(Bi0.51 Na0.47)TiO3 based lead free ceramics with high energy density and efficiency

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Abstract
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Keywords
density, energy, efficiency, high, na0.47)tio3, ceramics, free, lead, (bi0.51

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1. Introduction

The demand of energy storage technologies has been dramatically increased due to the increasing energy consumption within the next 50 years, coupled with renewable energy harness and sustainable society development. The efficient energy storage solutions include, but not limit to, chemical energy storage devices such as batteries and solid oxide fuel cells, flywheels, electrochemical capacitors and electrostatic capacitors. Dielectric capacitors belong to the electrostatic capacitors, possessing high power density based on their ultrafast charge-discharge capability, which make them suitable candidates for pulse power and high power applications. Currently, the commercially available dielectric capacitors are mainly made of dielectric polymers and/or dielectric ceramics [1–3]. Compared with fuel cells or batteries, they are lower cost, more thermally stable and mechanically robust, in addition to their high power density [4]. Dielectric ceramics exhibit stable energy storage properties over a broader temperature range than polymer counterparts. However, the energy density of dielectric ceramics is lower than that of polymers owing to their relatively low dielectric breakdown strength (BDS in short), which limits the application range of dielectric ceramics [5]. Thus, it is desired to explore new dielectric systems with high energy density in order to meet the requirement of electric and electronic devices towards the miniaturization, light-weight and integration [6–12].

The majority of ceramic materials used for dielectric capacitors consist of linear dielectrics, ferroelectrics, relaxor ferroelectrics and anti-ferroelectrics. In general, the recoverable energy storage density (Wrec) can be calculated by integrating the area between the polarization axis and the discharge curve of the polarization-field (P-E) hysteresis loops according to the following equations [13–15]:

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The dielectric properties were measured using a precision LCR meter (E4980A, Agilent Technology, Santa Clara, CA, USA) at various electric fields and temperatures, where the test specimens with a thickness of 0.1 mm were subject to an electric field through the MOSFET switch and the stored energy was discharged to a load resistor (RL). By an electric voltage MOSFET switch, where the ceramic sample was charged by a high-voltage power amplifier (Trek Model 610C, TREK, USA). Charge and discharge behaviors were measured by RC circuit performed by a capacitor charge-discharge test system (PK-CPR1701, PolyK Technologies, USA) with a high-voltage MOSFET switch, where the ceramic sample was charged by an electric field through the MOSFET switch and the stored energy was discharged to a load resistor (R_L = 2000Ω).

3. Results and discussion

3.1. Phase characterization and microstructure

The X-ray diffraction (XRD) patterns of the pure BNT and BNT-
BNT100x ceramics measured at room temperature are given in Fig. 1a. All compositions are found to exhibit single perovskite structure with no obvious secondary impurity phase. In Fig. 1b, the [111] peak of pure BNT exhibits an asymmetry while the [200] peak doesn’t split, showing a rhombohedral structure. With BZT increasing, sharp peaks of [111] and [200] profiles can be clearly seen, which implies that the BNT-BZT100x ceramics are in pseudocubic perovskite structure [31]. Besides, all diffraction peaks shift toward the lower angle with increasing BZT content, which can be clearly seen near the dashed lines drawn, indicating an increment in lattice constant and cell volume with the increase of BZT. This is due to the fact that Ba$^{2+}$ cations enter A-site and Zr$^{4+}$ cations occupy B-site of BNT lattice structure, respectively, where the ionic radius of Ba$^{2+}$ (0.161 nm) is bigger than that of (Bi$_{0.51}$Na$_{0.47}$)$_{2+}$ (0.133 nm) while the ionic radius of Zr$^{4+}$ (0.072 nm) is larger than that of Ti$^{4+}$ (0.0605 nm), leading to the increased lattice constants and downward-shift of the peak positions [27,32].

The SEM images of the fractured cross-sections for pure BNT and BNT-BZT100x ceramics are presented in Fig. 2. The close-packed grains can be observed in all BNT-BZT100x samples, suggesting the ceramics are dense with minimal porosity. However, it is worth noting that there is a small amount of second phase observed in x = 0.50 composition, indicating that 50 mol% of BZT exceeds the solubility of BNT, which cannot be confirmed from the XRD patterns because of the limitation of the detection resolution. The insets show the grain size distribution for each composition and the average grain size is obtained from the Gauss distribution curves. The average grain size of the ceramics is observed to decrease from 1.70 μm to 1.20 μm first, and then slightly increase with further increasing the BZT, which implies the relatively low BZT addition inhibits grain boundary mobility and suppresses the grain growth.

TEM images of the BNT-BZT40 sample are given in Fig. 3. SAED results from Fig. 3a indicate the existence of perovskite structure in the sample with a pseudocubic crystal structure, which is in good agreement with the XRMA measurement. The HRTEM image from Fig. 3b suggests the existence of nano polar regions in the sample with typical size around 5 nm, where no macroscopic ferroelectric domain configuration can be observed, showing a typical image of relaxor materials.

### 3.2. Dielectric properties

Fig. 4 shows the temperature dependence of the dielectric constant and dielectric loss at different frequencies for pure BNT and BNT-BZT100x ceramics. It can be seen that the dielectric constant versus temperature curves exhibit two dielectric anomalies. The first dielectric anomaly observed at lower temperature is identified as the depolarization temperature ($T_d$), corresponding to the phase transition from field-induced ferroelectric to relaxor, or from one polar phase to another nonpolar phase with different symmetry [33]. The curves show obvious frequency dispersion around $T_d$, where the peaks shift to higher temperatures with increasing frequency. Compared with pure BNT ($T_d$ ~166°C), the depolarization temperature of BNT-BZT100x ceramics is significantly decreased with the addition of Ba(Zr$_{0.3}$Ti$_{0.7}$)O$_3$, which is beneficial to the stabilization of the antiferroelectric phase at lower temperature or even at room temperature. The second dielectric anomaly detected at higher temperature is regarded as the Curie point ($T_m$), where the dielectric constant reaches a maximum value ($\varepsilon_m$). Detailed information about $T_d$, $T_m$, dielectric constant at room temperature ($\varepsilon_R$) and $\varepsilon_m$ are summarized in Table 1. With increasing BZT content, both $T_m$ and $\varepsilon_m$ decrease noticeably, which smears the Curie peaks and forms flat dielectric plateaus between $T_d$ and $T_m$. As a result, BNT-BZT100x ceramics with higher x values exhibit minimal dielectric variation over the plateau region, which is favorable for the temperature stability of dielectric and energy storage properties [24]. However, it is interesting to note that $T_m$ is not identified for x = 0.50 composition, which may be due to the greatly depressed dielectric maxima around the Curie point. Of particular significance is that the BZT addition has a significant effect on the improvement of dielectric constant at room temperature, where all of the BNT-BZT100x ceramics exhibit larger $\varepsilon_R$ than that of BNT. On the other hand, in the dielectric loss versus temperature curves, frequency dispersion can also be observed over a wider temperature range below $T_m$ for different compositions.

The diffuseness of dielectric anomalies and dielectric loss as a function of frequency is mainly ascribed to the presence of short range ordering (SROs), such as polar nanoregions (PNRs) or local structural heterogeneity [14,26,30]. In order to further characterize the dielectric dispersion behavior, a modified Curie-Weiss law is used [34,35]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C}$$

where $C$ is Curie constant and $\gamma$ corresponds to the degree of diffuseness with the value varying between 1 for normal ferroelectric and 2 for ideal relaxor. Fig. A1 (Supporting Information) shows the typical fitting curves according to Eq. (4) and the diffusion parameters $\gamma$ are listed in Table 1. It is apparent that the fitting values of $\gamma$ for BNT-BZT100x ceramics are larger than that of pure BNT with the exception of x = 0.50 composition, being close to that of ideal relaxor, indicating the addition of Ba(Zr$_{0.3}$Ti$_{0.7}$)O$_3$.
For $x = 0.50$ composition, the $\gamma$ shares almost the same value with that of pure BNT, mainly due to the fact that the dielectric around $T_m$, which represents the transition temperature from the nonpolar phase to paraelectric phase, is greatly depressed, giving rise to the decreased diffuseness [22]. Thereby, the expectation of designing BNT-based relaxor characteristic proposed in Section I is achieved, which will benefit the high energy storage density and efficiency for BNT-BZT100x ceramics, and meanwhile the flat dielectric plateau will guarantee the broadened temperature usage range.

3.3. Energy storage properties

Fig. 5 shows the hysteresis loops and current-electric field curves for BNT-BZT100x ceramics. In order to evaluate the potential for energy storage application, consistent experimental conditions were taken for each specimen and the electric field was fixed at 100 kV/cm. The parameters $P_r$, $P_{\text{max}}$, $W_{\text{rec}}$ and $\eta$ calculated from P-E loops are summarized in Table 2. As can be seen in Table 2, the remnant polarization decreases from ~1 $\mu$C/cm$^2$ to near zero with increasing BZT content, while the maximum polarization shows the same trend with the values decreasing from 23.1 $\mu$C/cm$^2$ to 11.5 $\mu$C/cm$^2$. Correspondingly, the P-E hysteresis loops show slimmer and more pinched shape in the compositions with higher $x$ values. As a result, the energy storage efficiency of the ceramics increases monotonically with increasing the BZT component, reaching the order of 90%, while the energy density decreases gradually owing to the obvious degradation of the maximum polarization. It is interesting to note that four weak current peaks can be observed in I-E curves, especially for the composition of $x = 0.20$, which is the characteristic of antiferroelectrics, and the I-E curve turns into rectangular shape for the composition of $x = 0.50$, exhibiting paraelectric-like behavior [36].

For dielectric energy storage application, high maximum polarization and low hysteresis are required. Based on this consideration, BNT-BZT40 ceramic with hysteresis of 7% and $P_{\text{max}}$ of 15.2 $\mu$C/cm$^2$ under the electric field of 100 kV/cm was selected to further evaluate the energy storage performance. This included the following aspects: dielectric breakdown strength, energy storage density and efficiency, charge and discharge behavior, temperature stability and fatigue endurance.
3.3.1. Dielectric breakdown strength

In order to explore the impact of BZT component on the breakdown strength of BNT matrix, the dielectric breakdown strengths were measured on pure BNT and BNT-BZT40 samples. The Weibull distribution has been widely employed to estimate the probability distribution of the breakdown strength for ceramics with perovskite structure [37]. The Weibull distribution can be described according to the following equations:

\[ X_i = \ln(E_i) \]  
\[ Y_i = \ln(-\ln(1 - i/(n + 1))) \]

where \( E_i \) is the specific breakdown strength of each sample in the experiment, \( n \) represents the count of samples in the same composition and \( i \) corresponds to the serial number which is defined by the relationship as follows:

\[ E_1 \leq E_2 \leq \cdots \leq E_l \leq E_n \]

The Weibull distribution function \( Y_i (X_i) \) displays linear relationship with \( X_i \). The slope of the fitting line is represented by \( \beta \) while the intercept on the \( x \)-axis is expressed by \( \ln x \), where \( x \) and \( \beta \) are the symbols of the scale parameter and shape parameter, respectively.

Fig. 6 shows the Weibull analysis of the breakdown strength for pure BNT and BNT-BZT40 ceramics with the same thickness of 0.1 mm. The shape parameter \( \beta > 9 \) can be observed for both compositions, suggesting the BDS data is in good agreement with the Weibull model. The average BDS of the BNT-BZT40 ceramic is extracted from the fitting line and found to be 270 kV/cm, which is much higher than that of pure BNT (~180 kV/cm) and other BNT-based ceramics [24,38,39]. The significant enhancement of the BDS in BNT-BZT40 ceramic is owing to the following two factors [3]:

1. The dense microstructure with minimal porosity, accompanying with the compositional homogeneity is achieved in BNT-BZT40 ceramic, where the corresponding EDS mapping images are given in Fig. A.2 (Supporting Information). Meanwhile, a few pores are observed in pure BNT ceramic, as shown in Fig. 2, the existence of which will greatly decrease the BDS. (2) The BaZrO3 component in the studied BNT-BZT100x samples possesses higher bandgap compared to BaTiO3, which is expected to positively impact the BDS values. The measured BDS results, again, validate the designing of BNT-BZT100x materials with enhanced BDS as proposed in Section I.

3.3.2. Energy storage density and efficiency

The unipolar hysteresis loops of BNT-BZT40 ceramic measured under different electric fields at room temperature are shown in Fig. 7a. The electric field increases from 100 kV/cm to 280 kV/cm during the test. The maximum polarization increases up to 29 \( \mu \)C/cm\(^2\) with increasing electric field, while the hysteresis is found to remain the similar value. To better depict the energy storage properties as a function of electric field, the energy storage density and efficiency are summarized in Fig. 7b. The energy storage density increases linearly with increasing electric field, benefited from the enhanced maximum polarization, while the energy efficiency maintains the similar value being on the order of >91%, due to the contribution from the relaxor feature. The maximum energy storage density of 3.1 J/cm\(^3\), together with high energy efficiency of 91%, is achieved simultaneously at the electric field of 280 kV/cm in BNT-BZT40 sample with thickness of 0.1 mm, indicating that the higher electric field prior to the BDS is beneficial to larger \( W_{\text{rec}} \) [40].

The dielectric energy storage materials are often used in high

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Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>( T_d ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( \epsilon _)</th>
<th>( \epsilon_m )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure BNT</td>
<td>166</td>
<td>327</td>
<td>770</td>
<td>2370</td>
<td>1.72</td>
</tr>
<tr>
<td>( x = 0.20 )</td>
<td>76</td>
<td>297</td>
<td>1340</td>
<td>2310</td>
<td>1.97</td>
</tr>
<tr>
<td>( x = 0.30 )</td>
<td>72</td>
<td>265</td>
<td>1250</td>
<td>1720</td>
<td>1.94</td>
</tr>
<tr>
<td>( x = 0.40 )</td>
<td>65</td>
<td>230</td>
<td>1140</td>
<td>1300</td>
<td>1.91</td>
</tr>
<tr>
<td>( x = 0.50 )</td>
<td>61</td>
<td>/</td>
<td>1090</td>
<td>1130</td>
<td>1.71</td>
</tr>
</tbody>
</table>

---

Fig. 4. Dielectric constant and dielectric loss as a function of temperature measured at frequencies from 1 kHz to 1000 kHz for a) pure BNT and BNT-BZT100x ceramics: b) \( x = 0.20 \), c) \( x = 0.30 \), d) \( x = 0.40 \) and e) \( x = 0.50 \).
temperature applications, especially in the inverter capacitor for HEVs and pulse power systems. In this case, the energy storage performance at elevated temperature should be taken into consideration. Fig. 7c shows the unipolar hysteresis loops of BNT-BZT40 ceramic measured under different electric fields and at the elevated temperature of 160 °C. The maximum polarization increases up to 25 \( \mu \)C/cm\(^2\) under the critical electric field of 220 kV/cm, while the P-E loops exhibit the stronger relaxor antiferroelectric characteristic as the test temperature is far above the \( T_d \) (~65 °C). However, the BDS decreases compared to that at room temperature, which is caused by the increased electronic/ionic conduction and subsequent deterioration of the insulation. The detailed information of the energy storage density and efficiency at 160 °C are summarized in Fig. 7d. The energy storage density increases monotonically with increasing electric field while the energy efficiency shows minimal variation below 4%. The maximum energy storage density of 2.3 J/cm\(^3\), together with the nearly ideal energy efficiency of 96%, is achieved simultaneously at the electric field of 220 kV/cm with thickness of 0.1 mm at 160 °C, indicating that the BNT-BZT40 ceramic possesses outstanding energy storage performance at elevated temperature. Again this ultrahigh energy efficiency is attributed to the dominated relaxor feature at elevated temperature.

3.3.3. Charge and discharge behavior

The energy discharge behavior of BNT-BZT40 ceramic under different electric fields was investigated using a resistance-capacitance (RC) circuit, in which the discharge energy was measured by a load resistor (RL) in series with the ceramic sample. The discharge energy density of the ceramics can be calculated according to the following formula [6]:

<table>
<thead>
<tr>
<th>Composition</th>
<th>( P_r(\mu )C/cm(^2))</th>
<th>( P_{max}(\mu )C/cm(^2))</th>
<th>( W_{rec}(J/cm^3) )</th>
<th>( \eta(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.20 )</td>
<td>1.01</td>
<td>23.1</td>
<td>1.00</td>
<td>79.5</td>
</tr>
<tr>
<td>( x = 0.30 )</td>
<td>1.21</td>
<td>21.0</td>
<td>0.93</td>
<td>82.7</td>
</tr>
<tr>
<td>( x = 0.40 )</td>
<td>0.37</td>
<td>15.2</td>
<td>0.71</td>
<td>93.0</td>
</tr>
<tr>
<td>( x = 0.50 )</td>
<td>0.10</td>
<td>11.5</td>
<td>0.56</td>
<td>96.7</td>
</tr>
</tbody>
</table>

Fig. 6. Weibull distribution of dielectric breakdown strength of pure BNT and BNT-BZT40 ceramics.

Table 2
The parameters \( P_r, P_{max}, W_{rec} \) and \( \eta \) of BNT-BZT100x ceramics measured at 10 Hz and 25 °C.

Fig. 5. Bipolar P-E loops and corresponding I-E curves of BNT-BZT100x ceramics measured at 10 Hz and 25 °C under a moderate applied electric field of 100 kV/cm: a) \( x = 0.20 \), b) \( x = 0.30 \), c) \( x = 0.40 \) and d) \( x = 0.50 \).
\[ W = \int I^2(t)R dt \]  

(8)

where \( R \) is the total load resistor and \( I(t) \) represents the discharge current detected by the oscilloscope.

The discharge energy density as a function of time is demonstrated in Fig. 8. In the measurement, the test sample (with the capacitance of 500 pF) was subject to various electric fields. The energy density measured from the discharge curve is slightly lower than that measured in the P-E loops from Fig. 7b, which can be attributed to the following two factors: the energy losses to the equivalent series resistor in the RC circuit measurement and thickness fluctuation of different samples for the two measurements. The time constant of energy discharge can be deduced by exponentially fitting discharge voltage as a function of time, taking the electric field of 180 kV/cm as an example, which is found to be ~1.1 \( \mu \)s, as shown in the inset of Fig. 8. It should be noted that the product of the load resistance (2000 \( \Omega \)) in the RC circuit and the capacitance of BNT-BZT40 ceramic is 2000 \( \Omega \times 500 \) pF = 1.0 \( \mu \)s, sharing similar value with the time constant of energy discharge, implying that the discharge time of the BNT-BZT40 ceramic is controlled by the RC circuit in the measurement and as a result, the BNT-BZT40 ceramic should exhibit a much shorter discharge time of well below 1.1 \( \mu \)s. [16].

3.3.4. Temperature stability

Property thermal stability is regarded as one of the pivotal factors for electronic materials. To evaluate the feasibility for practical applications, the temperature stability of energy storage performance for BNT-BZT40 ceramic was investigated as a function of temperature. The hysteresis loops measured at different temperatures from 20 \(^\circ\)C to 160 \(^\circ\)C are presented and compared in Fig. A.3 (Supporting Information). From a viewpoint of practical applications, the applied electric field was determined to be approximately half of the critical electric field, namely 140 kV/cm in case of the breakdown of the ceramic samples [16]. Fig. A.3 suggests
that BNT-BZT40 ceramic displays slim P-E loops over the whole studied temperature range. As the temperature exceeds $T_d$ (−65 °C), more pinched hysteresis loops with negligible remnant polarization can be observed, implying the stabilized relaxor antiferroelectric phase at the temperature above $T_d$. Fig. 9 illustrates the energy storage properties as a function of temperature, where the recoverable energy density fluctuates slightly with increasing temperature, being in the range of 1.19–1.21 J/cm$^3$ with variation below 1.5% over the temperature range of 20–160 °C. Of particular significance is that the dissipated energy density shows the decreasing trend, leading to increased energy efficiency, being on the order of 97% at 160 °C, which is owing to the prevailing relaxor feature with degraded remnant polarization at elevated temperature.

3.3.5. Fatigue endurance

Fatigue endurance (cycling reliability) is considered to be another key indicator for electronic materials in practical energy storage applications. The hysteresis loops measured at room temperature under 140 kV/cm with a cumulative cycling number up to $10^6$ are shown in Fig. A.4 (Supporting Information). It is observed that the P-E loops remain almost the same shape as the cycling number accumulates to the order of $10^6$. In order to better manifest the effect of cumulative cycles on energy storage performance, $W_{rec}$, $W_{loss}$ and $\eta$ as a function of the cycling number are given in Fig. 10. Overall, BNT-BZT40 ceramic shows excellent cycling reliability. The recoverable energy density is found to slightly decrease from 1.20 J/cm$^3$ to 1.17 J/cm$^3$, with variation below 3% after $10^6$ charge/discharge cycles. The dissipated energy density shows an opposite trend with respect to the number of cycles compared to that of the recoverable energy density, leading to slightly decreased energy storage efficiency, being on the order of 90% after $10^6$ charge/discharge cycles, with variation below 3%. This is ascribed to the increment of the hysteresis loss, which is thought to be associated with volume changes during phase transition and domain wall pinning with cycles up to $10^6$ [41].

4. Conclusion

In summary, a series of BNT-BZT100x lead free relaxor ferroelectric ceramics were successfully fabricated via solid state reaction method, where strong relaxor and high BDS characteristics were introduced in BNT-based solid solution due to the addition of relaxor end member BZT, which met our design expectation. The strong relaxor feature and increased BDS are responsible for the improved energy storage density and energy efficiency, where a high energy storage density of 3.1 J/cm$^3$ and high energy efficiency of 91% were simultaneously achieved in BNT-BZT40 ceramic (0.1 mm in thickness) at room temperature. Together with the high temperature stability over the temperature range of 20–160 °C and excellent cycling reliability up to $10^6$ cycles, it demonstrates that the BNT-BZT40 ceramic possesses a great potential for high power energy storage applications over broad temperature range.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmat.2019.03.006.

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