Large energy-storage density and high temperature stability in high textured (111)-oriented Pb_{0.8}Ba_{0.2}ZrO_{3} relaxor thin film with coexistence of antiferroelectric and ferroelectric

High textured (111)-oriented Pb_{0.8}Ba_{0.2}ZrO_{3} (PBZ) relaxor thin film with coexistence of antiferroelectric and ferroelectric was prepared on Pt/TiO_{x}/SiO_{2}/Si(100) substrate by using a sol-gel method. A large recoverable energy storage density of 40.18 J/cm^{3} along with efficiency of 64.1% was achieved at room temperature. A high temperature stability of the energy storage density with variation of below 5% was obtained from room temperature to 250 ºC. The high energy storage performance was endowed by large dielectric breakdown strength, great relaxor dispersion, high texture orientation and the coexistence of the FE/AFE phases. The PBZ thin film is believed to be an attractive material for applications in energy storage systems in a wide temperature range.

**Keywords:** energy storage, relaxor, antiferroelectric, textured, sol-gel

1. **Introduction**

Recently, with the rapid development of microelectronic devices towards miniaturization, lightweight and integration, new dielectric capacitors with higher energy-storage density, fast charge/discharge and low cost, etc., are eagerly desired, due to the wide applications in power electronics and pulsed power systems, etc.\(^1\)\(^-\)\(^5\)

Antiferroelectrics (AFEs) have been predicted to might be a promising candidate for energy storage application as early as 1962.\(^2\)\(^,\)\(^6\) However, little attention for a long time has been paid to them, because of the low energy storage density in their bulk
ceramics. For example, it was reported that the maximum energy storage density is only 2.75 \text{ J/cm}^3. It was recognized that the relatively low dielectric breakdown strength (normally less than 100 \text{ kV/cm}) was one of the main reasons for the low energy-storage density.

With the development of modern thin film technology such as sol-gel, pulsed laser deposition (PLD), and molecular beam epitaxy (MBE), etc., the higher dielectric breakdown strength can be achieved in thin or thick films. Thus, the investigations on energy-storage properties of AFE films have reignited an attracted increasing attention. For instance, an improved energy-storage density of about 14 - 18 \text{ J/cm}^3 was obtained in Pr, La, Sr, and Eu-doped PbZrO\textsubscript{3} thin film at room temperature. Only recently, a huge energy density of 53 \text{ J/cm}^3 and 56 \text{ J/cm}^3 at about 3500 \text{ kV/cm} was reported in relaxor antiferroelectric (Pb\textsubscript{0.92}La\textsubscript{0.08})(Zr\textsubscript{0.9}T\textsubscript{10.05})O\textsubscript{3} and (Pb\textsubscript{0.97}La\textsubscript{0.02})(Zr\textsubscript{0.55}Sn\textsubscript{0.4}T\textsubscript{10.05})O\textsubscript{3} thick films, respectively. In addition to the doping of elements and the optimization of compositions, other many efforts have been made to improve the value of the energy storage density in antiferroelectric films, such as, optimization of grain size, purification and crystallinity of phase, orientation of thin film, etc. However, in practical applications, for a competent energy storage material, not only high value of energy storage density is required, but also high temperature stability is necessary. So far, to our knowledge, large energy storage density simultaneously with high temperature stability in antiferroelectric films is rarely reported.

In this study, a high textured, (111)-oriented Pb\textsubscript{0.8}Ba\textsubscript{0.2}ZrO\textsubscript{3} relaxor thin film with
coexistence of antiferroelectric and ferroelectric was fabricated by a sol-gel method. Large energy storage density (40.18 J/cm$^3$ at 2801 kV/cm) with high temperature stability (the variations of the energy density from room temperature to 250 °C are below 5%) were achieved. Moreover, it is found that highly textured structure can greatly improve the energy storage performance.

2. Results and discussions

2.1. Structure

Fig.1 shows the XRD pattern of the PBZ thin film prepared by using the deposition way of layer-by-layer crystallization. The thin film exhibits a good crystallization quality and a pure perovskite phase with (111) preferential orientation. In addition to the rhombohedral ferroelectric phase, an orthorhombic antiferroelectric phase with superlattice reflections indices (130)/(112), (161)/(321) and (332) also coexisted in the PBZ thin film, which is consistent with the report by Pokharel. Atomic force microscope (AFM) micrograph in the inset of Fig.1 reveals that the thin film has a low surface roughness, and the average Ra and Rq are 1.62 nm and 1.3 nm, respectively.

Fig.2 shows the cross-sectional TEM image of the (111)-oriented PBZ thin film. The TEM cross-sectional image revealed that the microstructure of the PBZ thin film is uniform, homogeneous, and crack free, and with thickness of 320 nm. Nanocrystals with average grain size of 20 nm in a highly ordered columnar-like texture can be visible clearly in an enlarged image of the thin film, as shown in the inset (a) of Fig.2. In the inside of some nanocrystals, lamellar nanodomains with ~1 nm wide (the red dot circles) and ~2 nm wide (the blue solid circles) can be observed. The
corresponding selected area electron-diffraction (SAED) pattern which is labeled by using pseudo cubic rather than the orthorhombic or rhombohedral indicated that the columnar-like texture is (111)-oriented, as shown in the inset (b) of Fig.2.

2.2. Phase transition

In order to understand the structure change of the high textured (111)-oriented PBZ thin film, Raman scattering spectrum was measured from 100 cm\(^{-1}\) to 900 cm\(^{-1}\) at 5 K interval in the temperature range between 298 K and 463 K. Representative plots of them are shown in Fig. 3. Previous research work suggests that the appearance and change of the band at 277 cm\(^{-1}\) which is assigned to Zr-O-Zr bending mode can reflect the existence and change of antiferroelectric phase in PbZrO\(_3\) thin film.\(^{23}\) An additional active band at about 830 cm\(^{-1}\) was considered to be related to the appearance of the ferroelectric phase in 3\% W-doping PbZrO\(_3\) thin film.\(^{23,24}\) For the highly textured (111)-oriented PBZ thin film, the Zr-O-Zr bending mode exhibits a slight shift due to internal stress in the film.\(^{23}\) The inset (a) of Fig.3 shows the temperature dependence of the Zr-O-Zr bending mode. It can be seen that the scattering intensity of the Zr-O-Zr bending mode degraded gradually with the increase of temperature and disappeared at about 345 K, indicating that a phase transition of antiferroelectric to ferroelectric. Meanwhile, a wide band around 830 cm\(^{-1}\) was found to become more and more obvious with the increase of temperature, which further confirmed the existence of the phase transition of antiferroelectric to ferroelectric.\(^{23}\)

The phase transition of antiferroelectric to ferroelectric can also be observed on the maximum value of polarization versus temperature curve (\(P_{\text{max}}-T\)) by drawing on data from the \(P-E\) loops measured at 156 kV/cm, as shown in the inset (a) of Fig.3. The
more subtle phase transition process of antiferroelectric to ferroelectric can be
detected by the temperature dependence of the dielectric permittivity and the
dielectric loss of the highly textured (111)-oriented PBZ thin film, as shown by the
red arrow in the inset (b) of Fig.3. The colored solid lines around the dielectric peak
exhibited the best fitting result of the Lorentz-type relation, \( \frac{\varepsilon_A}{\varepsilon_0} = 1 + \frac{(T-T_A)^2}{2(\delta_A)^2} \). The
relevant detailed description on the equation could be found in previous research
work.\textsuperscript{25,26} A large parameter \( \delta_A (97.73) \) for 10 kHz is obtained and is close to that
(103.6) of the prototypical relaxor Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} ceramics, indicating that a much
higher degree of relaxor dispersion in the thin film. The extrapolated value at the left
part of the dielectric peak is gradually far and below from its real value with the
decrease in temperature from the phase transition of antiferroelectric to ferroelectric,
which further indicates the coexistence of antiferroelectric and ferroelectric phases in
PBZ thin film at room temperature.

2.3. Energy storage

The recoverable energy density \( (W_{\text{energy}}) \) of a dielectric-based compound could be
estimated from the P-E loops, which is calculated with the following equation:

\[
W_{\text{energy}} = \int_{P_r}^{P_{\text{max}}} E dP , \quad 0 \leq E \leq E_{\text{max}} ;
\]

where \( E \) is the applied electric field that causes the variation in electric polarization \( P \),
\( P_r \) is the remnant polarization, and \( P_{\text{max}} \) is the maximum polarization under the
applied field.\textsuperscript{1-5} According to Eq. (1), materials simultaneously with smaller \( P_r \), larger
\( P_{\text{max}} \) and higher breakdown strength are more suitable for energy storage. They are
realized in the highly textured (111)-oriented PBZ relaxor film through the
coexistence of FE and AFE phases, where the FE phase helps maintain a high $P_{\text{max}}$, the AFE phase keeps a low $P_r$, and the relaxation characteristic contributes to release the large phase transition stress.\textsuperscript{27}

Fig. 4 shows the $P$-$E$ loops of the highly textured Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film at selected applied electric field. It can be seen that the $P$-$E$ loop transformed gradually from a slim double hysteresis loop into a single hysteresis loop when the applied electric field increased from 156 kV/cm to 2801 kV/cm, indicating that a field-induced nanscale AFE to FE phase transition. The maximum polarization $P_{\text{max}}$ and the remanant polarization $P_r$ at 2801 kV/cm, is 19.76 µCcm$^{-2}$ and 78.68 µCcm$^{-2}$, respectively. By integrating the discharging portion of the $P$-$E$ loop according to Eq. (1), an energy density ($W_{\text{energy}}$) of 40.18 Jcm$^{-3}$ (as painted by the cyan shaded area) at 2801 kVcm$^{-1}$ can be achieved on the highly textured (111)-oriented PBZ thin film.

For energy storage applications, good electric field endurance is another one of the crucial factors to consider for high energy-storage capacitors. The inset (a) in Fig. 4 depicts Weibull distribution of electric field strength for the highly textured PBZ thin film. The relevant detailed description on Weibull distribution could be found in previous research work.\textsuperscript{28} According to the data given in the inset, a statistical breakdown strength values 2902 kV/cm can be obtained from the x intercept of the fitting lines. The high breakdown strength of samples was attributed to their denser microstructure.

In practical application, apart from higher recoverable energy density $W_{\text{energy}}$ values, larger energy-storage efficiency ($\eta$) is also always desired, which is defined as the
ratio of the discharging (output) energy to the charging (input) energy,
\[
\eta = \frac{W}{W + W_{\text{loss}}} ;
\]
(2)
where \( W_{\text{loss}} \) is the energy loss density, calculated by the numerical integration of closed area of the \( P-E \) hysteresis loops.\(^1\)\(^-\)\(^5\) The inset (b) in Fig. 4 depicts the electric field dependence of the energy density \( W_{\text{energy}} \), the energy loss density \( W_{\text{loss}} \) and the energy-storage efficiency \( \eta \). It can be seen that the \( W_{\text{energy}} \) increased gradually with the increase of the applied electric field and reached about 40.18 Jcm\(^{-3}\) at 2801 kV/cm, however, the \( W_{\text{loss}} \) increased first and then tended to be a constant about 22.5 Jcm\(^{-3}\) at 2801 kV/cm. Similar to the \( W_{\text{energy}} \), the energy-storage efficiency \( \eta \) increased with the increase of the applied electric field and reached 64.1\% at 2801 kV/cm. Assumed that a larger breakdown strength value could be achieved for the highly textured PBZ thin film, based on the above analysis results, it is easy to infer that a larger \( \eta \) could be achieved for the case of a constant \( W_{\text{loss}} \) under a larger electric field. The \( \eta \) can be further improved by an appropriate content of special elements doping, which can enhance the degree of relaxor dispersion and maintain the antiferroelectric property, such as rare earth element-La. Moreover, the \( \eta \) can also be enhanced by using oxide electrodes as contact electrodes such as LaNiO\(_3\),\(^1\)\(^2\) which can reduce the influence of the interfacial layer between film and contact electrode on the hysteresis loop of the film to obtain higher \( W_{\text{energy}} \) and lower \( W_{\text{loss}} \).

In addition to the above mentioned, thermal stability of the energy-storage performance should also be considered as an important parameter in real capacitor applications. Fig.5 shows \( P-E \) loops of the highly textured Pb\(_{0.8}\)Ba\(_{0.2}\)ZrO\(_3\) thin film in
a wide temperature range of 293-583 K, which is measured at 2726 kV/cm slightly lower than 2801 kV/cm to prevent from the high temperature thermal breakdown. The inset (a) of Fig.5 summarized the temperature dependence of the energy density $W_{\text{energy}}$, the energy loss density $W_{\text{loss}}$ and the energy-storage efficiency $\eta$. Clearly, the $W_{\text{energy}}$ increased slightly first from room temperature (39.17 Jcm$^{-3}$) up to 523 K (40.98 Jcm$^{-3}$) and then decreased sharply. The variations of the energy density $W_{\text{energy}}$ from room temperature to 250 ºC are below 5% (as shown by the blue solid line), indicating good temperature stability of the energy-storage performance. The good temperature stability may be ascribed to the great relaxor dispersion of the highly textured PBZ thin film as shown in the inset (b) of Fig.3. Differently to the $W_{\text{energy}}$, the $\eta$ decreased slowly first from room temperature (63.84%) up to 523 K (54.26%) and then dropped sharply. The variations of the $\eta$ in the wide temperature range are about 15%. The two sharp decreases of the $W_{\text{energy}}$ and the $\eta$ above 523 K may be attributed to the reduction in polarization and the increase in leakage current (as shown by the round ends of the green $P$-$E$ loop in Fig.5)

To get an insight into the effect of texture on the energy storage performance of the highly textured (111)-oriented PBZ thin film, a less textured PBZ thin film was prepared by adjusting the deposition process of thin film. Different from the deposition way of the layer-by-layer crystallization of the highly textured PBZ thin film, in the less textured PBZ thin film, each layer was dried at 350 ºC for 3 min and then pyrolized at 550 ºC for 5 min on hotplates, after the deposition of desired layers, the film was crystallized finally at 750 ºC for 30 min in a tube furnace in air. As
shown by the inset (a) of Fig. 6, in addition to the diffraction of (111) (for convenience, the lattice indices are labeled as pseudo-cubic structure), very strong diffractions of (110) and (100) can also be detected in the XRD pattern, indicating the existence of a less textured film structure. The less textured film structure can also be confirmed by its cross-sectional TEM image and the corresponding SAED, as shown by the inset (b) of Fig. 6, where no obvious texture features can be detected.

Fig. 6 shows the $P-E$ loops of the highly textured and less textured Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film. A lower $P_{\text{max}}$ (73.42 µCcm$^{-2}$) and a higher $P_r$ (31.7 µCcm$^{-2}$) were obtained for the less textured PBZ thin film, as well as a bigger coercive field $E_c$ (167 kV/cm). The $W_{\text{energy}}$ and the $\eta$ of the low textured PBZ thin film are 33.9 Jcm$^{-3}$ and 37%, respectively. Compared to them in the less textured PBZ thin film, the $W_{\text{energy}}$ (40.18 Jcm$^{-3}$) in the highly textured PBZ thin film was increased by 18.5% and the $\eta$ (64.1%) was remarkably increased by 73.2%. These results indicate that highly textured structure can help improve the energy storage performance, especially in the energy efficiency $\eta$. Therefore, a larger $W_{\text{energy}}$ and a higher $\eta$ can be expected in a highly (111)-oriented single crystal PBZ thin film.

3. Conclusions

A large recoverable energy storage density of 40.18 J/cm$^3$ and simultaneously a high temperature stability (the variation of below 5% in the energy storage density from room temperature to 250 °C) were achieved in the highly textured (111)-oriented Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ relaxor thin film with coexistence of antiferroelectric and ferroelectric. This is accomplished by the large dielectric breakdown strength, great relaxor
dispersion, high texture orientation and the coexistence of the FE/AFE phases. The excellent energy storage performance of the thin film may make it a promising material for applications in energy storage devices in a wide temperature range.

4. Experimental procedure

Fabrication of Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$:

Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ (PBZ) thin film was grown by using a sol-gel method. Pb(OAc)$_2$ 3H$_2$O with 20% excess Pb and Ba(CH$_3$COO)$_2$ were dissolved in glacial acetic and deionized water. Simultaneously, appropriate acetylacetone was added to a mixture of 2-methoxyethanol and Zr(OnPr)$_4$. The Pb/Ba and Zr solutions were then mixed and stirred for 2 h at room temperature. The final concentration of the PBZ precursor solution is 0.3 M. After they aged for 24 h, the PBZ thin film was deposited on Pt(111)/TiO$_x$/SiO$_2$/Si(100) substrate through a multiple-step spin-coating technique. Each layer of PBZ film was spin-coated at 4000 rpm for 30 s. To eliminate the formation of cracks, every wet film was first dried at 350 ºC for 3 min and subsequently pyrolyzed at 550 ºC for 3 min on hotplates, and finally crystallized at 800 ºC for 3 min in a tube furnace in air. Layer-by-layer, the spin-coating and heat-treatment were repeated several times to obtain the desired thickness. The final thickness of the PBZ thin film was about 320 nm determined by the crossing-section micrographs.

Characterization:

The crystallinity of the PBZ thin film was analyzed by X-ray diffraction (XRD, Rigaku 9 KW Smartlab, Japan). The cross-sectional morphology of the film was
examined by scanning electron microscope (SEM, FEI Sirion 200). The microstructure of the film was studied by transmission electron microscopy (TEM; JEOL JEM-2100F). The out-of-plane feature of the film was investigated by scanning probe microscope (SPM; Bruker Multimode 8). The Raman scattering spectra was acquired by Raman spectrometer (Horiba HR800) with excitation source of 488 nm laser. For the measurements of electrical properties, Au/Cr layers of 150 µm in diameter were evaporated on the surface through a patterned photoresist mask to form sandwich electrode structure. Dielectric permittivity measurement were carried out using an impedance analyzer (Wayne-Kerr Electronics, West Sussex, UK) with a perturbation voltage $V_{ac} = 100$ mV. Polarization-electric field hysteresis loops ($P$-$E$) and current-voltage curves ($I$-$V$) were obtained by means of a ferroelectric tester (Precision Premier II, Radiant Technologies Inc.) at 10 kHz. The energy storage performance was calculated according to the $P$-$E$ results.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. XRD pattern of the high textured (111)-oriented Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film. Inset: AFM micrograph.

Figure 2. Cross-sectional TEM image of the high textured (111)-oriented Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film. Inset: (a) an enlarged image of thin film (b) the corresponding SAED.

Figure 3. Raman scattering spectra of the high textured (111)-oriented Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film. Inset: (a) Temperature dependences of the Zr-O-Zr bending mode and the $P_{max}$ measured at 156 kV/cm and (b) $\varepsilon(T)$ and tan $\delta(T)$. 
Figure 4. $P$-$E$ loops of the high textured (111)-oriented Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film at selected applied electric fields. The shaded area represents 40.18 Jm$^{-3}$ being stored. Inset: $W_{\text{energy}}$, $W_{\text{loss}}$ and $\eta$ & $E$.

Figure 5. $P$-$E$ loops of Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film at selected temperatures. Inset: $W_{\text{energy}}$, $W_{\text{loss}}$ and $\eta$ vs. $T$.

Figure 6. $P$-$E$ loops of high textured and low textured Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film. Inset: (a) XRD pattern and (b) cross-sectional TEM image and the corresponding SAED of low textured Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ thin film.


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Large Energy Storage Density and High Thermal Stability in a Highly Textured (111)-Oriented Pb0.8Ba0.2ZrO3 Relaxor Thin Film with the Coexistence of Antiferroelectric and Ferroelectric Phases

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