



Review

Thickness-dependent electrocaloric effect of $\text{Pb}_{0.82}\text{Ba}_{0.08}\text{La}_{0.10}(\text{Zr}_{0.90}\text{Ti}_{0.10})\text{O}_3$ antiferroelectric thick films



Hongcheng Gao^a, Xihong Hao^{a,*}, Qiwei Zhang^a, Shengli An^a, Ling Bing Kong^b

^a School of Materials and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, China

^b School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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ABSTRACT

Effects of thickness on dielectric properties and electrocaloric effect (ECE) of $\text{Pb}_{0.82}\text{Ba}_{0.08}\text{La}_{0.10}(\text{Zr}_{0.90}\text{Ti}_{0.10})\text{O}_3$ (PBLZT) antiferroelectric (AFE) thick films were systematically studied. As the thickness was increased, the Curie temperature of the thick films was increased, while their diffusing behavior was reduced. A giant reversible adiabatic temperature change of $\Delta T = 25.1$ °C at room temperature was achieved in the PBLZT AFE thick film with a thickness of 1.0 μm . At the same time, the 1.0- μm -thick film had an electrocaloric coefficient of $\Delta T/\Delta E = 0.036$ K cm/kV and a refrigeration efficiency of $\text{COP} = 6.0$ at room temperature. In addition, all samples had a low leakage current density of $<10^{-6}$ A/cm² at room temperature. These results indicated that the PBLZT AFE thick films could be used for applications in solid-cooling devices by properly controlling their thickness.

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1. Introduction

The electrocaloric effect (ECE) refers to the isothermal entropy change (ΔS) and the adiabatic temperature change (ΔT) in the application or withdraw of an electric field under adiabatic conditions [1–3]. In recent years, ECE has attracted great interest because it can be used to fabricate domestic and industrial refrigeration, so as to effectively reduce greenhouse gas emission and energy consumption. Because of the low electric breakdown field of bulk ceramics and single crystal, they usually exhibit very weak ECE, and can not meet the requirement of practical applications [4–6]. Differently, a giant ECE was obtained in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$

antiferroelectric (AFE) thin film [7] and relaxor ferroelectric (FE) polymer [8], due to their excellent electric field endurance, which offered a new opportunity to develop cooling systems based on ECE. Currently, the present studies on ECE are mainly focused on the FE/AFE-paraelectric (PE) transition switching process, because of the large entropy change during the structure phase transition [9,10]. However, the phase transition of AFE/FE-PE usually occurs at a higher temperature, which usually is quite above room temperature.

In fact, the phase transition between AFE and FE could also be realized by applying an external field in a wide temperature range near room temperature, and is accompanied by a large entropy change. The first work on the ECE of AFEs was reported by Thacher in 1968, in which a temperature change of $\Delta T = 1.6$ K at 328 K was observed in $\text{Pb}(\text{Zr}_{0.455}\text{Sn}_{0.455}\text{Ti}_{0.09})\text{O}_3$ bulk ceramic during the FE-

* Corresponding author.

E-mail address: xhhao@imust.cn (X. Hao).

AFE phase switching [11]. Recently, a giant ECE peak ($\Delta T = 37.1$ K) at room temperature was also reported in a ZrO₂-buffered PLZST AFE thick films [12]. Therefore, it is expected that large ECE near room temperature could be obtained in AFEs by using the electric field-induced phase transition. However, to the best of our knowledge, the ECE of AFEs has not been extensively studied up to now [13,14].

Comparatively, it has been accepted that thick films, which have high critical breakdown field like thin films and also possess large volume like bulk ceramics, are more likely to be used in practice. However, the effects of thickness on ECE of AFE thick films are rarely reported. Various factors have been evaluated to influence the ECE of AFE/FE in thin-film and bulk-ceramic form, including the chemical composition, thickness, orientation, and so on [15–17]. Thus, in this work, Pb_{0.82}Ba_{0.08}La_{0.10}(Zr_{0.90}Ti_{0.10})O₃ AFE thick films with different thicknesses were prepared by using a sol-gel route. The thickness-dependent dielectric properties and ECE of thick films were systematically investigated, with an aim to control the film thickness to adjust the cooling properties of AFE thick films.

2. Experimental procedures

Pb_{0.82}Ba_{0.08}La_{0.10}(Zr_{0.90}Ti_{0.10})O₃ (PBLZT) thick films were prepared by using a sol-gel method. Starting chemicals were lanthanum acetate hydrate, titanium isopropoxide, zirconium propoxide, lead acetate trihydrate and barium acetate. Acetate and deionized water were used as solvents. Firstly, lead acetate trihydrate with 20% excess, barium acetate and lanthanum acetate hydrate were dissolved in acetic acid at 110 °C with a ratio according to the predetermined compositions. After the solution was cooled to room temperature, zirconium propoxide and titanium isopropoxide were added, and stirred for 30 min.

To improve mechanical properties of the films, ethylene glycol was added into the solution in a ratio of 1 mol ethylene glycol to 1 mol lead. The final concentration of the PBLZT precursor solution was 0.5 M. Conductive LaNiO₃ (LNO) layers with (100) orientation were used as bottom electrodes, which were deposited on Si (100) substrates by using a chemical solution deposition route similar to that reported in Ref. [12].

After the precursor solution was aged for 24 h, PBLZT thick films were deposited on the LaNiO₃/Si(100) substrates by using a multistep spin-coating technique. Each layer was spin-coated at 3000 rpm for 40 s. In order to form a uniform film, every wet film was first dried at 350 °C for 10 min and then pyrolyzed at 600 °C for 10 min to remove the organics. The spin coating and heat treatment were repeated several times to obtain films with desired thicknesses. To compensate the loss of lead and thus form a single phase perovskite, a capping layer of PbO from 0.4 M solution of lead acetate trihydrate was deposited, before the films were finally anneal at 700 °C for 20 min. Final thicknesses of the thick films were 1.0, 1.5 and 2.0 μm, estimated from their cross-sectional SEM images.

Phase composition of the PBLZT thick films was analyzed by using X-ray diffraction (XRD Bruker D8 Advanced Diffractometer, German). Surface morphology of the films were examined by using a field-emission scanning electron microscopy (FE-SEM ZEISS Supra 55, German). To measure electrical properties, gold pads of 0.20 mm in diameter were coated on the film surface as top electrodes by using a DC sputtering. Temperature, frequency and electric field dependences of dielectric properties of the thick films were measured by using a computer-controlled Agilent E4980A LCR analyzer. Field-induced hysteresis loops and leakage current characteristics of the PBLZT thick films were measured by using a Ferroelectric tester (Radiant Technologies, Inc., Albuquerque, USA). The ECE performance of the films was calculated according to the *P-E* results.

3. Results and discussion

Fig. 1(a) shows XRD patterns of the PBLZT films with different thicknesses annealed at 700 °C. It is shown that all the samples are well crystallized with a perovskite structure. Moreover, with the thickness increasing, the PBLZT thick films were changed from (100)-preferred orientation to random orientation. Fig. 1(b) shows the (100)-preferential ratios (α), calculated according to the following formula [18]:

$$\alpha = \frac{I(100)}{\{I(100) + I(110) + I(111)\}}, \quad (1)$$

where $I(hkl)$ is the corresponding XRD peak intensity. As the thickness was increased from 1.0 to 2.0 μm, (100)-preferential ratio was decreased from 91% to 52%. The (100)-preferred orientation of PBLZT films was induced by the (100)-preferred LNO bottom electrodes, due to the small mismatch between the AFE films and LNO [12]. As the thickness was increased, the effect of the LNO was decreased. Thus, the preferred orientation was also declined. Moreover, it was reported that the (100)-preferred orientation of the lead-based films also strongly dependent on the lead content [19]. Therefore, PBLZT films with higher thickness were inevitably experienced more times heat-treatment process, which led to much lead loss. As a result, the preferred degree was reduced. Similar results were also observed in PZT thin films [20]. The declined orientation maybe has an effect on the dielectric properties of the films.

FE-SEM images of the thick films are shown in Fig. 2(a–c). All samples have a smooth, dense and void-free microstructure. The cross-sectional SEM images of the films are shown in Fig. 2(d–f), further confirming their uniform structure. The PBLZT thick films with thicknesses of 1.0, 1.5 and 2.0 μm had average grain sizes of about 650, 720 and 690 nm, respectively. Due to the small difference, the effect of grain size on the dielectric properties of these thick films could be neglected.

Frequency-dependent dielectric constant (ϵ_r) and dielectric loss of the PBLZT AFE thick films, measured from 1 kHz to 1 MHz at room temperature, are plotted in Fig. 3. With the frequency increasing, a gradual decrease in the dielectric constant is observed in all the films, which could be understood by taking into account the different response times of different dipoles [21]. Moreover, the change of the thickness of the films has an obvious effect on their dielectric constant [22,23]. Clearly, the dielectric constant has an increased tendency as the film thickness is increased, while the dielectric loss is slightly varied. The similar results were also observed in PZT and PLZT films [24,25]. Generally, a dead layer (\leq a few nanometers) with an extremely low dielectric constant is often formed at the interface between the film and electrode, which leads to the reduction of the overall measured dielectric constant [26]. Moreover, when thus a dead layer is present at the metal-dielectric interface, a depolarization field is also created, which also reduce the dielectric constant of the films [25]. As the thickness increases, the effect of dead layer could be reduced [27]. As a result, the films with a larger thickness usually possess an improved dielectric constant. The corresponding values of dielectric constant and dielectric loss at 1, 100 kHz and 1 MHz are listed in Table 1. It should be noted here that the slightly reduction in dielectric constant of the films with a thickness of 2.0 μm should be contributed to its declined (100)-preferred orientation [19].

Fig. 4(a) shows the electric field-induced polarization (*P-E*) of the PBLZT films, measured at 1 kHz and 400 kV/cm. All the *P-E* curves are slim double hysteresis loops, indicating their AFE nature. A small remnant polarization (P_r) is detected in the films, as shown in the inset of Fig. 4(a), which is decreased with the thickness

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