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Effect of Zr:Sn ratio in the lead lanthanum zirconate stannate titanate anti-ferroelectric ceramics on energy storage properties

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Abstract

$(Pb_{0.87}Ba_{0.1}La_{0.02})(Zr_xSn_{0.95-x}Ti_{0.05})O_3$ (PBLZST, $x=0.6$–0.8) anti-ferroelectric ceramics have been prepared by the conventional solid-state reaction process, and the dependence of phase structure, unit cell volume, anti-ferroelectric properties and energy storage properties on the Zr:Sn ratio has been studied. When $x=0.675$, the sample has a high saturation polarization of 43.5 $\mu C/cm^2$, a large stored energy density of 2.05 J/cm^3, and a high energy efficiency of 68.5%, and exhibits the largest recoverable energy density of 1.4 J/cm^3, which is about seven times higher than that of PBLZST with $x=0.6$ or 0.8. The results indicate that varying the Zr:Sn ratio is an effective method to improve the energy storage properties of the PBLZST anti-ferroelectric ceramics.

Keywords: PBLZST ceramics; Energy storage properties; Anti-ferroelectric properties; Zr:Sn ratio

1. Introduction

Recently, the rapid development of high energy electrical storage systems has advanced the active investigation and development of energy storage materials [1,2]. The target devices for these materials are primarily the electric armor, electric guns, particle beam accelerators, high power microwave sources, and ballistic missile systems [3]. In order to minimize the size and weight of these devices, energy storage materials with high energy density are required [3]. Generally ferroelectric (FE) and anti-ferroelectric (AFE) ceramics are used as energy storage materials because they possess high energy density [4–8]. The energy density can be obtained by calculating the area between the polarization axis and the hysteresis loops [8]. The saturation polarization and coercive electrical field (or the AFE-to-FE phase switching electric field) of FE and AFE ceramics are high. Therefore, the area between the polarization axis and the hysteresis loops is large and the energy density of these two kinds of materials is high.

Compared with FE materials, the energy density of AFE materials is higher [6,7], since they have double hysteresis loops. However, the effective energy density is equal to the area between the polarization axis and the FE-to-AFE switching hysteresis loops, because the energy represented by the area between the AFE-to-FE and FE-to-AFE switching hysteresis loops is exhausted during the depolarization process; in other words, the exhausted energy is mainly due to the hysteresis loss during the phase transformation between the AFE and FE states [8]. Hence, in order to fabricate AFE ceramics with high energy efficiency and density, firstly it is essential to increase the saturation polarization and the AFE-to-FE and FE-to-AFE phase switching electric field, for increasing the stored energy density represented by the area between the polarization axis and the hysteresis loops, and secondly it is necessary to reduce the width of the double hysteresis loops, for decreasing the energy loss represented by the area between the double hysteresis loops of AFE-to-FE and FE-to-AFE phase transitions.

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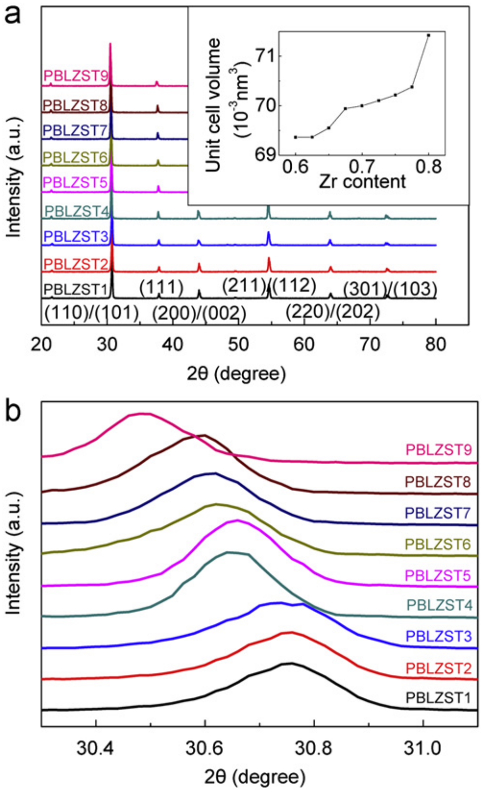

Fig. 1. (a) X-ray diffraction patterns and unit cell volume (inset), and (b) the magnified picture of (110)/(101) peaks of the PBLZST samples with various Zr contents.

Lead zirconate titanate and lead zirconate stannate titanate are typical AFE ceramics used as energy storage materials. With a view to increase the stored energy density, several dopants, such as Sr and Eu, have been doped to increase the saturation polarization and reduce the width of the AFE-to-FE and FE-to-AFE switching hysteresis loops [6,8–10]. In addition to introducing dopants, changing the autologous ions ratio, for instance, modulating the Zr:Sn or Sn:Ti ratio, is another effective method to optimize the double hysteresis loop of AFE ceramics [11–13]. It is reported that the microstructure, such as grain cell parameter, grain size, density and phase structure, and the electrical properties, such as dielectric constant, Curie temperature, spontaneous polarization, and phase switching field, are obviously affected by the Zr:Sn or Sn:Ti ratio [11–14]. However, the improvement of energy storage properties as a result of changing of autologous ions ratio has been neglected. Up to now, few studies report the relationship between the energy storage properties of lead zirconate stannate titanate AFE ceramics and the Zr:Sn (or Sn:Ti) ratio, grain lattices, double hysteresis loops.

In this study, $(Pb_{0.87}Ba_{0.1}La_{0.02})(Zr_xSn_{0.95-x}Ti_{0.05})O_3$ (PBLZST, $x=0.6$–0.8) AFE ceramics are prepared by the conventional solid-state reaction process. The effect of the Zr:Sn ratio on the microstructure (such as phase structure and unit cell volume) and the electrical properties (such as anti-ferroelectric and energy storage properties) of the PLBZST specimens has been investigated. It is revealed that the energy storage properties of PLBZST can be effectively improved by varying the Zr:Sn ratio. And the possible reasons have been discussed.

2. Experimental procedures

The starting materials were analytical-grade metal oxides and carbonate powders: PbO (99.9%), La_2O_3 (99.9%), TiO_2 (99.8%), ZrO_2 (99.6%), $BaCO_3$ (99.8%), and SnO_2 (99.6%). The powders were weighed according to the formula $(Pb_{0.87}Ba_{0.1}La_{0.02})(Zr_xSn_{0.95-x}Ti_{0.05})O_3$ with 5 mol% excess PbO and then thoroughly milled for 4 h. The dried slurries were calcined at 900 °C for 3 h, and then ball milled again for 4 h. Polyvinyl alcohol (PVA) was added to the mixtures as a binder for granulation, and the compacts were pressed at about 5 MPa with the diameter of 20 mm. Next, the samples were buried in the PbO powders and sintered at 1250 °C in the muffle furnace for 3 h. The specimens with $x=0.6$, 0.625, 0.65, 0.675, 0.7, 0.725, 0.75, 0.775, and 0.8 were denoted as PBLZST1, PBLZST2, PBLZST3, PBLZST4, PBLZST5, PBLZST6, PBLZST7, PBLZST8, and PBLZST9, respectively.

The crystal structures of the samples were determined through using an X-ray diffractometer. Polarization versus electric field hysteresis loops were measured by a standard Sawyer–Tower circuit with high voltage power supply. And the energy storage density was calculated by integrating the hysteresis loops: $J=\int E\,dP$, where E is the applied electric field and P is the polarization [8].

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns of the samples with various Zr:Sn ratios. From the XRD patterns it can be seen that there is only perovskite structure in all the specimens, without additional phases, such as pyrochlore phase. The 2θ of diffraction peaks increases as the content of Sn decreases. For example, the (110) peaks shift to a higher degree when the Sn content reduces, as shown in Fig. 1(b). This means that the unit cell volume increases as the content of Zr increases. The unit cell volume calculated on the basis of the least square refinement with over six peaks of diffraction patterns is shown in the inset of Fig. 1(a). It is indicated that the ionic radius of Zr^{4+} (0.079 nm) is larger than that of Sn^{4+} (0.071 nm), and accordingly the cell volume increases as the Zr:Sn ratio increases. It is notable that the cell volume increases markedly when x increases from 0.65 to 0.675 and from 0.775 to 0.8. It is well known that the ferroelectric and anti-ferroelectric properties are significantly affected by the unit cell parameters [15], and thus the obvious change in the electrical properties could be expected when the Zr content increases from 0.65 to 0.675 and from 0.775 to 0.8.

Fig. 2(a) and (b) shows the hysteresis loops of the PBLZST ceramic samples. All samples other than PBLZST1 and PBLZST9 show double hysteresis loops. The hysteresis loops indicate that the PBLZST ceramics are anti-ferroelectrics when the Zr content increases from 0.625 to 0.775, but they

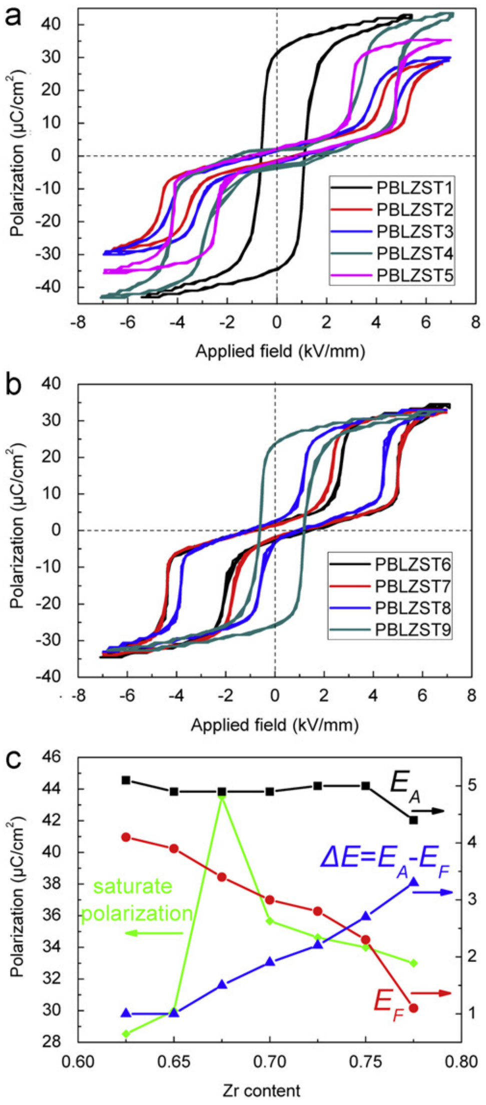

Fig. 2. (a,b) The hysteresis loops and (c) the saturation polarization and phase transition field of the PBLZST samples with various Zr contents.

are ferroelectrics when the Zr content is higher than 0.8 or lower than 0.6. As is known to us, when $x=0.6$, the PBLZST is anti-ferroelectrics [12]. However, the AFE phase is unstable and thus can be induced to the FE phase by an AC electric field. In this study, all the hysteresis loops were tested with an AC electric field of 50 Hz. The FE phase corresponding to $x=0.6$ is induced by applied AC electric field, and the FE phase is unstable and easy to recover to AFE phase again at some conditions [13,16].

The saturation polarization of the anti-ferroelectric PBLZST samples is presented in Fig. 2(c). When the Zr content is below 0.675, the saturation polarization increases as the Zr content increases. Particularly when the Zr content increases from 0.65 to 0.675, the saturation polarization increases markedly from 30 μC/cm^2 to 43.5 μC/cm^2. However, when the Zr content exceeds 0.675, the increase of Zr content leads to the decrease of saturation polarization. It is reported that the spontaneous polarization of ferroelectric and anti-ferroelectric materials is determined by the relative displacement of the B site ions (for PBLZST, Zr^{4+}, Sn^{4+}, and Ti^{4+} are the B site ions), and the larger relative displacement between the O^{2-} ions and B site ions, the higher saturate polarization [15]. Based on the analysis of the XRD patterns, the unit cell volume increases as the Zr:Sn ratio increases because the radius of Zr^{4+} is larger than that of Sn^{4+}, but the relationship between the unit cell volume and the Zr:Sn ratio is nonlinear. It is noticeable that the unit cell volume increases remarkably when the Zr content increases from 0.65 to 0.675, as shown in Fig. 1(a); however, when the Zr content exceeds 0.675, the unit cell volume increases slightly with the increase of Zr content. We suggest that the nonlinear relationship between the unit cell volume and the Zr:Sn ratio results in the increase and decrease of the saturate polarization. When the Zr:Sn ratio increases from 0.625 to 0.675, especially increases from 0.65 to 0.675, though the B sites are occupied by the Zr^{4+} ions of larger radius, the noticeable increase of the unit cell volume results in the enlargement of the B site ions' activity space and relative displacement, and then leads to the increase of saturate polarization. In contrast to the above result, when the Zr content increases from 0.675 to 0.775, although the unit cell volume increases, the increased unit cell volume is so small that the activity space and relative displacement of B site ions are decreased. As a result, the saturate polarization decreases with the further increase of Zr content. Based on the above analysis, it is concluded that the Zr:Sn ratio can change the unit cell volume and then modify the saturate polarization, and the maximum saturation polarization of 43.5 μC/cm^2 can be achieved when the Zr content is 0.675 for PLZBST anti-ferroelectric ceramics. It is quite clear that the high saturation polarization is conducive to the increase of energy density, and therefore changing the Zr:Sn ratio is an important and effective method to improve the energy storage properties of PLBZST anti-ferroelectric ceramics.

Fig. 2(c) also shows the AFE-to-FE phase switching electric field (E_F), the FE-to-AFE phase switching electric field (E_A) and the hysteresis switch $\Delta E=E_F-E_A$ of the anti-ferroelectric ceramics. The E_A is about 5 kV/mm and it varies slightly when the Zr content increase from 0.625 to 0.75. This result indicates that the forward (AFE-to-FE) phase switching field is independent of the Zr:Sn ratio when the Zr content is between 0.625 and 0.775. However, when the Zr content increases to 0.775, the material is close to the AFE–FE phase boundary, the stability of the anti-ferroelectric phase decreases, so it is easy for PLBZST8 to transit from the anti-ferroelectric phase to the ferroelectric phase with a lower switching field. Unlike the E_A, the E_F decreases as the Zr:Sn ratio increases, and the decrease of E_A leads to the increase of the hysteresis switch ΔE. This is consistent with the investigation performed by Xu et al., who changed the Zr:Sn ratio in $Pb_{0.97}La_{0.02}(Zr_{0.65}Sn_{0.31}Ti_{0.04})O_3$ anti-ferroelectric ceramics [12]. The hysteresis switch ΔE is a crucial parameter to evaluate the diffuseness of the AFE–PE phase transition, and the samples with smaller ΔE and slim-loop hysteresis have higher diffuseness of AFE–PE phase transition [12]. It has been found

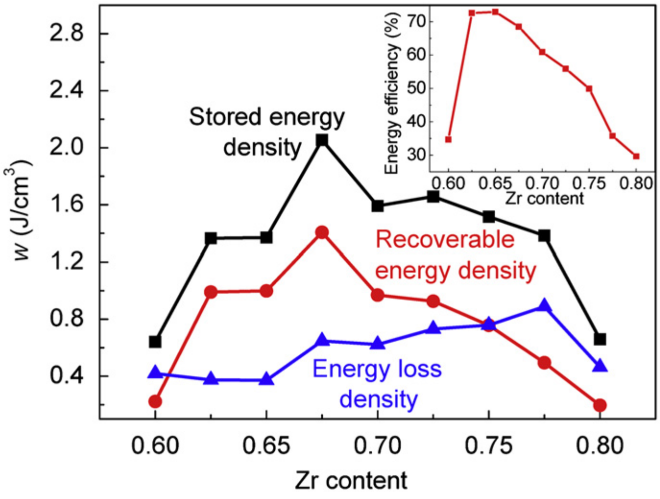

Fig. 3. Stored energy density, recoverable energy density, energy loss density and energy efficiency of the PBLZST samples with various Zr contents.

that in PLBZST anti-ferroelectric ceramic, the high Sn content can introduce the intrusion of a multi-cell cubic state and make the transition from multi-cell AFE phase to single-cell PE phase [17]. The presence of single-cell PE phase originates from the compositional heterogeneity that is caused by the high Sn content because the end member, "$PbSnO_3$" of the crystalline solution is known to be thermodynamically unstable [18]. The compositional inhomogeneity due to high Sn content may directly enhance the diffuseness of the AFE–PE phase transition, as in the diffuse phase transition phenomenon in relaxor ferroelectrics [19]. Due to the above-mentioned reasons, samples with high Sn content possess slim-loop hysteresis and small hysteresis switch ΔE. For energy storage materials, small ΔE is required to increase the energy efficiency [8]. Therefore, an appropriate increase of Sn content is necessary.

The stored energy densities, recoverable energy density, energy loss density and energy efficiency are plotted in Fig. 3. PLBZST1 and PLBZST9 are ferroelectrics, and their recoverable energy density are small because of the low stored energy density and low energy efficiency. When the Zr content increases from 0.625 to 0.675, the stored energy density increases from 1.36 J/cm^3 to 2.05 J/cm^3, owing to the increase of saturate polarization. However, further increase of Zr content results in the decrease of stored energy density, which is also because of the reduction of saturation polarization. The energy loss density increases as the Zr content increases, for reasons of the decrease in diffuseness of AFE–PE phase transition and the increase of ΔE. The recoverable energy density and the energy efficiency increase as the content of Zr increases when the Zr content is below 0.675, and PLBZST4 shows a maximum recoverable energy density of 1.4 J/cm^3, which is about seven times higher than PLBZST1 and PLBZST9, due to its high stored energy density, low energy loss density and high energy efficiency. However, further increase of Zr content leads to the decrease of recoverable energy, for the decrease of the stored energy density and energy efficiency.

4. Conclusions

In summary, Zr:Sn ratio is an important parameter to determine the energy storage properties of PLBZST anti-ferroelectric ceramics. For PLBZST with Zr content of 0.675, the highest recoverable energy density of 1.4 J/cm^3, which is about seven times higher than that of samples with 0.6 or 0.8 Zr content, can be achieved, and the obvious improvement of the energy storage properties is attributed to the increase of unit cell volume caused by the change of Zr:Sn ratio. Thus, it can be concluded that varying the Zr:Sn ratio is an effective method to improve the microstructure (such as phase structure and unit cell volume) and the electrical properties (such as anti-ferroelectric and energy storage properties) of the PLBZST anti-ferroelectric ceramics.

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