

## Superior energy-storage properties in (Pb,La)(Zr,Sn,Ti)O<sub>3</sub> antiferroelectric ceramics with appropriate La content

Y Dan, K Zou, G. Chen, Y Yu, Y Zhang, QF Zhang, Y Lu, Q Zhang, Y. He

### Abstract

Antiferroelectric (AFE) ceramics based on Pb(Zr,Sn,Ti)O<sub>3</sub> (PZST) have shown great potential for applications in pulsed power capacitors because of their fast charge-discharge rates (on the order of nanoseconds). However, to date, it has been proven very difficult to simultaneously obtain large recoverable energy densities  $W_{re}$  and high energy efficiencies  $\eta$  in one type of ceramic, which limits the range of applications of these materials. Addressing this problem requires the development of ceramic materials that simultaneously offer a large ferroelectric-antiferroelectric (FE-AFE) phase-switching electric field  $E_A$ , high electric breakdown strength  $E_b$ , and narrow polarization-electric field ( $P$ - $E$ ) hysteresis loops. In this work, via doping of La<sup>3+</sup> into (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramics, large  $E_A$  and  $E_b$  due to respectively enhanced AFE phase stability and reduced electric conductivity, and slimmer hysteresis loops resulting from the appearance of the relaxor AFE state, are successfully obtained, and thus leading to great improvement of the  $W_{re}$  and  $\eta$ . The most superior energy storage properties are obtained in the 3 mol% La<sup>3+</sup>-doped (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramic, which simultaneously exhibits at room temperature a large  $W_{re}$  of 4.2 J/cm<sup>3</sup> and a high  $\eta$  of 78%, being respectively 2.9 and 1.56 times those of (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramics with  $x = 0$  ( $W_{re} = 1.45$  J/cm<sup>3</sup>,  $\eta = 50\%$ ) and also being superior to many previously published results. Besides, both  $W_{re}$  and  $\eta$  change very little in the temperature range of 25–125 °C. The large  $W_{re}$ , high  $\eta$ , and their good temperature stability make the Pb<sub>0.955</sub>La<sub>0.03</sub>(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramic attractive for preparing high pulsed power capacitors useable in various conditions.

### Keywords

Relaxor antiferroelectrics, La<sup>3+</sup> content, Energy-storage density, Energy efficiency, Temperature stability

## 1. Introduction

In recently, much attention and research interest has been devoted to energy-storage devices in order to meet the needs of social sustainable development [1,2]. Present energy-storage devices mainly consist of electrochemical capacitors, batteries, dielectric capacitors and fuel cells. In all these energy-storage devices, dielectric capacitors have faster charge-discharge rate ( $<1 \mu\text{s}$ ), more excellent fatigue endurance, and lower energy loss, and thus are widely used in electromagnetic guns, particle beam accelerators, laser technology, and hybrid electrical vehicles, which require a rapid and gigantic energy release so as to acquire large pulsed power [3,4]. Dielectric materials used in dielectric capacitors are classified into four categories: ferroelectrics (FEs), linear dielectrics (LDs), antiferroelectrics (AFEs), and relaxor ferroelectrics (RFEs). Generally, AFEs can exhibit more superior energy-storage properties than FEs because of their near-zero remnant polarization, and than LDs and RFEs due to their larger saturation polarization [5,6]. Thus, in recent years, energy-storage properties of AFE materials, especially  $(\text{Pb,La})(\text{Zr,Sn,Ti})\text{O}_3$  AFE systems on account of their wide AFE phase region, have been widely studied and reported [[7], [8], [9], [10], [11]].

For AFE materials, as presented in Fig. 1, the total energy-storage density ( $W$ ), the recoverable energy-storage density ( $W_{\text{re}}$ ), and the energy efficiency  $\eta$  can be respectively defined as [12]: (1)  $W = W_{\text{re}} + W_{\text{loss}} = \int_0^{P_{\text{max}}} E dP$  (upon charging), (2)  $W_{\text{re}} = -\int_{P_{\text{max}}}^{P_{\text{r}}} E dP$  (upon discharging), (3)  $\eta = \frac{W_{\text{re}}}{W} \times 100\%$ , where the  $P_{\text{max}}$  and  $P_{\text{r}}$  are respectively the maximum and the remnant polarization, and the  $E$  is the applied external electric field. From Fig. 1 and Eqs. (1), (2), it is clear that increasing  $E_{\text{A}}$ , the electric breakdown strength ( $E_{\text{b}}$ ),  $P_{\text{max}}$ , and decreasing the electrical hysteresis ( $\Delta E = E_{\text{F}} - E_{\text{A}}$ ) improve  $W_{\text{re}}$  and  $\eta$ , respectively. Thus, AFEs which exhibit high  $E_{\text{A}}$ ,  $E_{\text{b}}$ ,  $P_{\text{max}}$  and slim double P-E hysteresis loops are best choice for developing and preparing dielectric capacitors possessing superior energy-storage properties.

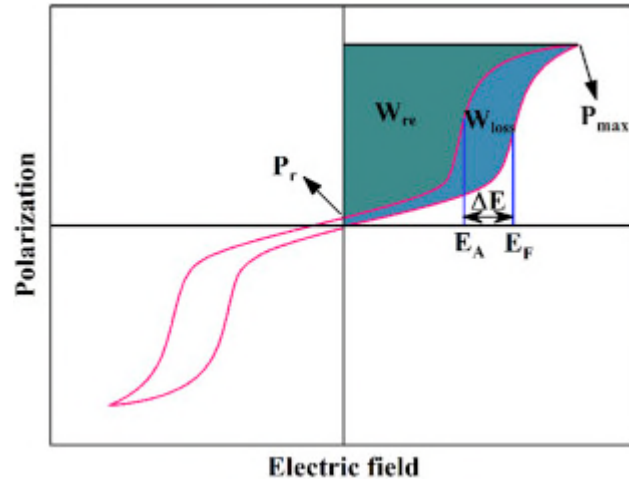


Fig. 1. Schematic diagram showing energy-storage properties of AFE materials.

In  $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$  AFE materials, the contents of Zr, Ti, Sn, and La all have obvious effects on  $E_A$ ,  $P_{\text{max}}$ ,  $E_b$ , and  $\Delta E$  [9,11,13,14]. For example, upon continuously increasing the  $\text{La}^{3+}$  content, the phase structure of  $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$  ceramics at room temperature transforms from AFE state to relaxor AFE state with slimmer hysteresis loops, larger  $E_A$ , and higher  $E_b$  [15,16]. This is good for improving  $W_{\text{re}}$  and  $\eta$ . However, to date, only two research groups have reported how the  $\text{La}^{3+}$  content affects energy-storage characteristics of  $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$  AFE ceramics. Because of inappropriate Zr:Sn:Ti ratios, the maximum  $W_{\text{re}}$  is only  $1.47 \text{ J/cm}^3$ , which is far less than that required for practical applications of dielectric capacitors [13,17]. Very recently, we found that  $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$  AFE ceramics with high Sn content have a superior energy-storage capacity because the introduction of elemental Sn can make the P-E hysteresis loops slimmer and increase  $E_b$  [11]. Thus, adding more  $\text{La}^{3+}$  into these AFE ceramics with high Sn content may lead to a larger  $W_{\text{re}}$  and a higher  $\eta$ .

Based on above discussion, in this work, we study the influence of the  $\text{La}^{3+}$  content on the phase structure, surface morphology, and energy-storage characteristics of  $(\text{Pb}_{1-1.5x}\text{La}_x)(\text{Zr}_{0.5}\text{Sn}_{0.43}\text{Ti}_{0.07})\text{O}_3$  AFE ceramics with high Sn content. With the optimum  $\text{La}^{3+}$  content, the ceramic exhibits simultaneously a large  $W_{\text{re}}$  of  $4.2 \text{ J/cm}^3$  and a high  $\eta$  of 78%,

which are respectively 2.9 and 1.56 times greater than those of (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramics with  $x = 0$  ( $W_{re} = 1.45 \text{ J/cm}^3$ ,  $\eta = 50\%$ ) and are also superior to many previously reported results. Furthermore, we attempted to correlate quantitatively the EF, EA, and  $\Delta E$  with the temperature variation.

## 2. Experimental procedures

(Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> (PLZST) ( $x = 0, 0.5\%, 1\%, 1.5\%, 2.5\%, 3\%, 4\%, 5\%$ ) AFE ceramics were prepared via the conventional ceramic fabrication technique, using PbO ( $\geq 99\%$ ), La<sub>2</sub>O<sub>3</sub> ( $\geq 99.99\%$ ), TiO<sub>2</sub> ( $\geq 98\%$ ), SnO<sub>2</sub> ( $\geq 99.5\%$ ) and ZrO<sub>2</sub> ( $\geq 99\%$ ) as raw materials. These powders were weighed on the basis of above chemical formula, ball milled and calcined at 870 °C for 2 h. The powders were ball milled again, pressed into discs of 1.5 mm thickness and 11.5 mm diameter, and sintered at 1230 °C for 2 h. In order to measuring electrical properties, the sintered ceramics were covered with silver electrodes at 550 °C for 10 min.

The apparent density of the sintered sample was measured by the Archimedes method. The phase and crystal structure of the ceramics were examined by the powder x-ray diffraction (XRD; D8 Advance; Bruker, Karlsruhe, Germany). The micrographs of the fresh ceramics were performed by the scanning electron microscopy (SEM; JSM 6510LV; Jeol, Tokyo, Japan). Elemental mappings were done using a SEM (FE-SEM; SIGMA 500; Zeiss, Oberkochen, Germany). The polarization-electric field (P-E) hysteresis loops were characterized at 10 Hz with a precision ferroelectric measurement system (PolyK Technologies, State College, Pennsylvania, USA).

## 3. Results and discussion

Fig. 2(a) gives XRD patterns of PLZST ceramics with different La<sup>3+</sup> contents at the room temperature. The results clearly demonstrate that all ceramics have a pure perovskite structure without secondary or impure phase. To characterize more clearly the phase structure of PLZST ceramics, we examine fine scanning XRD patterns in the  $2\theta$  range of 43°–45°, as given in Fig.

2(b). Two split peaks of (200) and (002) are apparently shown, indicating a tetragonal phase structure of the ceramics. In addition, upon increasing the La<sup>3+</sup> content from x = 0 to x = 5%, both the (200) and (002) peaks shift to higher angles, indicating an decrease in the lattice parameters, as shown in Fig. 3. The decrease of lattice parameters a and c with increasing La<sup>3+</sup> content in the PLZST ceramics is attributed to smaller ionic radius of La<sup>3+</sup> (1.36 Å) compared with Pb<sup>2+</sup> (1.49 Å).

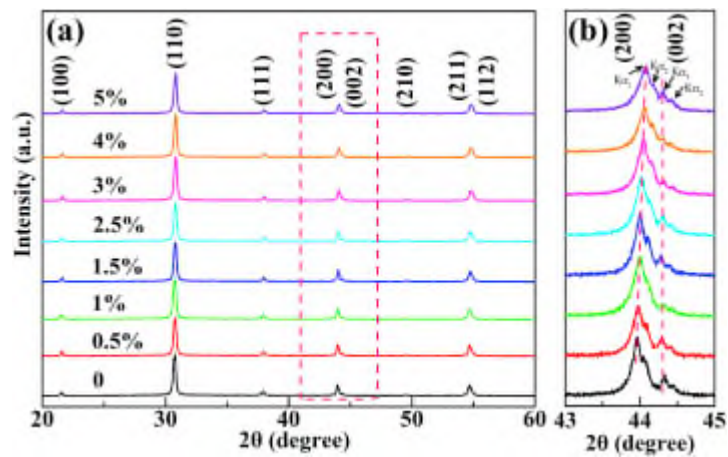


Fig. 2. (a) XRD patterns of PLZST ceramics with different La<sup>3+</sup> contents. (b) Fine-scan XRD patterns of the PLZST ceramics in 2θ range of 43o-45°; Kα1 and Kα2 indicate the diffraction peaks from Cu Kα1 and Kα2 radiations ( $\lambda_{K\alpha1} = 1.5406 \text{ \AA}$  and  $\lambda_{K\alpha2} = 1.5444 \text{ \AA}$ ),

respectively.

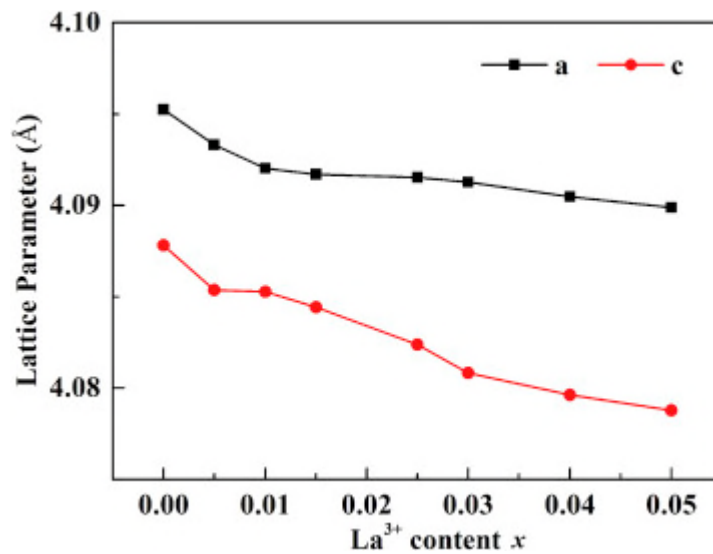


Fig. 3. Lattice parameters a and c of the PLZST ceramics with different La<sup>3+</sup> contents.

Fig. 4(a)-4(h) show scanning electron micrographs of the fresh PLZST ceramics with various  $\text{La}^{3+}$  contents. The  $\text{La}^{3+}$  content distinctly affects the grain size. Upon increasing the  $\text{La}^{3+}$  content from  $x = 0$  to 0.5%, the grain size clearly increases, which may be associated with the higher grain-growth rate caused by quicker diffusion of the smaller  $\text{La}^{3+}$  ion in place of the larger  $\text{Pb}^{2+}$  ion. As the  $\text{La}^{3+}$  content further increases, the ceramic grain size decreases obviously. Introducing additional  $\text{La}^{3+}$  leads to the formation of  $\text{Pb}^{2+}$  vacancies with a negative charge, which can be easily segregated at the grain boundary. These vacancies can attract the positively charged  $\text{La}^{3+}$  ion, thereby creating  $\text{La-VPb}''$  pairs near the grain boundary through Columbic interactions. These vacancy-aliovalent ion pairs impede the movement of the grain boundary and thus suppress the grain growth leading to reduced grain size [18,19]. In addition, when the  $\text{La}^{3+}$  content is less than 3 mol%, all ceramics have a dense microstructure, whereas pores start to appear upon further increasing the  $\text{La}^{3+}$  content to 4 mol%. Higher  $\text{La}^{3+}$  content leads to larger lattice distortion and thus more defects in the ceramics.

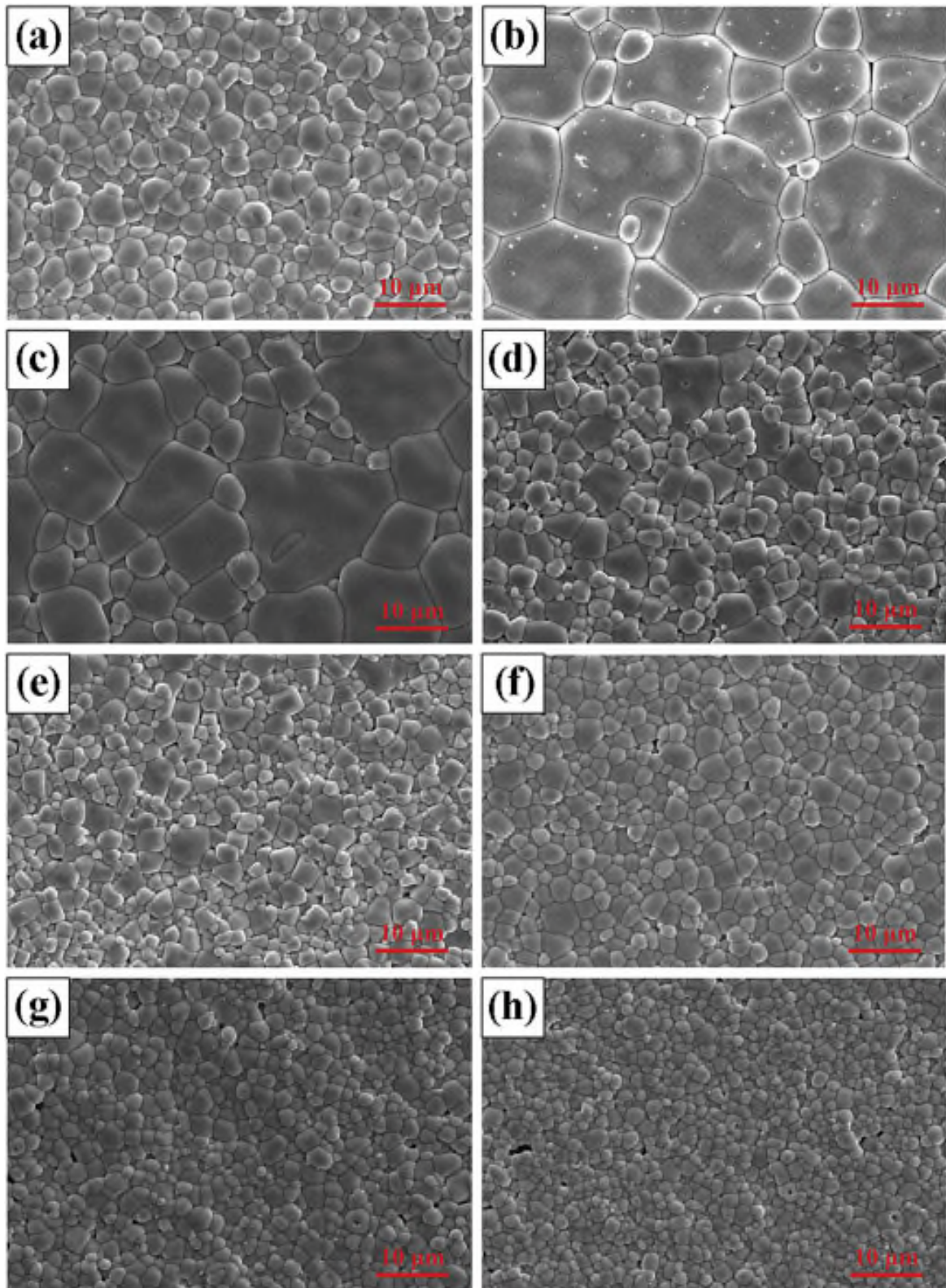


Fig. 4. SEM micrographs of  $(\text{Pb}_{1-1.5x}\text{La}_x)(\text{Zr}_{0.5}\text{Sn}_{0.43}\text{Ti}_{0.07})\text{O}_3$  ceramics with different  $\text{La}^{3+}$  contents: (a)  $x = 0$ , (b)  $x = 0.5\%$ , (c)  $x = 1\%$ , (d)  $x = 1.5\%$ , (e)  $x = 2.5\%$ , (f)  $x = 3\%$ , (g)  $x = 4\%$ , and (h)  $x = 5\%$ .

Fig. 5 gives densities of the PLZST ceramics with different La<sup>3+</sup> contents. As seen from the figure, when the La<sup>3+</sup> content increases from x = 0 to x = 3%, both apparent and relative densities of the ceramics increase from 7.92 g/cm<sup>3</sup> and 92% to 8.25 g/cm<sup>3</sup> and 97%, respectively. This means that suitable La<sup>3+</sup> content benefits the densification of ceramics during the sintering process. However, when the La<sup>3+</sup> content is beyond 3 mol%, the apparent density and the relative density both decrease obviously, as a consequence of formation of pores in the ceramics as affirmed by the SEM observation.

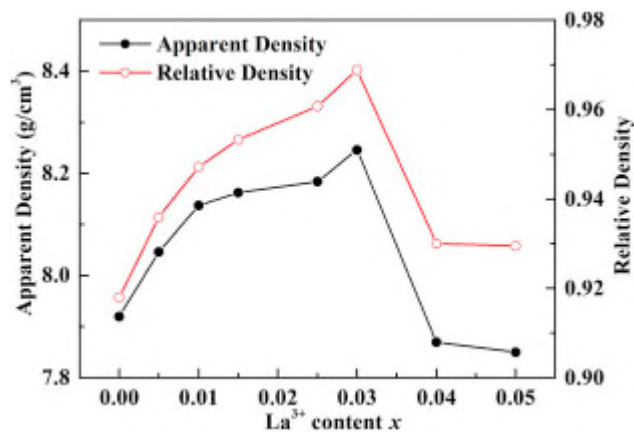


Fig. 5. The apparent density and relative density of the PLZST ceramics with different La<sup>3+</sup> contents.

Elemental mappings of all ceramics were done using energy-dispersive spectrometry (FESEM/EDS). Fig. 6 displays representative EDS spectra along with a micrograph for the ceramic with x = 3%. All EDS spectra corresponding to various elements were recorded within the same area as in Fig. 6(a). As seen from Fig. 6(b)-6(g), all elements in the PLZST AFE ceramic are detected and evenly distributed without agglomeration. An integrated-area spectrum appears in Fig. 6(h) and is tabulated by atoms and the weight percentage of constituent elements. The atomic ratio given from the area EDS analysis is nearly the same as the stoichiometric formula of the ceramic, which is beneficial for obtaining superior energy-storage properties in this ceramic.



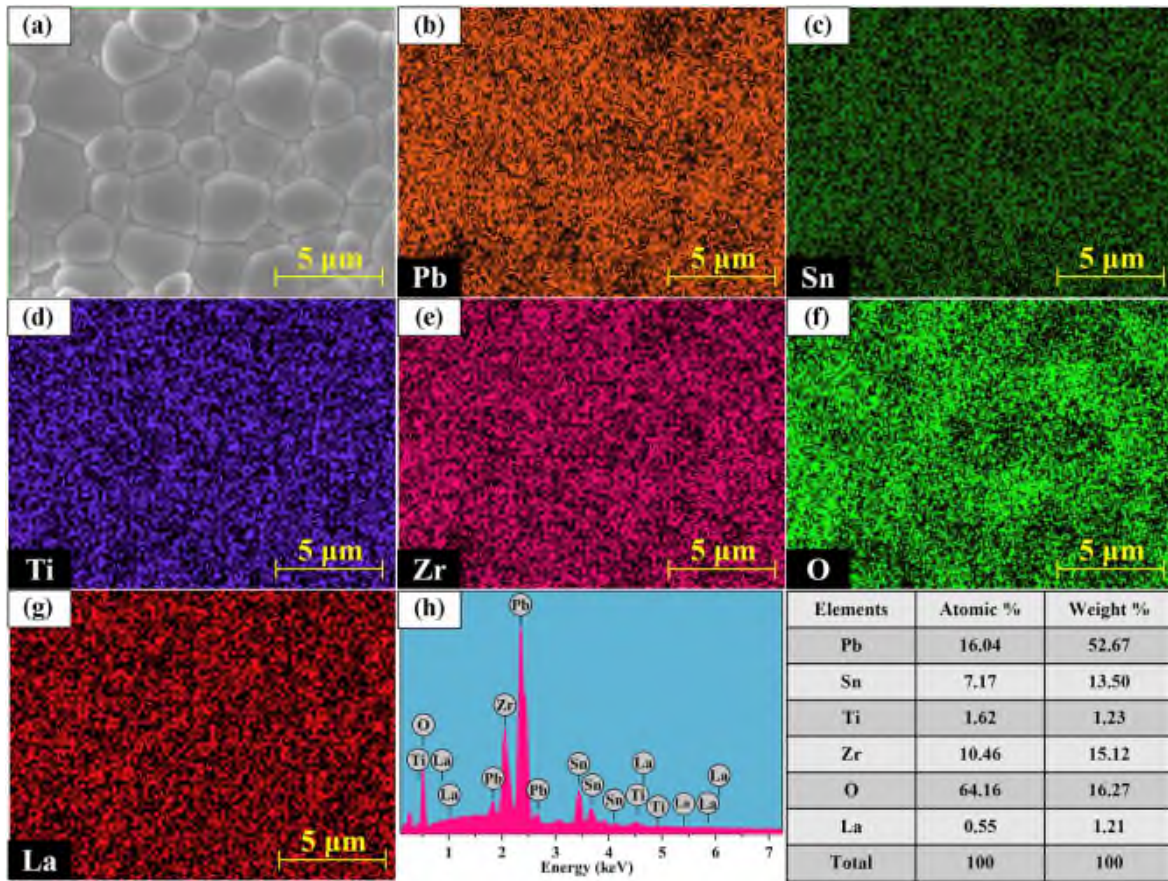


Fig. 6. FESEM-EDS elemental mapping of  $(\text{Pb}_{1-1.5x}\text{La}_x)(\text{Zr}_{0.5}\text{Sn}_{0.43}\text{Ti}_{0.07})\text{O}_3$  ceramics with  $x = 3\%$ : (a) surface microstructure, and elementals mapping of (b) Pb, (c) Sn, (d) Ti, (e) Zr, (f) O, and (g) La. (h) EDS spectrum (left panel) and quantitative atomic and weight percent of various elements (right table).

The  $\text{La}^{3+}$  content not only affects the microstructure of PLZST AFE ceramics, but also may strongly influence the energy-storage properties. Therefore, it is desirable to find a suitable  $\text{La}^{3+}$  content for obtaining the best energy-storage characteristics. Fig. 7(a) and (b) show P-E hysteresis loops and current-electric field (I-E) curves, respectively, measured at 10 Hz and room temperature for all ceramics. Fig. 7(c) and (d) present EF, EA,  $\Delta E$ , W,  $W_{re}$ , and  $\eta$  of the ceramics with various  $\text{La}^{3+}$  contents, where EF, EA, and  $\Delta E$  are determined from the I-E curves, and W,  $W_{re}$ , and  $\eta$  are calculated from the P-E hysteresis loops. All ceramics exhibit double P-E hysteresis loops, confirming the AFE symmetry of these ceramics. Besides, as the  $\text{La}^{3+}$  content increases,  $E_b$  first increases and then decreases. Generally, the Pb-based ceramics

exhibit p-type conductivity due to the volatilization of PbO at high sintering temperature. In this study, La<sup>3+</sup> ions with higher valence substituted for Pb<sup>2+</sup> ions are considered as donor doping, which neutralizes the hole carriers and thus increases the electric resistivity and breakdown strength of the ceramic. The decrease of the E<sub>b</sub> is attributed to the deterioration of the sintering behavior, as affirmed by the SEM observation above. In addition, when the La<sup>3+</sup> content increases, the shapes of P-E hysteresis loops change from square to slim-slanted and become slimmer, indicating the reduction of the ΔE and thus the increase of the η. Moreover, as seen from Fig. 7(b) and (c), increasing the La<sup>3+</sup> content clearly improves both E<sub>F</sub> and E<sub>A</sub>, which is on account of the enhancement of the AFE phase stability. Generally, the stability of the perovskite structure is evaluated by the tolerance factor t, which is expressed as [20]:  $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$ , where r<sub>A</sub>, r<sub>B</sub>, and r<sub>O</sub> are respectively the ionic radii of A-site cation, B-site cation, and oxygen anion. The ferroelectric phase can be stabilized when the tolerance factor is more than 1, and the antiferroelectric phase can be stabilized when the tolerance factor is less than 1. The ionic radius of La<sup>3+</sup> ions (1.36 Å) is smaller than that of Pb<sup>2+</sup> (1.49 Å), and thus substitution of La<sup>3+</sup> for Pb<sup>2+</sup> in the A-site will suppress the FE state and stabilize the AFE state. The increased E<sub>A</sub>, E<sub>b</sub> and reduced ΔE contribute to the improved energy-storage properties, as seen in Fig. 7(d). When the La<sup>3+</sup> content is 3 mol%, the ceramic exhibits optimum energy-storage characteristics, with a large W<sub>re</sub> of 4.2 J/cm<sup>3</sup> and a high η of 78%, which are respectively 2.9 and 1.56 times greater than those of (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramics with x = 0 (W<sub>re</sub> = 1.45 J/cm<sup>3</sup>, η = 50%). Upon further increasing the La<sup>3+</sup> content to x = 4%, the energy-storage capacity of the ceramic drops because of the decreased E<sub>b</sub>.

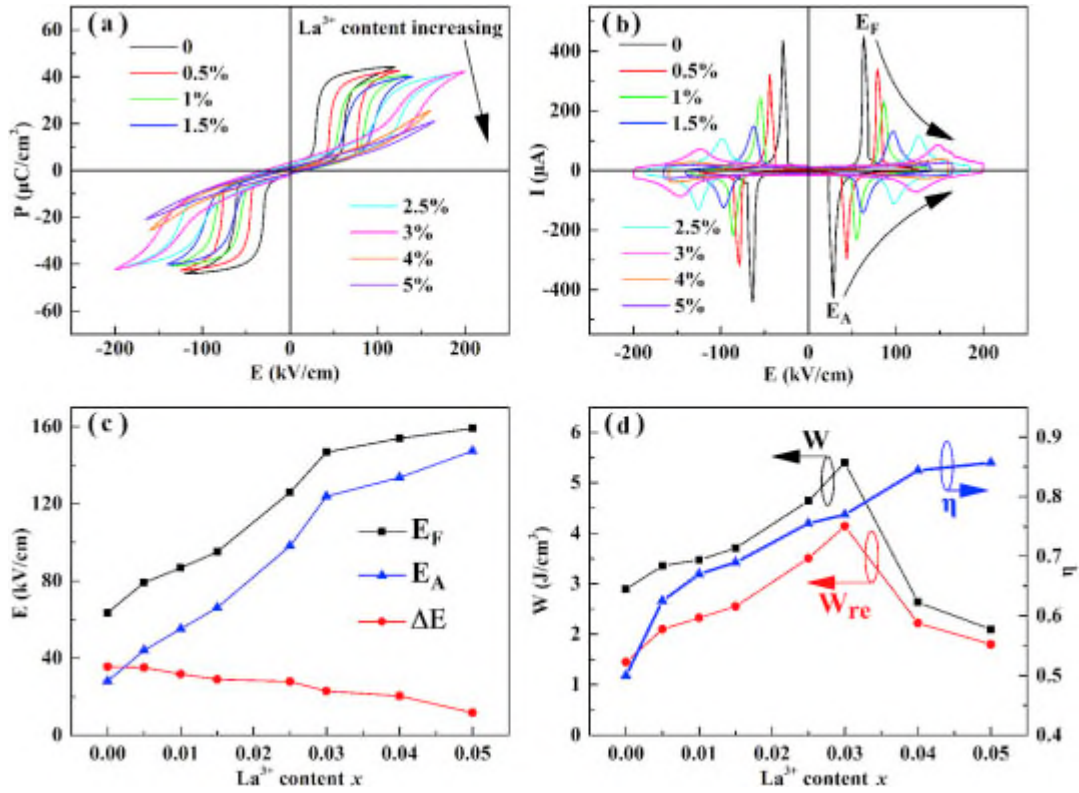


Fig. 7. (a) P-E hysteresis loops, (b) I-E curves, (c) E<sub>F</sub>, E<sub>A</sub>, ΔE, and (d) W, W<sub>re</sub>, and η of PLZST ceramics with different La<sup>3+</sup> contents.

Fig. 8 compares the room-temperature W<sub>re</sub> and η of recently reported (Pb,La)(Zr,Sn,Ti)O<sub>3</sub> AFE ceramics [[8], [9], [10], [11], [12],[21], [22], [23], [24], [25], [26], [27], [28]]. In previously reported work, it was hardly possible to acquire simultaneously large W<sub>re</sub> and high η in a single material. For instance, (Pb<sub>0.858</sub>Ba<sub>0.1</sub>La<sub>0.02</sub>Y<sub>0.008</sub>)(Zr<sub>0.65</sub>Sn<sub>0.3</sub>Ti<sub>0.05</sub>)O<sub>3</sub>- (Pb<sub>0.97</sub>La<sub>0.02</sub>)(Zr<sub>0.9</sub>Sn<sub>0.05</sub> Ti<sub>0.05</sub>)O<sub>3</sub> AFE ceramics possess an excellent W<sub>re</sub> of 6.40 J/cm<sup>3</sup>, whereas the η is only about 62.4% [21]. Conversely, Pb<sub>0.88</sub>La<sub>0.04</sub>Sr<sub>0.06</sub>[(Zr<sub>0.6</sub>Sn<sub>0.4</sub>)<sub>0.84</sub>Ti<sub>0.16</sub>]O<sub>3</sub> AFE ceramics have a very high η of 93.3% but suffer from a low W<sub>re</sub> of 1.52 J/cm<sup>3</sup> [22]. In contrast, the Pb<sub>0.955</sub>La<sub>0.03</sub>(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramic in the present work has simultaneously a very large W<sub>re</sub> and a fairly high η, which makes it overall superior to other lead-based AFE ceramics in terms of energy-storage properties.

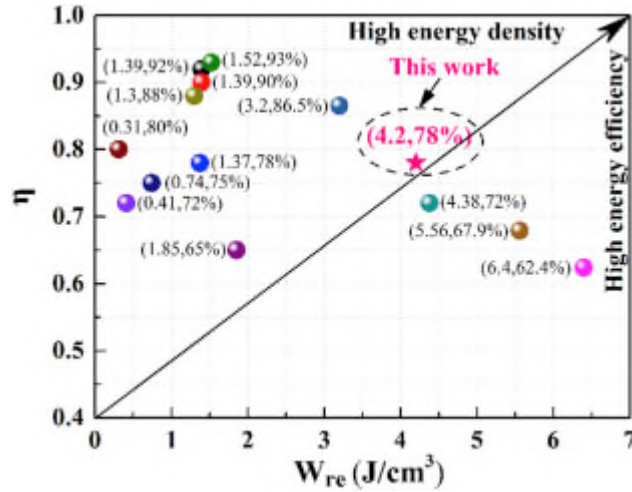


Fig. 8. Comparison of energy densities and efficiencies of recently reported (Pb,La)(Zr,Sn,Ti)O<sub>3</sub> AFE ceramics.

Besides large  $W_{re}$  and high  $\eta$ , the temperature stability of the energy-storage characteristics is also of great importance for AFE materials, because dielectric capacitors always have to work over a wide range of temperatures in practical applications. For this reason, we further study in the following the influence of the temperature on energy-storage characteristics for 3 mol% La-doped  $(Pb_{1-1.5x}La_x)(Zr_{0.5}Sn_{0.43}Ti_{0.07})O_3$  ceramics (see Fig. 9). As seen in Fig. 9(a), the ceramic exhibits typical double P-E hysteresis loops of AFE materials between 25 °C and 125 °C, and the hysteresis loops become slimmer with increasing measuring temperature. The  $P_{max}$ ,  $P_r$ ,  $\Delta P = P_{max} - P_r$ ,  $EF$ ,  $EA$ , and  $\Delta E$ , which are determined from P-E hysteresis loops and I-E curves [Fig. 9(b)], are presented in Fig. 9(c) as functions of temperature.  $EF$ ,  $EA$ ,  $\Delta E$ , and  $P_{max}$  clearly decrease upon increasing the temperature. When the measurement temperature rises, the ceramic transforms from the AFE state gradually to paraelectric (PE) state, and thus the AFE phase stability reduces. This decreases the coupling strength between electric dipoles in the AFE state. In other words, the electric-dipole interaction energy  $W_{inter}$  is reduced. In addition, increasing the temperature makes it easier for reorientation of electric dipoles, leading to the decrease of the strain energy  $W_{str}$ . Hence, the  $EF$ ,  $\Delta E$  and  $P_{max}$ , which are respectively proportional to  $W_{inter} + W_{str}$ ,  $2W_{str}$  and the stability of AFE phase, reduce with the increase

of the measurement temperature. The reduction of the EA (proportional to  $W_{\text{irr}} - W_{\text{str}}$ ) may be a result of faster decrease of the  $W_{\text{irr}}$  than the  $W_{\text{str}}$  [11]. The  $W$ ,  $W_{\text{re}}$ , and  $\eta$  measured at 150 kV/cm and different temperature are given in Fig. 9(d). Clearly, in the temperature range of 25–125 °C, the  $W_{\text{re}}$  exceeds 2 J/cm<sup>3</sup>, the  $\eta$  is higher than 85%, and their variations are very slight, indicating good temperature stability. These results distinctly make (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramics with 3 mol% content a potential candidate material for preparing power capacitors that can operate at a high temperature.

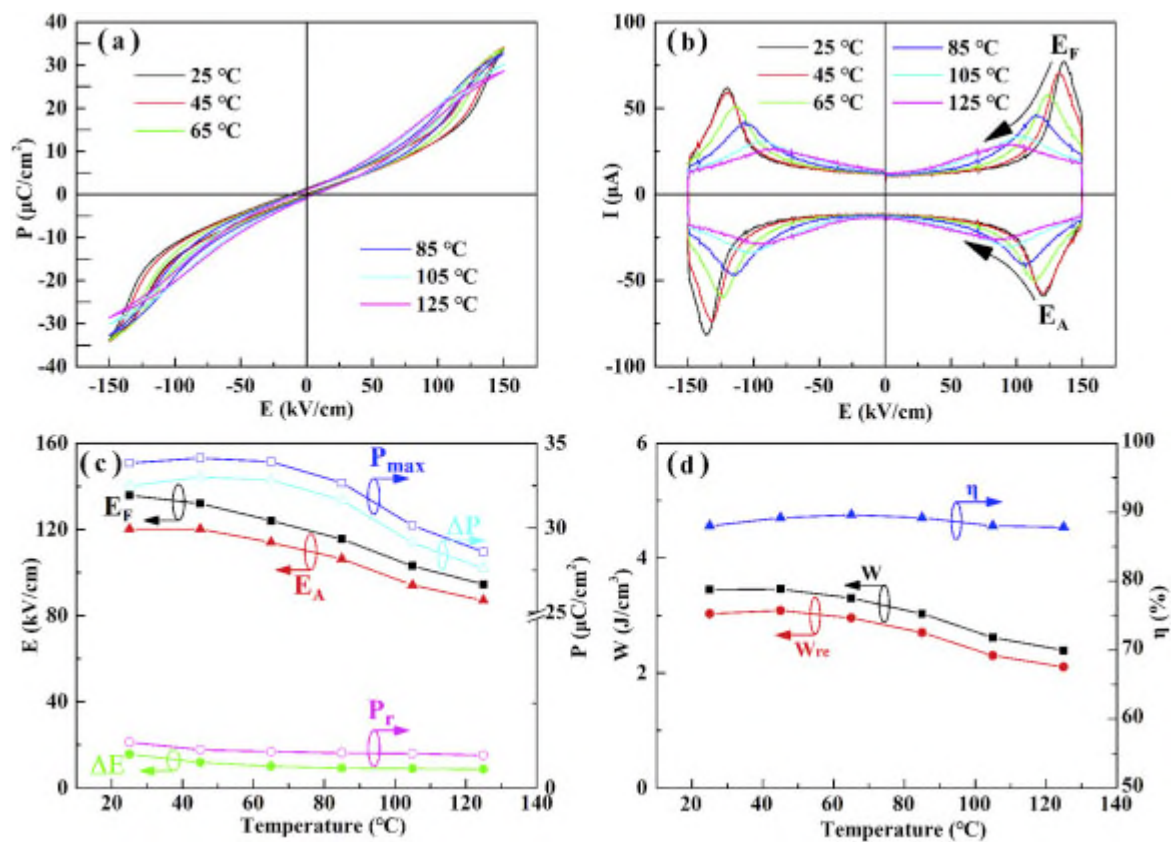


Fig. 9. (a) P-E hysteresis loops measured at 150 kV/cm, (b) I-E curves, (c)  $E_F$ ,  $E_A$ ,  $\Delta E$ ,  $P_{\text{max}}$ ,  $P_r$  and  $\Delta P$ , and (d)  $W$ ,  $W_{\text{re}}$ , and  $\eta$  of (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramic with  $x = 3\%$  in the temperature range of 25–125 °C.

#### 4. Conclusions

In summary, we prepare (Pb<sub>1-1.5x</sub>La<sub>x</sub>)(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE ceramics with different La<sup>3+</sup> contents in the pure perovskite phase by the traditional ceramic fabrication method, and

then study how the La<sup>3+</sup> content affects the crystal structure, microscopic morphology, and energy-storage properties of these ceramics. Upon increasing the La<sup>3+</sup> content, the electric conductivity of the ceramic reduces, the AFE phase stability improves, and the AFE state gradually transforms to the relaxor AFE state with slimmer P-E hysteresis loops, which result in the increase of EA and Eb, and the decrease of ΔE. Thus, the Wre and η improve from 1.45 J/cm<sup>3</sup> and 50% (x = 0) to 4.2 J/cm<sup>3</sup> and 78% (x = 0.03). However, upon further increasing the La<sup>3+</sup> content to 4 mol%, the Eb of the ceramic decreases because of the increase of pores, so the Wre reduces to 2.2 J/cm<sup>3</sup>. Besides, the Wre and η of the ceramic with 3 mol% La<sup>3+</sup> show good temperature stability between 25 °C and 125 °C. These results indicate the potential of the Pb<sub>0.955</sub>La<sub>0.03</sub>(Zr<sub>0.5</sub>Sn<sub>0.43</sub>Ti<sub>0.07</sub>)O<sub>3</sub> AFE material for fabricating advanced pulsed capacitors.

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# Superior energy-storage properties in (Pb,La)(Zr,Sn,Ti)O-3 antiferroelectric ceramics with appropriate La content

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