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Orientation-dependent energy-storage performance and electrocaloric effect in PLZST antiferroelectric thick films

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ABSTRACT

The enhancement of the energy-storage performance and electrocaloric effect (ECE) was achieved via orientation control. The 1.5-μm-$(Pb_{0.97}La_{0.02})(Zr_{0.73}Sn_{0.22}Ti_{0.05})O_3$ (PLZST) antiferroelectric (AFE) thick films with (111), (110), and (100) crystallographic orientations were successfully prepared via a sol-gel method. It was found that both the enhanced energy-storage density of 13.5 J/cm^3 at 900 kV/cm and the corresponding temperature reduction of $\Delta T = 28.1\,^\circ C$ at room temperature were obtained in the PLZST thick film with (111) orientation due to a high polarization. Moreover, these films with different orientations display a small leakage current density at the room temperature. These results suggest that both energy-storage properties and cooling performance in AFEs could be optimized by the proper orientation control.

1. Introduction

In order to reduce the dependency on fossil based energy reserves, the successful production, distribution, and storage of electricity will form a cornerstone for the development and growth of society and technology in the coming century. The generation of electricity from renewable and non-conventional resources is being investigated and is attracting much attention. High energy-storage density dielectric capacitors as a means for storage of electric energy form an indispensible part of all modern electronic and electrical devices [1–4].

In generasmall remnant polarizationl, the recoverable energy-storage density W and the energy-storage efficiency η are two crucial parameters, which can be calculated according to the equations as below [5]:

$$W = \int_{P_r}^{P_{max}} EdP, \tag{1}$$

$$W_{loss} = \int EdP, \tag{2}$$

$$\eta = \frac{W}{W + W_{loss}}, \tag{3}$$

where E is the applied electric field, P is the polarization, P_r is remanent polarization, P_{max} is the maximum polarization, and W_{loss} is the energy loss density. Obviously, the high energy-storage density depends on smaller P_r, larger P_{max} and good electric field endurance. Antiferroelectrics (AFEs) play a key role in the dielectric energy-storage capacitors due to the high maximum polarization and large electric field induced-strain. In recent years, PbZrO-strain$_3$-based AFE materials, such as $Pb_{0.97}La_{0.02}(Zr_{0.97}Ti_{0.03})O_3$, $(Pb_{0.97}La_{0.02})(Zr_{0.95-x}Sn_xTi_{0.05})O_3$, $Pb_{0.8}Ba_{0.2}ZrO_3$, Sr-doped $PbZrO_3$, Eu-doped $PbZrO_3$, and Nb-doped $PbZr_{0.4}Ti_{0.6}O_3$, were widely investigated in the high energy-storage performancewidely investigated in the high energy-storage density capacitors storage performance [6–10].

Like dielectric capacitors, a highly efficient and environmentally friendly solid-state cooling technology also has attracted much attention for the micro-electromechanical systems [11,12]. It offers an alternative to the traditional vapor-compression cooling

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method accompanied hazardous gases, which is widely used in household and industrial applications. There are several technologies being developed by using of various solid-state cooling technology, such as electrocaloric, magnetocaloric and mechanocaloric effects. Electrocaloric effect (ECE) refers to a change in temperature under adiabatic application of external electric fields [13–15]. Alternatively, it can be described as an isothermal change in entropy. To achieve a large electrocaloric effect, a phase transition is desirable, where the entropy change (ΔS) is maximized. For example, the giant ECE observed in the $0.9PbMg_{1/3}Nb_{2/3}O_3$-$0.1PbTiO_3$ film, $PbZr_{0.95}Ti_{0.05}O_3$ film, and $Pb(Zr_{0.455}Sn_{0.455}Ti_{0.09})O_3$ bulk ceramic are associated with ferroelectric (FE)-paraelectric (PE), AFE-PE, and AFE-FE phase transitions, respectively [16–18]. Compared with FE (or AFE)-PE phase transition, the FE-AFE phase transition could be easily realized in a wide temperature range near 25 °C. Moreover, a considerable pyroelectric effect is also formed during FE-AFE transition, which is even larger than that caused by FE (or AFE)-PE phase transition. Therefore, good ECE should also be obtained during FE-AFE phase transition. Quite recently, a giant ECE ($\Delta T = 53.8\,°C$ and $\Delta S = 63.9\ J\,K^{-1}\,kg^{-1}$) with an electrocaloric coefficient of 0.060 K cm/kV was also achieved at 5 °C in our work on 2-μm-$Pb_{0.97}La_{0.02}(Zr_{0.75}Sn_{0.18}Ti_{0.07})O_3$ AFE thick film, which is comparable with the best results in FE materials [19]. These results indicate that ECE originated from FE-AFE phase transition is a promising route for the practical cooling applications.

Energy-storage performance and ECE of the dielectric materials are strongly dependent on their polarization character, which could be tuned by the phase structure, grain size, stress, interface layer, growth orientation, and so on. Orientation is a powerful tool, through which, for instance, enhanced the energy-storage performance, tuned the ferroelectric-antiferroelectric phase transition, and improved the ECE [20–22]. Based on these results, in this work, we report that a typical lead-based AFE thick films of $(Pb_{0.97}La_{0.02})(Zr_{0.73}Sn_{0.22}Ti_{0.05})O_3$ exhibits an orientation-dependent energy storage performance and electrocaloric effect.

2. Experimental procedure

The composition of $(Pb_{0.97}La_{0.02})(Zr_{0.73}Sn_{0.22}Ti_{0.05})O_3$ (PLZST) was selected to study, which is located in the morphotropic phase boundary (MPB). The PLZST precursor solution was deposited on Pt(111), $LaNiO_3$(110)/Pt(111) and $LaNiO_3$(100)/Pt(111) substrates via a sol-gel method, respectively. The detailed process could be found in reference [23]. The only difference is that the PLZST films deposited on Pt(111) was annealed at 700 °C for 25 min and the film deposited on $LaNiO_3$(110)/Pt(111) and $LaNiO_3$(100)/Pt(111) were annealed at 700 °C for 30 min in order to reduce discrepancy of grain size. The final thickness of all the PLZST AFE thick film was about 1.5 μm.

Here, $LaNiO_3$ thin films were prepared on the Pt(111) by sol-gel method similar to Ref. [24]. Lanthanum nitrate $[La(NO_3)_3]$ and nickel acetate $[Ni(CH_3COO)_2 \cdot 4H_2O]$ were used as the start materials, and acetic acid and water were used as the solvents. In order to avoid cracking during heating, formamide was also added to the system. The concentration of the precursor solution was adjusted to 0.2 M. The $LaNiO_3$ precursor solution was spin coated on the Pt(111) substrates at 3000 rpm for 20 s. For $LaNiO_3$(110) film, each wet film was heat treated at 450 °C for 10 min. This procedure was repeated several times. The process was repeated several times. Finally, the $LaNiO_3$ films were annealed at 700 °C for 60 min to obtain a well-crystallized structure. The whole thermal treatment was completed in a tube furnace [24]. For $LaNiO_3$(100) film, each wet film was fired at 160 °C for 300 s, then pyrolyzed at 400 °C for 360 s and finally annealed at higher temperatures for 240 s. The process was repeated several times. Finally, the $LaNiO_3$ films were annealed at 700 °C for 45 min to obtain desired thickness $LaNiO_3$(100) films. The whole thermal treatment was completed in an RTP furnace [25]. The thickness of both $LaNiO_3$(110) film and $LaNiO_3$(100) film are about 400 nm. In order to obtain the same grain size of both $LaNiO_3$ (110) and $LaNiO_3$ (100) films, the annealing time of $LaNiO_3$ (100) film was shortened by 15 min than that in our previous work [23]. For convenience, the PLZST AFE thick films deposited on Pt(111), $LaNiO_3$(110)/Pt(111) and $LaNiO_3$(100)/Pt(111) substrates are abbreviated as PLZST(111), PLZST(110), and PLZST(100) films, respectively.

The microstructure of the PLZST AFE thick films was analyzed by X-ray diffraction (XRD Bruker D8 Advanced Diffractometer, German) and field-emission scanning electron microscopy (FE-SEM ZEISS Supra 55, German), respectively. For the electrical measurements, gold pads of 0.20 mm in diameter were coated on the films surface as top electrodes by using a DC sputtering method. A computer-controlled Agilent E4980A LCR analyzer was employed for measuring the frequency, and temperature-dependent dielectric properties with the AC drive amplitude of 50 mV. The polarization-electric field hysteresis loops (P–E) at 1 kHz and the leakage current characteristic of the films were measured by a Ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM).

3. Results and discussion

Fig. 1 shows the XRD patterns of PLZST AFE thick films grown on Pt(111), $LaNiO_3$(110)/Pt(111) and $LaNiO_3$(100)/Pt(111) substrates after annealing at 700 °C. For convenience, the lattice indexes of the diffraction peaks are labeled as pseudocubic structure. All the thick films have crystallized into a pure perovskite phase without any other phases. Apparently, the PLZST film on the Pt(111) substrate shows well (111)-preferred orientation, while PLZST films on the $LaNiO_3$(110)/Pt(111) and $LaNiO_3$(100)/Pt(111) substrates display (110) and (100)-preferred orientations, respectively. In order to estimate the orientation degree of the PLZST films on three substrates, orientation factor $\alpha_{(111)}$, $\alpha_{(110)}$, and $\alpha_{(100)}$ are given according to the following well known formulas [26]:

$$\alpha_{(111)} = \frac{I_{(111)}}{I_{(111)} + I_{(110)} + I_{(100)}}, \tag{4}$$

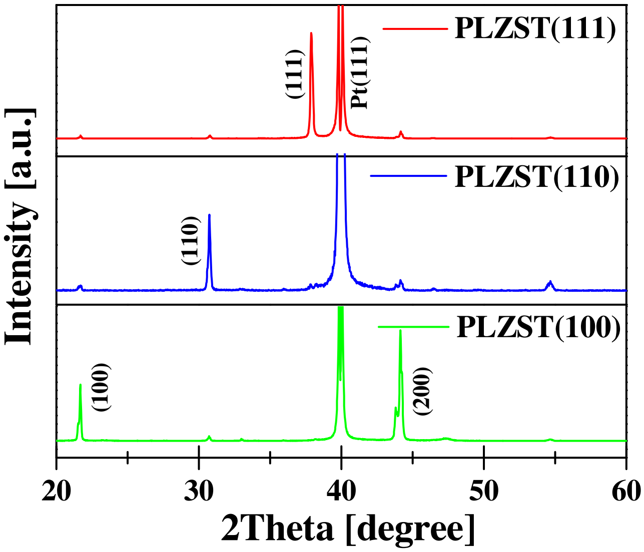

Fig. 1. XRD patterns of the PLZST(111), PLZST(110) and PLZST(100) AFE thick films.