Elastocaloric Effect in $PbTiO_3$ Thin Films with 180° Domain Structure: A Phase Field Study *

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The elastocaloric effect of $PbTiO_3$ thin films with 180° domain structure is studied using the phase field method. The influence of external stress σ_{33}, misfit strain u_m and domain wall energy on the adiabatic temperature change (ΔT_σ) at room temperature are carried out. The calculation results indicate that $|\Delta T_\sigma|$ increases as $|\sigma_{33}|$ or $|u_m|$ increases. The largest ΔT_σ value of $-7.8\,K$ is obtained at $\sigma_{33} = 2\,GPa$ and $u_m = -0.02$. Furthermore, the domain switching behaviors under different gradient coefficients are different, and finally affect the elastocaloric effect in PTO thin films. These results could provide a guide to choose the substrate and the preparation process in experiments.

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The caloric effects of ferroelectric thin films have attracted a great deal of attention since the giant electrocaloric effect was reported.[1−3] Most recently, a giant elastocaloric effect that occurs under the stress-induced phase transformation in ferroelectrics has been reported in $BaTiO_3$ (BTO) ultrathin films, which further expands the application of ferroelectric thin films as solid-state devices.[4,5]

Similar to the electrocaloric effect, the elastocaloric effect of ferroelectric thin films is closely associated with the domain structure, which is naturally linked to the polarization change.[6,7] It is well known that the caloric effect of ferroelectric materials is closely related to the domain structure. It has been found that the electrocaloric effect can be greatly enhanced at the proper volume fraction of *c*-domains in the field direction of $PbTiO_3$ (PTO) thin films.[8] Karthik *et al.* found that the electrocaloric effect in an epitaxial BTO thin film with the poly-domain $ca_1/ca_2/ca_1/ca_2$ is a phase larger than that in the monodomain *c* phase.[9] Our previous research predicted that 90° and 180° domain walls could make great contributions to the electrocaloric effect of ferroelectric thin films.[10,11] Moreover, the influences of the 90° domain on the elastocaloric effect in a two-dimensional PTO have been studied.[12] However, it will be of interest to investigate the elastocaloric effect of the thin film including substrate under the practical conditions. It is reported that the misfit strain induced by the substrate could strongly affect the properties of ferroelectric thin films.[13,14] Furthermore, the misfit strain could affect the electrocaloric effect in epitaxial thin films of the prototypical ferroelectric BTO and related materials.[15,16] Interestingly, it was demonstrated that the elastocaloric effect of BTO thin films has responses to the epitaxial strain.[17] Therefore, it is important to study the effects of misfit strain on the elastocaloric effect of ferroelectric thin films, and the domain wall energy plays an important role in the domain structure of thin films.[18]

In this Letter, the phase field simulation and thermodynamics analysis are developed to study the influence of misfit strain and gradient energy on the elastocaloric effect of PTO thin films with 180° domain structure at room temperature.

To study the elastocaloric effect of the PTO ferroelectric thin film with 180° domain structure, the phase field is applied to obtain the domain structure where the spontaneous polarization $\boldsymbol{P} = (P_1, P_2, P_3)$ is chosen as the order parameter. Then, the domain structure of the PTO thin film can be obtained by solving the time-dependent Ginzburg–Landau (TDGL) equation[19]

$$\frac{\partial P_i(r,t)}{\partial t} = -L\frac{\delta F}{\delta P_i(r,t)}, \quad i = 1,2,3, \tag{1}$$

where $\boldsymbol{r} = (x_1, x_2, x_3)$ denotes the spatial vector, t denotes the time, and P_i, L and F represent the spontaneous polarization, kinetic coefficient and the total free energy, respectively. It is crucial to define the expression of the total free energy. For the thin film, the expression for the total free energy contains four parts: the bulk free energy F_L, the domain wall energy F_G, the electric energy F_{ele}, and the elastic energy F_{ela},[20]

$$F = F_L + F_G + F_{ele} + F_{ela}. \tag{2}$$

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The bulk free energy described by a six-order Landau–Devonshire polynomial has the form[18–21]

$$\begin{aligned} F_{\rm L}(P_i) =& \alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4) \\ &+\alpha_{12}(P_1^2P_2^2+P_2^2P_3^2+P_1^2P_3^2) \\ &+\alpha_{111}(P_1^6+P_2^6+P_3^6)+\alpha_{112}[P_1^4(P_2^2 \\ &+P_3^2)+P_2^4(P_1^2+P_3^2)+P_3^4(P_1^2+P_2^2)] \\ &+\alpha_{123}P_1^2P_2^2P_3^2, \end{aligned} \tag{3}$$

where α_{ij} and α_{ijk} are phenomenological coefficients. Based on the Curie–Weiss law, $\alpha_1 = (T-T_0)/2\varepsilon_0 C_0$, where T and T_0 are the temperature and the Curie temperature, respectively, $\varepsilon_0 = 8.85\times10^{-12}\,{\rm Fm}^{-1}$ is the dielectric constant of the vacuum, and C_0 represents the Curie constant.

The domain wall energy originates from the spontaneous polarization gradient energy and has the invariant form of

$$F_{\rm G} = \frac{1}{2}g_{ijkl}(\partial P_i/\partial x_j)(\partial P_k/\partial x_l), \tag{4}$$

where g_{ijkl} is the gradient energy coefficients, and $P_{i,j} = \partial P_i/\partial x_j$ represents the derivative of the polarization components.

The electric energy is comprised of an electrostatic field $E_i^{\rm d}$, which is caused by the depolarization field and an external electric field. The value of $E_i^{\rm d}$ is obtained by the negative gradient of the electrostatic potential $E_i^{\rm d} = -\varphi_i$, where the electrostatic potential obtained by solving the electrostatic equilibrium equation $\nabla\cdot(-\varepsilon_0\kappa\nabla_\varphi + P) = 0$.

The spontaneous strains are associated with spontaneous polarizations. The spontaneous eigenstrains are linked to the spontaneous polarization components in the form of $\varepsilon_{ij}^0 = Q_{ijkl}P_kP_l$, where Q_{ijkl} are the electrostrictive coefficients. When an externally homogeneous stress σ_{kl} is applied on the film, the elastic e_{ij} can be calculated by[21]

$$e_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^0 + S_{ijkl}\sigma_{kl}, \tag{5}$$

where ε_{ij} is the total strain, and S_{ijkl} represents the elastic compliance tensor. Finally, the elastic energy under the cubic approximation is given by

$$\begin{aligned} F_{\rm ela} =& \frac{1}{2}C_{11}(\varepsilon_{11}^2+\varepsilon_{22}^2+\varepsilon_{33}^2) \\ &+C_{12}(\varepsilon_{11}\varepsilon_{22}+\varepsilon_{22}\varepsilon_{33}+\varepsilon_{33}\varepsilon_{11}) \\ &+2C_{44}(\varepsilon_{12}^2+\varepsilon_{23}^2+\varepsilon_{13}^2), \end{aligned} \tag{6}$$

where C_{11}, C_{12} and C_{44} are the second order elastic stiffness tensors. When the substrate is considered, the misfit strain is part of the total strain with the form of $u_{\rm m} = (a_{\rm s}-a_{\rm f})/a_{\rm s}$, where $a_{\rm s}$ and $a_{\rm f}$ are the in-plane lattice parameters of the cubic substrate and the stress-free thin film, respectively.

The indirect method via the Maxwell relationship $(\frac{\partial\varepsilon}{\partial T})_\sigma = (\frac{\partial S}{\partial\sigma})_T$ has been used to obtain the adiabatic temperature change ΔT_σ,[4]

$$\Delta T_\sigma = -\frac{T}{C}\int\left(\frac{\partial\varepsilon}{\partial T}\right)_\sigma d\sigma, \tag{7}$$

where C denotes the heat capacity. The change of entropy S of ferroelectrics can be obtained by

$$\Delta S_\sigma = \frac{1}{2\varepsilon_0 C}[P_\sigma^2(T) - P_0^2(T)]. \tag{8}$$

Then, ΔT_σ can be evaluated in terms of the polarization change rather than the strain change, which is directly supported by first-principles calculations[6] and a thermodynamic approach.[7]

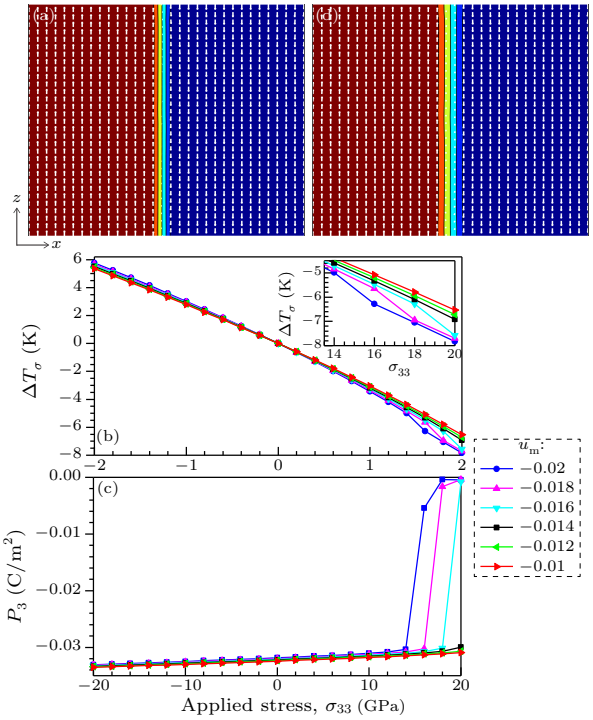

Fig. 1. (a) The 180° domain structure of PTO thin film under $u_{\rm m} = -0.016$; (b) ΔT_σ and (c) the mean polarization P_z as functions of σ_{33} and $u_{\rm m}$; and (d) the domain structure of PTO thin film under $\sigma_{33} = 1.8$ GPa and $u_{\rm m} = -0.016$.

It is reported that the total 180° domain structures can be formed under the large compressive misfit strain at normal temperature.[22] Figure 1(a) shows a typical 180° domain structure of PTO thin films with either positive or negative polarization along the out-of-plane axis obtained by solving the TDGL equation under the compressive strain $u_{\rm m} = -0.016$ without an applied stress. The stress field σ_{33} was applied along the z direction, ranging from −2 to 2 GPa. It is noted that an applied stress field larger than 2 GPa is avoided to prevent the experimental cracks.[6,23] The compressive strain from −0.02 to −0.01 has been chosen. The domain structures were demonstrated to be stable 180° domain structures at each compressive strain without the applied stress, which were used as the initial 180° domain structures on all simulation

processes. Figure 1(b) displays the adiabatic temperature change ΔT_σ obtained under different stress fields and misfit strains u_m. It is demonstrated that the value of ΔT_σ is negative when σ_{33} is positive, and $|\Delta T_\sigma|$ increases as σ_{33} increases under the tensile stress field. Meanwhile, the value of ΔT_σ is positive under the compressive stress field, and ΔT_σ increases as $|\sigma_{33}|$ increases. In addition, $|\Delta T_\sigma|$ increases as the compressive strain $|u_\mathrm{m}|$ increases which is in keeping with that of BTO thin films obtained by thermodynamic calculations.[17] Moreover, the largest negative ΔT_σ found here is about -7.8 K when the tensile stress field $\sigma_{33} = 2$ GPa and the compressive strain $u_\mathrm{m} = -0.02$, which is much larger than -4 K of bulk PTO calculated by a molecular dynamics simulation,[23] and -3.8 K of two-dimensional PTO with 90° domain structure obtained in our previous work.[12] Furthermore, from the enlarged figure shown inset of Fig. 1(b), a sudden change of ΔT_σ appears when the external stress and the compressive strain are large enough, such as $\sigma_{33} > 1.8$ GPa at $u_\mathrm{m} = -0.016$, $\sigma_{33} > 1.6$ GPa at $u_\mathrm{m} = -0.018$ and $\sigma_{33} > 1.4$ GPa at $u_\mathrm{m} = -0.02$. The elastocaloric effect of ferroelectric thin films is closely associated with the polarization change.[6,7] The corresponding changes in the mean polarization P_z are shown in Fig. 1(c). The distributions indicate that P_z increases with σ_{33} or $|u_\mathrm{m}|$, and P_z suddenly increases from about -0.033 to 0, which induces the sudden change of ΔT_σ. Moreover, the domain structure under the conditions of $\sigma_{33} = 1.8$ GPa and $u_\mathrm{m} = -0.016$ is present in Fig. 1(d). It can be found that the domain wall is wider than that of no applied stress.

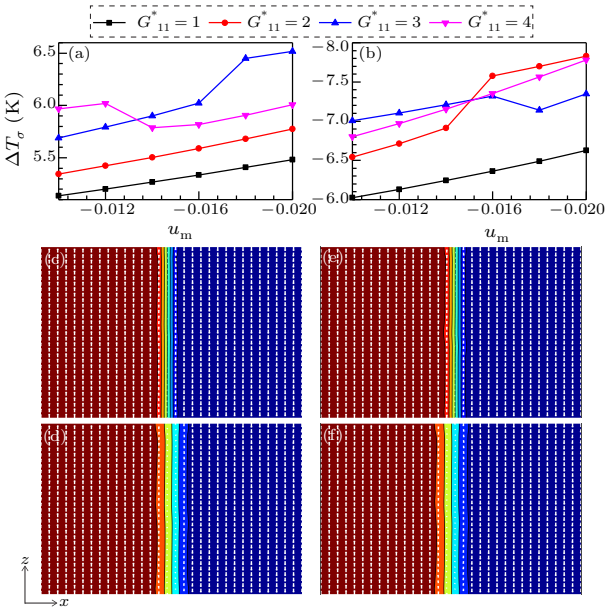

Fig. 2. The value of ΔT_σ at various u_m and G^*_{11} under (a) $\sigma_{33} = -2$ GPa and (b) $\sigma_{33} = 2$ GPa. The domain structures of PTO thin films under (c) $u_\mathrm{m} = -0.016$, (d) $u_\mathrm{m} = -0.018$, $G^*_{11} = 3$ at $\sigma_{33} = -2$ GPa, (e) $u_\mathrm{m} = -0.012$, and (f) $u_\mathrm{m} = -0.014$, $G^*_{11} = 4$ at $\sigma_{33} = 2$ GPa.

From the above, it is obvious that the domain structure has a great influence on the elastocaloric effect of ferroelectric thin films. Actually, the domain and domain wall can be dominant by the domain wall energy. Then, the value of the dimensionless gradient coefficient G^*_{11} is set from 1 to 4 to demonstrate the influence of the gradient function on the elastocaloric effect of PTO thin films. In Figs. 2(a) and 2(b), ΔT_σ under different G^*_{11} and various misfit strains at $\sigma_{33} = -2$ and 2 GPa have been detected, respectively. It can be seen that at some G^*_{11}, $|\Delta T_\sigma|$ linearly increases with $|u_\mathrm{m}|$, and at some G^*_{11}, ΔT_σ suddenly changes at certain u_m. By carefully comparing the domain structures before and after the sudden changes of ΔT_σ, it is found that they are related with the domain switching. Taking the domain structure (shown in Figs. 2(c)–2(f)) under $u_\mathrm{m} = -0.016$ and -0.018, $G^*_{11} = 3$ and $u_\mathrm{m} = -0.012$ and -0.014, $G^*_{11} = 4$ at $\sigma_{33} = -2$ GPa for example, it can be seen that the polarization switching accomplished by domain wall motion occur when $u_\mathrm{m} = -0.016$ increases to -0.018 at $G^*_{11} = 3$, and the domain wall widens when $u_\mathrm{m} = -0.012$ increases to -0.014 at $G^*_{11} = 4$. These domain switching behaviors finally affect the rise and drop of ΔT_σ. Experimentally, the contribution of the domain wall energy to the total energy can be adjusted through the introduction of defects which always have pinning interactions with the domain walls.[24,25] Therefore, the misfit strain and the defects could control the elastocaloric effect in the ferroelectric thin films, and our works will provide a guide to choose the substrate and the preparation process in experiments.

In summary, the influences of misfit strain and domain wall energy on the elastocaloric effect in PTO thin films with 180° domain structure at room temperature have been theoretically studied. The calculations indicate that $|\Delta T_\sigma|$ increases as $|\sigma_{33}|$ or $|u_\mathrm{m}|$ increases. The largest ΔT_σ value of -7.8 K is obtained at $\sigma_{33} = 2$ GPa and $u_\mathrm{m} = -0.02$. Furthermore, the domain switching behaviors are different under different gradient coefficients, and finally affect the elastocaloric effect in PTO thin films.

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