

# Tunable Temperature Range of Stress-Enhanced Electrocaloric Effects in Composition Gradient Bilayers

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## Abstract

We investigated a tunable temperature range of stress-enhanced electrocaloric effects in composition gradient bilayers by using the phenomenological Landau-Devonshire thermodynamic theory. A tunable temperature range of entropy change was obtained from 265 ~ 270 K for the specific composition of BaSrTiO<sub>3</sub> bilayers. Theoretical analysis shows that the external stress can tune the temperature range of electrocaloric effects from 220 K to 286 K, and the stress can tune the maximum temperature change 13 K per GPa. The thickness ratio of composition gradient films also can vary the adiabatic temperature change under constant stress. The present study therefore contributes to the understanding of stress effects of electrocaloric cooling and provides guidance for experiments to design high-efficiency cooling devices.

**Keywords:** Electrocaloric effect, ferroelectric gradient bilayers, thermodynamic calculation, tunable temperature range.

## 1. Introduction

Ferroelectric materials naturally possess spontaneous electric polarizations that can be tuned with external stimuli (electric field, stress, or temperature, etc.). The electrocaloric effect (ECE) is described as the changes of temperature and entropy of dielectric materials induced by the application or withdrawal of an electric field under adiabatic conditions<sup>1–8</sup>. The ECE has attracted a great deal of attention because it can be used to fabricate domestic and industrial refrigeration systems<sup>9–13</sup> based on solid-state cooling technology<sup>14–20</sup>. Previous studies on the ECE mainly focused on bulk ceramics and single crystals, but their breakdown fields are too low to get a giant enough ECE for commercial applications. Until the giant ECE was realized in PbZr<sub>0.95</sub>Ti<sub>0.05</sub>O<sub>3</sub> (PZT)<sup>21</sup>, PVDF-TrFE<sup>22</sup> ferroelectric thin films and Ba<sub>0.67</sub>Sr<sub>0.33</sub>TiO<sub>3</sub> nanowire arrays<sup>23</sup> under the ultrahigh electric fields, which obtain large entropy changes near ferroelectric-paraelectric (FE-PE) phase transitions. The discovery of giant ECE in thin films appeals to researchers interested in investigating the ECE in ferroelectric materials. For example, BaTiO<sub>3</sub> thick films exhibited a giant ECE of  $\Delta T = 7.1$  K and  $\Delta S = 10.1$  J K<sup>-1</sup> kg<sup>-1</sup> at 80 MV m<sup>-1</sup><sup>24</sup>, wherein the  $\Delta T$  was just 0.9 K with a lower electric field of 1.2 MV m<sup>-1</sup> in the single-crystal BaTiO<sub>3</sub><sup>25</sup>. Saranaya *et al.* reported a larger ECE temperature change ( $\Delta T = 31$  K) at 413 K and 74.7 MV m<sup>-1</sup> in Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)<sub>0.65</sub>Ti<sub>0.35</sub>O<sub>3</sub> thin films deposited by means of pulsed laser deposition<sup>26</sup>. The results revealed that the giant  $\Delta T$  values in thin films are due to the large isothermal entropy changes near ferroelectric-paraelectric (FE-PE) phase transitions, which are attributed to the much higher applied electric field compared with that of bulk materials.

In many ceramics, larger ECE values have been obtained within a narrow temperature range compared to the relaxor ferroelectric materials<sup>27</sup> around the temperature of FE-PE phase transitions above room temperature, which severely limits their applications. A tunable temperature range can improve the efficiency of ECE cooling. Therefore, the most important issue is how to make the operating temperature tunable and simultaneously achieve a giant ECE temperature/entropy change. In previous studies, Hou and Zhang *et al.*<sup>28</sup> reported that the electrocaloric response in composition gradient Ba(ZrTi)O<sub>3</sub> bilayers is significantly enhanced compared with that in homogeneous thick films. Zhao *et al.*<sup>29</sup> reported that the adiabatic temperature change among all compositions of Ba(Ti<sub>1-x</sub>Y<sub>x</sub>)O<sub>3-x/2</sub> ceramics shows a broad temperature range of 50 K. Liu *et al.*<sup>30</sup> studied experimentally that the maximum ECE in compositionally graded Ba<sub>(1-x)</sub>Sr<sub>x</sub>TiO<sub>3</sub> (BST) films is much larger than that in the uniform films with the same thickness and external field. They pointed out that the reduction of the Sr content can reduce the ferroelectric transition temperature to lower temperatures, which further tuned the temperature range. In addition, other studies demonstrated that the compressive or tensile strain induced by external stimuli (electric field, stress, pressure) can markedly change the spontaneous polarization of ferroelectrics<sup>31–35</sup>. What will happen if the compressive and tensile stress is loaded simultaneously on a compositionally graded film? Therefore, the main goal of this work is to analyze the effect of stress-enhanced adiabatic temperature change and operating temperature range of compositionally graded films of ferroelectrics, when the ferroelectrics are simultaneously subjected to compressive and tensile strains.

Although, the change of temperature and entropy of barium strontium titanate solid solution [Ba<sub>(1-x)</sub>Sr<sub>x</sub>TiO<sub>3</sub>

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(BST)] are inferior to that of lead-containing ferroelectrics such as  $\text{Pb}_{0.85}\text{La}_{0.1}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$  (PLZT)<sup>36</sup>, it is an important lead-free and environment-friendly ferroelectric on account of its low and easily controlled ferroelectric transition temperature based on alteration of the Sr content<sup>37–38</sup>. In this work, we aim to enhance the electrocaloric response over a tunable temperature range in composition gradient BST-based bilayers by using the phenomenological Landau-Devonshire theory. We calculated the temperature changes of different compositionally graded BST-based bilayers simultaneously compressive and tensile strains and discuss the results in Section III.

## II. Theoretical Description

In this work, for two different composition gradient (001) BST films epitaxially grown on a thick (001) cubic substrate, the total Gibbs free energy density  $\Delta G$  as a function of polarization  $\mathbf{P}$ , applied field  $\mathbf{E}$ , under external stress  $\sigma$  is given by,

$$\Delta G = f_{\text{LGD}} + f_{\text{elas}} + f_{\text{elec}} \quad (1)$$

where  $f_{\text{LGD}}$ ,  $f_{\text{elas}}$ , and  $f_{\text{elec}}$  are the Landau energy density, elastic energy density and electrostatic energy density. The Landau energy density can be calculated with:

$$\begin{aligned} f_{\text{LGD}} = & \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \\ & \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{123} (P_1^2 P_2^2 P_3^2) + \\ & \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} [P_1^2 (P_2^4 + P_3^4) + \\ & P_2^2 (P_1^4 + P_3^4) + P_3^2 (P_1^4 + P_2^4)] + \alpha_{1111} (P_1^8 + P_2^8 + P_3^8) + \\ & \alpha_{1122} (P_1^4 P_2^4 + P_1^4 P_3^4 + P_2^4 P_3^4) + \alpha_{1112} [P_1^6 (P_2^2 + P_3^2) + \\ & P_2^6 (P_1^2 + P_3^2) + P_3^6 (P_1^2 + P_2^2)] + \alpha_{1123} (P_1^4 P_2^2 P_3^2 + \\ & P_1^2 P_2^4 P_3^2 + P_1^2 P_2^2 P_3^4) \end{aligned} \quad (2)$$

where  $P_1, P_2, P_3$  are the three components of the polarization vector;  $\alpha_1, \alpha_{11}, \alpha_{12}, \alpha_{111}, \alpha_{112}, \alpha_{123}, \alpha_{1111}, \alpha_{1122}, \alpha_{1112}, \alpha_{1123}$  are the higher-order Landau coefficients. The elastic energy density can be expressed by,

$$\begin{aligned} f_{\text{elas}} = & -\frac{1}{2} s_{11} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) - \\ & s_{12} (\sigma_1 \sigma_2 + \sigma_1 \sigma_3 + \sigma_2 \sigma_3) - \frac{1}{2} s_{44} (\sigma_4^2 + \sigma_5^2 + \sigma_6^2) - \\ & Q_{11} (\sigma_1 P_1^2 + \sigma_2 P_2^2 + \sigma_3 P_3^2) - Q_{12} [\sigma_1 (P_2^2 + P_3^2) + \\ & \sigma_2 (P_1^2 + P_3^2) + \sigma_3 (P_1^2 + P_2^2)] - \\ & Q_{44} (\sigma_4 P_2 P_3 + \sigma_5 P_1 P_3 + \sigma_6 P_2 P_1) \end{aligned} \quad (3)$$

where  $s_{11}, s_{12}$  and  $s_{44}$  are the elastic compliance constants at constant polarization, and  $Q_{11}, Q_{12}$  and  $Q_{44}$  the corresponding electrostrictive coefficients,  $\sigma$  is the  $i$ th component of applied stress in Voigt notation. The electrostatic energy density can be expressed by,

$$f_{\text{elec}} = -(E_1 P_1 + E_2 P_2 + E_3 P_3) \quad (4)$$

Indeed, we are considering here relatively thick perovskite films between the top and bottom electrodes. In this case, the calculations take into account the actual finite conductivity of a ferroelectric film, showing that the depolarizing field is negligible. All the Landau potential coefficients in Eq. (2) are assumed to be temperature-independent except  $\alpha_1$ .  $\alpha_1$  is linearly dependent on temperature and obeys the Curie-Weiss law,  $\alpha_1 = (T - T_C)/2\epsilon_0 C$ . Here,  $T_C$  and  $C$  are the Curie-Weiss temperature and constant, and  $\epsilon_0$  is the vacuum permittivity. According to the phase

diagram of BST thin film, we focus on the transition from cubic phase ( $P_1 = P_2 = P_3 = 0$ ) to tetragonal phase ( $P_1 = P_2 = 0, P = P_3 \neq 0$ ) here, which are the stable phases for epitaxial BST thin film at room temperature ( $\text{RT} = 25^\circ\text{C}$ ).

Because we are focusing on the electrocaloric response enhanced over a tunable temperature range in this work, under an external stress, the applied stress tensors satisfy  $\sigma_1 = p$ , ( $p$  is the external stress)  $\sigma_2 = \sigma_3 = \sigma_4 = \sigma_5 = \sigma_6 = 0$ , and Eq. (1) becomes,

$$\Delta G = f_{\text{LGD}} - \frac{1}{2} s_{11} p^2 - Q_{11} p P_1^2 - Q_{12} p P_1 (P_2^2 + P_3^2) - (E_1 P_1 + E_2 P_2 + E_3 P_3) \quad (5)$$

This study was based on indirect measurements using the Maxwell relation  $(\partial P / \partial T)_E = (\partial S / \partial E)_T$ <sup>39</sup>. It is suggested that the reversible adiabatic change in entropy ( $\Delta S$ ) can be calculated using the following relations,

$$\Delta S = - \int_{E_a}^{E_b} \left( \frac{\partial P}{\partial T} \right)_E dE \quad (6)$$

Furthermore, the corresponding ECE temperature change ( $\Delta T$ ) can be determined with

$$\Delta T = - \int_{E_a}^{E_b} \frac{T}{C^E} \left( \frac{\partial P}{\partial T} \right)_E dE \quad (7)$$

where  $C^E$  is the heat capacity per unit volume of the material, the value of  $C^E = 3.05 \times 10^6 \text{ J K}^{-1} \text{ m}^{-3}$  reported for the similar compound  $\text{BaTiO}_3$  used here<sup>30,40</sup>,  $E_a$  and  $E_b$  are the initial and final applied electric fields, respectively. In this work, we calculate the temperature changes under  $E_a$  and  $E_b$ . The parameters for the calculation of the renormalized coefficients for BST film are obtained by averaging the corresponding parameters of  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  materials shown in Table 1.

## III. Results and Discussion

As shown in Fig. 1, we are investigating the bilayer thick films BST-1/BST-2. We are studying the compressive and tensile strains simultaneously on compositionally graded BST bilayer thick films BST-1/BST-2. The middle layer is substrate, BST-1 and BST-2 are two types of thick films that contain a different content of the Sr element ( $x$  value is different), which are deposited above and below the substrate, respectively. In the case, we assumed that the misfit strain equals zero owing to the relaxation of thick films. The application of an external stress on two terminals of the substrate can bend the model. The BST-1 layer is under tensile stress (we assume the tensile stress is positive,  $p > 0$ ) and the BST-2 layer is under compressive stress ( $p < 0$ ) while the external stress puts down, when the external stress in contrast to aforementioned can lead to distortion.

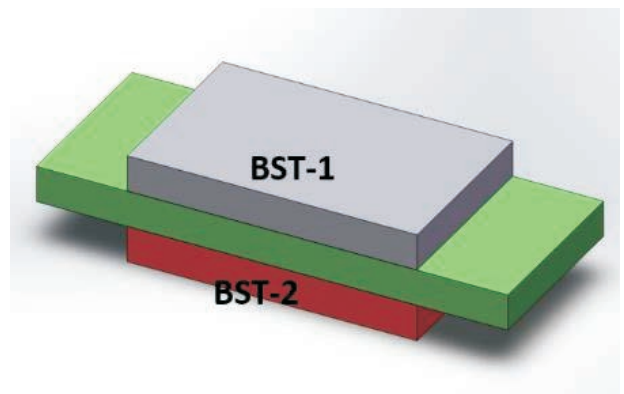
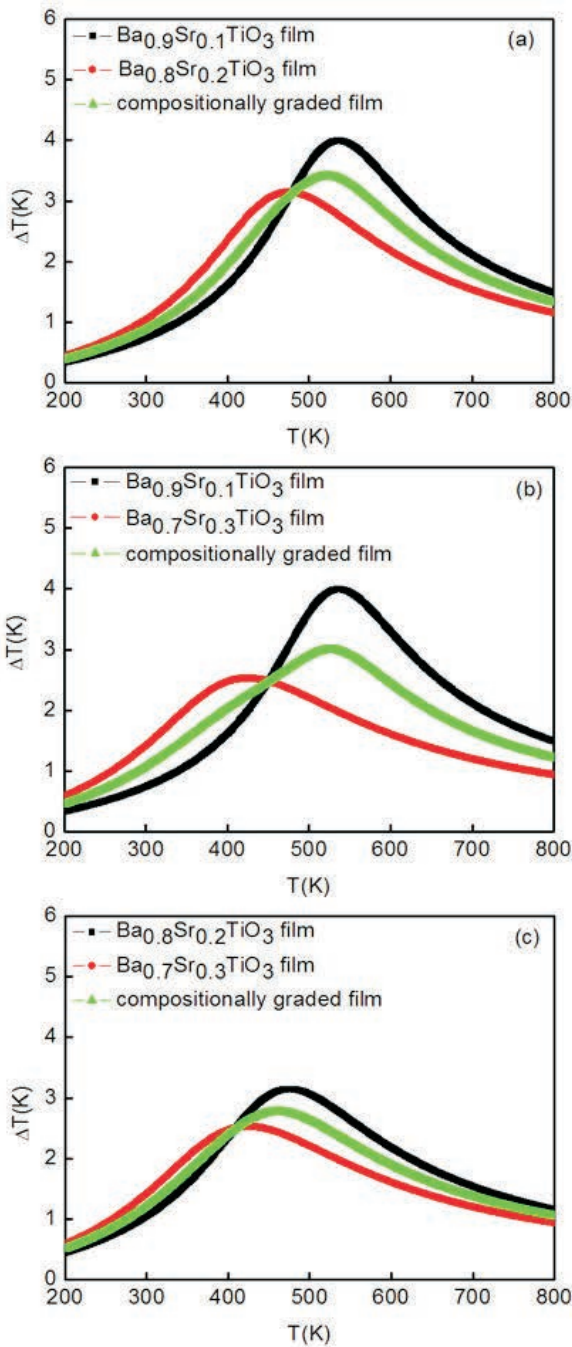


Fig. 1: Model of composition gradient BST bilayers.

**Table 1:** The coefficients for the calculation of the renormalized coefficients for  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  films.

Coefficient	$\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$	Coefficient	$\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$
$\alpha_1$	$5 \times 10^5 \times 160(\text{Coth}[\frac{160}{T}]-\text{Coth}[\frac{160}{390}])(1-x) + (4.05 \times 10^7(\text{Coth}[\frac{54}{T}]-\text{Coth}[\frac{54}{30}]))x$	$\alpha_{1122}$	$-2.221 \times 10^9$
$\alpha_{11}$	$-1.154 \times 10^8(1+0.037p)(1-x)+1.7 \times 10^9x$	$\alpha_{123}$	$-6.688 \times 10^9(1+0.023p)$
$\alpha_{111}$	$-2.106 \times 10^9(1+0.023p)$	$\alpha_{1123}$	$2.416 \times 10^{10}$
$\alpha_{1111}$	$7.59 \times 10^{10}$	$c_{11}$	$(1-x)(1.78 \times 10^{11})+3.156 \times 10^{11}x$
$\alpha_{12}$	$6.53 \times 10^8 \times (1+0.037p)(1-x)+1.37 \times 10^9x$	$c_{12}$	$(1-x)(0.964 \times 10^{11})+1.01 \times 10^{11}x$
$\alpha_{112}$	$4.091 \times 10^9(1+0.023p)$	$Q_{11}$	$0.11(1-x)+0.0457x$
$\alpha_{1112}$	$-2.193 \times 10^{10}$	$Q_{12}$	$-0.045(1-x)+(-0.0135)x$

**Fig. 2:** Electrocaloric temperature changes  $\Delta T$  of compositionally graded bilayers and uniform BST films under electric field  $\Delta E$  and zero external stress.

First, we consider the effect of different Sr content in the composition gradient BST bilayers on tunable temperature span. The ECE temperature changes of uniform and compositionally graded BST bilayers (the same thickness) with no external stress are presented in Fig. 2, respectively. We can easily see that the largest adiabatic temperature change  $\Delta T$  of  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3/\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  bilayers was 3.41 K, which is larger than other two conditions (3.00 K, 2.77 K, respectively). On the other hand, the temperature span of adiabatic temperature change above 2 K ( $\Delta T \geq 2$  K) was  $\sim 273$  K,  $\sim 253$  K,  $\sim 218$  K, respectively. Specifically, a large EC temperature change was obtained over a tunable temperature range in  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3/\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  bilayers, compared with that of  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3/\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  and  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3/\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  bilayers. Hence, we are using  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3/\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  bilayers to study the effect of bending on ferroelectric in the following discussion.

In addition, polarization and electrocaloric temperature changes  $\Delta T$  of compositionally graded bilayers and uniform BST films under different external stress as a function of temperature  $T$  are shown in Fig. 3 and Fig. 4. When the external stress applied is small, the polarization changes are not obvious (Fig. 3 (a) – (d)). But it is found that the temperature change  $\Delta T$  increases with slightly increasing stress (Fig. 4 (a) – (d)) and the largest temperature change  $\Delta T = 3.55$  K, temperature span is 267 K at  $p = 0.4$  GPa. Meanwhile, the temperature range changes barely as a result of small external stress. When the external stress applied to BST bilayers is large, the maximum value of  $\Delta T$  shows a significant decrease. However, the temperature span at  $p = 1$  GPa is about 285 K, which is broader than those at the other stress. If Fig. 2 (a) is compared with Fig. 4 (a) – (f), the tensile stress can shift the maximum in the ECE of  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$  film to a lower temperature, and the compressive stress shows the opposite trend to  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  film, which agrees with the previous publication in Refs. 41 and 42<sup>41–43</sup>. Because the diameter of Ba is greater than that of Sr, the lattice constant of BST films increases with the increasing content of Ba, the lattice constant of  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  is smaller than that of



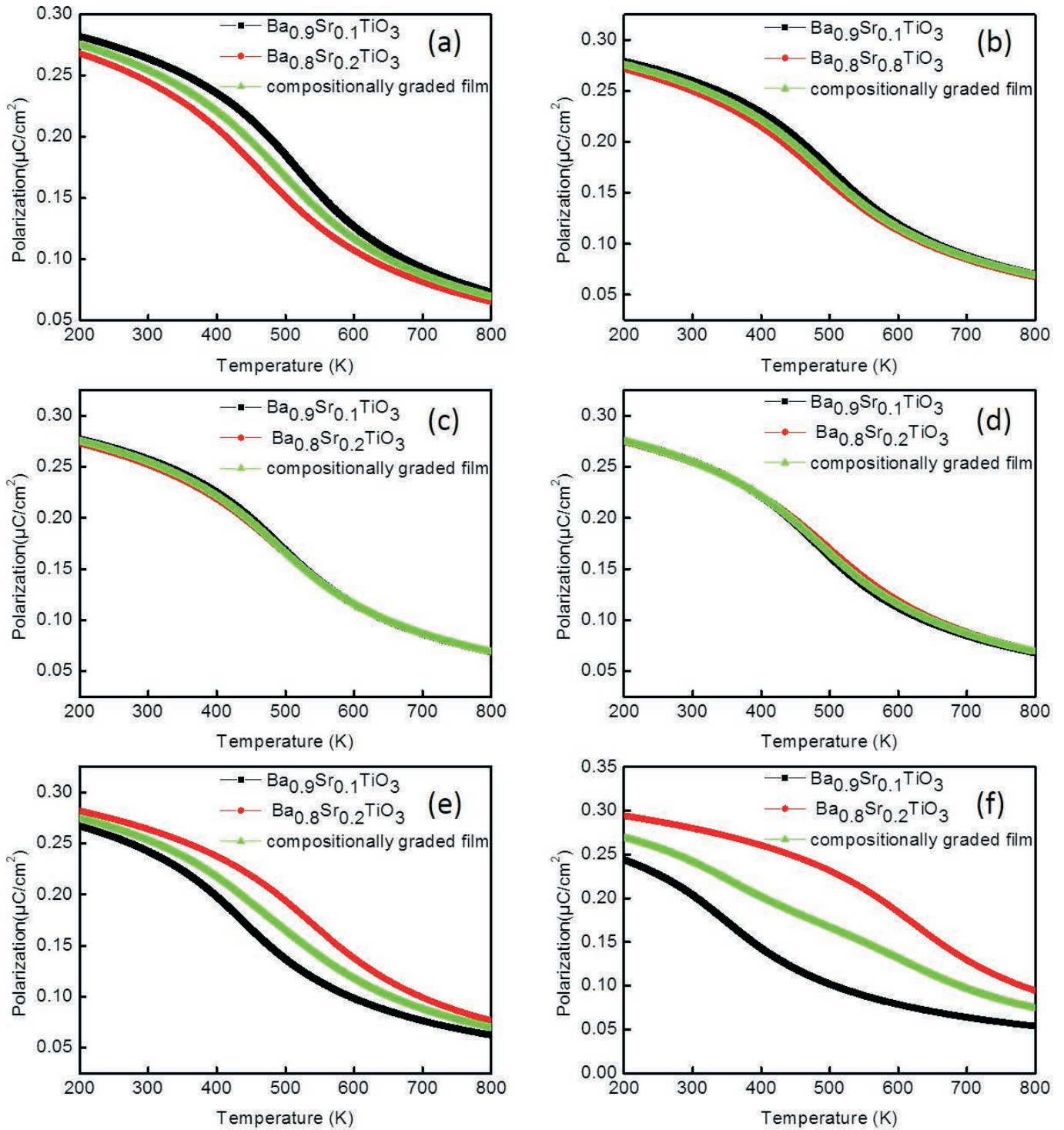
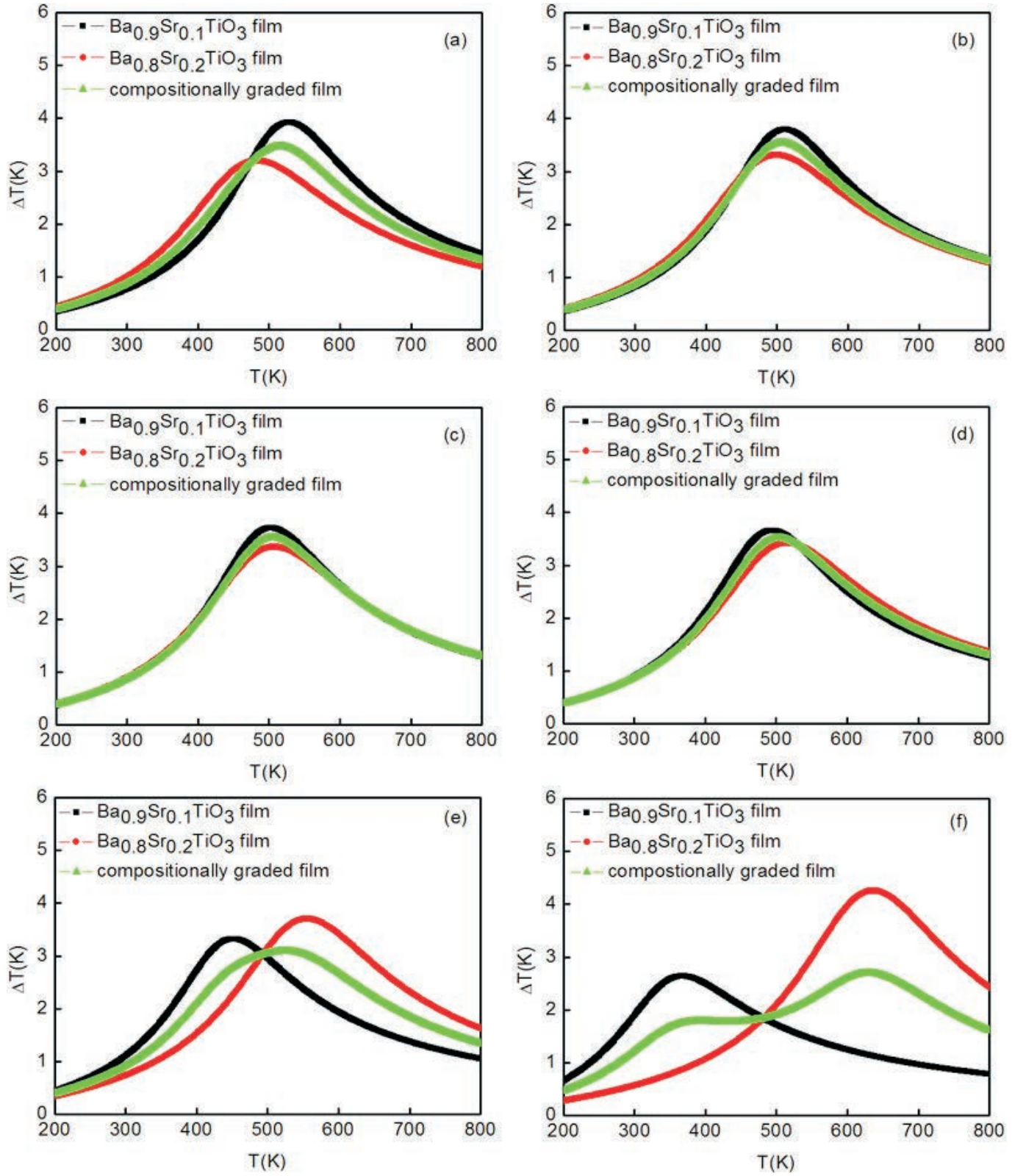


Fig. 3: Polarization of compositionally graded bilayers and uniform BST films under different external stress as a function of temperature  $T$  (a)  $p = 0.1$  GPa (b)  $p = 0.3$  GPa (c)  $p = 0.4$  GPa (d)  $p = 0.5$  GPa (e)  $p = 1.0$  GPa (f)  $p = 2.0$  GPa.

$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ . From a comparison of Fig. 4 (a) - (d) with Fig. 4 (e) - (f), we can easily see that the temperature range changes with adjustment of the external stress. As a result, the maximum of two films in the ECE almost overlap at  $p = 0.4$  GPa, we recommend this stress value as the best choice in this work.

In previous discussions, we assumed the thickness of  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$  film and  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  film is equivalent. But if the thickness affects the temperature change  $\Delta T$  and can tune the temperature range, then we should investigate it next. We calculated the maximum value of  $\Delta T$

and temperature range with different thickness ratio of  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$  film and  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  film at  $p = 0.4$  GPa, which is summarized in Fig. 5. As shown in Fig. 5, the temperature range remains almost unchanged and the temperature change increases linearly with the increase in the thickness ratio of the  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$  film. Therefore, we can conclude that the influence of the thickness ratio on the temperature range can be ignored and the influence of the thickness ratio on the temperature change  $\Delta T$  is significant.



**Fig. 4:** Electrocaloric temperature changes  $\Delta T$  of compositionally graded bilayers and uniform BST films under different external stress as a function of temperature  $T$  (a)  $p = 0.1$  GPa (b)  $p = 0.3$  GPa (c)  $p = 0.4$  GPa (d)  $p = 0.5$  GPa (e)  $p = 1.0$  GPa (f)  $p = 2.0$  GPa.

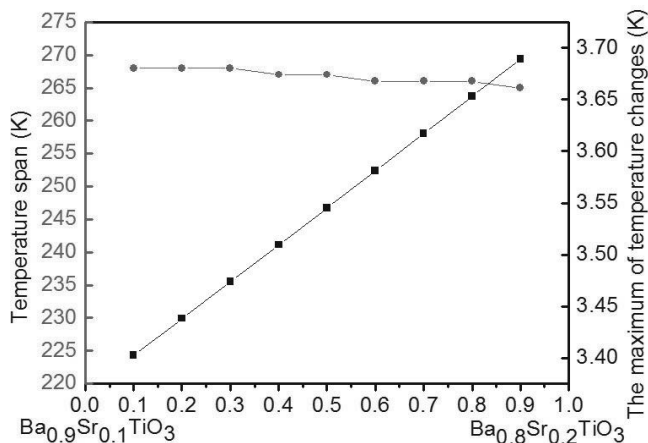


Fig. 5: Temperature range and the maximum of temperature changes as functions of thickness ratio, respectively.

#### IV. Conclusions

To summarize, the effect of bending on the compositionally graded BST bilayers has been demonstrated. We designed a model in order to discuss the effect of stress and thickness ratio on the EC effect of BST-based compositionally graded bilayers. The EC adiabatic temperature change and temperature range of  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3/\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  bilayers with the same thickness is 3.55 K and 267 K at  $p = 0.4$  GPa. The tunable temperature range is attributed to the stress effect, which applied a tensile stress and a compressive stress simultaneously. And the thickness ratio of composition gradient bilayers also can vary the adiabatic temperature change under constant stress. Next, we shall verify if the same design method used in other composition-controlled ferroelectric systems can obtain the large EC effect. As a result, we provide a potential way to design devices for refrigeration technology at a tunable temperature range.

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