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($\text{Pb}_{0.97}\text{La}_{0.02}$)($\text{Zr}_{1-x-y}\text{Sn}_x\text{Ti}_y$) O_3
antiferroelectric thin films

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Large strain and high energy storage density in orthorhombic perovskite (Pb_{0.97}La_{0.02})(Zr_{1-x}YSn_xTi_y)O₃ antiferroelectric thin films

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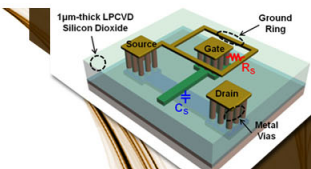
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Large strain and high energy storage density in orthorhombic perovskite $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{1-x-y}\text{Sn}_x\text{Ti}_y)\text{O}_3$ antiferroelectric thin films

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Antiferroelectric $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{1-x-y}\text{Sn}_x\text{Ti}_y)\text{O}_3$ (PLZST) thin films with orthorhombic perovskite structure were prepared on Si substrates by a chemical solution deposition process. A secondary pyrochlore phase, which was not detectable with x-ray diffraction, was revealed with transmission electron microscopy. The pyrochlore phase was effectively suppressed by the introduction of polyethylene glycol (PEG) in the precursor solution and applying PbO capping layer on the surface of the films. With the persistent and detrimental pyrochlore phase removed completely, our PLZST antiferroelectric thin films exhibited excellent electrical and electromechanical properties. A large energy storage density up to 13.7 J/cm^3 was exhibited from the polarization measurement, and a strain of 0.49% under the clamping of the substrate was also achieved in the thin film with high Zr content. © 2010 American Institute of Physics. [doi:10.1063/1.3497193]

Lanthanum-doped lead zirconate stannate titanate (PLZST) antiferroelectric (AFE) bulk ceramics and thin films possess large strain (maximum 0.87% and 0.32% as reported for bulk and thin film, respectively).^{1–6} Electric field induced AFE to ferroelectric (FE) transformation, which is the origin of the large strain,^{7–9} has been explored by *in situ* x-ray and electron diffraction analysis.^{10–12} In addition to the large strain, orthorhombic PLZST AFE materials are also promising for energy storage with their high storage density, resulting from their double hysteresis loop, large switching fields, and ideally zero remnant polarization.^{13–15} For bulk ceramic systems, the switching between the AFE and FE states occurs at low field (tenth of kilovolt per centimeter), leading to small energy storage density (0.41 J/cm^3)¹⁶ but large effective piezoelectric strain constant d_{33} (1891 pm/V)¹ which is much larger than that of bulk $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) (700 pm/V).¹⁷ For thin films, large switching field (a few hundred kilovolt per centimeter) results in much smaller effective d_{33} (80 pm/V),⁵ which is not substantially advantageous over high quality FE PZT thin films (110 pm/V),¹⁸ although the energy storage density is significantly higher (8.13 J/cm^3)^{15,19} compared to the bulk counterpart. However, it should be noted that all the achieved strain in PLZST thin films are far smaller than the bulk, and some possible reasons could be cracking and secondary phases in the films with the complex compositions.^{20,21}

In this work, secondary pyrochlore phase was effectively suppressed by the introduction of polyethylene glycol (PEG) in the precursor solution and completely eliminated by PbO capping layer on the surface of our AFE $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{1-x-y}\text{Sn}_x\text{Ti}_y)\text{O}_3$ (PLZST) thin films prepared by a chemical solution deposition process. A significantly improved energy storage density up to 13.7 J/cm^3 was exhibited from the polarization measurement, and a strain of 0.49% under the clamping of the substrate was also achieved in the thin film sample.

Four different compositions were studied as shown in Table I, covering the composition range corresponding to orthorhombic phase with the largest strain as reported for the bulk. Stoichiometric amounts of lead acetate trihydrate, lanthanum acetate hydrate, zirconium acetyl-acetonate, tin acetate and titanium isopropoxide were dissolved in 2-methoxyethanol to obtain 0.3M PLZST precursor solution. PEG was added to the solution with mole ratio of Pb:PEG=1:1. To compensate the Pb loss during heat treatment, 10 wt % excess lead precursor was added to the solution. Layers were continuously spin coated on Pt/Ti/SiO₂/Si substrates at 5000 rpm to achieve thickness in the range of 800–900 nm. A PbO capping layer was deposited prior to

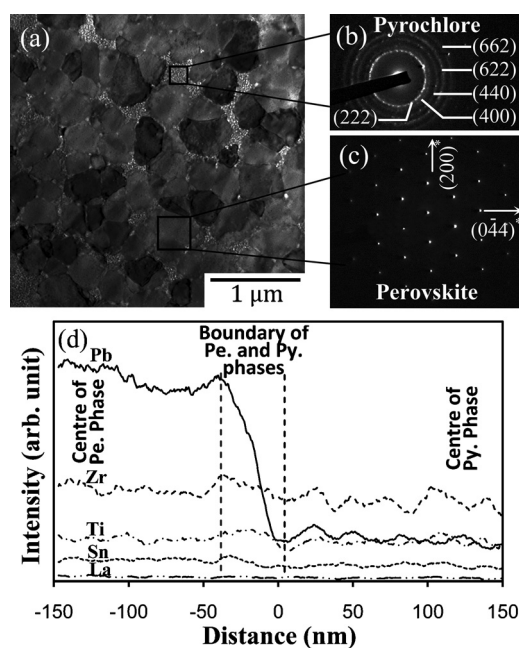


FIG. 1. (a) Bright field TEM micrograph of PLZST 65/30/05 without PbO capping layer, (b) SAED of pyrochlore (Py.) phase, and (c) of perovskite phase (Pe.). (d) EDS line profile of the same sample acquired from the center of perovskite phase to the center of pyrochlore phase.

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TABLE I. Summary of compositions, sample names, and properties of PLZST films.

Sample Composition	(Pb _{0.97} La _{0.02}) (Zr _{0.65} Sn _{0.30} Ti _{0.05})O ₃	(Pb _{0.97} La _{0.02}) (Zr _{0.75} Sn _{0.20} Ti _{0.05})O ₃	(Pb _{0.97} La _{0.02}) (Zr _{0.90} Sn _{0.05} Ti _{0.05})O ₃	(Pb _{0.97} La _{0.02}) (Zr _{0.85} Sn _{0.13} Ti _{0.02})O ₃
Sample designation	PLZST 65/30/05	PLZST 75/20/05	PLZST 90/05/05	PLZST 85/13/02
Saturation polarization ($\mu\text{C}/\text{cm}^2$)	25	29	39	34
Remnant polarization ($\mu\text{C}/\text{cm}^2$)	1.6	2.6	1.0	1.9
AFE to FE switching field (kV/cm)	110	140	260	190
FE to AFE switching field (kV/cm)	60	80	150	110
Dielectric constant at 1 kHz	352	348	318	238
Loss at 1 kHz	0.041	0.031	0.024	0.027
Energy storage density (J/cm^3)	11.1	10.1	13.7	10.8
Strain (%)	0.26	0.27	0.49	0.35

final annealing at 700 °C in air, while some samples were prepared without the capping layer for comparison. For electrical property testing, Au layer was deposited on the top surface to form sandwich electrode structure.

The crystalline phase and morphology of the thin films were examined by x-ray diffraction (XRD, D8-Advance, Bruker AXS GmbH, Karlsruhe, Germany), transmission electron microscopy (TEM, JSM-6100F, JEOL, Ltd., Japan), and field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL, Ltd., Japan). Dielectric constant (ϵ_r) and dielectric loss (D) were measured with an impedance analyzer (HP4194A). Polarization-electric field (P - E) characteristics were evaluated with a standard RT66A (Radiant Technologies, USA) testing unit. A laser scanning vibrometer (OFV-056, PolyTech GmbH, Germany) was used to measure electric field induced strain.

Only orthorhombic perovskite phase was observed in XRD spectra for all the films derived from the solution with PEG introduced (see Ref. 22) but two types of crystals were found in bright field TEM micrographs. As shown in Fig. 1(a), small grains with average size of approximately 10 nm are mixed with large grains with average size of 500 nm. TEM-energy dispersive x-ray spectroscopy (EDS) line scan from the center of one large grain to the center of colony of small grains is presented in Fig. 1(d). Pb content decreased while crossing the boundary of the two areas from the large to small grains. Indexing selected area electron diffraction (SAED) micrograph of the two types of crystals [Figs. 1(b) and 1(c)] revealed that, the small crystals are $\text{A}_2\text{B}_2\text{O}_{7-\delta}$ pyrochlore phase while the bigger ones are orthorhombic perovskite phase. These results were further confirmed with high resolution TEM (see Ref. 22). Figure 2 shows the FESEM micrograph of sample PLZST 90/05/05 without [Fig. 2(a)] and with [Fig. 2(b)] PbO capping layer. The pyrochlore phase was completely eliminated, and the grain size and crystallinity for the perovskite phase were improved after applying the PbO capping layer.

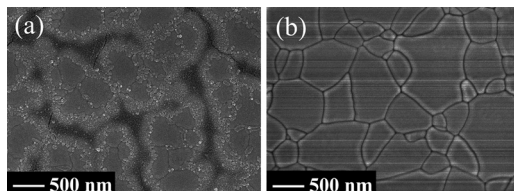


FIG. 2. FESEM micrographs of PLZST 90/05/05 film annealed at 700 °C without (a) and with (b) PbO capping layer.

Electrical properties of the PLZST films with pyrochlore phase removed are summarized in Table I. Dielectric constant and loss values ranged from 238 to 318 and 0.024 to 0.041, respectively, and were slightly decreasing with increasing frequency (see Ref. 22). These values decreased with increasing Zr:Sn ratio, which is consistent with the trend reported by Xu *et al.*¹⁵ and Hao *et al.*²⁰ for PLZST thin films. For PLZST 85/13/02, dielectric constant was smaller than PLZST 90/05/05 due to the low Ti content as proposed in the literature.³

Room temperature polarization hysteresis loops of the PLZST thin films with pyrochlore phase removed are shown in Fig. 3. All the samples exhibited double hysteresis loops and small remnant polarization. This indicates that all the films were AFE, however, small amount of FE phase remained after removing the field.²³ Saturation polarization, forward and backward switching fields increased from 25 $\mu\text{C}/\text{cm}^2$ to 39 $\mu\text{C}/\text{cm}^2$, 110 kV/cm to 260 kV/cm, and 60 kV/cm to 150 kV/cm, respectively, and hysteresis loop changed from slanted to square shape as the Zr:Sn ratio increased. Energy storage density is equal to the area between the polarization axis and back arm of the hysteresis loop.¹³ It is equal to 11.1 J/cm^3 , 10.1 J/cm^3 , 10.8 J/cm^3 , and 13.7 J/cm^3 at applied field of 1.5 MV/cm for PLZST 65/30/05, PLZST 75/20/05, PLZST 85/13/02, and PLZST 90/05/05, respectively. These results are significantly larger than those reported previously for PLZST bulk ceramic (0.41 J/cm^3)¹⁶ and films (8.13 J/cm^3).¹⁵

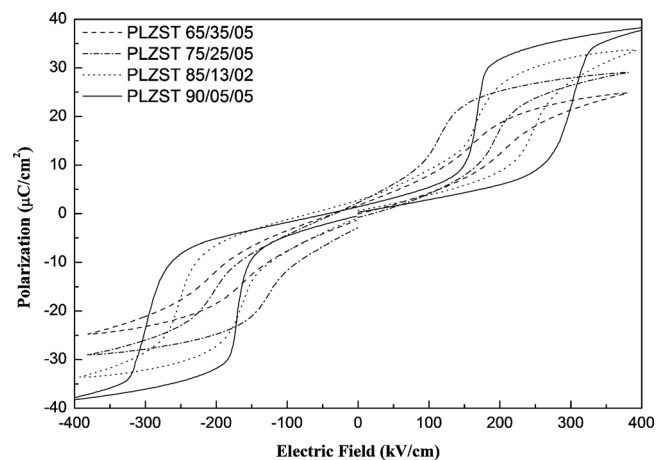


FIG. 3. Polarization-electric field hysteresis loops of PLZST thin film samples at room temperature.

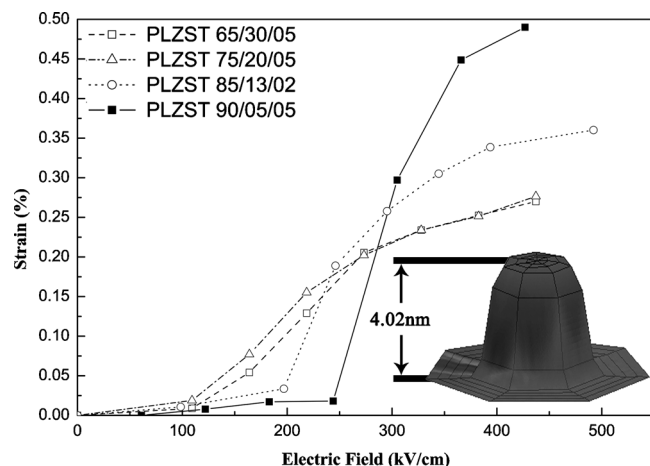


FIG. 4. Electric field induced strain for PLZST films. Inset shows the field induced displacement profile of the PLZST 90/05/05 film over the area of top electrode with electric field applied.

Strain measurements over different electric fields revealed that with increasing Zr:Sn ratio, the film response changes from gradual to steep, which is consistent with the change in type of the polarization hysteresis loops from slanted to square shape (Fig. 4). The forward switching field increased with Zr content which is in agreement with the polarization hysteresis measurements. Similar to the bulk PLZST, electric field induced dilatation increased with Zr:Sn ratio.³ The dilatation magnitude reached 4.02 nm for PLZST 90/05/05 (inset of Fig. 4) yielding in strain of 0.49% (effective d_{33} of 123 pm/V), which is a significant improvement over the previously obtained largest strain of 0.32% (effective d_{33} of 80 pm/V)⁵ for PLZST films under the constraint of the substrate, and the effective d_{33} is competitive to high quality polycrystalline PZT films (110 pm/V).¹⁸ The strain of 0.49% for our PLZST thin film is still lower than the maximum strain of 0.87% in bulk sample,¹ and the main reason is believed to be the in-plan substrate clamping effect for the thin films deposited on substrates.

The large energy storage density and large field induced strain demonstrated in our PLZST thin films are attributed to the single phase perovskite structure without any pyrochlore phase. Even if minor pyrochlore phase exists, which is not detectable by conventional XRD, it is substantially detrimental to the performance properties, particularly to the energy storage density and electric field excited strain. The promotion of perovskite phase with appropriate polymer additives has been observed in lead-based FE systems prepared through chemical solution approach.^{24–28} Application of PbO capping layer has also been conducted to suppress the formation of the pyrochlore phase in other lead-based FE systems.^{29–31} Here a combination of the two approaches completely eliminated the persistent and detrimental pyrochlore phase in PLZST AFE thin films, leading to the large energy storage density and large field induced strain.

In summary, AFE $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{1-x-y}\text{Sn}_x\text{Ti}_y)\text{O}_3$ (PLZST) thin films with orthorhombic perovskite structure were prepared on Si substrates by a chemical solution deposition process. A secondary pyrochlore phase, which was not detectable with XRD, was revealed with TEM. The pyrochlore phase was effectively suppressed by the introduction of the PEG in the precursor solution and applying PbO capping layer on the surface of the films. With the persistent and detrimental pyrochlore phase removed completely, our PLZST AFE thin films exhibited excellent electrical and electromechanical properties. A large energy storage density up to 13.7 J/cm³ was exhibited from the polarization measurement, and a strain of 0.49% under the clamping of the substrate was also achieved in the thin film with high Zr content.

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