

## **High energy storage density and large strain in Bi(Zn<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>-Doped BiFeO<sub>3</sub>-BaTiO<sub>3</sub> ceramics**

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# High Energy Storage Density and Large Strain in

## Bi(Zn<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>-Doped BiFeO<sub>3</sub>-BaTiO<sub>3</sub> Ceramics

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### ABSTRACT

High recoverable energy density ( $W_{rec} \sim 2.1 \text{ J/cm}^3$ ) was obtained in (0.7-x)BiFeO<sub>3</sub>-0.3BaTiO<sub>3</sub>-xBi(Zn<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>+0.1wt% Mn<sub>2</sub>O<sub>3</sub> (BF-BT-xBZN, x = 0.05) lead-free ceramics at < 200 kV/cm. Fast discharge speeds (< 0.5  $\mu\text{s}$ ), low leakage ( $\sim 10^{-7} \text{ A/cm}^2$ ) and small temperature variation in  $W_{rec}$  ( $\sim 25\%$  from 23 to 150 °C) confirmed the potential for these BiFeO<sub>3</sub> based compositions for use in high energy density capacitors. A core-shell microstructure composed of a BiFeO<sub>3</sub>-rich core and BaTiO<sub>3</sub>-rich shell was observed by scanning and transmission electron microscopy which may contribute to the high value of energy density. In addition, for x = 0.005, a large electromechanical strain was observed with  $S_{pos} = 0.463\%$  and effective  $d_{33}^* \sim 424 \text{ pm/V}$ , suggesting that this family of ceramics may also have potential for high strain actuators.

**Keywords:** energy storage, bismuth ferrite, lead-free ceramics, piezoelectrics, dielectrics, capacitors

## INTRODUCTION

The current research into new energy storage materials is mainly driven by concerns regarding the continued use of fossil fuels for automotive applications. Therefore, low cost, sustainable and environmentally-friendly energy storage materials with high energy densities are required.<sup>1-3</sup> Among current energy storage devices, ceramic capacitors are emerging as promising technological alternatives to fuel cells and batteries, because of their high power densities combined with fast charge-discharges rates, which are favoured in advanced pulse power applications.<sup>4-7</sup> This drives the search for dielectrics exhibiting both high energy and power densities, to satisfy for power supply components incorporated into portable electronics, electric vehicles and other high power and energy storage applications.<sup>8-10</sup>

To attain high recoverable energy density ( $W_{rec}$ ) and efficiency ( $\eta$ ), a polarization maximum ( $P_{max}$ ), a small remnance ( $P_r$ ) and an optimised breakdown strength (BDS) are simultaneously required. Furthermore, the stability of devices in a range of temperature is also a critical parameter. For example, for hybrid electric vehicles these devices are expected to operate at temperatures ranging from -40 °C to 140 °C.<sup>1,11</sup> Consequently, ferroelectrics (FE) and antiferroelectrics (AFE) are promising candidates due to their high  $P_{max}$  and Curie temperature ( $T_C$ ). The total energy density ( $W$ ),  $W_{rec}$  and  $\eta$  of FE and AFE ceramics is given by:

$$W = \int_0^{P_{max}} EdP, \quad (1)$$

$$W_{rec} = \int_{P_r}^{P_{max}} EdP, \quad (2)$$

$$\eta = W_{rec}/W \quad (3)$$

where  $P$ ,  $P_{max}$  and  $P_r$  are the polarization, polarization maximum and remnance, respectively.

Although there are commercial energy storage devices based on La doped lead zirconate titanate, concerns over the toxicity of PbO have led to a large body of recent research on lead free replacements such as BaTiO<sub>3</sub> (BT), (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> (KNN) and (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub> (BNT) based

ceramics.<sup>12-25</sup> Oxide additives such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO enhance both  $W_{rec}$  and BDS in BT-based ceramics<sup>12-14</sup> but BT-Bi(M,N)O<sub>3</sub> (M = Li, Mg, Zn, N = Nb, Ti, Zr) ceramics show greater promise, with  $W_{rec}$  up to 2.5 J/cm<sup>3</sup>.<sup>15-21</sup> In addition, Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub>-KNbO<sub>3</sub> (BNT-BT-KN) and Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub>-NaTaO<sub>3</sub> (BNT-BT-NT) also exhibit large  $W_{rec}$  of 1.72 and 1.2 J/cm<sup>3</sup>, respectively.<sup>22,23</sup> In a recent study, Du et al. showed a commensurate improvement in  $W_{rec}$  to ~ 4 J/cm<sup>3</sup> in KNN-ceramics due to an enhancement of BDS (300~400 kV/cm), which was achieved by a careful control of grain growth.<sup>24,25</sup> BiFeO<sub>3</sub>-BaTiO<sub>3</sub> (BF-BT) ceramics are characterised by high values of Curie maximum ( $T_C$ ) and  $P_{max}$  ( $> 40 \mu\text{C}/\text{cm}^2$ )<sup>26-32</sup>, but because their dielectric  $\tan\delta$  and  $P_r$  are relatively large, their energy storage characteristics have been seldom studied. Recently, Nb<sub>2</sub>O<sub>5</sub>, La(Mg<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub>, Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> have been used as either dopants in, or in solid solution with, BF-BT with  $W_{rec}$  of 0.71, 1.66, 1.56, and 1.82 J/cm<sup>3</sup>, respectively, reported<sup>33-36</sup> Nd doped BF-BT multilayers showed particular promise with both high  $W_{rec} \sim 6.74 \text{ J}/\text{cm}^3$  and  $\eta \sim 77\%$ , from RT to 125 °C.<sup>36</sup>

Wu et al. theoretically predicted that FE ceramics with core-shell microstructure could achieve enhanced energy density and reduced energy loss.<sup>37</sup> However, to our knowledge, up to now the energy storage characteristics of BF-based ceramics featuring a core-shell microstructure remain elusive, as no experimental evidence has been provided. Also Bi(Zn<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> (BZN) doped BF-BT materials were recently reported to have excellent piezoelectric properties<sup>27</sup> but their energy storage performance is yet to be determined, despite each effect relying on a large remanent/induced polarisation. In this work, a unique core-shell microstructure was induced by the substitution of BZN into BF-BT, its impact on the structure-property relationships, in particular on the energy storage characteristics, evaluated.

## EXPERIMENTAL SECTION

**Ceramic synthesis and characterisation:** (0.7-x)BiFeO<sub>3</sub>-0.3BaTiO<sub>3</sub>-xBi(Zn<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> + 0.1wt% Mn<sub>2</sub>O<sub>3</sub> (BF-BT-xBZN, x = 0, 0.005, 0.01, 0.02, 0.05, 0.08) ceramics were fabricated using solid state reaction.<sup>26,36</sup> In order to increase the resistivity of ceramics, 0.1 wt% Mn<sub>2</sub>O<sub>3</sub> was added into the

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3 calcined powder of BF-BT-xBZN.<sup>26,28,36</sup> Mn-ions are considered to form defect dipoles with oxygen  
4 vacancies and decrease their mobility. Densities of ceramics were determined by the Archimedes  
5 immersion method and were typically >95%. The phase structure of sintered ceramics was determined  
6 at RT by X-ray powder diffraction (XRD) using a Bruker D2 Phaser. Grain and sub-grain structures  
7 were evaluated by scanning electron microscope (SEM) and transmission electron microscopy (TEM)  
8 using an FEI Inspect F50 equipped with a backscattered (BSE) detector and a Tecnai G2-F20,  
9 respectively. For SEM, ceramics were ground/polished to a mirror finish using wet abrasive paper and  
10 diamond paste (MetPrep Ltd.). For TEM, BF-BT-0.05BZN ceramics were ground to 120  $\mu\text{m}$ , 3 mm  
11 disks ultrasonically cut and their centers dimpled down to 10  $\mu\text{m}$ . Prior to Ar-ion milling to achieve  
12 electron transparency, samples were annealed at 650  $^{\circ}\text{C}/0.5$  h to ensure that residual stresses were  
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25 **Electrical properties:** Fired-on gold paste electrodes were applied to both surfaces of the ceramics.  
26 100-120  $^{\circ}\text{C}$  was used to pole the electroded ceramics at fields of 40 ~ 60 kV/cm. A ferroelectric tester  
27 (aixACCT TF 2000E) was employed to measure the polarization and the electric-field induced strain  
28 from -50  $^{\circ}\text{C}$  to 150  $^{\circ}\text{C}$  using a 1 Hz triangular signal at provided by a TREK power supply. Leakage  
29 current density was also measured using the aixACCT TF 2000E. The dielectric properties as a  
30 function of temperature were evaluated from RT to 650  $^{\circ}\text{C}$  using an LCR meter (Agilent 4184A). AC  
31 impedance spectroscopy was carried out at 400  $^{\circ}\text{C}$  using a second LCR Meter (Agilent E4980A).  
32 Charging-discharge characteristics were determined using a capacitor discharge circuit.<sup>16,36</sup> A  
33 Tektronix DPO 4104 oscilloscope together with a Pearson 6585 coil were employed to obtain the  
34 discharge current waveforms. The discharge energy was then measured using ceramics connected in  
35 series with a load resistor (RL).  
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## 49 RESULTS AND DISCUSSION

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52 Room temperature XRD data in the 20 $^{\circ}$ ~70 $^{\circ}$  2 $\theta$  range for BF-BT-xBZN ceramics are illustrated in  
53 Fig. 1(a). Reflections are ascribed to either a single-phase perovskite or a mixture of perovskite  
54 phases, without any detectable secondary impurity phases for  $x < 0.08$ . Secondary peaks however,  
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3 were observed for  $x = 0.08$ , denoting the solid solubility limit for  $Zn_{1/3}/Nb_{2/3}$  self-compensated doping  
4 in BF-BT. The average ionic radii,  $R$ , of  $(Zn_{2/3}Nb_{1/3})^{3+}$  ions is given by  $R = 2/3R(Zn^{2+}) + 1/3R(Nb^{5+}) =$   
5  $0.707 \text{ \AA}$  ( $0.74 \text{ \AA}$  and  $0.64 \text{ \AA}$  are the respective ionic radii of  $Zn^{2+}$  and  $Nb^{5+}$ ),<sup>38</sup> which is larger than that  
6 of  $Fe^{3+}$  and  $Ti^{4+}$  ( $0.645 \text{ \AA}$  and  $0.605$ , respectively) and consistent with the diffraction peaks shifting to  
7 lower diffraction angle with increasing BZN concentration (Fig.1). The likely crystal symmetry is  
8 often determined by (021)/(110) peak splitting at  $\sim 2\theta = 32^\circ$ . In the present case, expanded XRD  
9 patterns reveal an apparent coexistence of rhombohedral ( $R$ ) and pseudocubic ( $PC$ ) symmetries at  
10 room temperature in BF-BT- $x$ BZN ceramics, as corroborated by broad multiple peaks. To confirm the  
11 phase assemblage, Rietveld refinement of BF-BT-0.05BZN was carried out using a two-phase  
12 refinement method ( $R3c + Pm\bar{3}m$ ) in the GSAS+EXPGUI package.<sup>39,40</sup> Observed and calculated  
13 patterns were in good agreement for BF-BT-0.05BZN as demonstrated in Fig. 1(b) ( $R_p = 7.6\%$ ,  $R_{wp} =$   
14  $9.7\%$  and chi-squared ( $\chi^2$ ) = 2.3), corroborating the presence of  $PC$  ( $Pm\bar{3}m$ ) and  $R$  ( $R3c$ ) symmetries.

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29 The relative permittivity ( $\epsilon_r$ ) and dielectric loss ( $\tan \delta$ ) for BF-BT- $x$ BZN ceramics from RT to  $550 \text{ }^\circ\text{C}$   
30 measured at 100 kHz are illustrated in Fig. 1(c). BF-BT and BF-BT-0.005BZN exhibit a relatively  
31 sharp peak in  $\epsilon_r$  at  $476 \text{ }^\circ\text{C}$  and  $480 \text{ }^\circ\text{C}$ , respectively, associated with a ferroelectric to paraelectric  
32 transition ( $T_C$ ) on heating but with increasing BZN concentration, two broad dielectric maxima are  
33 observed, each at lower temperatures. Furthermore, compared with BF-BT and BF-BT-0.005BZN, the  
34 maximum dielectric permittivity ( $\epsilon_m$ ) of BF-BT- $x$ BZN ( $x > 0.005$ ) decreases significantly and is  
35 accompanied by the emergence of broad frequency-dependent dielectric peaks (Fig. 1c). These two  
36 modifications are a manifestation of polar coupling disruption brought in by replacement of  
37  $(Zn_{2/3}Nb_{1/3})^{3+}$  for  $Fe^{3+}$ . Despite these changes,  $\tan \delta$  remains  $< 0.15$  at  $< 230 \text{ }^\circ\text{C}$ , and then increases  
38 greatly (Fig. 1c), presumably due to a rise in  $dc$  conductivity. To evaluate the electrical homogeneity,  
39 impedance spectroscopy (IS) analysis was performed at  $400 \text{ }^\circ\text{C}$ , Fig. 1(d) and Fig. S1. Indeed,  
40 electrical homogeneity can be qualitatively assessed from  $Z''$  and  $M''$  spectroscopic plots constructed  
41 from IS data.<sup>41,42</sup> It is evident that the peak positions of  $Z''$  and  $M''$  are almost coincident for BF-BT  
42 (Fig. S1a of ESI), however a frequency offset between the  $Z''$  and  $M''$  peak is observed for BF-BT-  
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3 0.02BZN and BF-BT-0.05BZN (Fig. 1d and Fig. S1b of ESI). This shows the latter compositions to  
4 be electrically heterogeneous, which we interpret on balance of evidence as arising from  
5 compositional inhomogeneity.  
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10 The SEM images of as-sintered and polished surface for BF-BT-xBZN are illustrated in Fig. S2 and  
11 Fig. 2(a-c), respectively. All samples present a single modal grain size distribution around an average  
12 of  $\sim 4 \mu\text{m}$  (Fig. S2 of ESI). Except for BF-BT and BF-BT-0.005BZN ceramics, there is evidence of  
13 core shell microstructure for BF-BT-xBZN (Fig. 2a-c), with dark and light contrast relating to  
14 BaTiO<sub>3</sub>-rich and BiFeO<sub>3</sub>-rich regions according to energy dispersive X-ray spectroscopy (EDS)  
15 mapping (Fig. 2d-k). The EDS elemental maps of polished BF-BT-0.05BZN samples are shown in  
16 Fig. 2(d-k). The Ba and Ti signals are weaker in the brighter regions of the SEM image, associated  
17 with the grain cores (Fig. 2d and e). Conversely, Bi and Fe exhibit a slightly increased intensity in the  
18 brighter areas (Fig. 2f, g). These results indicate that the observed core-shell microstructure in BF-BT-  
19 xBZN are associated with the micro-segregation of Ba and Ti into the shell, while Bi and Fe are  
20 concentrated in the core regions.<sup>41-47</sup> Murakami et al. investigated the role of composition and  
21 quenching on core-shell formation in BiMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> doped BF-BT ceramics.<sup>41,42</sup> They concluded that  
22 the major influence was the onset of immiscibility on cooling from the sintering temperature, driven  
23 by the electronegativity difference of the dopant species. Effectively, the more covalent the dopants,  
24 the greater the tendency for immiscibility.  
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41 To examine the core-shell microstructure, TEM was conducted on BF-BT-0.05BZN ceramics. For  
42 further data on undoped systems the reader is referred to ref. 36. Fig. 3a is bright-field (BF) TEM  
43 image of a grain close to a  $\langle 211 \rangle_{pc}$  zone axis. The dark spherical region in the grain center  
44 corresponds to the bright regions in the SEM images in Figure 2 and is thus BiFeO<sub>3</sub> rich.  $\langle 211 \rangle_{pc}$   
45 zone axis diffraction patterns (Fig. 2a) from the BiFeO<sub>3</sub> rich core have  $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  superstructure  
46 reflections arising from antiphase O-octahedral tilting consistent with an *R3c* phase.<sup>36</sup> These  
47 superstructure reflections are absent in the shell regions which are BaTiO<sub>3</sub>-rich, suggesting that they  
48 are *PC*. The weak aligned contrast in the shell region is consistent with relaxor-like phases in which  
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there is nano- rather than micro- or meso-range correlation of dipoles, commensurate with the diffuse frequency dependent Curie maxima, Fig. 3(b). The core and shell structures shown in Fig 3(a) and in Fig. 2 have been tentatively assigned to the high (BiFeO<sub>3</sub>-rich) and low (BaTiO<sub>3</sub>-rich) temperature broad Curie maxima in Fig. 3(b).

Field-induced polarization ( $P$ - $E$ ), bipolar strain ( $S$ - $E$ ) and unipolar strain curves for BF-BT- $x$ BZN ceramics measured at 100 kV/cm are illustrated in Fig. 4(a-c) (no field-induced strain for BF-BT-0.08BZN was detected).  $P_r$ , coercive field ( $E_C$ ) and electric-field induced positive ( $S_{pos}$ ) and negative strain ( $S_{neg}$ ) as a function of  $x$  are summarized in Fig. 4(d,e). The large signal piezoelectric strain coefficient ( $d_{33}^*$ ) and hysteresis ( $SH$ ) are calculated by

$$d_{33}^* = S_{max}/E_{max}, \quad (5)$$

$$SH = H_{E_{max}/2}/S_{max}, \quad (6)$$

where  $S_{max}$ ,  $E_{max}$  and  $H_{E_{max}/2}$  is the average electric field induced maximum strain obtained from the unipolar strain loops, the maximum electric field and the width of the loop at half the applied field, respectively.<sup>48</sup> BF-BT and BF-BT-0.005BZN ceramics exhibit saturated polarization loops and butterfly-shaped strain loops at 100 kV/cm (Fig. 4a,b), which also corroborate the high electrical resistivity of these ceramics. With increasing BZN content, the  $P$ - $E$  and  $S$ - $E$  loops become slimmer and are no longer saturated (Fig. 4a,b), along with  $P_r$ ,  $E_C$ ,  $d_{33}$  and  $S_{neg}$  continuously decreasing (Fig. 4d,e), suggestive of relaxor-like behavior, which is commensurate with both the broad  $\epsilon_m$  (Fig. 1c) and nanodomain structure (Fig. 3). The largest  $P_r \sim 24.6 \mu\text{C}/\text{cm}^2$ ,  $E_C \sim 32.8 \text{ kV}/\text{cm}$ ,  $d_{33} \sim 180 \text{ pC}/\text{N}$ ,  $S_{neg} \sim 0.079\%$  values and smallest  $HS \sim 18.4\%$  value are exhibited by BF-BT ceramics (Fig. 4d,e,f), due to coexistence of  $R3c$  and  $PC$  symmetries (Fig. 1).<sup>26,36</sup> On the other hand, the largest  $S_{pos} \sim 0.463\%$  and  $d_{33}^* \sim 424 \text{ pm}/\text{V}$  values are exhibited by BF-BT-0.005BZN ceramics (Fig. 4e,f), which arises from a field-induced transition from short- to long-range dipolar order at the transition from a normal to a relaxor ferroelectric (Fig. 4a,b and Fig. 1c).<sup>26,36</sup>

Because of their slim  $P$ - $E$  loops (Fig. 4a), BF-BT-0.05BZN and BF-BT-0.08BZN exhibit a greater potential for energy storage and were selected for further characterization. Unipolar  $P$ - $E$  loops are

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3 illustrated in Fig. 5(a,b), with corresponding values of  $P_{max}$ ,  $P_r$  and  $\Delta P$  ( $P_{max} - P_r$ ) at different electric  
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5 fields given in Fig. S3. As the increase of electric field,  $P_{max}$  and  $\Delta P$  are found to increase linearly  
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7 with a marginal improvement of  $P_r$  for both samples (Fig. S3). The highest values of  $P_{max}$  and  $\Delta P$  are  
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9 36.7 and 32.8  $\mu\text{C}/\text{cm}^2$  for BF-BT-0.05BZN at 180 kV/cm, 26.4 and 24.5  $\mu\text{C}/\text{cm}^2$  for BF-BT-0.08BZN  
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11 at 190 kV/cm, respectively. Equations 1-3 are employed to calculate  $W$ ,  $W_{rec}$  and  $\eta$ , Fig. 5(c,d). As  
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13 field increases,  $W$  and  $W_{rec}$  increase, reaching 3.7 and 2.06  $\text{J}/\text{cm}^3$  for BF-BT-0.05BZN at 180 kV/cm,  
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15 and 2.9 and 1.98  $\text{J}/\text{cm}^3$  for BF-BT-0.08BZN at 190 kV/cm, respectively. The  $\eta$  values, however,  
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17 decrease for both compositions to 53% for BF-BT-0.05BZN at 180 kV/cm and 68% for BF-BT-  
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19 0.08BZN at 190 kV/cm.  
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23 The discharge behaviour, leakage current and temperature stability are critical for high power  
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25 capacitors. The discharge behaviour of BF-BT-0.05BZN and BF-BT-0.08BZN as a function of  
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27 applied field is given in Fig. 6. The current increases as the electric field increases from 40  
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29 kV/cm to 70 kV/cm and all discharge processes occur within  $\sim 0.5$   $\mu\text{s}$ , as shown in Fig. 6(a,b).  
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31 The time for the discharge energy in the load to achieve 90% of the final value ( $\tau_{90}$ ), is  
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33 obtained from the  $W_{rec}$  curves (Fig. 6c,d).  $\tau_{0.9}$  of both composition under different electric  
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35 fields is less than 0.1  $\mu\text{s}$ .  
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39 *In-situ* temperature dependence of leakage current density ( $J$ ) and unipolar  $P$ - $E$  loops at 120  
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41 kV/cm for BF-BT-0.05BZN are shown in Fig. 7(a,b). The corresponding values of  $J$ ,  $P_{max}$ ,  $P_r$   
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43 and  $\Delta P$  are given in Fig. 7(c) and Fig. S4.  $W$ ,  $W_{rec}$  and  $\eta$  are also calculated and plotted in Fig.  
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45 7(d). The value of  $J$  below 50  $^\circ\text{C}$  is of the order of  $10^{-7}$   $\text{A}/\text{cm}^2$  in the high field region (Fig.  
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47 7a,c),  $\sim$  one order magnitude less than reported for BF-based ceramics at RT.<sup>49,50</sup> From -50  $^\circ\text{C}$   
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49 to 150  $^\circ\text{C}$ ,  $J$  consistently increases (Fig. 7a,c), indicating increased conductivity at high  
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51 temperatures. As temperature increases, saturated  $P$ - $E$  loops are obtained at  $\sim 150$   $^\circ\text{C}$ , giving  
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53 increased values of  $P_{max}$  and  $P_r$  (Fig. S4), which is attributed to lower activation energy of the  
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55 transition from relaxor to ferroelectric.<sup>26,36</sup>  $W$  increases with temperature, while  $W_{rec}$  and  $\eta$   
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3 increase before decreasing from a maximum of  $1 \text{ J/cm}^3$  and 59% at 75-100 °C, Fig. 7(d). The  
4 variation in  $W_{rec}$  is  $\sim 25\%$  between RT and 150 °C, which is attractive for commercial  
5 applications.  
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10 A comparison of  $W_{rec}$  and strain for ceramics is plotted in Fig. 8.<sup>12-25, 26-36, 48-92</sup>  $W_{rec}$  generally increases  
11 with electric field but lead-based ceramics still exhibit larger  $W_{rec}$  values compared to the lead-free  
12 ceramics (Fig. 8a). To our knowledge, BF-BT-0.05BZN has one of the highest value of  $W_{rec} \sim 2.1$   
13  $\text{J/cm}^3$  among current lead-free FE ceramics with an electric field  $< 220 \text{ kV/cm}$ , which is ascribed to  
14 the high BDS  $\sim 190 \text{ kV/cm}$ ,  $P_{max} \sim 36.7 \text{ } \mu\text{C/cm}^2$  and  $\Delta P \sim 32.8 \text{ } \mu\text{C/cm}^2$ . In Fig. 8(b), BF-BT-  
15 0.005BZN has one of the highest values of strain  $\sim 0.463\%$  amongst ferroelectric ceramics, with a  
16 medium value of  $d_{33}^* \sim 424 \text{ pm/V}$  and a low value of strain hysteresis  $\sim 38\%$  (in comparison with  
17 BNT),<sup>82-89</sup> which is attractive for actuator applications. Core-shell structures in FE ceramics are  
18 reported to alleviate inhomogeneity of local electric fields and weakens dielectric nonlinearity,  
19 resulting in slimmer hysteresis loops.<sup>37</sup> Although the work presented does not conclusively prove the  
20 arguments presented by the authors of ref. 37, enhanced energy storage is observed for core-shell BT-  
21 BF-xBZN compositions. Furthermore, we note that recent multilayering of Nd doped BF-BT ceramics  
22 improved  $W_{rec}$  from 1.82 to 6.74  $\text{J/cm}^3$  and  $\eta$  from 50 to 77%.<sup>36</sup> Similar improvements for multilayers  
23 of BF-BT-xBZN whose bulk ceramics have superior energy storage properties would suggest that  
24 they have potential for commercialization should lead based systems fail to gain exemption from  
25 future environmental legislation. Moreover, BT-BF-xBZN compositions are rare-earth (RE)-free,  
26 lowering their cost and enhancing their potential for sustainable manufacturing.  
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## 46 CONCLUSIONS

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48 Dense BF-BT-xBZN lead-free ceramics were fabricated using solid state reaction. *R* and *PC* phases  
49 coexisted in all studied BF-BT-xBZN compositions at RT. As BZN concentration increased, a core-  
50 shell microstructure was observed with a  $\text{BaTiO}_3$ -rich shell and  $\text{BiFeO}_3$ -rich core, confirmed by SEM,  
51 EDS, IS, TEM and LCR measurements. With the increase of BZN concentration, relaxor-like  
52 behaviour dominated with  $P_r$ ,  $E_C$ ,  $d_{33}$  and  $S_{neg}$  decreasing. The highest values of  $P_r \sim 24.6 \text{ } \mu\text{C/cm}^2$ ,  $E_C \sim$   
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3 32.8 kV/cm,  $d_{33} \sim 180$  pC/N,  $S_{\text{neg}} \sim 0.079\%$  and  $HS \sim 18.4\%$  were achieved for the undoped BF-BT.  
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5 The highest value of  $S_{\text{pos}} \sim 0.463\%$  and  $d_{33}^* \sim 424$  pm/V was obtained for BF-BT-0.05BZN. For  
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7 energy storage properties, with increasing electric field,  $W$  and  $W_{\text{rec}}$  increased from 3.7 and 2.06 J/cm<sup>3</sup>  
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9 for BF-BT-0.05BZN at 180 kV/cm, and 2.9 and 1.98 J/cm<sup>3</sup> cm<sup>2</sup> for BF-BT-0.08BZN at 190 kV/cm,  
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11 respectively.  $\eta$  decreased however, to 53% for BF-BT-0.05BZN at 180 kV/cm and 68% for BF-BT-  
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13 0.08BZN at 190 kV/cm, respectively. A fast discharge speed (less than 0.5 ms), leakage current  $\sim 10^{-7}$   
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15 A/cm<sup>2</sup> and a small temperature variation in  $W_{\text{rec}}$  ( $\sim 25\%$  in a temperature range between RT and  
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17 150 °C) were also obtained, suggesting that the BF-BT-xBZN is a potential lead-free candidate for  
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19 pulsed power capacitors and electromechanical actuators.  
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## 22 ASSOCIATED CONTENT

### 23 Supporting Information.

24 This material is available free of charge via the Internet at <http://pubs.acs.org>.

25 Spectroscopic plots of  $Z''$  and  $M''$  for (a) BF-BT and (b) BF-BT-0.02BZN. SEM images of BF-BT-  
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27 xBZN (a)  $x = 0$ , (b)  $x = 0.005$ , (c)  $x = 0.01$ , (d)  $x = 0.02$ , (e)  $x = 0.05$  and (f)  $x = 0.08$ .  $P_{\text{max}}$ ,  $P_r$  and  $\Delta P$   
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29 for (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN. Temperature dependence of  $P_{\text{max}}$ ,  $P_r$  and  $\Delta P$  for  
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31 BF-BT-0.05BZN at 120 kV/cm. The schematic diagram of the discharge circuit.  
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### 46 Notes

47 The authors declare no competing financial interest.  
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49 **Figure Captions:**

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51 **Fig. 1.** a) Room temperature XRD patterns of BF-BT-xBZN from 20°~70° 2θ. b) Rietveld refinement  
52 analysis of BF-BT-0.05BZN using the GSAS+EXPGUI package. c) Temperature dependence of  $\epsilon_r$   
53 and  $\tan\delta$  for BF-BT-xBZN; (d) Spectroscopic plots of  $Z''$  and  $M''$  for BF-BT-0.05BZN.  
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3 **Fig. 2.** SEM images of polished surfaces for BF-BT-xBZN (a) BF-BT, (b) BF-BT-0.02BZN and (c)  
4 BF-BT-0.05BZN. EDS elemental mapping results of polished BF-BT-0.05BZN samples (d) Ba, (e) Ti,  
5 (f) Bi, (g) Fe, (h) O, (i) Zn, (j) Nb and (k) elemental layered image.

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8 **Fig. 3.** a) Bright field TEM image of a grain in BF-BT-0.05BZN, illustrating a BiFeO<sub>3</sub> rich core and  
9 BaTiO<sub>3</sub> rich shell; <211> zone axis diffraction patterns reveal the absence of  $\frac{1}{2}\{000\}$  superstructure  
10 reflections in the shell (up) compared with core regions (down). b) The BiFeO<sub>3</sub> and BaTiO<sub>3</sub> core-shell  
11 regions are tentatively ascribed to the high and low temperature dielectric anomalies.

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14 **Fig. 4.** High electric field (a) bipolar P-E, (b) bipolar S-E and (c) unipolar S-E loops of BF-BT-xBZN  
15 samples at 100 kV/cm. (d)  $P_r$  and  $E_C$  as a function of BZN concentration. (e)  $S_{pos}$  and  $S_{neg}$  as a function  
16 of BZN concentration. (f)  $d_{33}^*$  and  $SH$  as a function of BZN concentration.  $d_{33}$  as a function of BZN  
17 concentration is in the inset of (d).

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20 **Fig. 5.** Unipolar P-E loops under different electric fields for (a) BF-BT-0.05BZN and (b) BF-BT-  
21 0.08BZN.  $W$ ,  $W_{rec}$  and  $\eta$  as a function of electric field for (c) BF-BT-0.05BZN and (d) BF-BT-  
22 0.08BZN.

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25 **Fig. 6.** Time dependence of the pulsed discharge current for (a) BF-BT-0.05BZN and (b) BF-BT-  
26 0.08BZN. Time dependence of  $W_{rec}$  for (c) BF-BT-0.05BZN and (d) BF-BT-0.08BZN.

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29 **Fig. 7.** *In-situ* temperature dependence of (a)  $J$  and (b) unipolar P-E loops for BF-BT-0.05BZN at an  
30 electric field of 120 kV/cm. (c)  $J$  as a function of temperature at different electric fields. (d)  $W$ ,  $W_{rec}$   
31 and  $\eta$  as a function of temperature.

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34 **Fig. 8.** Comparison of (a)  $W_{rec}$  vs electric field and (b) strain vs  $d_{33}^*$  among lead-based and lead-free  
35 ceramics.<sup>12-25, 26-36, 48-92</sup>

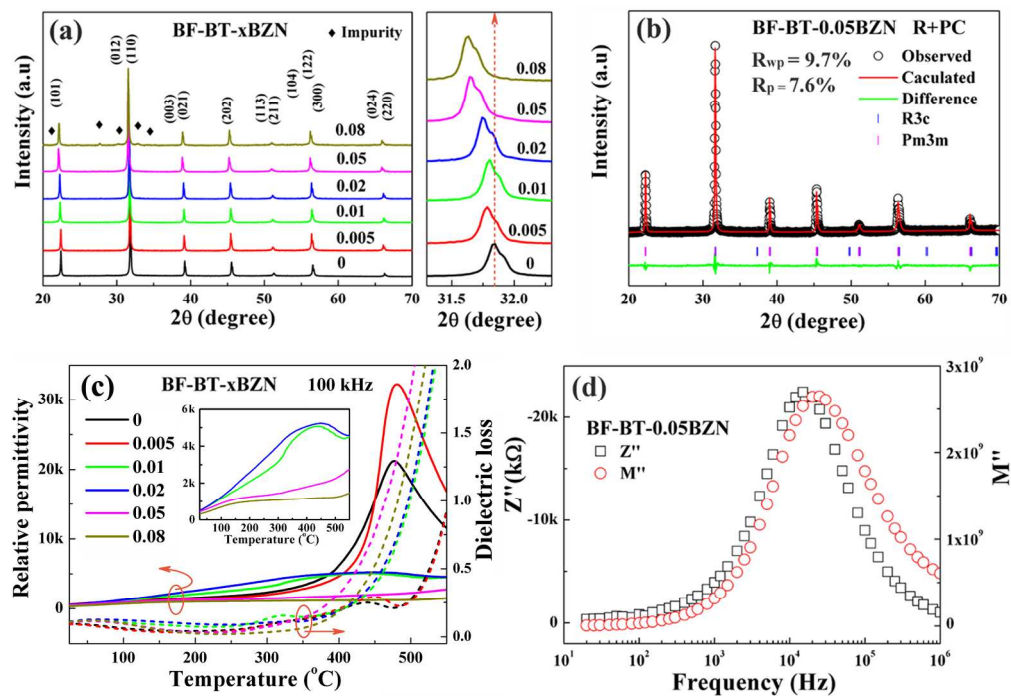


Fig. 1. a) Room temperature XRD patterns of BF-BT-xBZN from  $20^\circ \sim 70^\circ$   $2\theta$ . b) Rietveld refinement analysis of BF-BT-0.05BZN using the GSAS+EXPGUI package. c) Temperature dependence of  $\epsilon_r$  and  $\tan\delta$  for BF-BT-xBZN; d) Spectroscopic plots of  $Z''$  and  $M''$  for BF-BT-0.05BZN.

182x127mm (300 x 300 DPI)



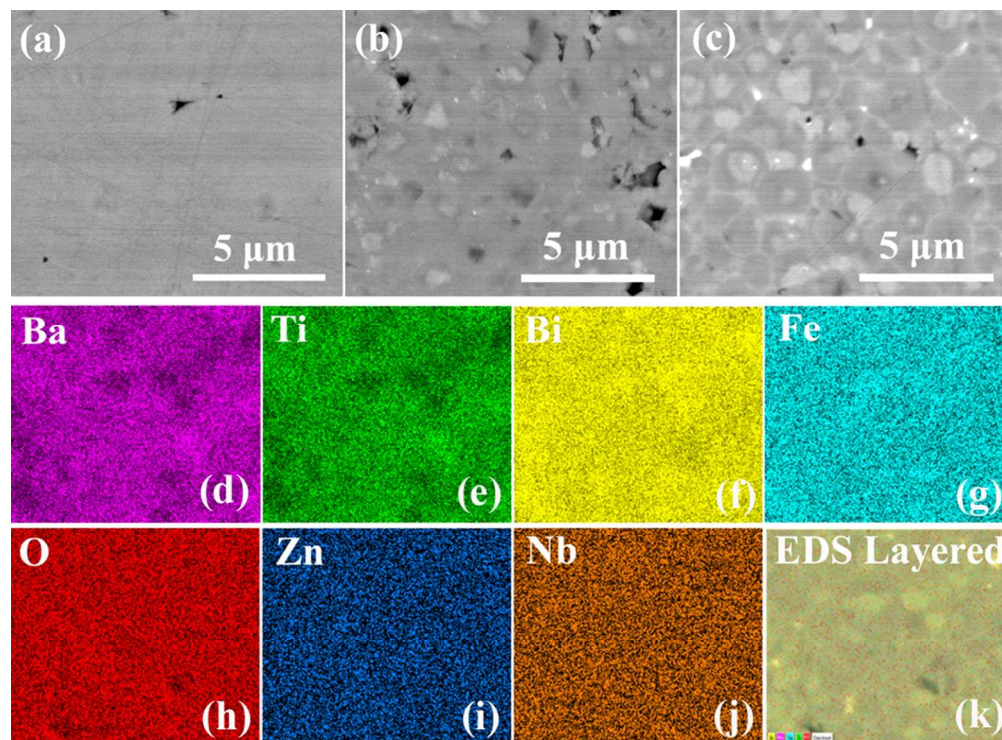
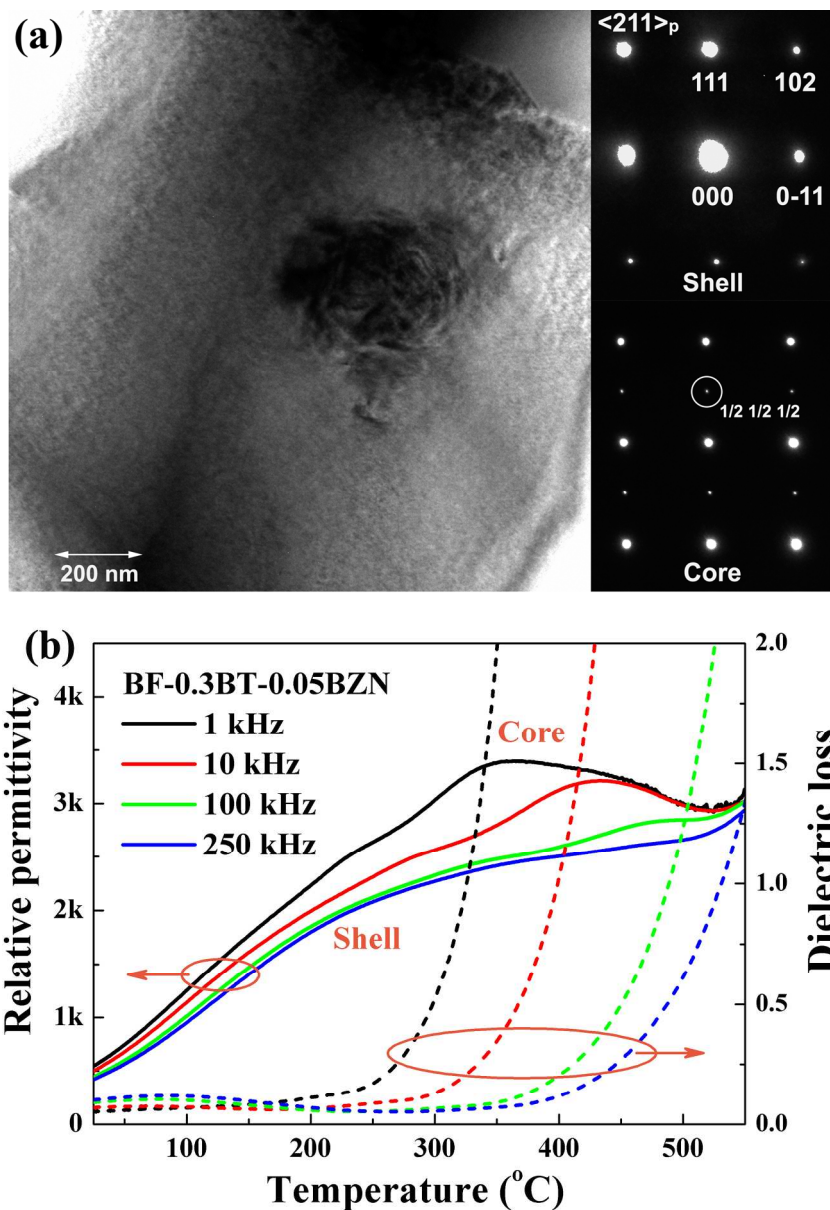


Fig. 2. SEM images of polished surfaces for BF-BT-xBZN (a) BF-BT, (b) BF-BT-0.02BZN and (c) BF-BT-0.05BZN. EDS elemental mapping results of polished BF-BT-0.05BZN samples (d) Ba, (e) Ti, (f) Bi, (g) Fe, (h) O, (i) Zn, (j) Nb and (k) elemental layered image.

84x62mm (300 x 300 DPI)



169x242mm (300 x 300 DPI)

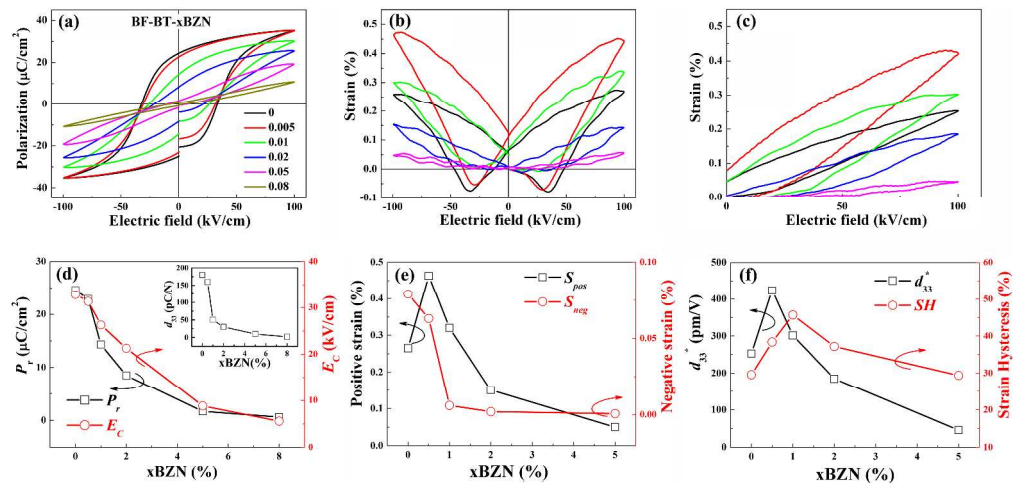


Fig. 4. High electric field (a) bipolar P-E, (b) bipolar S-E and (c) unipolar S-E loops of BF-BT-xBZN samples at 100 kV/cm. (d)  $P_r$  and  $E_c$  as a function of BZN concentration. (e)  $S_{pos}$  and  $S_{neg}$  as a function of BZN concentration. (f)  $d_{33}^*$  and SH as a function of BZN concentration.  $d_{33}$  as a function of BZN concentration is in the inset of (d).

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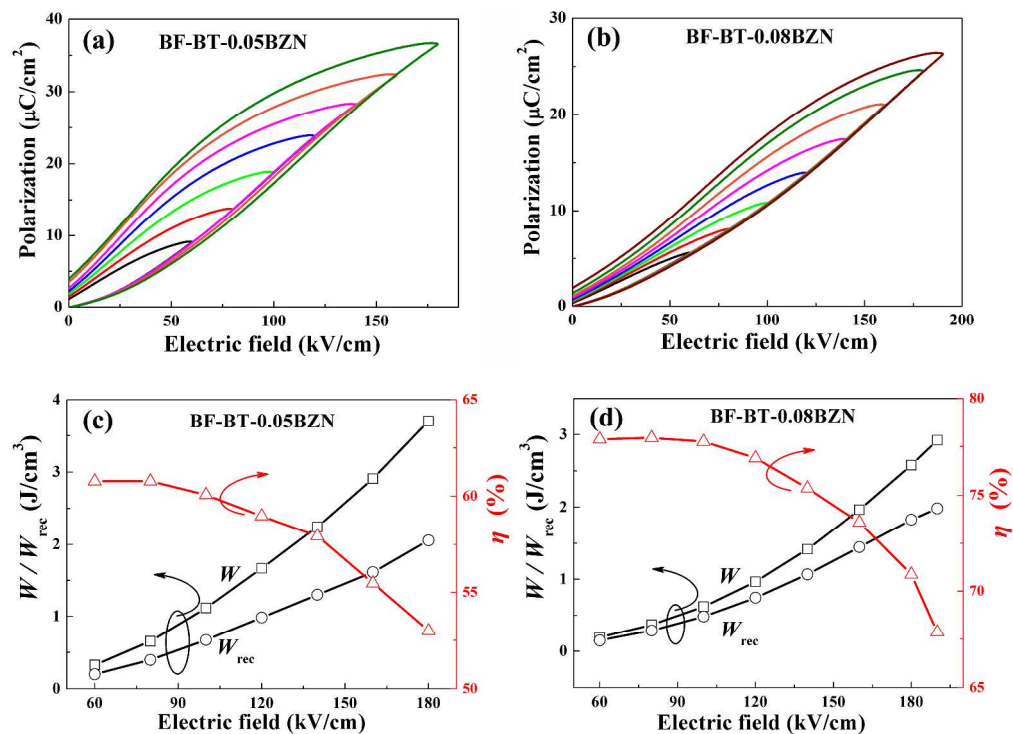


Fig. 5. Unipolar P-E loops under different electric fields for (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN.  $W$ ,  $W_{\text{rec}}$  and  $\eta$  as a function of electric field for (c) BF-BT-0.05BZN and (d) BF-BT-0.08BZN.

508x368mm (300 x 300 DPI)

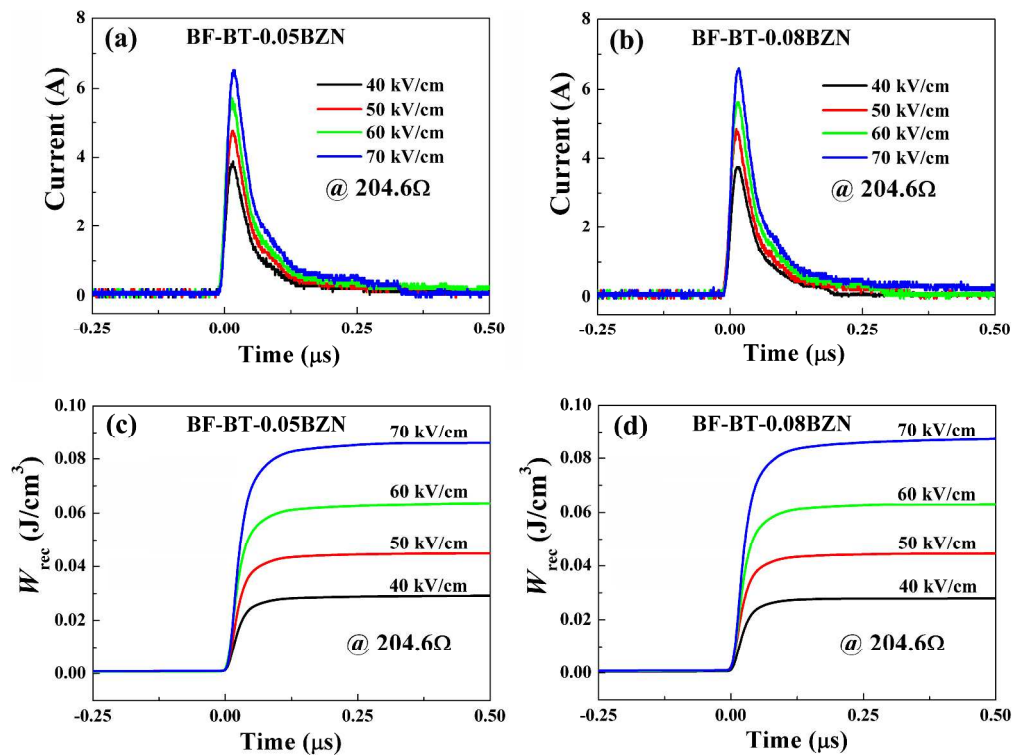


Fig. 6. Time dependence of the pulsed discharge current for (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN. Time dependence of  $W_{rec}$  for (c) BF-BT-0.05BZN and (d) BF-BT-0.08BZN.

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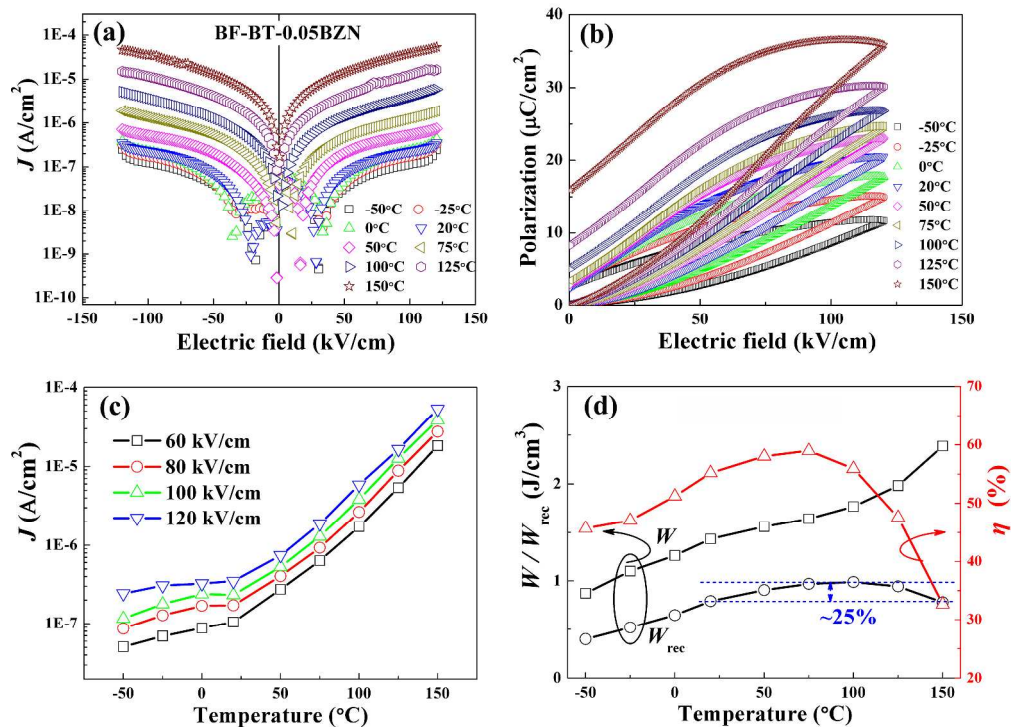


Fig. 7. In-situ temperature dependence of (a)  $J$  and (b) unipolar P-E loops for BF-BT-0.05BZN at an electric field of 120 kV/cm. (c)  $J$  as a function of temperature at different electric fields. (d)  $W$ ,  $W_{rec}$  and  $\eta$  as a function of temperature.

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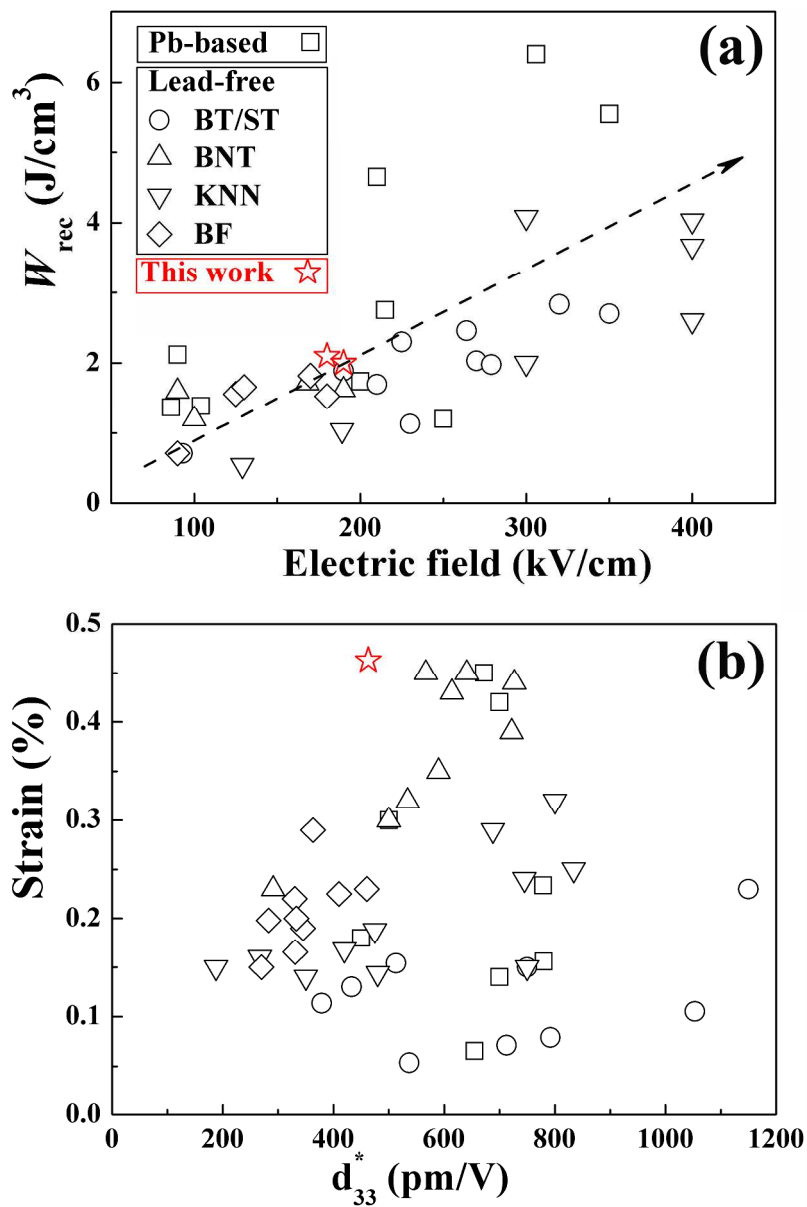
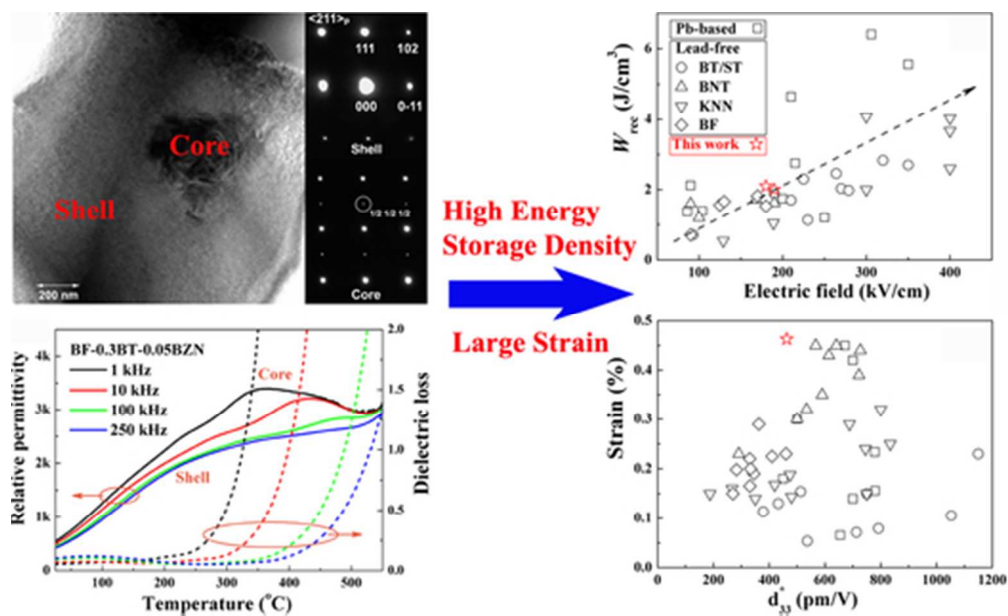


Fig. 8. Comparison of (a)  $W_{rec}$  vs electric field and (b) strain vs  $d_{33}^*$  among lead-based and lead-free ceramics.12-25, 26-36, 45-86

423x636mm (300 x 300 DPI)



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