Composition and misfit strain dependence of electrocaloric effect of $Pb_{1-x}Sr_xTiO_3$ thin films*

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A Landau–Devonshire thermodynamic theory is employed to investigate the effects of composition and misfit strain on the room-temperature electrocaloric effect of epitaxial $Pb_{1-x}Sr_xTiO_3$ thin films. The "temperature–misfit strain" phase diagrams with the Sr composition x of 0.1, 0.3, and 0.5 are constructed. The introduction of Sr composition reduces the Curie temperature greatly, and enhances the electrocaloric effect. Moreover, the electrocaloric effect largely depends on the misfit strain. Therefore, the Sr composition and the misfit strain can be controlled to obtain the giant room-temperature electrocaloric effect.

Keywords: phase diagram, phase transition, electrocaloric effect

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1. Introduction

Electrocaloric (EC) effect refers to temperature change of a material upon the application or withdrawal of an electric field under adiabatic conditions, and has attracted great attention in the use of refrigeration devices and thermodielectric power converters since the 1960s.[1–3] Due to the small adiabatic temperature change reported in experiments,[4] the EC effect of ferroelectric materials was insufficient for practical applications. However, the EC effect has been extensively investigated recently, since the giant EC effect was reported in $Pb(Zr_{0.95}Ti_{0.05}O_3)$ thin films.[5] A giant EC effect of 12 K at 25 V was found in $Pb(Zr_{0.95}Ti_{0.05}O_3)$ thin films near the phase transition temperature of 222 °C.[5] Later on, the $Pb(Zr_{1-x}Ti_x)O_3$ thin films with different Ti compositions have also been investigated in the frame of the Ginzburg–Landau–Devonshire theory.[6–8] The EC effects of $BaTiO_3$ thin films,[9–13] whose Curie temperature is about 110 °C, were studied both experimentally and theoretically, and can be comparable with that observed in $Pb(Zr_{0.95}Ti_{0.05}O_3)$ thin films. Other ferroelectric materials, such as relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$[14–17] and ferroelectric polymers,[18,19] have been found to show a giant EC effect near their Curie temperature. These materials have giant EC effects, however, their Curie temperature, which produces the maximal EC effect, is far away from room temperature. This hinders the practical applications in cooling systems at room temperature.

To our delight, ferroelectric $Pb_{1-x}Sr_xTiO_3$ systems have extremely high pyroelectric properties and low dielectric loss,[20–23] and the Curie temperature was found to vary linearly with the composition x.[24] Most importantly, the $Pb_{1-x}Sr_xTiO_3$ systems with $x \leq 0.3$ for solid solution[24] and $x \leq 0.5$ for thin films[25] have a Curie temperature below the room temperature. Moreover, the physical properties of the $Pb_{1-x}Sr_xTiO_3$ system are highly dependent upon the composition. Thus, as the inverse electrothermal conversion of the pyroelectric effect, it is predicted that the $Pb_{1-x}Sr_xTiO_3$ system has the giant room-temperature EC effect, which greatly depends on the Sr composition. In addition, the EC effect of the ferroelectric thin films can be adjusted by controlling the misfit strain between the thin film and the substrate.[11,26,27] The most intense EC effect can be obtained at a critical misfit strain.[26] Consequently, control over the Sr composition and the misfit strain can be used to achieve the giant room-temperature EC effect in $Pb_{1-x}Sr_xTiO_3$ thin films. However, the EC effect of $Pb_{1-x}Sr_xTiO_3$ thin films has not been studied.

In this work, we investigate the effect of Sr composition and the misfit strain on the room-temperature EC effect of $Pb_{1-x}Sr_xTiO_3$ thin films using the Landau–Devonshire thermodynamic theory. The "temperature–misfit strain" phase diagrams with different Sr compositions are constructed. Theoretical analysis indicates that the $Pb_{1-x}Sr_xTiO_3$ thin films exhibit giant room-temperature EC effect, which largely depends on the Sr composition and the misfit strain.

2. Model and method

We consider the single domain (001) $Pb_{1-x}Sr_xTiO_3$ thin films epitaxially grown on a thick cubic substrate with the surface parallel to the (001) crystallographic planes. The thermodynamic potential $\tilde{G}$ of the thin films as a function of polariza-

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tion P_i $(i = 1,2,3)$, misfit strain S_m, and applied electric field E_i is given by[28]

$$\begin{aligned}\tilde{G} = {} & \alpha_1^*(P_1^2+P_2^2)+\alpha_3^*P_3^2+\alpha_{11}^*(P_1^4+P_2^4)\\ & +\alpha_{33}^*P_3^4+\alpha_{12}^*P_1^2P_2^2+\alpha_{13}^*(P_1^2+P_2^2)P_3^2\\ & +\alpha_{111}(P_1^6+P_2^6+P_3^6)+\alpha_{112}[P_1^4(P_2^2+P_3^2)\\ & +P_2^4(P_1^2+P_3^2)+P_3^4(P_1^2+P_2^2)]\\ & +\alpha_{123}P_1^2P_2^2P_3^2-E_1P_1-E_2P_2-E_3P_3+\frac{S_m^2}{s_{11}+s_{12}}, \quad (1)\end{aligned}$$

where

$$\alpha_1^* = \alpha_1 - \frac{Q_{11}+Q_{12}}{s_{11}+s_{12}}S_m, \quad (2)$$

$$\alpha_3^* = \alpha_1 - \frac{2Q_{12}}{s_{11}+s_{12}}S_m, \quad (3)$$

$$\alpha_{11}^* = \alpha_{11} + \frac{1}{2}\frac{[(Q_{11}^2+Q_{12}^2)s_{11}-2Q_{11}Q_{12}s_{12}]}{s_{11}^2-s_{12}^2}, \quad (4)$$

$$\alpha_{33}^* = \alpha_{11} + \frac{Q_{12}^2}{s_{11}+s_{12}}, \quad (5)$$

$$\alpha_{12}^* = \alpha_{12} - \frac{[(Q_{11}^2+Q_{12}^2)s_{12}-2Q_{11}Q_{12}s_{11}]}{s_{11}^2+s_{12}^2} + \frac{Q_{44}^2}{2s_{44}}, \quad (6)$$

$$\alpha_{13}^* = \alpha_{12} + \frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}, \quad (7)$$

where α_1, α_{ij}, and α_{ijk} are dielectric stiffness coefficients at constant stress, s_{ij} is the elastic compliance at constant polarization, and Q_{ij} is the electrostrictive coefficient. The composition-dependent Landau coefficients of $Pb_{1-x}Sr_xTiO_3$ thin films have been constructed as a linear combination of the well-known Landau coefficients of the end members, $PbTiO_3$ and $SrTiO_3$.[25] The temperature dependence of ferroelectricity is mainly governed by the dielectric stiffness coefficient α_1, since the other dielectric stiffness coefficients may be taken as temperature-independent parameters. The parameters used for the calculation of the renormalized coefficients for $Pb_{1-x}Sr_xTiO_3$ thin films result from Ref. [25].

The misfit strain dependence of polarizations with different Sr compositions is given under the equilibrium conditions $\partial\tilde{G}/\partial P_i = 0$ $(i = 1,2,3)$. For the constant electric field and stress, the variation of the excess entropy ΔS can be written as[6,9]

$$\Delta S = -\left(\frac{\partial\tilde{G}}{\partial T}\right)_E. \quad (8)$$

In the presence of a uniform applied electric field E along the direction of [001], the electrocaloric coefficient p is given by[6,9]

$$p = \left(\frac{\partial\Delta S}{\partial E}\right)_T. \quad (9)$$

Reversible adiabatic temperature change ΔT of a ferroelectric material due to an electric field change ΔE is expressed as[9]

$$\Delta T = -T\int_{E_a}^{E_b}\frac{1}{C_E(T,E)}\left(\frac{\partial P}{\partial T}\right)_E \mathrm{d}E, \quad (10)$$

where $C_E(T,E)$ is the heat capacity per unit volume at constant electric field, and $\Delta E = E_b - E_a$ is the difference in the applied electric field.

3. Results and discussion

By using Eqs. (1)–(7), the equilibrium thermodynamic states of the thin films are determined by minimizing the potential $\tilde{G}$ with respect to polarization components with fixed values of the misfit strain and the temperature. The "temperature–misfit strain" phase diagrams with different Sr compositions are constructed in Fig. 1. Here, we introduce the following notations for different equilibrium states that may occur in the thin films: (i) the para-electric phase, where $P_1 = P_2 = P_3 = 0$; (ii) the c phase, where $P_1 = P_2 = 0$, and $P_3 \neq 0$; (iii) the aa phase, where $P_1 = P_2 \neq 0$, and $P_3 = 0$; (iv) the γ phase, where $P_1 = P_2 \neq 0$, and $P_3 \neq 0$. Theoretical calculation indicates that the phase transitions from the c phase to the aa phase in $Pb_{0.9}Sr_{0.1}TiO_3$ thin films and from the c phase to the γ phase are of the first order, and all the other phase transitions are of the second order. The introduction of the Sr composition decreases the Curie temperature greatly. At room temperature ($T = 298$ K), the c phase, the para-electric phase, and the aa phase are the stable phases in $Pb_{0.5}Sr_{0.5}TiO_3$ thin films whose Curie temperature is below the room temperature, while the c phase, the γ phase, and the aa phase can exist for $x = 0.1$ and 0.3.

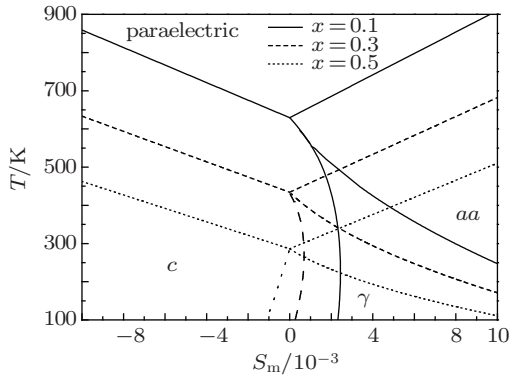


Fig. 1. "Temperature–misfit strain" phase diagrams of $Pb_{0.5}Sr_{0.5}TiO_3$ thin films with the Sr composition x =0.1, 0.3, and 0.5. The thin and thick lines denote the second- and first-order phase transitions, respectively.

The effect of misfit strain on the polarization of $Pb_{0.5}Sr_{0.5}TiO_3$ thin films with different Sr compositions is presented in Fig. 2. The applied electric field along the [001] direction transforms the para-electric phase and aa phase to the c phase and γ phase, respectively. Hence, only the c phase and γ phase are stable phases for $Pb_{0.5}Sr_{0.5}TiO_3$ thin films under the applied electric field at room temperature. The applied electric field undoubtedly increases the polarization P_3, and decreases the polarization P_1 and P_2 ($P_1 = P_2$) because the electric field is along the [001] direction. The polarizations at the phase

boundary between the c phase and the γ phase are all discontinuous because of the first-order phase transition from the c phase to the γ phase. The decrease of the compressive misfit strain decreases the polarization P_3, while the increase of the tensile misfit strain increases the polarizations P_1 and P_2, and has an opposite effect on the polarization P_3. As can be seen from Fig. 2, the polarization of $Pb_{0.5}Sr_{0.5}TiO_3$ thin films is smaller than that of $Pb_{0.7}Sr_{0.3}TiO_3$ and $Pb_{0.9}Sr_{0.1}TiO_3$ thin films due to the introduction of the Sr composition.

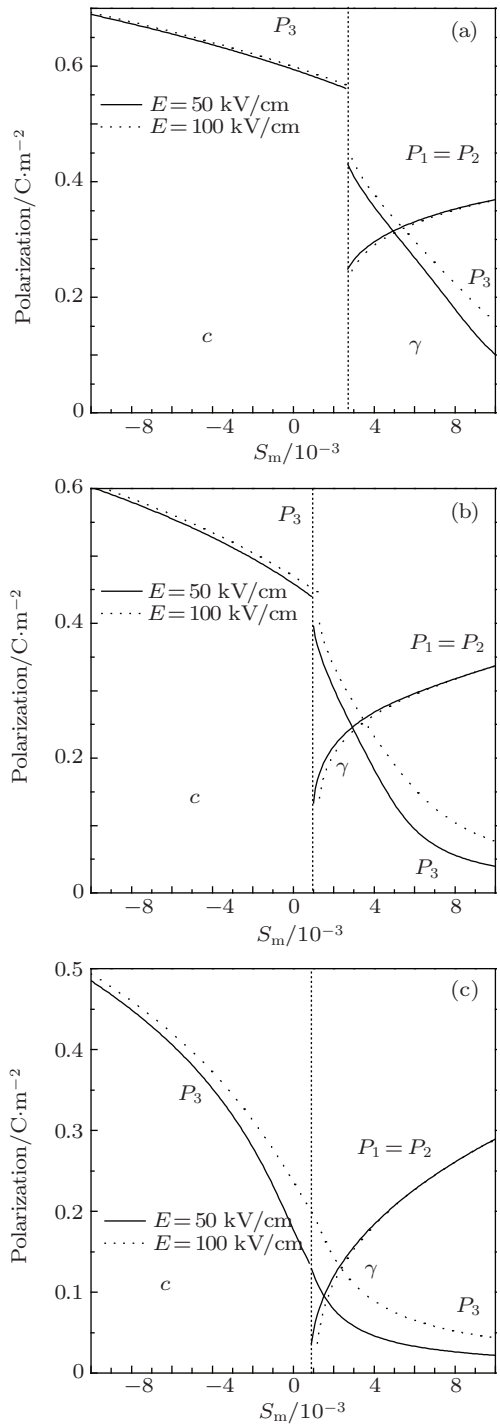


Fig. 2. Effects of Sr composition and misfit strain on the polarization of $Pb_{1-x}Sr_xTiO_3$ thin films for (a) $x = 0.1$, (b) $x = 0.3$, and (c) $x = 0.5$.

Figure 3 shows the effects of misfit strain and Sr composition on the EC coefficient of $Pb_{1-x}Sr_xTiO_3$ thin films. Because of the first-order phase transition from the c phase to the γ phase, the EC coefficient is discontinuous at the phase boundary, which is in agreement with the result for $Pb(Zr_{1-x}Ti_x)O_3$ thin films.[6] The $Pb_{1-x}Sr_xTiO_3$ thin films have giant room-temperature EC coefficient. Moreover, the EC coefficient of $Pb_{0.5}Sr_{0.5}TiO_3$ thin films is larger than that of $Pb_{1-x}Sr_xTiO_3$ ($x = 0.1$ and 0.3) thin films. As an example, $P = 3.1 \times 10^{-3}$ C/m^{2}K for $E = 50$ kV/cm, which is also much larger than that of $BaTiO_3$ thin films (e.g., $p = 9.2 \times 10^{-4}$ C/m^{2}K for $E = 50$ kV/cm).[9] The variation of the polarization induced by the electric field in $Pb_{0.5}Sr_{0.5}TiO_3$ thin films is larger than the other thin films, and results in greater change of the entropy which can be used to explain it. On the other hand, the EC coefficient of the c phase is larger than that of the γ phase. The applied electric field decreases the EC coefficient and enhances the misfit strain which corresponds to the maximum of

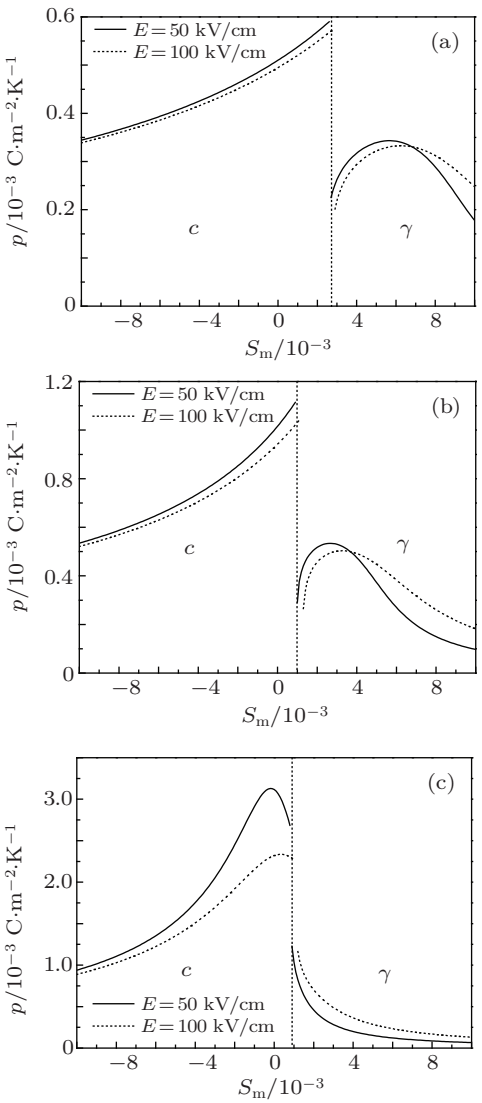


Fig. 3. Electrocaloric coefficient p of $Pb_{1-x}Sr_xTiO_3$ thin films with the Sr composition of (a) 0.1, (b) 0.3, and (c) 0.5.

the EC coefficient. This is in accordance with the results of the EC effect.[27] As mentioned above, the EC coefficient largely depends on the Sr composition and the misfit strain.

The misfit strain dependence of the adiabatic temperature change ΔT of $Pb_{1-x}Sr_xTiO_3$ ($x = 0.1$, 0.3, and 0.5) thin films is shown in Fig. 4. From Eq. (10), we know that the adiabatic temperature change ΔT depends on both the initial electric field E_a and the field change $\Delta E = E_b - E_a$. For comparison, we perform the integration for $\Delta E = 50$ kV/cm and 100 kV/cm with the initial electric field $E_a = 50$ kV/cm.

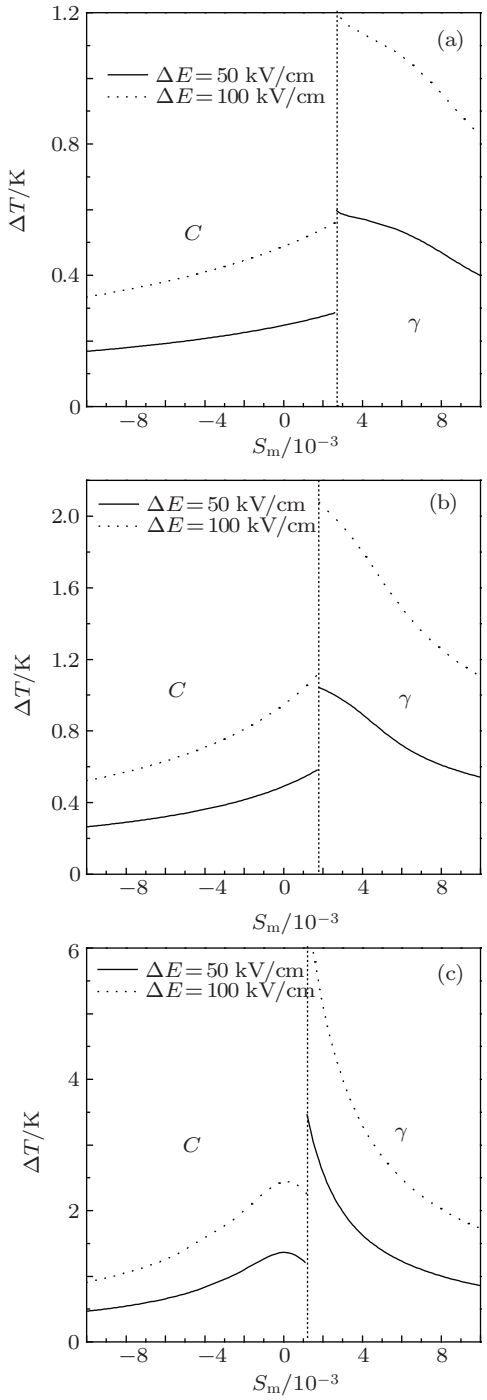


Fig. 4. Misfit strain dependence of the adiabatic temperature change ΔT of $Pb_{1-x}Sr_xTiO_3$ thin films with the Sr composition of (a) $x = 0.1$, (b) $x = 0.3$, and (c) $x = 0.5$.

The absolute value of specific heat $C_E(T,E)$ used for theoretical calculations in Eq. (10) is considered to be a linear relation of $(1-x)C_{PT} + xC_{ST}$ for simplicity, where the specific heat $C_{PT} = 3.2 \times 10^6$ J/m^{3}K is approximately equal to the value of single crystal $PbTiO_3$, and $C_{ST} = 2.78 \times 10^6$ J/m^{3}K is the value of single crystal $SrTiO_3$.[29] As seen from this figure, the adiabatic temperature change ΔT is not continuous at the phase boundary because of the first-order phase transition from the c phase to the γ phase, which is in agreement with the result of $SrTiO_3$ thin films.[26] The $Pb_{0.5}Sr_{0.5}TiO_3$ thin films have the largest adiabatic temperature change among the three different Sr compositions, which agrees with the result of the EC coefficient. Moreover, the giant adiabatic temperature change ΔT of $Pb_{0.5}Sr_{0.5}TiO_3$ thin films, e.g., $\Delta T = 6$ K with $\Delta E = 100$ kV/cm, is much larger than that of $BaTiO_3$ thin films ($\Delta T = 1$ K).[11] In addition, the $Pb_{1-x}Sr_xTiO_3$ thin films with the tensile misfit strain have larger adiabatic temperature change than that of the compressive misfit strain. On the other hand, it is expected that an increase in the field change ΔE can lead to a linear increase in the magnitude of adiabatic temperature change ΔT due to the EC effect.[5,18] It is concluded that the adiabatic temperature change depends on the Sr composition and the misfit strain. Therefore, a giant room-temperature EC effect can be obtained by controlling the Sr composition and the misfit strain. Most importantly, it may provide the potential for practical room-temperature applications in cooling systems.

4. Conclusion

In summary, a Landau–Devonshire thermodynamic theory is applied to investigate the effects of Sr composition and the misfit strain on the room-temperature electrocaloric effect of epitaxial $Pb_{1-x}Sr_xTiO_3$ thin films. Theoretical calculations demonstrate that the Curie temperature and the electrocaloric effect largely depend on the Sr composition and the misfit strain. The introduction of the Sr composition decreases the Curie temperature and enhances the electrocaloric effect. Moreover, $Pb_{1-x}Sr_xTiO_3$ thin films show giant room-temperature electrocaloric effect which is stronger than that of the other ferroelectric materials. Therefore, the Sr composition and the misfit strain can be chosen to obtain the giant room-temperature electrocaloric effect.

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