Temperature-dependent energy storage characterization of Pb-free relaxor ferroelectrics

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Received 12 January 2020; Revised 20 March 2020; Accepted 14 April 2020; Published 4 July 2020

The energy storage properties of (1−x)Bi0.3Na0.7TiO3−xBaTiO3 (x = 0.08) (BNT–BT) ceramics obtained via sol–gel method are determined from the polarization versus electric field (P−E) loops at various temperatures. The energy storage densities are observed to increase with increase in temperature and this may be attributed to the presence of antiferroelectric (AFE) phase at higher temperature (≥120 °C). Obvious changes are observed in the saturation polarization (Ps) and remnant polarization (Pr) with increasing temperature. The maximum energy storage density of 0.6 J/cm³ is observed for x = 0.06 in the AFE phase at 150 °C for 90 kV/cm of applied electric field. BNT–BT can be a promising candidate for energy storage devices to be used in above-room-temperature environment.

Keywords: Lead-free; perovskites; relaxor; antiferroelectrics; energy storage.

1. Introduction

Dielectric materials are being used frequently to store electrical energy based on electric polarization by an external applied electric field.1 Antiferroelectric (AFE) materials possess relatively higher energy storage density (W) compared to the ferroelectric (FE) and the linear dielectric materials.1,2 The lead (Pb)-based FE and AFE dielectrics, such as lead zirconate (PZ), lead zirconate titanate (PZST) and lead zirconate lanthanum titanate (PZLT), possess relatively better energy storage properties.2,3 However, due to the hazardous nature of Pb-based compounds, researchers are in search of Pb-free alternatives for capacitors and other electronic devices.3,5 In this regard, perovskite-structured, Pb-free Bi0.3Na0.7TiO3 (BNT) and its compounds may be better candidates to replace the Pb-based counterparts.5 Among the BNT-based compounds, Bi10.5Na0.5TiO3−BaTiO3 (BNT–BT) has attracted considerable attention as there exist a morphotropic phase boundary (MPB) and an AFE phase above the room temperature (T > 120 °C).7–9 BNT–BT exhibits relatively better ferroelectric properties and can be investigated for energy storage properties.10,11 The energy storage densities (W) of ferroelectric and antiferroelectric materials can be calculated by

\[ W = \int_{P_r}^{P_s} Edp. \]  

where E is the external applied electric field, P is the polarization, \( P_s \) is the remnant polarization and \( P_r \) is the saturation polarization. Equation (1) indicates that W is directly proportional to the electric field and the difference between \( P_s \) and \( P_r \). The values of W are calculated by numerical integration of the area in the polarization versus electric field (P−E) loop as shown in Fig. 3.10–12 The area covered by the P−E curve on the vertical axis gives the recoverable energy storage density.10–12

The (1−x)BNT–xBT ceramics possess rhombohedral–tetragonal MPB which is reported to be existing in the range of x = 0.06–0.1.13 The AFE phase of BNT–BT is more favorable for relatively higher energy storage applications due to the presence of pinched and double P−E hysteresis loops with higher \( P_s \) and lower \( P_r \) values.13,14 In this work,
the energy storage properties of \((1-x)\)B\(_{10.5}\)N\(_{a0.5}\)TiO\(_3\)-xBaTiO\(_3\)(0\(\leq x \leq\)0.08) are explored at various temperatures.

2. Materials and Methods

Solid solutions of \((1-x)\)B\(_{10.5}\)N\(_{a0.5}\)TiO\(_3\)-xBaTiO\(_3\) (0\(\leq x \leq\)0.08) are prepared via the sol–gel method. Solutions of research-grade Bi(CH\(_3\)COO)\(_3\), Na(CH\(_3\)COO) and Ba(CH\(_3\)COO)\(_2\) in stoichiometric ratios are separately prepared in acetic acid on a hot plate with a magnetic stirrer at 60°C. The solution of C\(_{16}\)H\(_{36}\)O\(_4\)Ti is prepared in ethanol to which acetyl acetone is added drop-wise for stabilization. All four solutions are mixed in a flask on a hot plate with stirrer. A dark yellow colored gel is obtained by heating the stock solution at 80°C for 4 h on a hot plate. The gel is dried on a hot plate at 100°C and calcined in air at 800°C and calcined in air at 800°C for 2 h in air with 5°C/min heating and cooling rates. For each sample, two drops of polyvinyl alcohol (PVA) are added and mixed with calcined powders as a binder and then this mixture is pressed by uniaxial presser at 100 MPa in disk shapes of 15-mm drops of polyvinyl alcohol (PVA) are added and mixed with calcined powders as a binder and then this mixture is pressed by uniaxial presser at 100 MPa in disk shapes of 15-mm diameter. The pellets are sintered at 1200°C for 2 h with 5°C/min heating and cooling rates in air.

The phase analyses of fabricated samples are carried out via X-ray diffractometer (XRD; Bruker D8 Advance) using cobalt-K\(_\alpha\) radiation (\(\lambda = 0.17902\) nm). The microstructural analyses are carried out via scanning electron microscopy (SEM). The temperature-dependent relative permittivity (\(\varepsilon_r\)) and loss tangent (\(\tan \delta\)) of ceramics are measured at different frequencies using impedance analyzer (HP4192A). The temperature-dependent \(P-E\) hysteresis loops are obtained by temperature-controlled TF Analyzer at a frequency of 10 Hz. The energy storage properties at selected temperatures are calculated using Eq. (1) and utilizing the \(P-E\) hysteresis loops.

3. Results and Discussion

3.1. Phase and microstructural analyses

The room-temperature XRD patterns of \((1-x)\)B\(_{10.5}\)N\(_{a0.5}\)TiO\(_3\)-xBaTiO\(_3\) (0\(\leq x \leq\)0.08) ceramics [Fig. 1(a)] revealed the formation of single-phase perovskite-structured compositions. The (110) peaks are shifted to relatively lower 2\(\theta\) values with increasing BT content [Fig. 1(b)]. This shift may be attributed to the incorporation of relatively larger Ba\(^{2+}\) (\(R_{Ba} = 1.61\) Å) ions for smaller Bi\(^{3+}\)/Na\(^{+}\) (\(R_{Bi}/R_{Na} = 1.40\) Å/1.39 Å) ions on the A-site of the perovskite unit cell.\(^{15}\)

The emergence of an obvious (002) shoulder peak at 53.5° along with (200) peak for \(x = 0.08\) indicated the coexistence of the rhombohedral (R\(_{3m}\)) and tetragonal (P\(_{4mm}\)) phases, consistent with previous studies which reported the existence of MPB at 0.05\(\leq x \leq\)0.1 in \((1-x)\)BNT–xBT ceramics.\(^{13,16}\)

The secondary-electron SEM images of BNT–BT ceramic samples calcined at 800°C and sintered at 1200°C for 2 h in air are shown in Fig. 2. The pellets are polished and thermally etched at 1000°C for 20 min. The grain morphologies are observed to change from rough-edged spheroidal shape to relatively sharp-edged cuboidal shape with increasing BT content. The grains in each sample are nearly of uniform size (\(\sim 1 \times 1\) μm\(^2\)) for 0\(\leq x \leq\)0.08. Some slightly elongated (\(\sim 1 \times 1.2\) μm\(^2\)) grains are also observed. Previous studies on BNT–BT ceramics reported a decrease in grain size with increasing BT content.\(^{11,16}\)

3.2. Phase transition analysis

The phase transition phenomenon with increasing temperature in the fabricated \((1-x)\)B\(_{10.5}\)N\(_{a0.5}\)TiO\(_3\)-xBaTiO\(_3\) (0\(\leq x \leq\)0.08) ceramic samples is indirectly investigated via temperature-dependent dielectric properties as shown in Fig. 3.

Fig. 1. (a) The XRD patterns of \((1-x)\)B\(_{10.5}\)N\(_{a0.5}\)TiO\(_3\)-xBaTiO\(_3\) (0\(\leq x \leq\)0.08) ceramics indicating single-phase perovskite-structured compositions. (b) The (110) peaks being shifted to lower 2\(\theta\) values.
The values of the dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) are plotted versus temperature ($T$) at different frequencies. Two anomalies are observed on $\varepsilon_r$ versus $T$ curves at temperatures denoted by $T_d$ and $T_m$ corresponding to the depolarization and maximum dielectric constant, respectively. The first anomaly observed at around 120 °C may be attributed to the FE–AFE phase transition consistent with the tan $\delta$ versus $T$ curve showing an anomaly at the same temperature. The second anomaly observed at $T_m$ (250 °C–320 °C) may be attributed to the AFE–paraelectric (PE) phase transition associated with the Curie point ($T_c$). The broadness of all the relative permittivity curves along with a frequency dispersion obvious at $T_m$ demonstrates the relaxor behavior of $(1 - x)$BNT–xBT ceramics and somewhat diffuse

Fig. 2. Secondary-electron SEM images of selected $(1 - x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$–xBaTiO$_3$ ceramic samples for (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.06$ and (d) $x = 0.08$.

Fig. 3. Plots of $\varepsilon_r$ and tan $\delta$ versus $T$ of $(1 - x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$–xBaTiO$_3$ ceramics for (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.06$ and (d) $x = 0.08$, showing the FE–AFE and AFE–PE phase transitions.
phase transition from FE to AFE phase and then to a centrosymmetric cubic PE phase.\textsuperscript{17,18} $T_m$ is observed to decrease from 320 °C to 250 °C with an increase in BT content. The dielectric constant ($\varepsilon_r$) increases with increase in BT content specifically around $T_m$ which may be attributed to the substitution of relatively larger ions of Ba\textsuperscript{2+} for Bi\textsuperscript{3+} and Na\textsuperscript{+} at A-site of the perovskite unit cell.\textsuperscript{15} The observed increase in $\tan \delta$ at higher temperatures (> 210 °C) may be due to increase in conductivity of samples caused by thermal excitation.\textsuperscript{9}

3.3. Ferroelectric properties

The polarization versus electric field ($P$–$E$) hysteresis loops of (1 $-$ $x$)BNT–$x$BT ceramics at various temperatures are shown in Fig. 4. All plots indicated similar trend of a rise in

![Fig. 4. Temperature-dependent P–E loops of selected (1 $-$ $x$)BNT–$x$BT ceramic samples at different temperatures for (a) $x$ = 0.04, (b) $x$ = 0.05, (c) $x$ = 0.06 and (d) $x$ = 0.08.](image-url)
In the FE phase ($T < 120^\circ C$) and a fall gradually in the AFE phase ($T > 120^\circ C$) as summarized in Fig. 5. The temperature-dependent values of $P_s$ obtained for BNT–BT [Fig. 5(a)] in this study are found consistent with a previous work.\textsuperscript{19} Thermal excitation with increase in temperature below $T_d$ ($T < 120^\circ C$) may align some antiparallel dipoles with the electric field and hence causes an increase in $P_s$.\textsuperscript{19} Samples with high BT contents are found to have relatively higher dielectric strength and possess relatively larger $P_s$ values. It is observed that $P_s$ increases with increase in $T$ while $P_r$ increased at temperatures below $T_d$ and decreased for those above $T_d$ (Figs. 4 and 5). The values of coercive electric field ($E_c$) decreased with increasing the temperature which is consistent with previous studies on BNT–BT.\textsuperscript{19,20} The $P$–$E$ hysteresis loops deform with the increase in temperature and pinched loops start appearing at about $120^\circ C$ for the BNT–BT ceramics (Fig. 4). Pinched and thin $P$–$E$ hysteresis loops indicate the presence of AFE phase above $T_d$ in the BNT–BT compositions.\textsuperscript{21}

### 3.4. Energy storage properties

The energy storage densities ($W$) of $(1 - x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$–$x\text{BaTiO}_3$ ($0 \leq x \leq 0.08$) samples are calculated using Eq. (1) from the $P$–$E$ loops for different BT contents at various values of temperature. The maximum value of $W$ obtained is 0.6 J/cm$^3$ at $150^\circ C$ for $x = 0.06$ under 90 kV/cm$^3$ of applied electric field. Our obtained results for $W$ are comparable with the previously reported value of 0.485 J/cm$^3$ for BNT–BT at room temperature, synthesized via solid-state route.\textsuperscript{22} Recently, Li \textit{et al.}\textsuperscript{23} reported an energy storage density of 1.2 J/cm$^3$ for 15% BaSnO$_3$-doped 0.94BNT–0.06BT at 115 kV/cm. The value of energy storage density of BNT–BT [Fig. 6(a)] increases from 0.18 J/cm$^3$ to 0.6 J/cm$^3$ with the increase in BT contents from 0.04 to 0.06. However, for $x = 0.08$, $W$ decreased slightly which may be attributed to the increase in dielectric loss as indicated in Fig. 3(d).\textsuperscript{24} Figure 6(b) indicates that energy density of BNT–BT samples increases monotonically with the increase in temperature from $30^\circ C$ to $150^\circ C$ for all compositions. The increase in $W$
with increase in temperature may be attributed to the phase transformation from FE to AFE phase above 100 °C.8,16,20

In order to obtain higher values of $W$, two parameters need to be higher, namely the electric polarization produced and the applied external electric field.10 The electric polarization is an intrinsic property of a material related to the crystal symmetry while the maximum electric field that a material can withstand depends on its dielectric strength. Higher value of electric field in units of kV/cm can be achieved by utilizing thin films of dielectrics as obtained (12.4 J/cm³) by Zhao et al.25 for modified BNT at 1200 kV/cm. The energy storage density can be enhanced if multilayered thin films of dielectrics are utilized in the capacitors.25 Hence, as a whole it can be concluded that BNT-BT may be utilized in capacitors to be used effectively in relatively higher temperature environment.

4. Conclusions
Ceramic compounds of $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$ ($0 \leq x \leq 0.08$) were fabricated via the chemical sol–gel method. The temperature-dependent dielectric values revealed two phase transitions in the samples. The $P_r$ value increased monotonically with the increase in temperature while the $P_e$ value increased with the increase in temperature below $T_d$ and decreased above $T_d$. The decrease of $P_r$ above $T_d$ may be attributed to the presence of AFE phase above $T_d$. The maximum energy storage density of 0.6 J/cm³ at 150 °C was observed for 0.94BNT–0.06BT compound for 90 kV/cm of applied electric field. BNT–BT fabricated via the sol–gel method can be a better candidate for the energy storage applications at higher temperature.

Acknowledgments
This work was supported by the Foshan Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, China. The authors also acknowledge the financial support extended by the technology Innovation Commission of Shenzhen, China and the Higher Education Commission (HEC), Pakistan.

References
1Z. Hao, A review on the dielectric materials for high energy-storage application, J. Adv. Dielect. 3, 1330001 (2013).
2M. S. Mirshekarloo, K. Yao and T. Sriharan, Large strain and high energy storage density in orthorhombic perovskite $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{1-x}\text{Sn}_{x}\text{Ti})_3\text{O}_9$ antiferroelectric thin films, Appl. Phys. Lett. 97, 142902 (2010).
3X. F. Chen, X. L. Dong, G. S. Wang, F. Cao and Y. L. Wang, Doped Pb(Zr,Sn,Ti)O$_3$ slim-loop ferroelectric ceramics for high-power pulse capacitors application, Ferroelectrics 363, 56 (2008).
4J. Rödel, W. Jo, K. T. P. Seifert, E.-M. Anton, T. Granzow and D. Damjanovic, Perspective on the development of lead-free piezoceramics, J. Am. Ceram. Soc. 92, 1153 (2009).
5Y. Zhang, M. Cao, Z. Yao, Z. Wang, Z. Song, A. Ullah, H. Hao and H. Liu, Effects of silica coating on the microstructures and energy storage properties of BaTiO$_3$ ceramics, Mater. Res. Bull. 67, 70 (2015).
6W.-S. Kang and J.-H. Koh, $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$ lead-free piezoelectric ceramics for energy-harvesting applications, J. Eur. Ceram. Soc. 35, 2057 (2015).
7M. Cernea, E. Andronescu, R. Radu, F. Fochi and C. Galassi, Sol-gel synthesis and characterization of BaTiO$_3$-doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ piezoelectric ceramics, J. Alloys Compd. 490, 690 (2010).
8W. Jo, J. E. Daniels, J. L. Jones, X. Tan, P. A. Thomas, D. Damjanovic and J. Rödel, Developing morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$–BaTiO$_3$ piezoceramics, J. Appl. Phys. 109, 014110 (2011).
9X. Tan, E. Aulbach, W. Jo, T. Granzow, J. Kling, M. Marsilius, H.-J. Kleebe and J. Rödel, Effect of uniaxial stress on ferroelectric behavior of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$-based lead-free piezoelectric ceramics, J. Appl. Phys. 106, 044107 (2009).
10C.-S. Chen, C. S. Tu, P.-Y. Chen, Y. Ting, S.-J. Chiu, C. Hung, H.-Y. Lee, S.-F. Wang, J. Anthoniappan, V. H. Schmidt and R. R. Chien, Dielectric properties in lead-free piezoelectric $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$–$\text{BaTiO}_3$ single crystals and ceramics, J. Cryst. Growth 393, 129 (2014).
11A. Chauocchi, S. Kennour, S. d’Astorg, M. Rguif, C. Courtis, S. Marinell and M. Aliouat, Characterization of sol–gel synthesised lead-free $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$–$\text{BaTiO}_3$-based ceramics, J. Alloys Compd. 509, 9138 (2011).
12M. Liu, H. Zhu, Y. Zhang, C. Xue and J. Ouyang, Energy storage characteristics of BiFeO$_3$/BaTiO$_3$ Bi-layers integrated on Si, Materials 9, 935 (2016).
13P. Chen, J. Wang, W. Zeng, C. Zhou, Y. Zhang, Q. Li, J. Xu, H. Chen and C. Yuan, Dielectric behaviors and relaxor characteristics in $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$–$\text{BaTiO}_3$ ceramics, J. Adv. Dielect. 9, 1950038 (2019).
14T. Oh and M.-H. Kim, Phase relation and dielectric properties in $(\text{Bi}_{0.7}\text{Na}_{0.3})\text{TiO}_3$ lead-free ceramics, Mater. Sci. Eng. B 132, 239 (2010).
15R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr. A 32, 751 (1976).
16Y. S. Sung, J. M. Kim, J. H. Cho, T. K. Song, M. H. Kim and T. G. Park, nOroles of lattice distortion in $(1-x)\text{(Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$–$\text{BaTiO}_3$ ceramics, Appl. Phys. Lett. 96, 202901 (2010).
17W. Jo, S. Schaab, E. Sapper, L. A. Schmitt, H.-J. Kleebe, A. J. Bell and J. Rödel, On the phase identity and its thermal evolution of lead free $(\text{Bi}_{0.7}\text{Na}_{0.3})\text{TiO}_3$–$\text{BaTiO}_3$ ceramics, J. Appl. Phys. 109, 074106 (2011).
18W. Ge, H. Cao, C. DeVreugd, J. Li, D. Viehland, Q. Zhang and H. Luo, Influence of BaTiO$_3$ content on the structure and properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ crystals, J. Am. Ceram. Soc. 94, 3084 (2011).
19Y. Bai, G.-P. Zheng and S.-Q. Shi, Abnormal electrocaloric effect of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$–$\text{BaTiO}_3$ lead-free ferroelectric ceramics above room temperature, Mater. Res. Bull. 46, 1866 (2011).
20T. Zhang, A. B. Kounag, E. Aulbach and Y. Deng, Temperature-dependent electrical properties of 0.94$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$–0.06$\text{BaTiO}_3$ ceramics, J. Am. Ceram. Soc. 91, 3950 (2008).
21A. Pathak, R. Chatterjee and C. Prakash, Improvement in shape memory in magnesium niobate modified PZST, Ceram. Int. 36, 2263 (2010).
22. M. Chandrasekhar and P. Kumar, Synthesis and characterizations of BNT-BT and BNT-BT-KNN ceramics for actuator and energy storage applications, *Ceram. Int.* **41**, 5574 (2015).

23. Q. Li, M. Li, C. Wang, M. Zhang and H. Fan, Enhanced temperature stable dielectric properties and energy-storage density of BaSnO$_3$-modified (Bi$_{0.5}$Na$_{0.5}$)$_{1-x}$Ba$_{0.06}$TiO$_3$ lead-free ceramics, *Ceram. Int.* **45**, 19822 (2019).

24. M. Rawat and K. L. Yadav, Structural, dielectric and ferroelectric properties of Ba$_{1-x}$(Bi$_{0.5}$Na$_{0.5}$)$_x$TiO$_3$ ceramics, *Ceram. Int.* **39**, 3627 (2013).

25. Y. Zhao, X. Hao and M. Li, Dielectric properties and energy-storage performance of (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$ thick films, *J. Alloys Compd.* **601**, 112 (2014).

26. Y. Bai, G. P. Zheng and S. Q. Shi, Kinetic electrocalorific effect and giant net cooling of lead-free ferroelectric refrigerants, *J. Appl. Phys.* **108**, 104102 (2010).