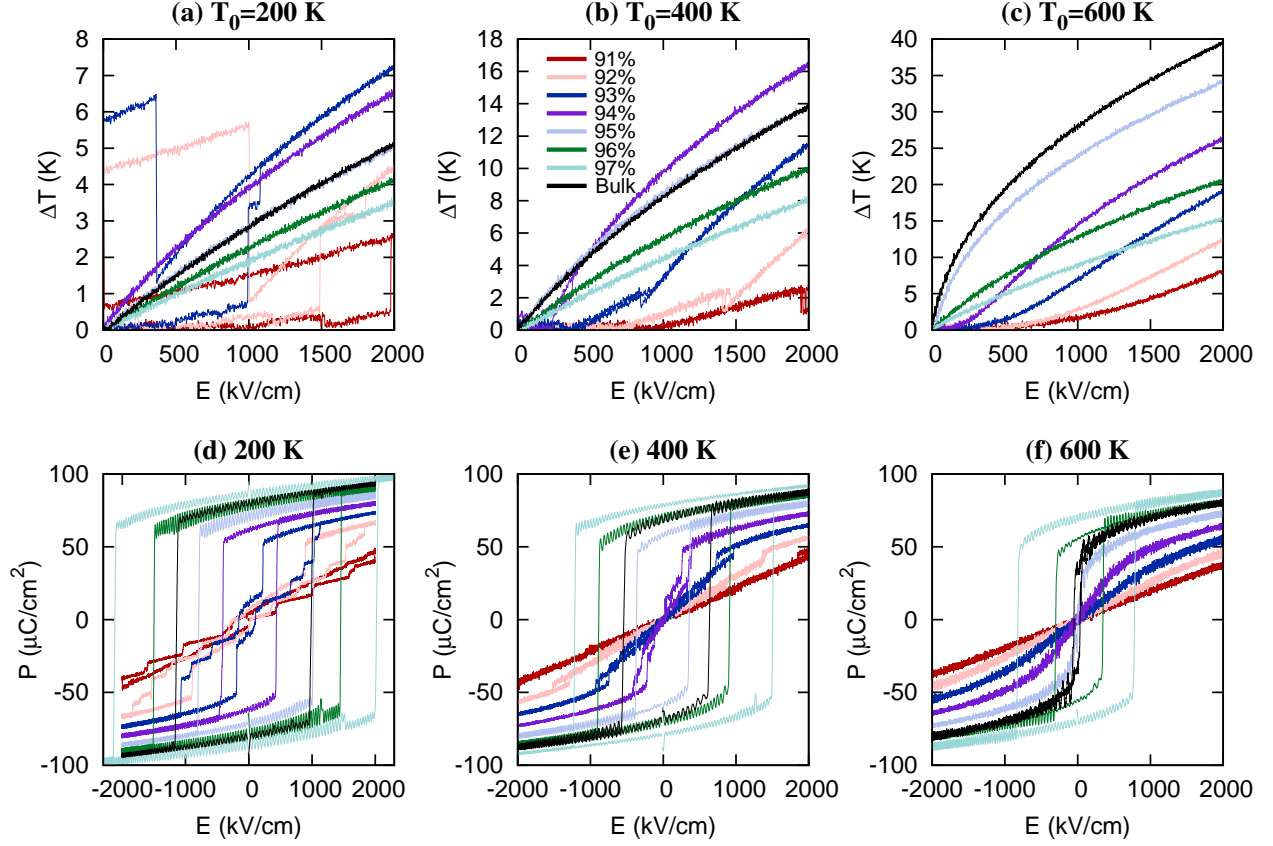


FIG. 2. (Color online). Panels (a)-(c) give the electrocaloric change in temperature as a function of the applied electric field for three different initial temperatures, T_0 . Panels (d)-(f) show the polarization as a function of the electric field as obtained in isothermal simulations under an *ac* electric field of 1 GHz frequency.

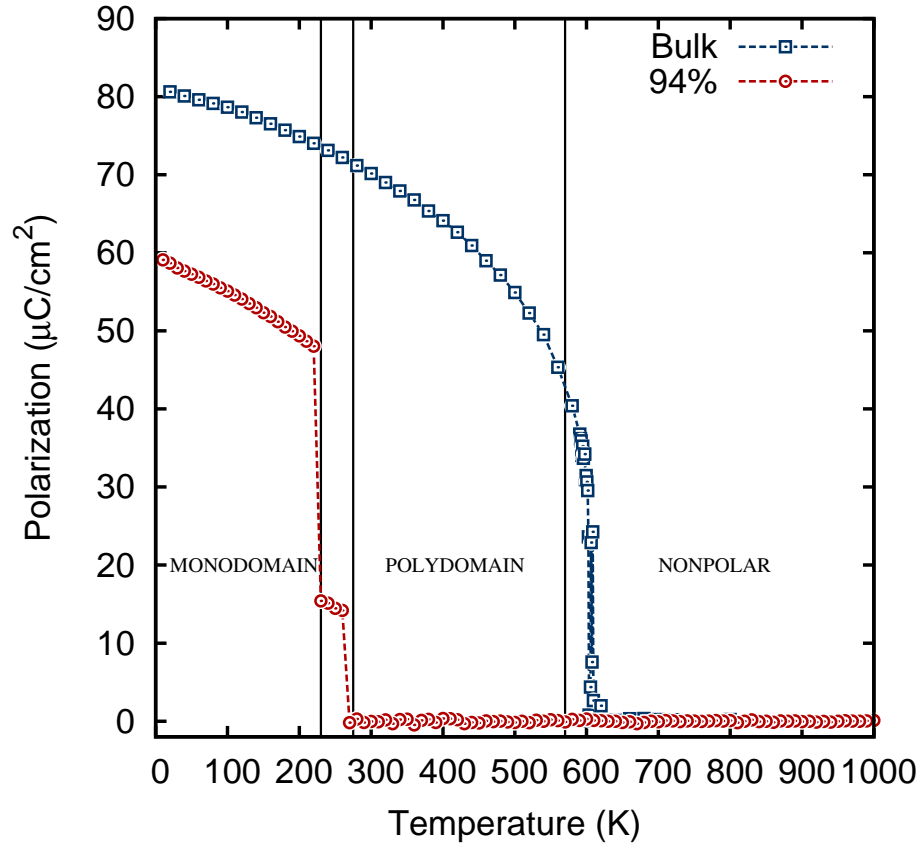


FIG. 3. (Color online). The temperature evolution of polarization in film with critical charge compensation of 94% and bulk. The vertical lines separate regions with different phases in the film.

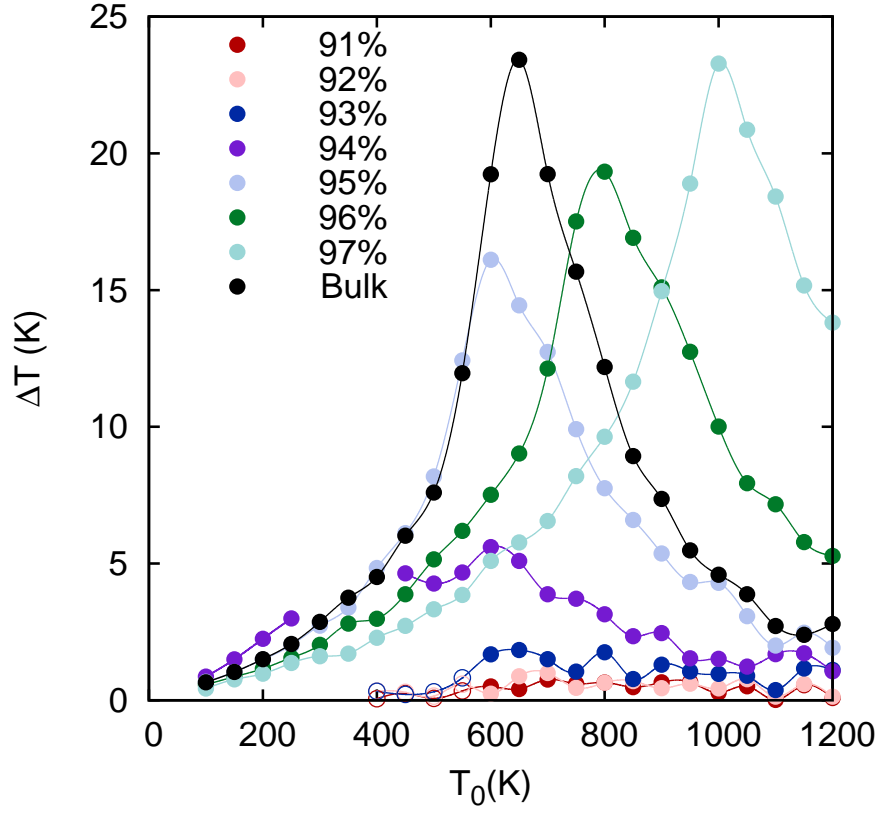


FIG. 4. (Color online). The change in temperature in response to the electric field of 500 kV/cm as a function of initial temperature. Filled (open) symbols indicate data for the films which undergo transition into a single domain (nanostripe domains) state. Only reversible ΔT are reported. For the film with critical charge compensation of 94% and in the temperature range of 450-550 K the supercell was polarized prior to ECE simulations.