Giant Electric Energy Density in Epitaxial Lead-Free Thin Films with Coexistence of Ferroelectrics and Antiferroelectrics

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Ferroelectrics/antiferroelectrics with high dielectric breakdown strength have the potential to store a great amount of electrical energy, attractive for many modern applications in electronic devices and systems. Here, it is demonstrated that a giant electric energy density (154 J cm\(^{-3}\)), three times the highest value of lead-based systems and five times the value of the best dielectric/ferroelectric polymer, together with the excellent fatigue-free property, good thermal stability, and high efficiency, is realized in pulsed laser deposited (Bi\(_{1/2}\)Na\(_{1/2}\))\(_{0.9118}\)La\(_{0.02}\)Ba\(_{0.0582}\)(Ti\(_{0.97}\)Zr\(_{0.03}\))O\(_3\) (BNLBTZ) epitaxial lead-free relaxor thin films with the coexistence of ferroelectric (FE) and antiferroelectric (AFE) phases. This is endowed by high epitaxial quality, great relaxor dispersion, and the coexistence of the FE/AFE phases near the morphotropic phase boundary. The giant energy storage effect of the BNLBTZ lead-free relaxor thin films may make a great impact on the modern energy storage technology.

1. Introduction

In recent years, there has been an increasing interest to develop new dielectric capacitors that possess high power density, fast charge/discharge (<1 µs), low cost, and high thermal and mechanical stability.\(^1\)\(^-\)\(^3\) These capacitors could find applications in defibrillators, detonators, power electronics, etc. that require high power density.\(^1\)\(^-\)\(^3\) However, compared with fuel cells, Li-ion batteries, and supercapacitors, the dielectric capacitors have the lowest energy density.\(^4\)\(^-\)\(^6\) To improve this, much attention has been particularly paid to antiferroelectric ceramics such as PZ,\(^7\)\(^,\)\(^8\) PLZT,\(^9\)\(^,\)\(^10\) PZN-PMN-PT,\(^4\) PLZST,\(^4\) etc., since they normally have higher energy density than ferroelectric and paraelectric ceramics at comparable electric field.\(^2\)

The energy density in bulk ceramics is usually less than 1 J cm\(^{-3}\) because of the limitation of low dielectric breakdown strength (<100 kV cm\(^{-1}\)).\(^11\)\(^,\)\(^12\) With the development of high-quality thin films by sol–gel, pulsed laser deposition (PLD), molecular beam epitaxy, etc., large energy density, mainly in lead-based antiferroelectric thin films, has been achieved due to the higher dielectric breakdown strength (>500 kV cm\(^{-1}\)).\(^3\)\(^,\)\(^9\)\(^,\)\(^13\)\(^,\)\(^14\) For example, a high energy density of 53 J cm\(^{-3}\) at 3500 kV cm\(^{-1}\) was obtained in relaxor antiferroelectric (Pb\(_{0.92}\)La\(_{0.08}\))(Zr\(_{0.9}\)Ti\(_{0.1}\))O\(_3\) sol–gel thin film.\(^9\) However, widespread applications of lead-based materials are prohibited due to the toxicity of lead. As a lead-free dielectric material, poly(vinylidene fluoride) (PVDF)-based polymer was also widely studied and a high energy density of 27 J cm\(^{-3}\) at 8000 kV cm\(^{-1}\) was reported.\(^1\)\(^4\) However, its lifetime and reliability are seriously impaired at the maximum operating temperature (typically less than 85 °C), seriously limiting its applications as capacitors.
In this study, \((\text{Bi}_{1/2}\text{Na}_{1/2})_{0.9118}\text{La}_{0.02}\text{Ba}_{0.0582}(\text{Ti}_{0.97}\text{Zr}_{0.03})\text{O}_3\) (BNLBTZ) epitaxial lead-free relaxor thin films with a coexistence of rhombohedral ferroelectric (FE) and tetragonal antiferroelectric (AFE) phases were deposited by the PLD method on (001) single-crystal \(\text{SrTiO}_3\) substrates. The film composition was exquisitely designed to be near the morphotropic phase boundary (MPB) of the \((1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{Ti}_x\text{BaTiO}_3\) (BNT-BT) solid solution, as shown in Figure 1.\(^{[15]}\) It should be noted that there are many debates on the AFE phase near the MPB of the BNT-BT system shown in Figure 1.) An appropriate content of La doping is to reduce the Curie temperature of the MPB composition \(0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{Ti}_{0.06}\text{BaTiO}_3\), improve the degree of relaxor dispersion, and maintain a certain amount of antiferroelectric phase. A small amount of Zr doping is to further gently adjust the Curie temperature. The deposited thin films have high saturation polarizations, low remnant polarizations, and slim \(P-E\) hysteresis loops, resulting in giant electric energy densities of 131 J cm\(^{-3}\) (efficiency \(\approx 95\%\)) and 154 J cm\(^{-3}\) (efficiency \(\approx 97\%\)) at 3500 kV cm\(^{-1}\) in (100)- and (111)-oriented thin films, respectively.

2. Results and Discussions

2.1. Structure

X-ray diffraction (XRD) patterns of the BNLBTZ thin film fabricated by PLD and bulk ceramic target synthesized by a sol-gel route are compared in Figure 2a. The BNLBTZ thin film exhibits a pure perovskite phase with preferential (100) orientation and a perfect epitaxial feature to the \(\text{La}_0.7\text{Sr}_0.3\text{MnO}_3\) (LSMO) bottom electrode because of the small lattice mismatch \((\alpha_{\text{LSMO}} = 3.85 \text{ Å and } \alpha_{\text{BNLBTZ}} = 3.91 \text{ Å})\). The rocking curve (inset of Figure 2a) of the (200) peak, whose full width at half maximum is less than 0.03°, indicates a highly single crystalline preferential growth orientation. The \(\phi\) scan of (110) (tilted about 45° away from the (100)) (inset of Figure 2a) further reveals a good fourfold rotational symmetry of the BNLBTZ epitaxial thin film. The slight deviation of the peak separation from the theoretical value of 90° indicates that the BNLBTZ thin film possesses a pseudo cubic structure.

The cross-sectional scanning electron microscope (SEM) image of the (100)-oriented BNLBTZ thin film (Supporting Information, Figure S1) shows clearly the epitaxial BNLBTZ film (thickness \(\approx 350\) nm), the bottom \(\text{La}_0.7\text{Sr}_0.3\text{MnO}_3\) (LSMO) electrode (thickness \(\approx 80\) nm), and the \(\text{SrTiO}_3\) substrate. The LSMO/STO and LSMO/BNLBTZ interfaces are all uniform and smooth, and no obvious grain boundaries can be detected, indicating a good epitaxial growth. Atomic force microscope micrograph shows that (100)-oriented BNLBTZ thin film has a low average surface roughness (\(R_a \approx 6.3\) nm and \(R_b = 7.9\) nm) (Supporting Information, Figure S2), a feature of good epitaxial growth.\(^{[16]}\) A direct evidence of the good epitaxial growth can be observed from the high-resolution transmission electron microscopy (HRTEM) image (Figure 2b) of the interface between the BNLBTZ thin film and the LSMO bottom electrode, where the selected area electron diffraction (SAED) shows the same set of pattern for both the film and the bottom electrode.

The cross-sectional transmission electron microscopy (TEM) image of the (100)-oriented BNLBTZ thin film (Figure 2c) shows lamellar nanodomains (indicated by black arrows in Figure 2c). The SAED pattern along pseudocubic [013] zone axis (inset of Figure 2d) shows bright 1/2[000] (\(o\) odd Miller indices) and weak 1/2[00e] (\(e\) even Miller indices) superlattice reflections, corresponding to a large portion of rhombohedral FE and a small portion of tetragonal AFE phases, respectively.\(^{[17]}\) Striking of the superlattice reflection can be observed along the [001] direction. It is believed that the doping of La on the A-site of the \(\text{ABO}_3\) perovskite structure disrupted the long range ordering of the AFE phase and led to the observed incommensurate modulations of the AFE phase.\(^{[18,19]}\) The piezoresponse force microscopy (PFM) vertical phase image (upper-right corner inset of Figure 2c) shows that the FE/AFE nanodomains can grow up into larger FE ones under the stimulus of an appropriate electric field.

2.2. Dielectric Properties

Figure 3 shows the temperature dependence of the relative dielectric permittivity \((\varepsilon(T))\) and the dielectric loss (tan \(\delta(T)\)) of BNLBTZ bulk ceramic and (100)-oriented thin film. The dielectric permittivity \((\varepsilon_{\text{BNLBTZ}}; \text{27 } ^\circ\text{C} = 1897)\) of the thin film at room temperature is much higher than that \((\varepsilon_{\text{BNLTZ}}; \text{27 } ^\circ\text{C} = 1618)\) of the bulk. However, the dielectric permittivity \((\varepsilon_{\text{BNLBTZ}}; \text{27 } ^\circ\text{C} = 1255)\) of the (111)-oriented BNLBTZ thin film is far below that of the bulk, implying that the rhombohedral phase is the dominant phase instead of the tetragonal one (consistent with the TEM result in Figure 2d) since for a rhombohedral phase the dielectric permittivity along the [111] direction is less than that along the [100] direction.\(^{[20]}\) In the bulk BNLBTZ, two dielectric permittivity maxima (at 10 kHz) can be observed at \(T_{m1} = 101 \text{ } ^\circ\text{C}\) and \(T_{m2} = 289 \text{ } ^\circ\text{C}\), which correspond to the phase transition temperatures of \(T_{\text{FE-AFE}}\) and \(T_{\text{AFE-PE}}\), respectively. By contrast, for the (100)-oriented BNLBTZ epitaxial thin film, the two dielectric permittivity maxima were smeared due to the relaxor dispersion in the thin film, especially near \(T_{m1}\).
The relaxor dispersion degree around $T_{m1}$ can be estimated by the Lorentz-type relation,
\[ \varepsilon_A / \varepsilon = 1 + (T - T_A)^2 / 2(\delta_A)^2, \]
where $T_A$ ($T_A \neq T_{m1}$) and $\varepsilon_A$ are the temperature of the dielectric permittivity peak and the extrapolated value of $\varepsilon$ at $T = T_A$, respectively. The parameter $\delta_A$ reflects the relaxor diffuseness of the dielectric peak. The greater the relaxor dispersion is, the larger the $\delta_A$ is. The Lorentz fitting parameters $\delta_A$ around $T_{m1}$ for the bulk and the thin film (the red dashed-dotted line in Figure 3) are 74 and 150, respectively, indicating a much higher degree of the relaxor dispersion in thin films, which can be attributed to composition difference between the thin film and the PLD target, small size effect, substrate constraint, interface charge, and other defects (such as vacancies).\(^{22–24}\)

Furthermore, the two dielectric permittivity maxima of the epitaxial thin film are both less than those of the bulk. One moves to the low temperature side of $T_{m1}$ and the other to the high temperature side of $T_{m2}$, leading to a wider temperature range of the AFE phase and a lower temperature coefficient of permittivity/capacitance (650–850 ppm K\(^{-1}\)) from room temperature up to 200 °C.

Due to the greater relaxor dispersion in the thin film, the dielectric loss ($\tan(\delta(T))$) of the (100)-oriented BNLBTZ thin film is much higher than that of the BNLBTZ bulk ceramic in the entire temperature range measured.

Previous research results showed that the reorientation of polar nanoclusters in relaxor FE/AFE phase plays a very important role in the electric field dependence of the dielectric permittivity, in addition to the contribution from intrinsic lattice phonon polarization.\(^{25}\) The room temperature dielectric permittivity ($\varepsilon(E)$) and the loss ($\tan(\delta(E))$) at 10 kHz exhibit a nonlinear dependence on the bias electric field (inset of Figure 3). Dielectric tunability and figure-of-merit (FOM) are defined as
\[ \varepsilon(E) = \varepsilon_s (0) / \left[ 1 + \lambda \varepsilon_s \varepsilon_r (0) E^2 \right]^{1/2} + \left( P_x / \varepsilon_s \right) [\cosh(Ex)]^{-2}, \]
\[ x = P_x / (2\varepsilon_s T). \]

**Figure 2.** XRD patterns and cross-sectional TEM images of the (100)-oriented BNLBTZ thin film. a) XRD pattern of the BNLBTZ bulk and thin film (the diffraction intensity is expressed in a logarithmic scale). Inset: The rocking curve of (200) and the $\phi$ scanning of (110). b) Cross-sectional TEM image of the interface between the BNLBTZ epitaxial thin film and the La$_0.7$Sr$_0.3$MnO$_3$ bottom electrode. The inset is the SAED pattern on a large area containing both the film and the substrate. c) TEM image. Lower-left corner inset: SAED pattern along [001] zone axis. Upper-right corner inset: PFM vertical phase image (red square section and peripheral area represent a single domain under 10 V DC bias and nanodomains under 0 V DC bias, respectively). d) TEM image. Inset: SAED pattern along [013] zone axis. Arrows indicate the 1/2[000] and 1/2[000] superstructure reflections, where $R$ means rhombohedral and $T$ tetragonal, and $o$ denotes the odd Miller index and $e$ the even Miller index.
Figure 3. $\varepsilon(T)$ and $\tan \delta(T)$ of the BNLBTZ bulk ceramic and (100)-oriented thin film. The inset is $\varepsilon(E)$ and $\tan \delta(E)$ at room temperature and 10 kHz, where the symbols represent experimental data, the black solid line is the fitting curve according to Equation (1), the red short dashed line is the contribution from polar nanoclusters, and the blue dotted line is the contribution from lattice phonons.

where $\varepsilon_0$ is the vacuum permittivity, $\lambda$ is a temperature-independent coefficient, $\varepsilon(E)$ is the relative dielectric permittivity at zero field, $P_r$ is the polarization of a polar nanocluster, $L$ is the cluster size (or correlation length), $k_B$ is the Boltzmann's constant, and $T$ is the temperature. The first term in Equation (1) represents the polarization contribution from lattice phonons, and the second stands for the reorientation contribution from polar nanoclusters. The black solid line (inset of Figure 3) fitted according to Equation (1) agrees quite well with the experimental data. Obviously, the nanoclusters make a significant contribution to $\varepsilon$ below $\approx 200$ kV cm$^{-1}$, which decreases quickly with increasing $E$ and almost disappears at an electric field above $300$ kV cm$^{-1}$. It can also be seen (inset of Figure 3) that the dielectric permittivity contributed by the nanoclusters ($\varepsilon_{\text{cluster}}$) is 1322 under zero bias, about 70% of the total dielectric permittivity ($\varepsilon_{\text{total}}$). The size of nanoclusters, according to the fitting, is $L = 3.9$ nm.

2.3. Energy Storage

The energy density ($W$) of a dielectric-based compound is given by

$$\quad W = \int_{P_r}^{P_{\text{max}}} E dP \quad 0 \leq E \leq E_{\text{max}}$$

(2)

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. It is obvious that, to have a high energy density $W$, the material should have a high $P_{\text{max}}$ and a low $P_r$. They are realized in the BNLBTZ films through the coexistence of relaxor FE and AFE phases, where the relaxor FE phase helps maintain a high $P_{\text{max}}$ and both the relaxor FE and AFE phase keep a low $P_r$. From the $P–E$ hysteresis loop of the (100)-oriented thin film (Figure 4) it can be seen that the $P_{\text{max}}$ and $P_r$ are 72.1 and 4.03 $\mu$C cm$^{-2}$, respectively, and the breakdown field exceeds $2180$ kV cm$^{-1}$ (Figure 4). A careful examination on the $P–E$ loop shows that it is not an FE-type single loop since four peaks can be observed in the corresponding $I–E$ curve (inset of Figure 4). The four peaks occur at a relatively low electric field of $125$ kV cm$^{-1}$ and are indicative of a relaxor AFE nature of the epitaxial thin film. One may argue that double hysteresis loops are not necessarily indicative of antiferroelectricity. As originally shown by Merz,[24] double loops also occur for first-order FE transitions over a temperature range of a few degrees above $T_c$, where the applied field induces spontaneous polarization. In BaTiO$_3$, this occurs over a temperature range from the Curie temperature $T_c$ to $T_c + 11$ °C. However, this can be ruled out in the present case because there is no evidence for such a temperature dependence.

One may also propose that double hysteresis loops may be due to the aging of point defects.[23] This can also be ruled out since the double hysteresis loops were observed in our fresh samples without aging. By integrating the discharging portion of the $P–E$ loop according to Equation (2), an energy density of $43.9$ J cm$^{-3}$ at $2180$ kV cm$^{-1}$ can be achieved on the (100)-oriented thin film, which is $\approx 44$ times that of the bulk BNLBTZ ($=1$ J cm$^{-3}$ at $103$ kV cm$^{-3}$, as illustrated by the shaded area in Supporting Information Figure S4). The energy density of $43.9$ J cm$^{-3}$ achieved in this lead-free material is comparable to the best lead-containing PLZT at similar electric fields. It can be further improved by changing the epitaxial growth orientation from (100) to (111), where an energy density of $54.3$ J cm$^{-3}$ was achieved (Figure 4). The good quality of the (111)-oriented epitaxial film can be reflected from the XRD pattern, the rocking curve of (111), and the $\phi$ scan of (110) (Supporting Information, Figure S5). The higher energy density of the (111)-oriented film can be ascribed to the higher $P_{\text{max}}$ ($82.5$ $\mu$C cm$^{-2}$) along [111] which is the spontaneous polarization direction for a system with a dominant rhombohedral phase.

In real applications, capacitor efficiency ($\eta$) is also an important factor to consider, which is defined as the ratio of the discharging (output) energy to the charging (input) energy

$$\quad \eta = W / (W + W_{\text{loss}})$$

(3)

where $W_{\text{loss}}$ is the energy loss density, equivalent to the integrated area of the closed $P–E$ hysteresis loops. At an electric field of $2180$ kV cm$^{-1}$, the energy loss densities of the (100)- and (111)-oriented BNLBTZ thin films are $9.2$ and $10.3$ J cm$^{-3}$, respectively, which result in efficiencies of $79\%$ and $81\%$, respectively.
For energy storage applications, cycling life is another important factor to consider. An electrochemical supercapacitor can normally withstand a cycling number of $10^5$. In this study, after $10^8$ fatigue cycles (bipolar cycling), a relatively high $P_{\text{max}}$ (70.5 $\mu$C cm$^{-2}$) and a low $P_r$ (2.94 $\mu$C cm$^{-2}$) can still be maintained for the (100)-oriented BNLBTZ thin film under an electric field of 2180 kV cm$^{-1}$ (Figure 4), with a corresponding high energy density of 37.9 J cm$^{-3}$. Since, in real applications, dielectric capacitors normally undergo unipolar cycling, it is thus believed that the cycling number of our thin film capacitor can be well above $10^8$. The excellent antifatigue property of our epitaxial thin film is resulted from (1) the use of a highly conductive p-type oxide La$_{0.7}$Sr$_{0.3}$MnO$_3$ as the bottom electrode, and (2) the great relaxor dispersion and the unique nanodomain structure near MPB (Figure 2c,d) that help relieve the large strain associated with the AFE–FE phase transition under an applied electric field.

In addition to the above, thermal stability should also be considered in real capacitor applications. The $P$–$E$ loops of the (100)-oriented thin film at selected temperatures after $10^8$ fatigue cycles are shown in Supporting Information, Figure S6. From the inset (b) of Figure 4, it can be seen that the variations of the energy density and the efficiency are below 2.6% and 5%, respectively, from room temperature up to 110 °C. The slight increase in energy density as the temperature is increased from room temperature to 100 °C is due to the increased leakage current at higher temperatures, where the $P$–$E$ loop becomes more and more leaky (Supporting Information, Figure S6). It is noted that the temperature for the maximum energy density (black arrow in the inset (b) of Figure 4) is close to $T_{\text{m1}}$ (red arrow in Figure 3) of the bulk BNLBTZ, not that of the (100)-oriented thin film. One possible reason is that the applied electric field tends to turn the AFE phase into an FE one, resulting in enhanced FE–AFE transition temperature $T_{\text{m1}}$ of this epitaxial thin film.

According to Equation (2), a higher energy density can be achieved if the thin film can withstand a higher electric field. With the help of an external voltage amplifier (ferroelectric tester Precision Premier II) and to simulate the condition in a real application, a unipolar voltage pulse was used to charge the thin film capacitor. The resulting $P$–$E$ loops of the (100)- and (111)-oriented BNLBTZ epitaxial thin films (Figure 5) show that both of them can withstand a very high electric field, up to 3500 kV cm$^{-1}$. Extremely high $P_{\text{max}}$ has been achieved (90.55 $\mu$C cm$^{-2}$ in (100) film and 113.45 $\mu$C cm$^{-2}$ in (111) one). As a result, giant energy storage effect has been observed in (100) and (111) films, with $W = 131$ and 154 J cm$^{-3}$, respectively. The efficiencies are 95% and 97%, respectively, comparable to the Columbic efficiency of a good electrochemical supercapacitor.

Further increasing the electric field will cause a failure of the top electrode (inset (b) of Figure 5) due to the large leakage current at the beginning of charging (inset (a) of Figure 5). The leakage current measurement (Supporting Information, Figure S7) shows that, under a high electric field, the conduction in the (100) thin film satisfies a bulk-limited conduction mechanism, following a Poole–Frenkel relation.

It is believed that the flat film/electrode interface (Figure 2b and Supporting Information, Figure S1) is one of the reasons to achieve a high breakdown field. An even higher energy density is achievable if the film quality can be further improved and the top electrode can be optimized by using, for example, a LaNiO$_3$ electrode. The utilization of a “dead layer” at the film/electrode interface could
a number of promising materials previously reported (the BNLBTZ thin films in the present work are compared with applications in energy storage devices, the energy densities of ref. [14]; the navy dot: ref. [4]; the blue dot: ref. [7]; the wine dot: ref. [4]; the gray dot: ref. [4]; the green dot: ref. [14]; the navy dot: ref. [4]). By implementing a multilayer configuration, the BNLBTZ reported in this work will be a very promising, environmentally friendly, inexpensive (compared with scandium-based),[32] and thermally stable (compared with polymers) capacitor material for potential applications in electric energy storage, due to its ultrahigh energy density (154 J cm$^{-3}$–7.7 W h kg$^{-1}$).

3. Conclusions

In conclusion, a giant energy storage effect (137 and 154 J cm$^{-3}$ for (100)- and (111)-oriented thin films, respectively) with high efficiency, excellent antifatigue property ($10^8$ cycles), and thermal stability (variation below 2.6% at 2180 kV cm$^{-1}$ from room temperature to 110 °C) has been achieved in the lead-free relaxor BNLBTZ epitaxial thin films. This is accomplished by the high epitaxial quality, great relaxor dispersion, and the coexistence of FE/AFE phase near the MPB.

The giant energy storage density of the thin film with lead-free, fast charge/discharge, low cost, and high thermal stability may make it a promising material for modern energy storage technology, especially in electronic and electric systems.

4. Experimental Section

Fabrication of BNLBTZ Target: BNLBTZ target was fabricated by sol–gel and conventional solid-state reaction methods. Bi(OAc)$_3$, Na(OAc), La(NO$_3$)$_3$, and Ba(CH$_3$COO)$_2$ were dissolved in glacial acetic, 2-methoxyethanol, and deionized water. In order to compensate for the Bi and Na loss during sintering, 20% excess Bi and Na were added. Separately, acetylacetone and 2-methoxyethanol were added to a mixture of Zr(O$_n$Pr)$_4$ and titanium-4-butoxide, and the resulting solution was pyrolyzed at 350 °C for 30 min and then fired at 600 °C for 30 min, and finally calcined at 900 °C for 2 h in air in a tube furnace. After grinding for 2 h in an agate mortar, the calcined powders were then compacted into pellets with 20 mm in diameter and 3 mm in thickness under a 300 MPA cold isostatic pressing and were sintered at 1150 °C for 6 h in air, and then cooled to room temperature at a furnace cooling rate.

Fabrication of BNLBTZ Thin Films: The as-prepared BNLBTZ target exhibited a prominent pure perovskite crystalline phase in the XRD pattern (Figure 2). The BNLBTZ thin film was grown by PLD using a KrF laser excimer ($\lambda = 248$ nm) with a pulse repetition rate of 5 Hz. A 80 nm thick lattice matched La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) thin film was deposited as the bottom electrode between the BNLBTZ film and the SrTiO$_3$ (STO) substrate. The BNLBTZ/LSMO bilayers were deposited in situ at the substrate temperature of 700 °C, oxygen pressure of 30 Pa, and laser pulse energy density of 5 J cm$^{-2}$. After the deposition, the bilayer films were post-annealed in situ at the deposition temperature under an oxygen pressure of 400 Pa for 20 min before they were cooled to room temperature to minimize oxygen vacancies. The aforementioned PLD processing parameters and the corresponding plasma image for depositing BNLBTZ thin films are briefly summarized in Supporting

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Figure 5. P–E loops of (100)- and (111)-oriented BNLBTZ thin films at 3500 kV cm$^{-1}$ (close to the breakdown electric field of the thin film) and 10 kHz. The inset (a) is leakage current at 3500 kV cm$^{-1}$, and the inset (b) is the optical image of a broken electrode.

Figure 6. Energy densities of the lead-free BNLBTZ thin films reported in this work and a number of lead-based FE/AFE thin and thick films, as well as polymeric PVDF, at different applied electric fields. The red and the magenta dots are the (111)- and (100)-oriented BNLBTZ epitaxial thin films, respectively. The olive dot: ref. [9]; the black dot: ref. [10]; the blue dot: ref. [7]; the wine dot: ref. [4]; the gray dot: ref. [4]; the green dot: ref. [14]; the navy dot: ref. [4].
Information Table S2. The final thickness of the BNLBTZ film was about 350 nm. Circular Cr/Au top electrodes with about 100 μm in diameter were deposited by RF magnetron sputtering using a shadow mask.

**Characterization:** The crystallinity of the BNLBTZ film was monitored by XRD (Rigaku 9 KW Smartlab, Japan) on a diffractometer, using Cu Kα radiation (λ = 1.5406 Å). The cross-sectional morphology of the film was examined by SEM (JEOL JEM-2100F). The out-of-plane feature of the ferroic domains in the film was investigated by scanning probe microscope (Bruker Multimode 8). Dielectric permittivity measurements were carried out using an impedance analyzer (4294A, Agilent) with a perturbation voltage V_{ac} = 500 mV. The polarization-electric field (P–E) hysteresis loop and leakage current (I–E) were obtained by means of a ferroelectric tester (Precision Premier II, Radiant Technologies Inc.).

All samples were measured with top-to-bottom electrode configuration. The temperature of the sample was controlled via feedback from a thermocouple in contact with the sample, with an accuracy of 0.1 °C.

**Supporting Information**

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

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