Effect of misfit strain on the electrocaloric effect of polydomain epitaxial ferroelectric thin films*

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The effect of misfit strain on the electrocaloric effect in polydomain epitaxial $BaTiO_3$ thin films at room temperature is investigated using the Ginzburg–Landau–Devonshire thermodynamic theory. Numerical calculations indicate that the misfit strain has a large impact on the ferroelectric polarization states and the electrocaloric effect. Most importantly, the electrocaloric effect in the polydomain $ca_1/ca_2/ca_1/ca_2$ phase is much larger than that in the monodomain c phase and the other polydomain phases. Consequently, a large electrocaloric effect can be obtained by carefully controlling the misfit strain, which may provide potential applications in refrigeration devices.

Keywords: polydomain, electrocaloric effect, phase transition

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1. Introduction

Ferroelectric thin films with perovskite structure, such as $BaTiO_3$, $PbTiO_3$, and $Pb(Zr_{1-x}Ti_x)O_3$, have been the subject of intense theoretical and experimental studies due to their potential for use in a wide range of applications.[1−5] One application is the electrical refrigeration based on the electrocaloric (EC) effect. The EC effect is a change in the temperature of a material upon the application or withdrawal of an electric field under the adiabatic conditions. The EC effect provides an efficient and environment-friendly solution to cooling the integrated circuits, and therefore has attracted great attention since the 1960s.[6−12] The interest in the EC effect has recently been renewed due to the giant EC effect in ferroelectric $Pb(Zr_{0.95}Ti_{0.05})O_3$ thin films.[13] Mischenko *et al.* found a giant EC effect of 0.48 K/V in 350 nm $Pb(Zr_{0.95}Ti_{0.05})O_3$ thin film near its ferroelectric Curie temperature of 226 °C.[13]

Theoretically, Akcay *et al.* used a thermodynamic theory to study the intrinsic EC effect in the $BaTiO_3$ thin film.[14,15] They found that a compressive misfit strain shifts the maximum of the EC effect to a higher temperature, reduces its magnitude and dependence on temperature, while the tensile misfit strain results in the opposite effects. Qiu *et al.* demonstrated that the EC effect in the ferroelectric thin films strongly depends on the misfit strain and a large room temperature EC effect can be obtained at a critical misfit strain.[16,17] Zhang *et al.* showed that the $BaTiO_3$ thin films with the tensile misfit strain exhibit sizable EC effects in a wider temperature range in comparison with those with the compressive misfit strain.[18]

Most of the experimental and theoretical studies have investigated the effects of misfit strain and electric field on the EC effect of monodomain ferroelectric thin films, however, such monodomain states are stable only in ultrathin thin films,[19,20] and the thicker films, which are technologically important, possess the polydomain structure with polarized domains separated by planar domain walls.[21−23] Unfortunately, the EC effect in polydomain thin films has not been investigated expect the theoretical work by Karthik *et al.*[24] They investigated the EC effect in the polydomain $Pb(Zr_{1-x}Ti_x)O_3$ thin films by using the Ginzburg–Landau–Dovenshire thermodynamic theory. The EC effect of the polydomain $c/a/c/a$ phase is larger than that of the monodomain c phase. Although they provided a pathway to tune the EC effect in the polydomain thin films via the strain effect, the Curie temperatures of $Pb(Zr_{1-x}Ti_x)O_3$ thin films are far away from the room temperature, and the phase diagram is relatively simple.[25,26]

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Therefore, it is necessary to investigate the EC effect in the polydomain $BaTiO_3$ thin films, who have the lower Curie temperatures around 110 °C and possess an abundant misfit strain–temperature phase diagram, which may provide different means to adjust the EC effect in the polydomain thin films.[26,27]

In this paper, the Ginzburg–Landau–Devonshire thermodynamic theory is applied to investigate the effect of misfit strain on the EC effect in the polydomain $BaTiO_3$ thin films. Theoretical analysis shows that the EC effect strongly depends on the misfit strain. Moreover, the EC effect of the polydomain $ca_1/ca_2/ca_1/ca_2$ phase is much larger than that of the monodomain c phase and the the other polydomain phases.

2. Model and method

We now focus on the (001)-oriented perovskite film epitaxially grown on a thick cubic substrate with the surface parallel to the (001) crystallographic planes. For the bulk perovskite ferroelectrics, the thermodynamic potential as a function of polarization components P_i $(i = 1, 2, 3)$ is given by[28]

$$\begin{aligned} G =\ & \alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4) \\ & +\alpha_{12}(P_1^2P_2^2+P_1^2P_3^2+P_2^2P_3^2) \\ & +\alpha_{111}(P_1^6+P_2^6+P_3^6)+\alpha_{112}[P_1^4(P_2^2+P_3^2) \\ & +P_2^4(P_1^2+P_3^2)+P_3^4(P_1^2+P_2^2)] \\ & +\alpha_{123}P_1^2P_2^2P_3^2-\frac{1}{2}s_{11}(\sigma_1^2+\sigma_2^2+\sigma_3^2) \\ & -s_{12}(\sigma_1\sigma_2+\sigma_1\sigma_3+\sigma_2\sigma_3) \\ & -\frac{1}{2}s_{44}(\sigma_4^2+\sigma_5^2+\sigma_6^2) \\ & -Q_{11}(\sigma_1P_1^2+\sigma_2P_2^2+\sigma_3P_3^2) \\ & -Q_{12}[\sigma_1(P_2^2+P_3^2)+\sigma_2(P_1^2+P_3^2) \\ & +\sigma_3(P_1^2+P_2^2)]-Q_{44}(P_2P_3\sigma_4+P_1P_3\sigma_5 \\ & +P_1P_2\sigma_6), \end{aligned} \tag{1}$$

where σ_n are the internal mechanical stresses in the film, α_1, α_{ij}, and $\alpha_{i,j,k}$ are the dielectric stiffness coefficients under the constant stress, s_{mn} are the elastic compliances at constant polarization, and $Q_{i,j}$ are the electrostrictive constants of the paraelectric phase.[28] Since the standard Gibbs function (1) is not appropriate for the description of thin film, a modified thermodynamic potential or the Helmholtz free energy function $\tilde{G}$ should be used in this case.[28] The latter can be derived via the inverse Legendre transformation of G, which gives $\tilde{G} = G + \Sigma_{n=1}^{6}\sigma_n S_n$. Substituting Eq. (1) into this formula and eliminating the strains with the aid of thermodynamic relations $S_n = -\partial G/\partial\sigma_n$, after some manipulation, we obtain the energy density $\tilde{G}$ as a function of P_i and σ_n. We allow the possible presence of the internal electric field E in the film, and the electrostatic potentials of electrodes are fixed in our case but not their charge. For the relevant modified density $\tilde{F}$, the calculation gives

$$\begin{aligned} \tilde{F} =\ & \alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4) \\ & +\alpha_{12}(P_1^2P_2^2+P_1^2P_3^2+P_2^2P_3^2) \\ & +\alpha_{111}(P_1^6+P_2^6+P_3^6)+\alpha_{112}[P_1^4(P_2^2+P_3^2) \\ & +P_2^4(P_1^2+P_3^2)+P_3^4(P_1^2+P_2^2)] \\ & +\alpha_{123}P_1^2P_2^2P_3^2+\frac{1}{2}s_{11}(\sigma_1^2+\sigma_2^2+\sigma_3^2) \\ & +s_{12}(\sigma_1\sigma_2+\sigma_1\sigma_3+\sigma_2\sigma_3) \\ & +\frac{1}{2}s_{44}(\sigma_4^2+\sigma_5^2+\sigma_6^2) \\ & -\frac{1}{2}\varepsilon_0(E_1^2+E_2^2+E_3^2)-E_1P_1 \\ & -E_2P_2-E_3P_3, \end{aligned} \tag{2}$$

where ε_0 is the permittivity of the vacuum.

Since we consider only periodic domain structures that are composed of alternating domains of two types[25–27] here, the free energy density $\tilde{F}$ may be replaced by the mean energy density $\langle\tilde{F}\rangle = \phi\tilde{F}' + (1-\phi)\tilde{F}''$, where $\tilde{F}'$ and $\tilde{F}''$ are the characteristic energy densities in the inner regions of domains of the first and the second type, respectively, $\phi' = \phi$ and $\phi'' = 1-\phi$ are their volume fractions in the film, within which the polarization and the strain field are almost uniform. Note that the contributions of the domain walls and the depolarizing field are neglected in the relatively thick film.[26,27]

Using the mechanical and the electric boundary conditions,[25–27] we are possible to eliminate the stresses σ_i', σ_i'' and the internal electric fields E_i', E_i'' from the final expression of the average energy density $\langle\tilde{F}\rangle$. Thus, the average energy density $\langle\tilde{F}\rangle$ can be written as a function of polarizations P_i', P_i'' and volume fraction ϕ. Performing numerically the minimization of $\langle\tilde{F}\rangle(P_i', P_i'', \phi)$, we can find the equilibrium polarization states and the volume fractions in both domains as functions of in-plane misfit strain $S_{\rm m}$, temperature T, and the external electric field E_0. The external electric field along [001] is taken into account in our calculations.

According to the misfit strain–temperature phase diagram of the polydomain $BaTiO_3$ thin film,[27] the c phase ($P_1' = P_2' = 0, P_3' \neq 0, P_1'' = P_2'' = P_3'' = 0$),

the $c/a/c/a$ phase ($P_1' = P_2' = 0, P_3' \neq 0, P_1'' \neq 0, P_2'' = P_3'' = 0$), the $ca^*/aa^*/ca^*/aa^*$ phase ($P_1' = 0, P_2' \neq 0, P_3' \neq 0, P_1'' \neq 0, P_2'' \neq 0, P_3'' = 0$), the $ca_1/ca_2/ca_1/ca_2$ phase ($P_1' \neq 0, P_2' = 0, P_3' \neq 0, P_1'' = 0, P_2'' \neq 0, P_3'' \neq 0$), the $a_1/a_2/a_1/a_2$ phase ($P_1' \neq 0, P_2' = P_3' = 0, P_2'' \neq 0, P_1'' = P_3'' = 0$), and the $aa_1/aa_2/aa_1/aa_2$ phase ($P_1' \neq 0, P_2' \neq 0, P_3' = 0, P_1'' \neq 0, P_2'' \neq 0, P_3'' = 0$) are the stable phases at room temperature (25 °C).

2.1. The monodomain *c* phase

The free energy density of the c phase is given by

$$\begin{aligned}\langle\tilde{F}\rangle = & \frac{S_{\rm m}^2}{s_{11}+s_{12}} + (\alpha_1 - 2S_{\rm m}B)P_3'^2 \\ & + (\alpha_{11}+D)P_3'^4 + \alpha_{111}P_3'^6 \\ & - \frac{1}{2}\varepsilon_0 E_{03}^2 - E_{03}P_3',\end{aligned} \tag{3}$$

where

$$\begin{aligned}B &= \frac{Q_{12}}{s_{11}+s_{12}}, \\ D &= \frac{Q_{12}^2}{s_{11}+s_{12}}.\end{aligned} \tag{4}$$

2.2. The polydomain $c/a/c/a$ phase

The free energy density of the polydomain $c/a/c/a$ phase can be written as

$$\begin{aligned}\langle\tilde{F}\rangle = & \frac{S_{\rm m}^2}{s_{11}+s_{12}} + \phi[(\alpha_1 - 2S_{\rm m}B)P_3'^2 \\ & + (\alpha_{11}+\phi D)P_3'^4 + \alpha_{111}P_3'^6] \\ & + (1-\phi)[(\alpha_1 - S_{\rm m}A)P_1''^2 \\ & + (\alpha_{11}+(1-\phi)C)P_1''^4 + \alpha_{111}P_1''^6] \\ & + \phi(1-\phi)EP_1''^2P_3'^2 \\ & - \frac{1}{2}\varepsilon_0 E_{03}^2 - \phi E_{03}P_3',\end{aligned} \tag{5}$$

where

$$\begin{aligned}A &= \frac{Q_{11}+Q_{12}}{s_{11}+s_{12}}, \\ C &= \frac{s_{11}Q_{11}^2 + s_{11}Q_{12}^2 - 2s_{12}Q_{11}Q_{12}}{2(s_{11}^2 - s_{12}^2)}, \\ E &= \frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}.\end{aligned} \tag{6}$$

The spontaneous polarization of the c and a domains as a function of the misfit strain and temperature can be obtained by using the equilibrium conditions $\partial\langle\tilde{F}\rangle/\partial P_1'' = 0$, $\partial\langle\tilde{F}\rangle/\partial P_3' = 0$, and $\partial\langle\tilde{F}\rangle/\partial\phi = 0$ at the external electric field $E_{03} = 0$. The calculation shows that the spontaneous polarization $P_{\rm S}$ has the same magnitude in the c and a domains,

$$\begin{aligned}P_{\rm S}^2 = & -\frac{\alpha_{11}+Q_{12}^2/2s_{11}}{3\alpha_{111}} + \Bigg[\frac{(\alpha_{11}+Q_{12}^2/2s_{11})^2}{9\alpha_{111}^2} \\ & - \frac{\alpha_1 - (Q_{12}/s_{11})S_{\rm m}}{3\alpha_{111}}\Bigg]^{1/2}.\end{aligned} \tag{7}$$

The equilibrium volume fraction of the c domain is

$$\phi = 1 - \frac{(s_{11}-s_{12})(S_{\rm m} - Q_{12}P_{\rm S}^2)}{s_{11}(Q_{11}-Q_{12})P_{\rm S}^2}. \tag{8}$$

2.3. The polydomain $ca^*/aa^*/ca^*/aa^*$ phase

The free energy density of the polydomain $ca^*/aa^*/ca^*/aa^*$ phase is

$$\begin{aligned}\langle\tilde{F}\rangle = & \frac{S_{\rm m}^2}{s_{11}+s_{12}} + \phi[(\alpha_1 - S_{\rm m}A)P_2'^2 \\ & + (\alpha_1 - 2S_{\rm m}B)P_3'^2 + (\alpha_{11}+\phi C)P_2'^4 \\ & + (\alpha_{11}+\phi D)P_3'^4 + (\alpha_{12}+\phi E)P_2'^2P_3'^2 \\ & + \alpha_{111}(P_2'^6 + P_3'^6) \\ & + \alpha_{112}(P_2'^4P_3'^2 + P_2'^2P_3'^4)] \\ & + (1-\phi)[(\alpha_1 - S_{\rm m}A)(P_1''^2 + P_2''^2) \\ & + (\alpha_{11}+(1-\phi)C)(P_1''^4 + P_2''^4) \\ & + (\alpha_{12}+(1-\phi)F)P_1''^2P_2''^2 \\ & + \alpha_{111}(P_1''^6 + P_2''^6) \\ & + \alpha_{112}(P_1''^4P_2''^2 + P_1''^2P_2''^4)] \\ & + \phi(1-\phi)(FP_2'^2P_1''^2 + EP_3'^2P_1''^2 \\ & + 2CP_2'^2P_2''^2 + EP_3'^2P_2''^2) \\ & - \frac{1}{2}\varepsilon_0 E_{03}^2 - \phi E_{03}P_3',\end{aligned} \tag{9}$$

where

$$F = \frac{2s_{11}Q_{11}Q_{12} - s_{12}Q_{11}^2 - s_{12}Q_{12}^2}{s_{11}^2 - s_{12}^2}. \tag{10}$$

2.4. The polydomain $ca_1/ca_2/ca_1/ca_2$ phase

The free energy density of the polydomain $ca_1/ca_2/ca_1/ca_2$ phase is

$$\begin{aligned}\langle\tilde{F}\rangle = & \frac{S_{\rm m}^2}{s_{11}+s_{12}} + \phi[(\alpha_1 - S_{\rm m}A)P_1'^2 \\ & + (\alpha_1 - 2S_{\rm m}B)P_3'^2 + (\alpha_{11}+\phi C)P_1'^4 \\ & + (\alpha_{11}+\phi D)P_3'^4 + (\alpha_{12}+\phi E)P_1'^2P_3'^2 \\ & + \alpha_{111}(P_1'^6 + P_3'^6)\end{aligned}$$

$$
\begin{aligned}
&+ \alpha_{112}(P_1'^4 P_3'^2 + P_1'^2 P_3'^4)] \\
&+ (1-\phi)[(\alpha_1 - S_{\rm m}A)P_2''^2 \\
&+ (\alpha_1 - 2S_{\rm m}B)P_3''^2 \\
&+ (\alpha_{11} + (1-\phi)C)P_2''^4 \\
&+ (\alpha_{11} + (1-\phi)D)P_3''^4 \\
&+ (\alpha_{12} + (1-\phi)E)P_2''^2 P_3''^2 \\
&+ \alpha_{111}(P_2''^6 + P_3''^6) \\
&+ \alpha_{112}(P_2''^4 P_3''^2 + P_2''^2 P_3''^4)] \\
&+ \phi(1-\phi)(FP_1'^2 P_2''^2 + EP_1'^2 P_3''^2 \\
&+ EP_3'^2 P_2''^2 + 2DP_3'^2 P_3''^2) \\
&- \frac{1}{2}\varepsilon_0 E_{03}^2 - \phi E_{03}P_3' \\
&- (1-\phi)E_{03}P_3''. \qquad (11)
\end{aligned}
$$

2.5. The polydomain $a_1/a_2/a_1/a_2$ phase

The free energy density of the polydomain $a_1/a_2/a_1/a_2$ phase can be calculated as

$$
\begin{aligned}
\langle \tilde{F} \rangle = &\frac{S_{\rm m}^2}{s_{11}+s_{12}} + \phi[(\alpha_1 - S_{\rm m}A)P_1'^2 \\
&+ (\alpha_{11} + \phi C)P_1'^4 + \alpha_{111}P_1'^6] \\
&+ (1-\phi)[(\alpha_1 - S_{\rm m}A)P_2''^2 \\
&+ (\alpha_{11} + (1-\phi)C)P_2''^4 + \alpha_{111}P_2''^6] \\
&+ \phi(1-\phi)FP_1'^2 P_2''^2 - \frac{1}{2}\varepsilon_0 E_{03}^2. \qquad (12)
\end{aligned}
$$

The spontaneous polarization $P_{\rm S}$ has the same magnitude in the a_1 and a_2 domains and lies along the edges of the prototypic cubic cell, which are parallel to the film surfaces. The equilibrium volume fractions of the a_1 and the a_2 domains are found to be equal to each other at all the investigated misfit strain and temperature ($\phi = 0.5$).

2.6. The polydomain $aa_1/aa_2/aa_1/aa_2$ phase

The free energy density of the polydomain $aa_1/aa_2/aa_1/aa_2$ phase is

$$
\begin{aligned}
\langle \tilde{F} \rangle = &\frac{S_{\rm m}^2}{s_{11}+s_{12}} + \phi[(\alpha_1 - S_{\rm m}A)(P_1'^2 + P_2'^2) \\
&+ (\alpha_{11} + \phi C)(P_1'^4 + P_2'^4) \\
&+ (\alpha_{12} + \phi F)P_1'^2 P_2'^2 + \alpha_{111}(P_1'^6 + P_2'^6) \\
&+ \alpha_{112}(P_1'^4 P_2'^2 + P_1'^2 P_2'^4)] \\
&+ (1-\phi)[(\alpha_1 - S_{\rm m}A)(P_1''^2 + P_2''^2) \\
&+ (\alpha_{11} + (1-\phi)C)(P_1''^4 + P_2''^4) \\
&+ (\alpha_{12} + (1-\phi)F)P_1''^2 P_2''^2 \\
&+ \alpha_{111}(P_1''^6 + P_2''^6) \\
&+ \alpha_{112}(P_1''^4 P_2''^2 + P_1''^2 P_2''^4)] \\
&+ \phi(1-\phi)(2CP_1'^2 P_1''^2 + 2CP_2'^2 P_2''^2 \\
&+ FP_1'^2 P_2''^2 + FP_2'^2 P_1''^2) \\
&- \frac{1}{2}\varepsilon_0 E_{03}^2. \qquad (13)
\end{aligned}
$$

Similar to the polydomain $a_1/a_2/a_1/a_2$ phase, the spontaneous polarization components have the same magnitude in the aa_1 and aa_2 domains, and the equilibrium volume fractions of the aa_1 and aa_2 domains are equal to each other ($\phi = 0.5$).

The value of the polarization and its dependence on the misfit strain are determined by the equilibrium conditions $\partial\langle\tilde{F}\rangle/\partial P_i' = 0$, $\partial\langle\tilde{F}\rangle/\partial P_i'' = 0$, and $\partial\langle\tilde{F}\rangle/\partial\phi = 0$ ($i = 1, 2, 3$). The average out-of-plane polarization is $\langle P_3 \rangle = \phi P_3' + (1-\phi)P_3''$, where ϕ is the volume fraction of the domain of the first type.

For the constant electric field and stress, the variation of the entropy can be written as[29]

$$
\Delta S = -\left(\frac{\partial\langle\tilde{F}\rangle}{\partial T}\right)_{E_{03}}. \qquad (14)
$$

In the presence of a uniform external electric field E_{03} along [001], the electrocaloric coefficient p_3 is given by[29]

$$
p_3 = \left(\frac{\partial \Delta S}{\partial E_{03}}\right)_T. \qquad (15)
$$

3. Results and discussion

Figure 1 shows the effects of the misfit strain on the spontaneous polarization, the average out-of-plane polarization, and the domain fraction of the first type at room temperature. The theoretical analysis indicates that the polarization and the volume fraction strongly depend on the misfit strain. As shown in Fig. 1(a), all the polarization components are discontinuous, which suggests that all the phase transitions are of the first order, while Koukhor *et al.*[27] reported that the phase transitions between the c phase and the $c/a/c/a$ phase and between the $c/a/c/a$ phase and the $ca^*/aa^*/ca^*/aa^*$ phase were of the second order. Based on Fig. 2 of Ref. [26], the polarizations of the c phase and the $c/a/c/a$ phase in the $PbTiO_3$ thin films are discontinuous. In the polydomain $c/a/c/a$ phase, the spontaneous polarizations in the c and a domains have the same magnitude and gradually decrease with the decrease of the compressive misfit strain as well as the average polarization and the volume fraction of

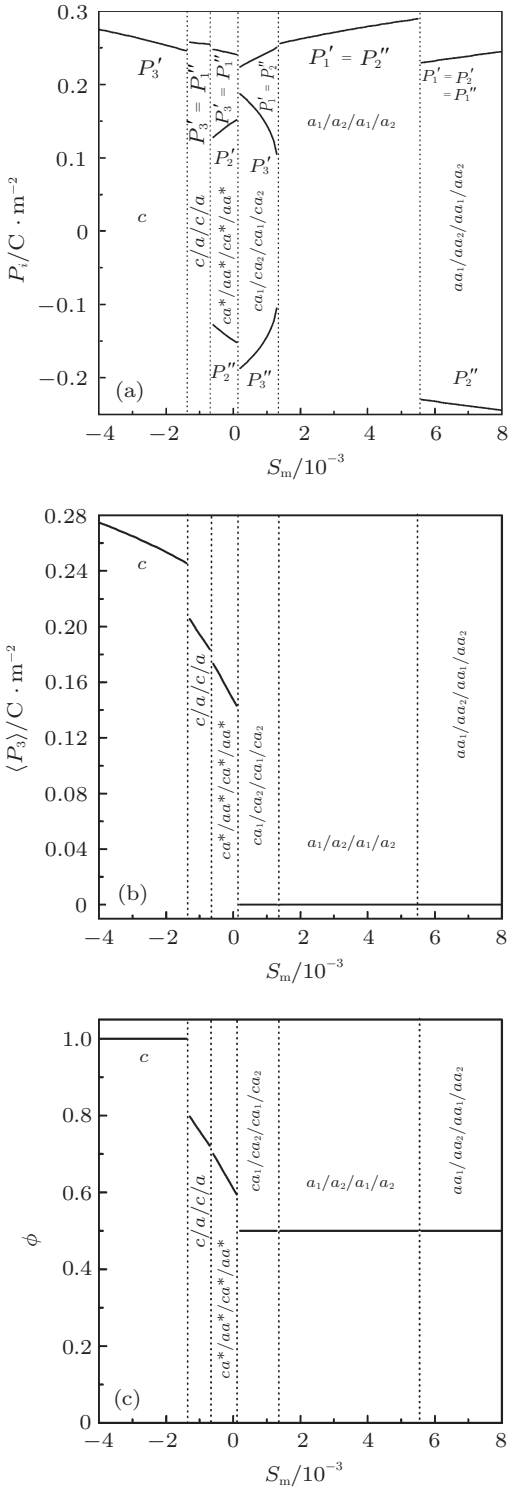


Fig. 1. The effects of the misfit strain on (a) the spontaneous polarization, (b) the average out-of-plane polarization, and (c) the volume fraction of the domain of the first type.

the c domain. Owing to the P_2 instability, the polydomain $c/a/c/a$ state transforms into a new polydomain $ca^*/aa^*/ca^*/aa^*$ state with a further reduction of the compressive misfit strain. The in-plane polarizations in neighboring domains have the opposite directions but the same magnitude ($P_2{}' = -P_2''$), and the out-of-plane polarization of the ca^* domain has the same magnitude as the polarization P_1'' of the aa^* domain. With the misfit strain varied from compressive to tensile, both the average polarization and the volume fraction of the ca^* domain decrease. In the polydomain $ca_1/ca_2/ca_1/ca_2$ phase, the out-of-plane and the in-plane polarizations in both domains have the same magnitude, but opposite directions for the out-of-plane polarizations. Therefore, the average polarization $\langle P_3\rangle$ is equals to zero, and the volume fractions of the ca_1 and ca_2 domains are equal to each other ($\phi = 0.5$). In the $a_1/a_2/a_1/a_2$ polydomain structure, the spontaneous polarizations in the a_1 and a_2 domains have the same magnitude and lie along the edges of the prototypic cubic cell, which are parallel to the film surfaces. The volume fractions of the a_1 and a_2 domains are found to be equal to each other at all the investigated misfit strains. In the polydomain $aa_1/aa_2/aa_1/aa_2$ state, the polarization patterning occurs along two in-plane face diagonals of the prototypic cubic cell. The volume fractions of the aa_1 and aa_2 domains are equal to each other ($\phi = 0.5$), and the spontaneous polarizations in these domains have the same magnitude. The polarization components in both the polydomain $a_1/a_2/a_1/a_2$ and $aa_1/aa_2/aa_1/aa_2$ phases increase as the misfit strain increases.

The misfit strain dependence of the electrocaloric coefficient p_3 at room temperature is presented in Fig. 2. The external electric field $E_{03} = 5$ kV/cm along [001] is deliberately set to be low to avoid the new phase transitions under the effect of the electric field. The EC effect vanishes in the polydomain $a_1/a_2/a_1/a_2$ and $aa_1/aa_2/aa_1/aa_2$ phases due to the zero polarization along the [001] direction. The EC effect in the polydomain $ca_1/ca_2/ca_1/ca_2$ phase is much larger than those in the monodomain c phase and the polydomain $c/a/c/a$ and $ca^*/aa^*/ca^*/aa^*$ phases. The maximum EC effect is obtained along the phase boundary between the polydomain $ca_1/ca_2/ca_1/ca_2$ phase and the $a_1/a_2/a_1/a_2$ phase at a small tensile misfit strain, which is in agreement with the result of the polydomain $Pb(Zr_{1-x}Ti_x)O_3$ thin films.[24] In the absence of the applied electric field, the out-of-plane polarizations of the ca_1 and ca_2 domains have the same magnitude but opposite directions. However, the applied electric field of 5 kV/cm along [001] changes the direction of the polarization component P_3'' in the ca_2 domain, which results in the largest variation of the entropy. It can be used to explain

why the polydoamin $ca_1/ca_2/ca_1/ca_2$ phase has the maximal EC effect. The maximum of the EC coefficient is 8×10^{-4} C/m^2·K at $E_{03} = 5$ kV/cm and $T = 25$ °C. As can be seen, the misfit strain has a large impact on the EC effect. Thus, the misfit strain may be used to adjust the EC effect.

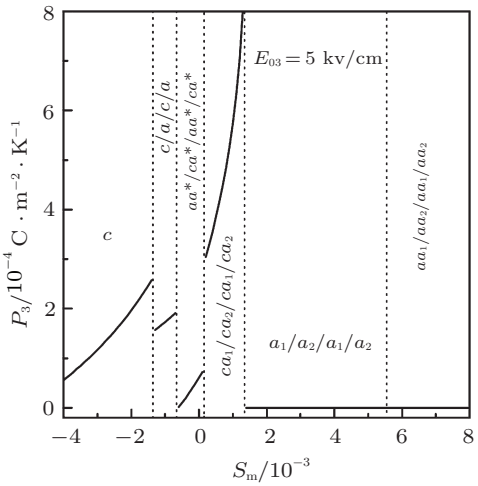


Fig. 2. Misfit strain dependence of the electrocaloric coefficient p_3 at room temperature.

4. Conclusion

In summary, the Ginzburg–Landau–Dovenshire thermodynamic theory is applied to investigate the effect of misfit strain on the electrocaloric effect in polydomain epitaxial $BaTiO_3$ thin films. Theoretical calculations demonstrate that the ferroelectric polarization states and the electrocaloric effect strongly depend on the misfit strain. Moreover, the maximum of the electrocaloric effect is obtained in the polydomain $ca_1/ca_2/ca_1/ca_2$ phase near the phase boundary between the polydomain $ca_1/ca_2/ca_1/ca_2$ phase and the $a_1/a_2/a_1/a_2$ phase, which has the larger electrocaloric effect than that of the monodomain c phase and the polydomain $c/a/c/a$ and $ca^*/aa^*/ca^*/aa^*$ phases. Therefore, choosing an appropriate polydomain state by controlling the misfit strain can be used to obtain the large electrocaloric effect, which can provide the potential application in cooling devices.

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