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Giant electrocaloric effect of $PbTiO_3$ thin film tuned in a wide temperature range by the anisotropic misfit strain

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ABSTRACT

The influence of anisotropic in-plane strains on the electrocaloric effect (ECE) in $PbTiO_3$ (PT) epitaxial ferroelectric thin films is investigated by using a Landau-Devonshire thermodynamic theory. The calculation results show that the anisotropic strain can tune the ECE of PT ferroelectric thin films to obtain a large adiabatic temperature change in a wide temperature range which is attributed to the shift of *c*-phase boundary of PT thin films under the anisotropic strains with an external electric field. These results indicate that the anisotropic strain can provide an efficient way to adjust the ECE of ferroelectric thin films to refrigerate in a wide temperature range.

1. Introduction

The strain engineering in ferroelectric thin films has attracted great interest because it can dramatically enhance the properties of ferroelectric thin films. The mechanism of the relationship between the properties of the ferroelectric thin film and the misfit strain which is induced by the lattice mismatch between the thin film and the substrate and has deep understood (Hirel et al., 2012; Pane et al., 2009; Qiu et al., 2010; Wang, 2011). So, choosing the substrate can provides an available way to tune the properties of ferroelectric thin films, such as Curie temperature (T_c), piezoelectric and dielectric properties. Recently, the adjustment of the misfit strain on the electrocaloric effect (ECE) which is the change in temperature of a material under adiabatic conditions in response to an applied electric field has aroused considerable interest among the various properties of the ferroelectric thin film. The ECE can provide an alternative solid-state cooling technology in devices refrigeration with the features of environmental-friendly and high efficiency. It is noted that many devices work on a wide temperature range. Therefore, the ferroelectric thin film is required to have a large adiabatic temperature change in the wide temperature range for commercial exploited. However, the large ECE reported in ferroelectric thin films mainly appears in a narrow temperature range near the ferroelectric–paraelectric (F–P) phase transition because of the existence of large entropy change (Cole et al., 2008; Lu and Zhang, 2009; Bai et al., 2010; Chen et al., 2009; Correia et al., 2011; Liu et al., 2010). In this sense, the strain can be used for achieving a large adiabatic temperature change in the wide temperature range in the ferroelectric thin film.

Recently, research works showed that the strain has large effects on the ECE of the ferroelectric thin film. Qiu et al. showed that the magnitude of the adiabatic temperature change in epitaxial $PbZr_{1-x}Ti_xO_3$ thin films largely depends on the isotropic misfit strain (Qiu and Jiang, 2008). Zhang et al. showed that the compressive substrates could enhance the ECE of the $SrTiO_3$ thin film (Zhang et al., 2012). Then, Alcay et al. reported that the isotropic misfit strain can tune the temperature dependence of ECE in the $BaTiO_3$ ferroelectric thin film which the compressive misfit strain reduces the ECE dependence on temperature and the tensile misfit strain has the opposite effect (Akcay et al., 2008). And our previous work pointed that the $BaTiO_3$ thin film with the tensile isotropic misfit strain exhibits a sizable ECE in a wider temperature range in comparison with those with compressive misfit strain (Zhang et al., 2011). It is found that the strain in the above works are isotropic strain, while the experiments result showed that the anisotropy strain has significantly effects on the properties of ferroelectric thin films (Lin et al., 2004). However, there are no works regarding how the anisotropic misfit strain influences the ECE of the ferroelectric thin film.

In this letter, the effect of anisotropic misfit strains which is introduced from the orthorhombic substrate on the ECE of the

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$PbTiO_3$ (PT) epitaxial ferroelectric thin film is investigated by using the Landau-Devonshire theory. The adiabatic temperature change of the PT thin film is calculated as a function of the anisotropic misfit strain. A large value of the adiabatic temperature change in a wide temperature range is found in the PT thin film. And the mechanism of this wide temperature range with large adiabatic temperature change is analyzed in detail.

2. Theoretical analysis

The Landau-Devonshire theory is used for investigating the ECE of the epitaxial PT thin film grown along [0 0 1] direction on the orthorhombic substrate. In the ferroelectric thin film, the misfit strain which is caused by the lattice mismatch at the interfaces and the different thermal expansion coefficient between the film and the substrate is taken in account (Chen, 2008) u_{m1} and u_{m2} stand for the misfit strain along the two directions of the in-plane strain, while the positive and negative value denote the compressive and tensile misfit strain, respectively. $u_{m1} = (a_1 - a_0)/a_0$ and $u_{m2} = (a_2 - a_0)/a_0$ where a_1 and a_2 are the lattice parameter of the strained ferroelectric film along [1 0 0] and [0 1 0] directions, respectively, a_0 is the lattice parameter of the ferroelectric thin film in its cubic states under the stress-free condition. In the case of the ferroelectric thin film grown on the orthorhombic substrate, the in-plane misfit strain $u_{m1} \neq u_{m2}$. A shear deformation $u_{m6} = \gamma - \pi/2$ is introduced by the substrate, but it should be zero because we concern $\gamma = \pi/2$ (Wang and Zhang, 2005). In this work, the electric field is applied along the [0 0 1] polarization direction (P_3). Hence, $E_1 = E_2 = 0$, $E_3 = |\vec{E}|$. From the Landau-Devonshire theory, the three-coupled polarizations $P_i(u_{m1}, u_{m2}, E, T)$, $(i = 1, 2, 3)$ follow the thermodynamic potential $\tilde{G}$ as (Wang and Zhang, 2005; Zembilgotov et al., 2005)

$$\begin{aligned}\tilde{G} &= \alpha_1^*(P_1^2+P_2^2)+\alpha_3^*P_3^2+\alpha_{11}^*(P_1^4+P_2^4)+\alpha_6^*P_1P_2+\alpha_{33}^*P_3^4\\&+\alpha_{13}^*(P_1^2P_3^2+P_2^2P_3^2)+\alpha_{12}^*P_1^2P_2^2+\alpha_{111}(P_1^6+P_2^6+P_3^6)\\&+\alpha_{112}(P_1^4(P_3^2+P_2^2)+P_2^4(P_3^2+P_1^2)+P_3^4(P_1^2+P_2^2))+\alpha_{123}P_1^2P_2^2P_3^2\\&+\frac{[s_{11}(u_{m1}^2+u_{m2}^2)-2s_{12}u_{m1}u_{m2}]}{(s_{11}{}^2-s_{12}{}^2)}+\frac{u_{m6}{}^2}{2s_{44}}-(E_3P_3)\end{aligned} \tag{1}$$

where

$$\begin{aligned}&\alpha_1^* = \alpha_1 + \frac{u_{m1}(Q_{12}s_{12}-Q_{11}s_{11})+u_{m2}(Q_{11}s_{12}-Q_{12}s_{11})}{(s_{11}{}^2-s_{12}{}^2)}, \quad \alpha_3^* = \alpha_1 - \frac{Q_{12}(u_{m1}+u_{m2})}{(s_{11}+s_{12})},\\&\alpha_2^* = \alpha_1 + \frac{u_{m2}(Q_{12}s_{12}-Q_{11}s_{11})+u_{m1}(Q_{11}s_{12}-Q_{12}s_{11})}{(s_{11}{}^2-s_{12}{}^2)}, \quad \alpha_6^* = -\frac{Q_{44}u_{m6}}{s_{44}},\\&\alpha_{11}^* = \alpha_{11} + \frac{1}{2}\frac{1}{s_{11}^2-s_{12}^2}[(Q_{11}^2+Q_{12}^2)s_{11}-2Q_{11}Q_{12}s_{12}], \quad \alpha_{33}^* = \alpha_{11}+\frac{Q_{12}^2}{s_{11}+s_{12}},\\&\alpha_{12}^* = \alpha_{12} - \frac{1}{s_{11}^2-s_{12}^2}[(Q_{11}^2+Q_{12}^2)s_{12}-2Q_{11}Q_{12}s_{11}]+\frac{Q_{44}^2}{2s_{44}}, \quad \alpha_{13}^* = \alpha_{12}+\frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}.\end{aligned} \tag{2}$$

All the dielectric spiffiness coefficients α_1, α_{ij}, α_{ijk}, electrostrictive coefficients Q_{ij} and elastic compliances s_{ij} are taken from Ref. Pertsev et al. (1998). By solving the Eula equation $\partial\tilde{G}/\partial P_i = 0$, $(i = 1, 2, 3)$, the polarizations P_i in the equilibrium phases under the different applied electric fields can be obtained. Then, the electrocaloric coefficient should be written as (Akcay et al., 2007)

$$p(u_{m1}, u_{m2}, E, T) = \frac{\partial S}{\partial E_3} = \frac{\partial P_3}{\partial T} \tag{3}$$

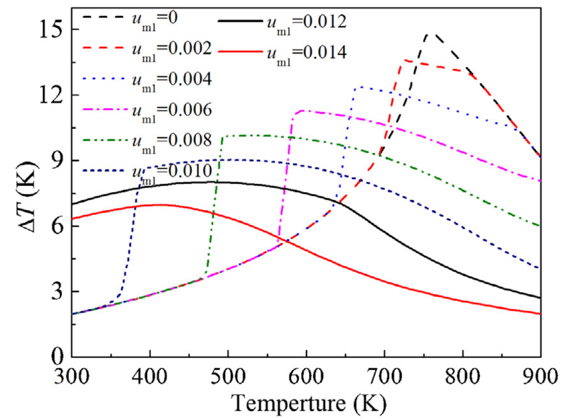

Fig. 1. Adiabatic temperature change in PT epitaxial ferroelectric thin films grown on orthorhombic substrates as functions of the anisotropic misfit strain and the temperature with $E_a = 0$ kV/cm and $E_b = 500$ kV/cm.

where S is the entropy and T is the absolute temperature. The adiabatic temperature change ΔT which is induced by the change in the applied electric field is given by

$$\Delta T(u_m, E, T) = -T\int_{E_a}^{E_b}\frac{1}{C_{E,\sigma}}\left(\frac{\partial P_3}{\partial T}\right)_{E,\sigma} dE \tag{4}$$

where $E_b - E_a = \Delta E$ is the difference in the applied electric field and $C_{E,\sigma}$ is the heat capacity per unit volume at the constant electric field (Akcay et al., 2008). The heat capacity

$$C_{E,\sigma} = 2.84\times 10^6 + 417T + \Delta C(T, E) \tag{5}$$

is estimated by the computed zero-field values of the excess specific heat

$$\Delta C(T, E) = -T \times \left(\frac{\partial^2\tilde{G}}{\partial T^2}\right)_E \tag{6}$$

and a simple fitted value (Härdtl and Rau, 1969; Rossetti et al., 1998).

3. Results and discussion

To investigate the ECE of the PT thin film grown on the orthorhombic substrate, we take a special series of the anisotropic misfit strain with a regular pattern of $u_{m1} = -u_{m2}$. Fig. 1 shows the adiabatic temperature change of the PT thin film as a function of the anisotropic misfit strain with $E_a = 0$ kV/cm and $E_b = 500$ kV/cm. It can be seen that the value of adiabatic temperature change sharply increases to 13.6 K at 720 K when the anisotropic misfit strain is 0.002. After that, the value of adiabatic temperature change gradually decreases to 13 K when the temperature increases to 810 K and thus leads to a platform of adiabatic temperature change. The magnitude of adiabatic temperature change quickly decreases with further increasing of the temperature. It is reasonable believe that the platform of adiabatic temperature change of ferroelectric thin