B-site non-stoichiometric $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_{3}$ antiferroelectric ceramics for energy storage

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1. Introduction

In recent years, the demand for dielectric materials with optimal energy storage performance has been on the rise. Among a variety of dielectric materials, antiferroelectrics (AFEs) have more potential for application in high-energy-storage capacitors due to their large maximum polarization and zero remnant polarization [1,2]. Furthermore, the phase transformation between AFE and ferroelectric (FE) phases, accompanied by a large strain or displacement and phase switching current because of changes in the orientation of dipoles, has received much attention [3,4]. Lead zirconate titanate (PZT) based ceramics, one typical AFE material in the AFE family, have wide potential usage in high-power energy storage, cooling devices and pulsed systems due to their excellent field induced phase transition and composition-tunable dielectric properties [5].

Up to now, AFE materials including PbZrO$_3$ (PZ), PbZr$_{1-x}$Ti$_x$O$_3$ (PZT), Pb$_{1-x}$La$_x$(Zr$_{1-y}$Ti$_y$)$_{3-x/4}$O$_{3-\delta}$ (PLZT) and Pb$_{1-x}$La$_x$(Zr$_{0.55}$Sn$_{0.35}$Ti$_{0.10}$)O$_3$ (PLZST) have been extensively studied and used in applications, expecting to improve the energy-storage performance [6–9]. Notably, it has been evaluated for some systems, that doping using La$^{3+}$ ions generally promotes the stability of the AFE phase over the FE phase [10].

Recent progress in the investigation on the physical properties of $(\text{Pb}_{0.99}\text{La}_{0.01})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_{3}$ (PLZT2/95/5) ceramics [11] revealed interesting behavior in the electric field dependence of polarization $(P-E$ hysteresis loops) at different temperatures. Results have shown that the energy-storage density and efficiency achieved about 0.83 J/cm$^3$ and 70%, respectively, which is an improvement compared to the previous works [12–15]. However, an ideal capacitor is expected to possess high power density, high energy density, good discharge efficiency, and low dielectric losses with its practical applications [16,17]. Therefore, the development of material with a high energy density for electrical capacitor is much sought. In our work, we first prepared non-stoichiometric $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})_{1+y}\text{O}_3$ (PLZT-100 $(1+y$) antiferroelectric ceramics. It’s worth mentioning that the study on the energy-storage performance of non-stoichiometric antiferroelectric materials has not been reported besides a few number of investigations on structure and electric properties of nonstoichiometric lead-free piezoelectric ceramics [18,19].

Then, under stimulation of an electric field $E$, the energy storage density $W_{\text{re}}$ and efficiency $\eta$ of the AFE ceramics as a function of $T$ and $f$, with $T$ $\text{(25°C-240°C)}$ and $f$ $(10\text{Hz})$, were measured. In this paper, We obtained high recoverable energy densities $(0.98 J/cm^3)$ and efficiency $(82.1\%)$ of the studied ceramics. In addition, the influence of the applied electric field and temperature on the phase switching features and the dielectric characteristics have been discussed, in order to appraise the suitability of the studied ceramics for prospective high-energy-storage application.
2. Experimental

(Pb_{0.97}La_{0.02})(Zr_{0.95}Ti_{0.05})_{1+y}O_{3} (y = −0.03, −0.01, 0.01 and 0.03) ceramics were fabricated by a conventional mixed oxide solid state reaction method. Raw materials of PbO, TiO_{2}, ZrO_{2}, and La_{2}O_{3} were weighed according to the formula PLZT2/95/5 in the required stoichiometry with 5 wt% excess PbO. Precursor oxides were mixed by ball milling in ethanol for 24 h, then dried and calcined at 850°C in an alumina crucible for 5 h. After remilling and drying, the calcined fine powder with 5 wt% PVA as a binder was cold pressed into cylindrical pellets of size 12 mm diameter and 1–2 mm thickness using a hydraulic press. The ceramics were fabricated by sintering at 1250°C for 5 h. In order to avoid the vaporization, PbO atmosphere for the sintering was maintained using Pb (Zr_{0.95}Ti_{0.05})_{3}O_{5} (PZT95/5) as spacer powder.

Ceramic samples were polished to the thickness of 0.7 mm for the measurement of electrical properties. Both sides of samples were electroded with silver paste and sintered at 650°C for 2 h. The crystal structure and orientation of the ceramic samples were characterized by using an X-ray diffractometer (XRD, D/MAX 2200 VPC, Rigaku, Japan) with working current and voltage of 20 mA and 36 kV, respectively. The bias electric field and temperature dependence of dielectric and impedance properties were measured by a precision LCR meter (Aglient 4790, Aglient Technologies Inc., Santa Clara, CA, USA) in the temperature range of 26–650°C with the heating rate of 3 °C/min. The polarization-electric field (P−E) loops were characterized by a Radiant Technologies Precision premier II (Albuquerque, NM) over the temperature range of 25–240°C.

3. Results and discussion

Figure 1 presents the XRD patterns of the (Pb_{0.97}La_{0.02})(Zr_{0.95}Ti_{0.05})_{1+y}O_{3} (PLZT2/95/5) (y = −0.03, −0.01, 0.01, and 0.03) ceramics measured at room temperature. It can be seen that perovskite phase of PLZT is predominant for all the samples after final sintering at 1250°C for 5 h. The XRD peaks positions were observed to shift to lower angles with decreasing y values, which should be related to the formation of cation and oxygen vacancies [19]. The (042) peak splits into two peaks and the ratio of intensity for the two peaks is about 2:1, corresponding to a orthorhombic phase with the space group Pnmb(62), as the Pb(Yb_{1/2}Nb_{1/2})O_{3} reported by Kwon and Choo [20]. In addition, the orthorhombic basis vectors of the room temperature unit cell have the following relationships with the basis vectors of the prototype phase: \( a_{o} = (a_{x} + b_{y}) \), \( b_{o} = 4(a_{x} + b_{y}) \), and \( c_{o} = 2c_{c} \). Here the subscript “o” refers to the orthorhombic lattice [20,21]. Table 1 shows the lattice parameters of the (Pb_{0.97}La_{0.02})(Zr_{0.95}Ti_{0.05})_{1+y}O_{3} ceramics (y = −0.03, −0.01, 0.01, and 0.03).

![Figure 2](image-url)
electro-ceramic materials, such as conductivity, dielectric behavior and relaxation characteristics [22]. Figure 3(a–d) shows complex impedance plane plots \((Z', Z'')\) collected at several temperatures. The \((Z', Z'')\) plots of all investigated ceramics show single semicircles, indicating that a single localized relaxation mechanism dominates the impedance in the measured temperature range. Besides, the radius of the semicircles decrease as the temperatures increases, illustrating a strong temperature dependence of resistance. When the temperature increases, the mobility of the space charges becomes higher and the accumulated charge carrier in the vicinity of grain boundaries have enough energy to pass through the barrier, leading to an intensive conductivity with the reduction in impedance. This interprets the diminishing in radius of semicircles with increasing temperature. Insert of Figure 3(a–d) indicates the normalized imaginary part of impedance \((Z'')\) with frequency at different temperatures. A obvious temperature-dependent peak under a characteristic frequency was obtained for all compositions, which shift towards the high frequency with an increasing temperature. Also, \(Z'' / Z''_{\text{max}}\) peak values will move toward higher frequency with increasing temperature, hopping mechanism could be account for it, in which the numbers of polaron will gradually decrease as it hopped with gradual decrease of electron lattice coupling [23].

In perovskite materials, the major mode of charge transport is multiple hopping processes. For a thermally activated relaxation process, the activation energy of relaxation units can be calculated by the Arrhenius law:

\[
\omega_p = \omega_0 \cdot \exp\left(-\frac{E_a}{k_BT}\right)
\]

where \(\omega_0\), \(E_a\), \(k_B\), \(T\) are characteristic frequency, activation energy, the Boltzmann constant, and absolute temperature, respectively. Experimental data fitted with the above equation was shown in Figure 4. For \((\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})_{1+y}\text{O}_3\) ceramics, the activation energy \(E_a\) were about 0.89, 1.08, 1.10 and 1.38 eV with \(y = -0.03, -0.01, 0.01\) and 0.03, respectively. Computational simulations of the ionic transport in perovskite oxides indicate that the \(E_a\) for oxygen-vacancy migration is approximately 1eV [24]. In PLZT-based ceramics, charged defects are always formed during the sintering process because of the volatilization of \(\text{Pb}^{2+}\).
The obtained $E_a$ are approximately 1 eV, implying the presence of oxygen vacancies in the ceramics. Steinsvik et al. reported that lower $E_a$ values always correspond to a higher concentration of oxygen vacancies in the ABO$_3$ perovskite structure [25]. The increase in $E_a$ from 0.89 to 1.38 eV as $y$ is increased from $-0.03$ to $0.03$ denotes a change in the oxygen vacancy concentration.

The $P$-$E$ hysteresis loops at 10Hz of these AFE ceramics are presented in Figure 5, which were measured at their critical breakdown field and at several temperatures. Evidently, all the samples showed the double polarization-electric field ($P$-$E$) loops, indicating the AFE nature, and there was no obvious effect of the non-stoichiometry on the hysteresis curve behavior. Similarly, it was clearly seen that temperature played a key role in defining the shape of $P$-$E$ loops. As an example, Figure 5(a) shows the polarization-electric field hysteresis loops of (Pb$_{0.97}$La$_{0.02}$)(Zr$_{0.95}$Ti$_{0.05}$)$_{1+y}$O$_3$ ceramics with compositions of $y = -0.03$ at electric fields of 60 kV/cm at several representative temperatures.
The $P-E$ loops looks like a linear curve (not shown here) at room temperature due to the large AFE/FE phase transition field. Besides, with the increasing test temperature at about 160°C, the $P-E$ loops turns into double hysteresis loops suddenly. Moreover, $E_{FE-AFE}$ declined slightly from 60 to 55 kV/cm, which was attributed to the decrease in free energy barrier between FE and AFE phases with the rising temperature [26]. Under the measurement conditions, the various phase transition fields of the ceramics probably contribute to the space charge polarization [27]. The same phenomenon was reported by some researchers [28,29], which is followed by a first order reversible AFE to FE phase transformation. The magnitude of the electric field required for the phase change depends on material composition and external parameters such as temperature and stress. Based on these facts (Figure 5), it can be concluded that the temperature played an important role in describing the shape of the $P-E$ hysteresis loops, which was ascribed to the AFE to FE phase transition. Moreover, as shown in the inserts of Figure 5, the temperature dependencies of $P_{max}$ increases as a function of temperature, with an inversion point at about 200°C, whereas $P_r$ monotonously increases with increasing temperature, demonstrating that the domain wall motion of the FE/ferrielectric phase becomes easier at elevated temperature [30].

According to the $P-E$ loops, the stored energy density $W_{st}$, recoverable energy density $W_{re}$ and energy efficiency $\eta$ can be calculated through the following formulas:

$$W_{st} = \int_{0}^{P_{max}} EdP$$  \hspace{1cm} (1)

$$W_{re} = -\int_{P_r}^{P_{max}} EdP$$  \hspace{1cm} (2)

$$\eta = W_{re}/W_{st}$$  \hspace{1cm} (3)

where $P_r$ and $P_{max}$ are the remanent polarization and maximum polarization, respectively. From Table 2.

Table 2. Electric field ($E$), maximum recoverable storage density ($W_{re}$), and energy storage efficiency ($\eta$) of PLZT ceramics with different $y$ values.

| Temperature(°C) | 195 | 195 | 195 | 200 |
|----------------|-----|-----|-----|-----|
| Electric field (kV/cm) | 60  | 50  | 50  | 50  |
| $W_{re}$ (J/cm$^3$) | 0.98 | 0.87 | 0.91 | 0.83 |
| $\eta$ (%) | 82.05 | 87.01 | 85.45 | 86.73 |
Table 2, the maximum recoverable energy density of 0.98 J/cm$^3$ at 195°C, under the electric field of 60 kV/cm, is obtained in PLZT ceramics with $y = -0.03$. Also, the $\eta$ is as high as 82.1%, which is superior to other reported antiferroelectric ceramics with energy efficiency lower than 80% [31–32]. This suggests the heat generated during the discharge test could be very small. To elucidate the effect of electric field on the energy storage properties, the $P$-$E$ loops of PLZT AFE ceramics with $y = -0.03$ measured in the electric field range of 40–60 kV/cm at several temperatures are presented in Figure 6(a). Moreover, Figure 6(b) shows the value of $W_{re}$ and $\eta$ under different applied fields. It can be seen that when the electric field ranges from 40 kV/cm to 60kV/cm, the $W_{re}$ increases monotonously with the increasing of electric fields, as a result of polarization enhancement induced by the field-forced AFE-FE phase transition.

4. Conclusions

In summary, non-stoichiometric (Pb$_{0.97}$La$_{0.02}$) (Zr$_{0.95}$Ti$_{0.05}$)$_1$yO$_3$ (PLZT2/95/5) AFE ceramics were successfully prepared by a conventional mixed oxide solid state reaction method. The hysteresis loops denote the observable phase transition of AFE, FE, and PE behavior with the increasing external temperature. It is found that the dielectric properties of the ceramics are weakly dependent on the content of $y$ content. The maximum BDS value of 60 kV/cm is obtained in the $y = -0.03$ ceramics. As a result, the energy-storage density and efficiency calculated from hysteresis loops achieved about 0.98 J/cm$^3$ and 82.1%, respectively. Moreover, the corresponding ceramics exhibited good energy stability in the temperature range from room temperature to 220°C. It indicated that these PLZT2/95/5 ceramics may be a promising material for energy storage ceramic capacitors applications.

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Disclosure statement

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