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ACS Appl. Energy Mater., **Just Accepted Manuscript** • DOI: 10.1021/acsaem.8b01099 • Publication Date (Web): 16 Jul 2018

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High Energy Storage Density and Large Strain in

Bi(Zn_{2/3}Nb_{1/3})O₃-Doped BiFeO₃-BaTiO₃ 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)BiFeO₃-0.3BaTiO₃-xBi(Zn_{2/3}Nb_{1/3})O₃ + 0.1wt% Mn₂O₃ (BF-BT-xBZN, x = 0.05) lead-free ceramics at < 200 kV/cm. Fast discharge speeds (< 0.5 μs), 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 BiFeO₃ based compositions for use in high energy density capacitors. A core-shell microstructure composed of a BiFeO₃-rich core and BaTiO₃-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.¹⁻³ 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.⁴⁻⁷ 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.⁸⁻¹⁰

To attain high recoverable energy density (W_{rec}) and efficiency (η), 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.^{1,11} 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 η 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 BaTiO₃ (BT), (K_{0.5}Na_{0.5})NbO₃ (KNN) and (Bi_{0.5}Na_{0.5})TiO₃ (BNT) based

ceramics.¹²⁻²⁵ Oxide additives such as Al₂O₃, SiO₂, MgO enhance both W_{rec} and BDS in BT-based ceramics¹²⁻¹⁴ but BT-Bi(M,N)O₃ (M = Li, Mg, Zn, N = Nb, Ti, Zr) ceramics show greater promise, with W_{rec} up to 2.5 J/cm³.¹⁵⁻²¹ In addition, Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-KNbO₃ (BNT-BT-KN) and Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-NaTaO₃ (BNT-BT-NT) also exhibit large W_{rec} of 1.72 and 1.2 J/cm³, respectively.^{22,23} In a recent study, Du et al. showed a commensurate improvement in W_{rec} to ~ 4 J/cm³ in KNN-ceramics due to an enhancement of BDS (300~400 kV/cm), which was achieved by a careful control of grain growth.^{24,25} BiFeO₃-BaTiO₃ (BF-BT) ceramics are characterised by high values of Curie maximum (T_C) and P_{max} (> 40 μ C/cm²)²⁶⁻³², but because their dielectric $\tan\delta$ and P_r are relatively large, their energy storage characteristics have been seldom studied. Recently, Nb₂O₅, La(Mg_{1/2}Ti_{1/2})O₃, Ba(Mg_{1/3}Nb_{2/3})O₃ and Nd₂O₃ 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/cm³, respectively, reported³³⁻³⁶ Nd doped BF-BT multilayers showed particular promise with both high W_{rec} ~ 6.74 J/cm³ and η ~ 77%, from RT to 125 °C.³⁶

Wu et al. theoretically predicted that FE ceramics with core-shell microstructure could achieve enhanced energy density and reduced energy loss.³⁷ 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_{2/3}Nb_{1/3})O₃ (BZN) doped BF-BT materials were recently reported to have excellent piezoelectric properties²⁷ 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)BiFeO₃-0.3BaTiO₃-xBi(Zn_{2/3}Nb_{1/3})O₃ + 0.1wt% Mn₂O₃ (BF-BT-xBZN, x = 0, 0.005, 0.01, 0.02, 0.05, 0.08) ceramics were fabricated using solid state reaction.^{26,36} In order to increase the resistivity of ceramics, 0.1 wt% Mn₂O₃ was added into the

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3 calcined powder of BF-BT-xBZN.^{26,28,36} 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 μm , 3 mm
11 disks ultrasonically cut and their centers dimpled down to 10 μm . 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
13 removed.
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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.^{16,36} 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 θ 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 \AA (0.74 \AA and 0.64 \AA are the respective ionic radii of Zn^{2+} and Nb^{5+}),³⁸ which is larger than that
6 of Fe^{3+} and Ti^{4+} (0.645 \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.^{39,40} 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 (χ^2) = 2.3), corroborating the presence of PC ($Pm\bar{3}m$) and R ($R3c$) symmetries.
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29 The relative permittivity (ϵ_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 ϵ_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 (ϵ_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.^{41,42} 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 BaTiO₃-rich and BiFeO₃-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.⁴¹⁻⁴⁷ Murakami et al. investigated the role of composition and
21 quenching on core-shell formation in BiMg_{1/3}Nb_{2/3}O₃ doped BF-BT ceramics.^{41,42} 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 BiFeO₃ rich. $\langle 211 \rangle_{pc}$
45 zone axis diffraction patterns (Fig. 2a) from the BiFeO₃ 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.³⁶ These
47 superstructure reflections are absent in the shell regions which are BaTiO₃-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 (BiFeO₃-rich) and low (BaTiO₃-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-xBZN 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 (*d₃₃^{*}*) 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.⁴⁸ 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*, *d₃₃* and *S_{neg}* continuously decreasing (Fig. 4d,e), suggestive of relaxor-like behavior, which is commensurate with both the broad ϵ_m (Fig. 1c) and nanodomain structure (Fig. 3). The largest *P_r* ~ 24.6 $\mu\text{C}/\text{cm}^2$, *E_C* ~ 32.8 kV/cm, *d₃₃* ~ 180 pC/N, *S_{neg}* ~ 0.079% values and smallest *HS* ~ 18.4% value are exhibited by BF-BT ceramics (Fig. 4d,e,f), due to coexistence of *R3c* and *PC* symmetries (Fig. 1).^{26,36} On the other hand, the largest *S_{pos}* ~ 0.463% and *d₃₃^{*}* ~ 424 pm/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).^{26,36}

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 ΔP ($P_{max} - P_r$) at different electric
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5 fields given in Fig. S3. As the increase of electric field, P_{max} and ΔP 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 ΔP 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 η , Fig. 5(c,d). As
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13 field increases, W and W_{rec} increase, reaching 3.7 and 2.06 J/cm^3 for BF-BT-0.05BZN at 180 kV/cm,
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15 and 2.9 and 1.98 J/cm^3 for BF-BT-0.08BZN at 190 kV/cm, respectively. The η 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 ~ 0.5 μs , 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 (τ_{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 μs .
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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 ΔP are given in Fig. 7(c) and Fig. S4. W , W_{rec} and η 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} A/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.^{49,50} 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 ~ 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.^{26,36} W increases with temperature, while W_{rec} and η
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3 increase before decreasing from a maximum of 1 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.^{12-25, 26-36, 48-92} 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 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),⁸²⁻⁸⁹ 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.³⁷ 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 J/cm^3 and η from 50 to 77%.³⁶ 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 BaTiO_3 -rich shell and 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_{rec} increased from 3.7 and 2.06 J/cm³
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9 for BF-BT-0.05BZN at 180 kV/cm, and 2.9 and 1.98 J/cm³ cm² for BF-BT-0.08BZN at 190 kV/cm,
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11 respectively. η 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/cm² and a small temperature variation in W_{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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21

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_{max} , P_r and ΔP
28
29 for (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN. Temperature dependence of P_{max} , P_r and ΔP 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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52 ACKNOWLEDGMENT

53 This work was supported by the Engineering and Physical Sciences Research Council (EP/L017563/1
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55 and EP/N010493/1) and National Natural Science Foundation of China (51602060 and 51402005).
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58
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60

REFERENCES

1. Chu B., Zhou X., Ren K., Neese B., Lin M., Wang Q., Bauer F., Zhang Q. M., A dielectric polymer with high electric energy density and fast discharge speed, *Science*, 2006, 313, 334-336.
2. Li Q., Chen L., Gadinski M. R., Zhang S., Zhang G., Li H., Haque A., Chen L., Jackson T., Wang Q., Flexible high-temperature dielectric materials from polymer nanocomposites, *Nature*, 2015, 523, 576-579.
3. Zhao L., Liu Q., Gao J., Zhang S., Li J. F., Lead-free antiferroelectric silver niobate tantalate with high energy storage performance, *Adv. Mater.* 2017, 29, 1701824-7pp.
4. Love G. R., Energy-storage in ceramic dielectrics, *J. Am. Ceram. Soc.*, 1990, 73, 323-328.
5. Kwon S., Hackenberger W., Alberta E., Furman E., Lanagan M., Nonlinear Dielectric Ceramics and Their Applications to Capacitors and Tunable Dielectrics, *IEEE Electr. Insul. Mag.*, 2011, 27, 43-55.
6. Hu W. B., Liu Y., Withers R. L., Frankcombe T. J., Noren L., Snashall A., Kitchin M., Smith P., Gong B., Chen H., Schiemer J., Brink F., Leung J. W., Electron-pinned defect-dipoles for high-performance colossal permittivity materials, *Nat. Mater.*, 2013, 12, 821-826.
7. Li Q., Zhang G., Liu F., Han K., Gadinski M. R., Xiong C., Wang Q., Solution-processed ferroelectric terpolymer nanocomposites with high breakdown strength and energy density utilizing boron nitride nanosheets, *Energy Environ. Sci.*, 2015, 8, 922-931.
8. Liu C., Li F., Ma L. P., Cheng H. M., *Advanced Materials for Energy Storage*, *Adv. Mater.*, 2010, 22, E28-E62.
9. Hadjipaschalis I., Poullickas A., Efthimiou V., Overview of current and future energy storage technologies for electric power applications, *Renew. Sust. Energy Rev.*, 2009, 13, 1513-1522.
10. Chen H., Cong T. N., Yang W., Tan C., Li Y., Ding Y., Progress in electrical energy storage system: A critical review, *Prog. Nat. Sci.*, 2009, 19, 291-312.
11. Wang Y. L., Chen X. L., Zhou H. F., Fang L., Liu L. J., Zhang H., Evolution of phase transformation behavior and dielectric temperature stability of BaTiO₃-Bi(Zn_{0.5}Zr_{0.5})O-3 ceramics system, *J. Alloys Compd.*, 2013, 551, 365-369.

12. Liu B. B., Wang X. H., Zhao Q. C., Li L. T., Improved Energy Storage Properties of Fine-Crystalline BaTiO₃ Ceramics by Coating Powders with Al₂O₃ and SiO₂, *J. Am. Ceram. Soc.*, 2015, 98, 2641–2646.
13. Zhang Q. M., Wang L., Luo J., Tang Q., Du J., Ba_{0.4}Sr_{0.6}TiO₃/MgO Composites with Enhanced Energy Storage Density and Low Dielectric Loss for Solid-State Pulse-Forming Line, *Int. J. Appl. Ceram. Technol.*, 2010, 7, E124–E128.
14. Huang Y. H., Wu Y. J., Qiu W. J., Li J., Chen X. M., Enhanced energy storage density of Ba_{0.4}Sr_{0.6}TiO₃-MgO composite prepared by spark plasma sintering, *J. Eur. Ceram. Soc.*, 2015, 35, 1469–1476.
15. Li W. B., Zhou D., Pang X., Enhanced energy storage density by inducing defect dipoles in lead free relaxor ferroelectric BaTiO₃-based ceramics, *Appl. Phys. Lett.*, 2017, 110, 132902-5pp.
16. Li W. B., Zhou D., Pang L. X., Xu R., Guo H. H., Novel barium titanate based capacitors with high energy density and fast discharge performance, *J. Mater. Chem. A*, 2017, 5, 19607–19612.
17. Yuan Q., Yao F., Wang Y., Ma R., Wang H., Relaxor ferroelectric 0.9BaTiO₃-0.1Bi(Zn_{0.5}Zr_{0.5})O₃ ceramic capacitors with high energy density and temperature stable energy storage properties, *J. Mater. Chem. C*, 2017, 5, 9552-9558.
18. Wang T., Jin L., Li C. C., Hu Q. Y., Wei X. Y., Relaxor Ferroelectric BaTiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ Ceramics for Energy Storage Application, *J. Am. Ceram. Soc.*, 2015, 98, 559–566.
19. Hu Q. Y., Jin L., Wang T., Li C. C., Xing Z., Wei X. Y., Dielectric and temperature stable energy storage properties of 0.88BaTiO₃-0.12Bi(Mg_{1/2}Ti_{1/2})O₃ bulk ceramics, *J. Alloys Compd.*, 2015, 640, 416–420.
20. Shen Z. B., Wang X. H., Luo B. C., Li L. T., BaTiO₃-BiYbO₃ perovskite materials for energy storage applications, *J. Mater. Chem. A*, 2015, 3, 18146–18153.
21. Wu L. W., Wang X. H., Li L. T., Lead-free BaTiO₃-Bi(Zn_{2/3}Nb_{1/3})O₃ weakly coupled relaxor ferroelectric materials for energy storage, *RSC Adv.*, 2016, 6, 14273–14282.

- 1
2
3 22. Xu Q., Xie J., He Z. C., Zhang L., Cao M. H., Huang X. D., Lanagan M. T., Hao H., Yao Z. H.,
4 Liu H. X., Energy-storage properties of Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-KNbO₃ ceramics fabricated by
5 wet-chemical method, *J. Eur. Ceram. Soc.*, 2017, 37, 99–106.
6
7
8
9 23. Xu Q., Liu H. X., Zhang L., Xie J., Hao H., Cao M. H., Yao Z. H., Lanagan M. T., Structure and
10 electrical properties of lead-free Bi_{0.5}Na_{0.5}TiO₃-based ceramics for energy-storage applications,
11 *RSC Adv.*, 2016, 6, 59280–59291.
12
13
14
15 24. Yang Z. T., Du H. L., Qu S. B., Hou Y. D., Ma H., Wang J. F., Wang J., Wei X. Y., Xu Z.,
16 Significantly enhanced recoverable energy storage density in potassium-sodium niobate-based
17 lead free ceramics, *J. Mater. Chem. A*, 2016, 4, 13778–13785.
18
19
20
21 25. Shao T. Q., Du H. L., Ma H., Qu S. B., Wang J., Wang J. F., Wei X. Y., Xu Z., Potassium-sodium
22 niobate based lead-free ceramics novel electrical energy storage materials, *J. Mater. Chem. A*,
23 2017, 5, 554–563.
24
25
26
27 26. Wang D., Khesro A., Murakami S., Feteira A., Zhao Q., Reaney I. M., Temperature dependent,
28 large electromechanical strain in Nd-doped BiFeO₃-BaTiO₃ lead-free ceramics, *J. Eur. Ceram.*
29 *Soc.*, 2017, 37, 1857–1860.
30
31
32
33 27. Lee M. H., Kim D. J., Park J. S., Kim S. W., Song T. K., Kim M. H., Kim W. J., Do D., Jeong I.
34 K., High-Performance Lead-Free Piezoceramics with High Curie Temperatures, *Adv. Mater.*,
35 2015, 27, 6976–6982.
36
37
38
39 28. Leontsevw S. O., Eitel R. E., Dielectric and Piezoelectric Properties in Mn-Modified (1-
40 x)BiFeO₃-xBaTiO₃ Ceramics, *J. Am. Ceram. Soc.*, 2009, 92, 2957–2961.
41
42
43 29. Fan Q., Zhou C., Zeng W., Cao L., Yuan C., Rao G., Li X., Normal-to-relaxor ferroelectric phase
44 transition and electrical properties in Nb-modified 0.72BiFeO₃-0.28BaTiO₃ ceramics, *J.*
45 *Electroceram.*, 2016, 36, 1–7.
46
47
48
49 30. Malik R. A., Hussain A., Song T. K., Kim W. J., Ahmed R., Sung Y. S., Kim M. H., Enhanced
50 electromechanical properties of (1-x)BiFeO₃-BaTiO₃-xLiNbO₃ ceramics by quenching process,
51 *Ceram. Inter.*, 2017, 43, S198–S203.
52
53
54
55
56
57
58
59
60

- 1
2
3 31. Kim S., Khanal G. P., Nam H. W., Fujii I., Ueno S., Moriyoshi C., Kuroiwa Y., Wada S.,
4 Structural and electrical characteristics of potential candidate lead-free BiFeO₃-BaTiO₃
5 piezoelectric ceramics, *J. Appl. Phys.*, 2017, 122, 164105.
6
7
8
9 32. Liu Z., Zheng T., Zhao C., Wu J., Composition design and electrical properties in BiFeO₃-
10 BaTiO₃-Bi(Zn_{0.5}Ti_{0.5})O₃ lead-free ceramics, *J. Mater. Sci.: Mater. Electron.*, 2017, 28, 13076–
11 13083.
12
13
14 33. Wang T., Jin L., Tian Y., Shu L. L., Hu Q. Y., Wei X. Y., Microstructure and ferroelectric
15 properties of Nb₂O₅-modified BiFeO₃-BaTiO₃ lead-free ceramics for energy storage, *Mater.*
16
17
18
19
20 34. Zheng D. G., Zuo R. Z., Zhang D. S., Li Y., Novel BiFeO₃-BaTiO₃-Ba(Mg_{1/3}Nb_{2/3})O₃ Lead-
21 Free Relaxor Ferroelectric Ceramics for Energy-Storage Capacitors, *J. Am. Ceram. Soc.*, 2015, 98,
22 2692–2695.
23
24
25
26 35. Zheng D. G., Zuo R. Z., Enhanced energy storage properties in La(Mg_{1/2}Ti_{1/2})O₃-modified
27 BiFeO₃-BaTiO₃ lead-free relaxor ferroelectric ceramics within a wide temperature range, *J. Eur.*
28
29
30
31
32 36. Wang D., Fan Z., Zhou D., Khesro A., Murakami S., Feteira A., Zhao Q., Tan X., Reaney I. M.,
33 Bismuth ferrite-based lead free ceramics and multilayers with high recoverable energy density, *J.*
34
35
36
37
38 37. Wu L., Wang X., Li L., Enhanced Energy Density in Core–Shell Ferroelectric Ceramics:
39 Modeling and Practical Conclusions, *J. Am. Ceram. Soc.*, 2016, 99, 930–937.
40
41
42 38. Shannon R. D., Revised effective ionic radii and systematic studies of interatomic distances in
43 halides and chalcogenides, *Acta Cryst.*, 1976, A32, 751–767.
44
45
46 39. Larson C., Von Dreele R. B., General Structure Analysis System (GSAS), Los Alamos: Los
47 Alamos National Laboratory Report LAUR; 2004.
48
49
50 40. Toby H., a graphical user interface for GSAS, *J. Appl. Cryst.*, 2001, 34, 210–213.
51
52 41. Murakami S., Ahmed N. T. A. F., Wang D., Feteira A., Sinclair D. C., Reaney I. M., Optimising
53 properties in BiMeO₃ (Me = Al, Ga, Sc, Y, Mg_{2/3}Nb_{1/3}, Zn_{2/3}Nb_{1/3}, Zn_{1/2}Ti_{1/2}) doped lead-
54
55
56
57
58
59
60

- 1
2
3 free BaTiO₃-BiFeO₃ based ceramics for actuator applications, *J. Eur. Ceram. Soc.*, 2018, 38,
4 4220-4231.
5
6
7 42. Murakami S., Wang D., Mostaed A., Khesr A., Feteira A., Sinclair D. C., Reaney I. M, High
8 strain (0.4%) Bi(Mg₂/3Nb₁/3)O₃-BaTiO₃-BiFeO₃ lead-free piezoelectric ceramics and
9 multilayers, *J. Am. Ceram. Soc.*, 2018, doi.org/10.1111/jace.15749
10
11
12 43. Calisir I., D. Hall A., Chemical heterogeneity and approaches to its control in BiFeO₃-BaTiO₃
13 lead-free ferroelectrics, *J. Mater. Chem. C*, 2018, 6, 134–146.
14
15
16 44. Calisir I., Amirov A. A., Klepped A. K., Hall D. A., Optimisation of functional properties in lead-
17 free BiFeO₃-BaTiO₃ ceramics through La³⁺ substitution strategy, *J. Mater. Chem. A*, 2018, 6,
18 5378-5397.
19
20
21 45. Lin D., Zheng Q., Li Y., Wan Y., Li Q., Zhou W., Microstructure, ferroelectric and piezoelectric
22 properties of Bi_{0.5}K_{0.5}TiO₃-modified BiFeO₃-BaTiO₃ lead-free ceramics with high Curie
23 temperature, *J. Eur. Ceram. Soc.*, 2013, 33, 3023–3036.
24
25
26 46. Yabuta H., Shimada M., Watanabe T., Hayashi J., Kubota M, Miura K, Fukui T, Fujii I, Wada S.,
27 Microstructure of BaTiO₃-Bi(Mg₁/2Ti₁/2)O₃-BiFeO₃ Piezoelectric Ceramics, *Jpn. J. Appl.*
28 *Phys.*, 2012, 51, 09LD04.
29
30
31 47. Guo Y., Wang T., Shi D., Xiao P., Zheng Q., Xu C., Lam K. H., Lin D., Strong piezoelectricity
32 and multiferroicity in BiFeO₃-BaTiO₃-NdCoO₃ lead-free piezoelectric ceramics with high Curie
33 temperature for current sensing application, *J. Mater. Sci.: Mater. Electron.*, 2017, 28, 5531–5547.
34
35
36 48. Wang D., Cao M., Zhang S., Investigation of ternary system PbHfO₃-PbTiO₃-
37 Pb(Mg₁/3Nb₂/3)O₃ with morphotropic phase boundary compositions, *J. Am. Ceram. Soc.*, 2012,
38 95, 3220–3228.
39
40
41 49. Guo Y., Xiao P., Wen R., Wan Y., Zheng Q., Shi D., Lam K. H., Liu M., Lin D., Critical
42 roles of Mn-ions in enhancing the insulation, piezoelectricity and multiferroicity of BiFeO₃,
43 *J. Mater. Chem. C*, 2015, 3, 5811-5824.
44
45
46 50. Liu N., Liang R., Liu Z., Zhou Z., Xu C., Wang G., Dong X., Large remanent polarization
47 and enhanced magnetic properties in non-quenched Bi(Fe,Ga)O₃-(Ba,Ca)(Zr,Ti)O₃
48 multiferroic ceramics, *Appl. Phys. Lett.*, 2017, 110, 112902.
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 51. Zhang L., Jiang S., Fan B., Zhang G., Enhanced energy storage performance in
4
5 $(\text{Pb}_{0.858}\text{Ba}_{0.1}\text{La}_{0.02}\text{Y}_{0.008})(\text{Zr}_{0.65}\text{Sn}_{0.3}\text{Ti}_{0.05})\text{O}_3(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.9}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_3$
6
7 anti-ferroelectric composite ceramics by Spark Plasma Sintering, *J. Alloys Compd.*, 2015, 622,
8
9 162-165.
- 10
11 52. Liu Z., Chen X., Peng W., Xu C., Dong X., Cao F., Wang G., Temperature-dependent stability of
12
13 energy storage properties of $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.58}\text{Sn}_{0.335}\text{Ti}_{0.085})\text{O}_3$ antiferroelectric ceramics
14
15 for pulse power capacitors, *Appl. Phys. Lett.*, 2015, 106, 262901.
- 16
17 53. Zhang Q., Tong H., Chen J., Lu Y., Yang T., Yao X., He Y., High recoverable energy density
18
19 over a wide temperature range in Sr modified $(\text{Pb},\text{La})(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ antiferroelectric ceramics with
20
21 an orthorhombic phase, *Appl. Phys. Lett.*, 2016, 109, 262901.
- 22
23 54. Xu R., Li B., Tian J., Xu Z., Feng Y., Wei X., Huang D., Yang L.,
24
25 $\text{Pb}_{0.94}\text{La}_{0.04}[(\text{Zr}_{0.70}\text{Sn}_{0.30})_{0.90}\text{Ti}_{0.10}]\text{O}_3$ antiferroelectric bulk ceramics for pulsed capacitors
26
27 with high energy and power density, *Appl. Phys. Lett.*, 2017, 110, 142904.
- 28
29 55. Zhang Q., Chen J., Lu Y., Yang T., Yao X., He Y., $(\text{Pb},\text{Sm})(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ Multifunctional
30
31 Ceramics with Large Electric-Field Induced Strain and High-Energy Storage Density, *J. Am.*
32
33 *Ceram. Soc.*, 2016, 99, 3853-3856.
- 34
35 56. Zhao Q., Lei H., He G., Di J., Wang D., Tan P., Jin H., Cao M., Effects of thickness on energy
36
37 storage of $(\text{Pb}, \text{La})(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ antiferroelectric films deposited on LaNiO_3 electrodes, *Ceram.*
38
39 *Int.*, 2016, 42, 1314-1317.
- 40
41 57. Yang H., Yan F., Lin Y., Wang T., Novel Strontium Titanate-Based Lead-Free Ceramics for
42
43 High-Energy Storage Applications, *ACS Sustainable Chem. Eng.*, 2017, 5,10215-10222.
- 44
45 58. Yan F., Yang H., Lin Y., Wang T., Dielectric and Ferroelectric Properties of SrTiO_3 -
46
47 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $\text{BaAl}_{0.5}\text{Nb}_{0.5}\text{O}_3$ Lead-Free Ceramics for High-Energy-Storage Applications,
48
49 *Inorg. Chem.*, 2017, 56, 13510-13516.
- 50
51 59. Yin J., Lv X., Wu J., Enhanced energy storage properties of $\{\text{Bi}_{0.5}[(\text{Na}_{0.8}\text{K}_{0.2})_{1-}$
52
53 $z\text{Li}_z]_{0.5}\}_{0.96}\text{Sr}_{0.04}(\text{Ti}_{1-x-y}\text{Ta}_x\text{Nb}_y)\text{O}_3$ lead-free ceramics, *Ceram. Inter.*, 2017, 43, 13541-
54
55 13546.
- 56
57
58
59
60

- 1
2
3 60. Pu Y., Yao M., Zhang L., Chen M., Enhanced energy storage density of $0.55\text{Bi}0.5\text{Na}0.5\text{TiO}_3$ -
4 $0.45\text{Ba}0.85\text{Ca}0.15\text{Ti}0.85\text{Zr}0.1\text{Sn}0.05\text{O}_3$ with MgO addition, *J. Alloys Compd.*, 2017, 702, 171-
5 177.
6
7
8
9 61. Tao H., Wu W., Wu J., Electrical properties of holmium doped $(\text{K},\text{Na})(\text{Nb},\text{Sb})\text{O}_3$ - $(\text{Bi},\text{Na})\text{HfO}_3$
10 ceramics with wide sintering and poling temperature range, *J. Alloys Compd.*, 2016, 689, 759-766.
11
12 62. Qu B., Du H., Yang Z., Liu Q., Liu T., Enhanced dielectric breakdown strength and energy
13 storage density in lead-free relaxor ferroelectric ceramics prepared using transition liquid phase
14 sintering, *RSC Adv.*, 2016, 6, 34381–34389.
15
16
17 63. Tao H., Wu J., Optimization of energy storage density in relaxor $(\text{K}, \text{Na}, \text{Bi})\text{NbO}_3$ ceramics, *J.*
18 *Mater. Sci.: Mater. Electron.*, 2017, 28:16199–16204.
19
20
21 64. Saito Y., Takao H., Tani T., Nonoyama T., Takatori K., Homma T., Nagaya T., Nakamura M.,
22 Lead-free Piezoceramics, *Nature*, 2004, 432, 84–87.
23
24
25 65. Zhang S., Kounga A. B., Aulbach E., Ehrenberg H., Rödel J., Giant strain in lead-free
26 piezoceramics $\text{Bi}0.5\text{Na}0.5\text{TiO}_3$ - BaTiO_3 - $\text{K}0.5\text{Na}0.5\text{NbO}_3$ system, *Appl. Phys. Lett.*, 2007, 91,
27 112906.
28
29
30
31 66. Wang D., Cao M., Zhang S., Investigation of ternary system $\text{Pb}(\text{Sn},\text{Ti})\text{O}_3$ - $\text{Pb}(\text{Mg}1/3\text{Nb}2/3)\text{O}_3$
32 with morphotropic phase boundary compositions, *J. Eur. Ceram. Soc.*, 2012, 32, 441–448.
33
34
35 67. Wang D., Li J., Cao M., Zhang S., Effects of Nb_2O_5 additive on the piezoelectric and dielectric
36 properties of PHT-PMN ternary ceramics near the morphotropic phase boundary, *Phys. Status*
37 *Solidi A*, 2014, 211, 226–230.
38
39
40
41 68. Qi H., Zuo R., Zheng D., Xie A., Evolution of relaxor behavior and high-field strain responses in
42 $\text{Bi}(\text{Mg}1/2\text{Ti}1/2)\text{O}_3$ - PbTiO_3 - $\text{Pb}(\text{Ni}1/3\text{Nb}2/3)\text{O}_3$ ferroelectric ceramics, *J. Alloys Compd.*, 2017,
43 724, 774–781.
44
45
46
47 69. Donnelly N. J., Shrout T. R., Randall C. A., Addition of a Sr, K, Nb (SKN) Combination to
48 PZT(53/47) for High Strain Applications, *J. Am. Ceram. Soc.*, 2007, 90, 490–495.
49
50
51
52 70. Zhang Q., Chen J., Lu Y., Yang T., Yao X., He Y., $(\text{Pb},\text{Sm})(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ Multifunctional
53 Ceramics with Large Electric-Field Induced Strain and High-Energy Storage Density, *J. Am.*
54 *Ceram. Soc.*, 2016, 99, 3853–3856.
55
56
57
58
59
60

- 1
2
3 71. Liu Z., Zhao C., Li J., Wang K., Wu J., Large strain and temperature-insensitive piezoelectric
4 effect in high-temperature piezoelectric ceramics, *J. Mater. Chem. C*, 2018, 6, 456-463
5
6
7 72. Tao H., Wu J., Xiao D., Zhu J., Wang X., Lou X., *ACS Appl. Mater. Interfaces*, 2014, 6,
8 20358–20364.
9
10 73. Zheng T., Wu J., Xiao D., Zhu J., High Strain in (K,Na)NbO₃-Based Lead-Free Piezoceramics,
11 *ACS Appl. Mater. Interfaces*, 2015, 7, 20332–20341
12
13 74. Qin Y., Zhang J., Yao W., Lu C., Zhang S., Domain Configuration and Thermal Stability of
14 (K_{0.48}Na_{0.52})(Nb_{0.96}Sb_{0.04})O₃-Bi_{0.50}(Na_{0.82}K_{0.18})_{0.50}ZrO₃ Piezoceramics with High d₃₃
15 Coefficient, *ACS Appl. Mater. Interfaces*, 2016, 8, 7257–7265.
16
17 75. Wang K., Yao F., Jo W., Gobeljic D., Shvartsman V. V., Lupascu D. C., Li J., Rödel J.,
18 Temperature-Insensitive (K,Na)NbO₃-Based Lead-Free Piezoactuator Ceramics, *Adv. Funct.*
19 *Mater.*, 2013, 23, 4079–4086.
20
21 76. Fu J., Zuo R., Qi H., Zhang C., Li J., Li L., Low electric-field driven ultrahigh electrostrains in
22 Sb-substituted (Na,K)NbO₃ lead-free ferroelectric ceramics, *Appl. Phys. Lett.*, 2014, 105, 242903.
23
24 77. Lee J., Kim D., Seo I., Kim J., Park J., Ryu J., Han S. H., Jang B., Nahm S., Large Strain in CuO-
25 added (Na_{0.2}K_{0.8})NbO₃ Ceramic for Use in Piezoelectric Multilayer Actuators, *J. Am. Ceram.*
26 *Soc.*, 2016, 99, 938–945.
27
28 78. Zhang M., Wang K., Du Y., Dai G., Sun W., Li G., Hu D., Thong H. C., Zhao C., Xi X., Yue Z.,
29 Li J., High and Temperature-Insensitive Piezoelectric Strain in Alkali Niobate Lead-free
30 Perovskite, *J. Am. Chem. Soc.* 2017, 139, 3889–3895
31
32 79. Wang X., Zheng T., Wu J., Xiao D., Zhu J., Wang H., Wang X., Lou X., Gu Y., Characteristics of
33 giant piezoelectricity around the rhombohedral-tetragonal phase boundary in (K,Na)NbO₃-based
34 ceramics with different additives, *J. Mater. Chem. A*, 2015, 3, 15951-15961.
35
36 80. Zhou J., Wang K., Yao F., Zheng T., Wu J., Xiao D., Zhu J., Li J., Multi-scale thermal stability of
37 niobate-based lead-free piezoceramics with large piezoelectricity, *J. Mater. Chem. C*, 2015, 3,
38 8780-8787.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
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- 1
2
3 81. Wang D., Hussain F., Khesro A., Feteira A., Tian Y., Zhao Q., Reaney I. M., Composition and
4 temperature dependence of structure and piezoelectricity in $(1-x)(K_{1-y}Na_y)NbO_{3-x}$
5 $(Bi_{1/2}Na_{1/2})ZrO_3$ lead-free ceramics, *J. Am. Ceram. Soc.*, 2017, 100, 627–637
6
7
8
9 82. Zhang S., Kouna A. B., Aulbach E., Granzow T., Jo W., Kleebe H. J., Rödel J., Lead-Free
10 Piezoceramics with Giant Strain in the System $Bi_{0.5}Na_{0.5}TiO_3$ – $BaTiO_3$ – $K_{0.5}Na_{0.5}NbO_3$. I.
11 Structure and Room Temperature Properties, *J. Appl. Phys.*, 2008, 103, 034107.
12
13
14 83. Wang Y., Kouna Njiwa A. B., Hoffmann C., WO/2011/012682, 2011
15
16
17 84. Bai W., Li P., Li L., Zhang J., Shen B., Zhai J., Structure evolution and large strain response in
18 BNT–BT lead-free piezoceramics modified with $Bi(Ni_{0.5}Ti_{0.5})O_3$, *J. Alloys Compd.*, 2015, 649,
19 772-781.
20
21
22 85. Maqbool A., Hussain A., Rahman J. U., Song T. K., Kim W., Lee J., Kim M., Enhanced electric
23 field-induced strain and ferroelectric behavior of $(Bi_{0.5}Na_{0.5})TiO_3$ – $BaTiO_3$ – $SrZrO_3$ lead-free
24 ceramics, *Ceram. Inter*, 2014, 40, 11905-11914.
25
26
27 86. Yoshii K., Hiruma Y., Nagata H., Takenaka T., Electrical Properties and Depolarization
28 Temperature of $(Bi_{1/2}Na_{1/2})TiO_3$ – $(Bi_{1/2}K_{1/2})TiO_3$ Lead-Free Piezoelectric Ceramics, *Jpn. J.*
29 *Appl. Phys.*, 2006, 45, 4493–6.
30
31
32
33 87. Pham K., Hussain A., Ahn C. W., Kim W., Jeong S. J., Lee J., Giant strain in Nb-doped
34 $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ lead-free electromechanical ceramics, *Mater. Lett.*, 2010, 64, 2219-
35 2222.
36
37
38
39 88. Nguyen V., Han H., Kim K., Dang D., Ahn K., Lee J., Strain enhancement in
40 $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ lead-free electromechanical ceramics by co-doping with Li and Ta,
41 *J. Alloys Compd.*, 2012, 511, 237–241.
42
43
44
45 89. Hiruma Y., Nagata H., Takenaka T., Formation of Morphotropic Phase Boundary and Electrical
46 Properties of $(Bi_{1/2}Na_{1/2})TiO_3$ – $Ba(Al_{1/2}Nb_{1/2})O_3$ Solid Solution Ceramics, *Jpn. J. Appl. Phys.*,
47 2009, 48, 09KC08.
48
49
50
51 90. Yang H., Yan F., Lin Y., Wang T., Enhanced recoverable energy storage density and high
52 efficiency of $SrTiO_3$ -based lead-free ceramics, *Appl. Phys. Lett.*, 2017, 111, 253903.
53
54
55
56
57
58
59
60

- 1
2
3 91. Yang H., Yan F., Lin Y., Wang T., He L., Wang F., A lead free relaxation and high energy
4 storage efficiency ceramics for energy storage applications, *J. Alloys Compd.*, 2017, 710, 436–
5 445.
6
7
8
9 92. Yang H., Yan F., Lin Y., Wang T., Wang F., Wang Y., Guo L, Tai W., Wei H., Lead-free
10 BaTiO₃-Bi_{0.5}Na_{0.5}TiO₃-Na_{0.73}Bi_{0.09}NbO₃ relaxor ferroelectric ceramics for high energy
11 storage, *J. Eur. Ceram. Soc.*, 2017, 37, 3303–3311.
12
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14
15
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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 ϵ_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 BiFeO₃ rich core and
9 BaTiO₃ 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 BiFeO₃ and BaTiO₃ 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 η 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 η 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.^{12-25, 26-36, 48-92}

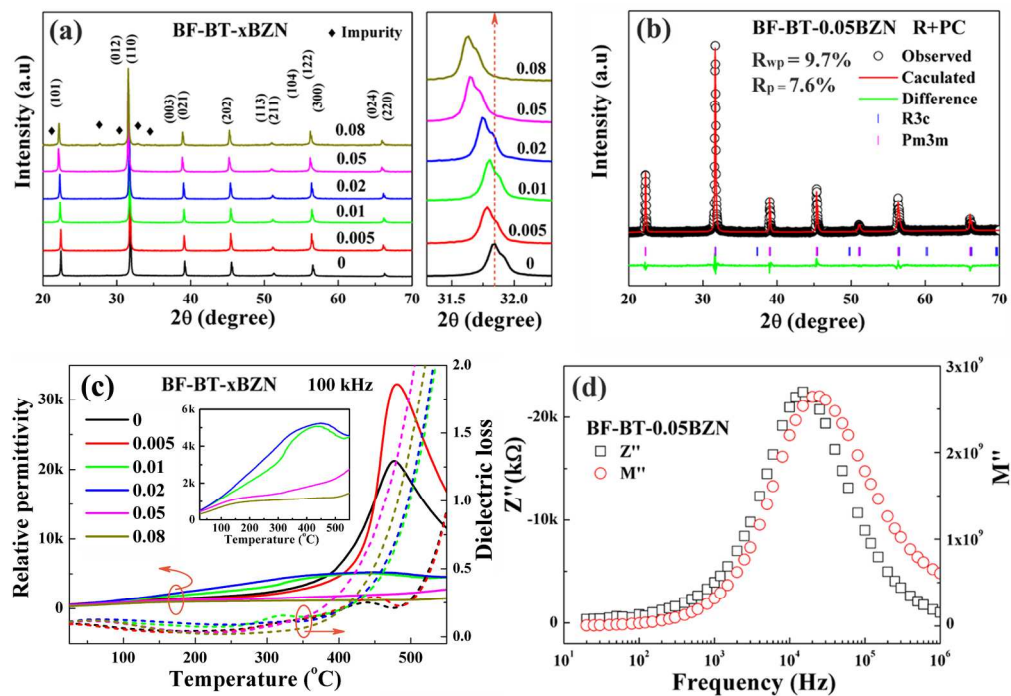


Fig. 1. a) Room temperature XRD patterns of BF-BT-xBZN from $20^\circ \sim 70^\circ$ 2θ . b) Rietveld refinement analysis of BF-BT-0.05BZN using the GSAS+EXPGUI package. c) Temperature dependence of ϵ_r and $\tan\delta$ for BF-BT-xBZN; (d) Spectroscopic plots of Z'' and M'' for BF-BT-0.05BZN.

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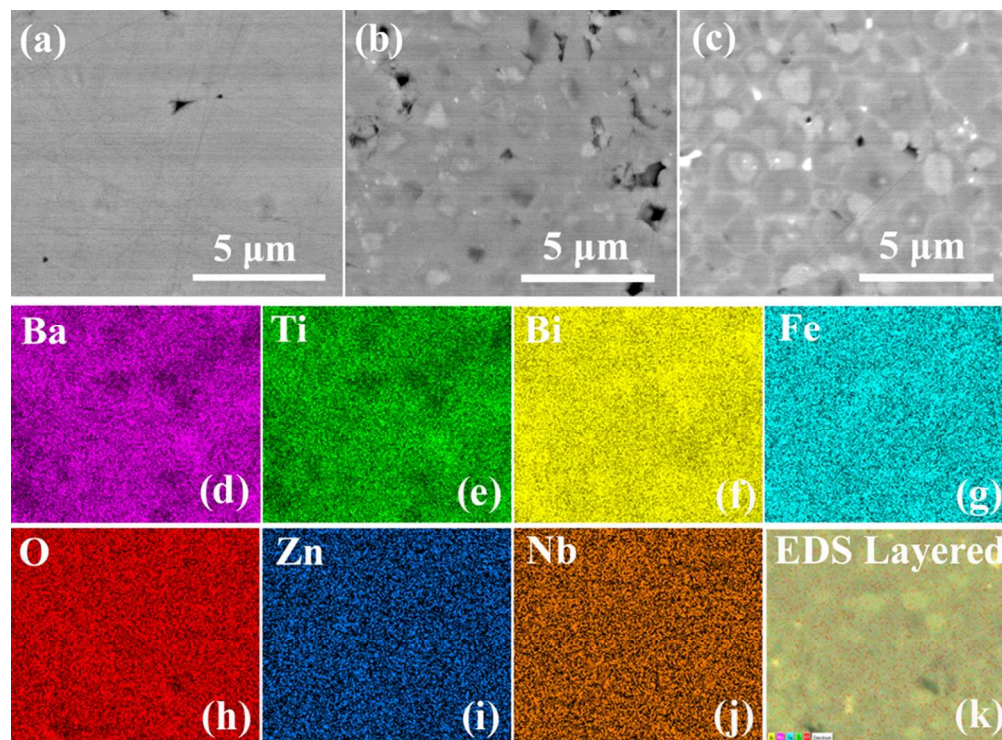
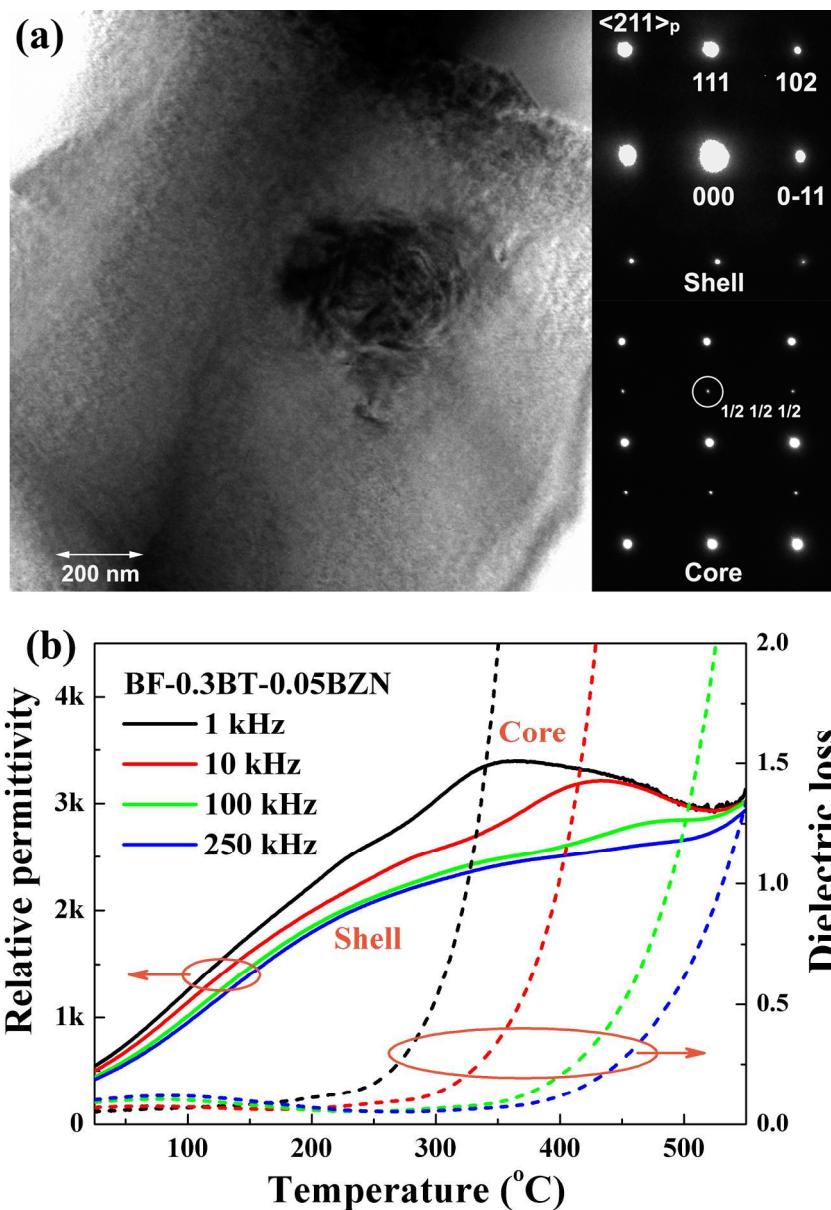


Fig. 2. SEM images of polished surfaces for BF-BT-xBZN (a) BF-BT, (b) BF-BT-0.02BZN and (c) BF-BT-0.05BZN. EDS elemental mapping results of polished BF-BT-0.05BZN samples (d) Ba, (e) Ti, (f) Bi, (g) Fe, (h) O, (i) Zn, (j) Nb and (k) elemental layered image.

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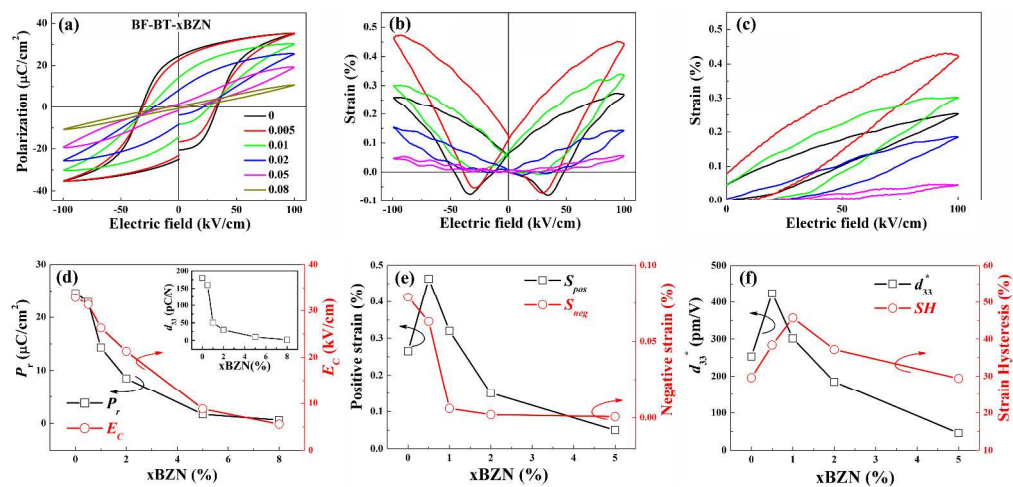


Fig. 4. High electric field (a) bipolar P-E, (b) bipolar S-E and (c) unipolar S-E loops of BF-BT-xBZN samples at 100 kV/cm. (d) P_r and E_C as a function of BZN concentration. (e) S_{pos} and S_{neg} as a function of BZN concentration. (f) d_{33}^* and SH as a function of BZN concentration. d_{33} as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

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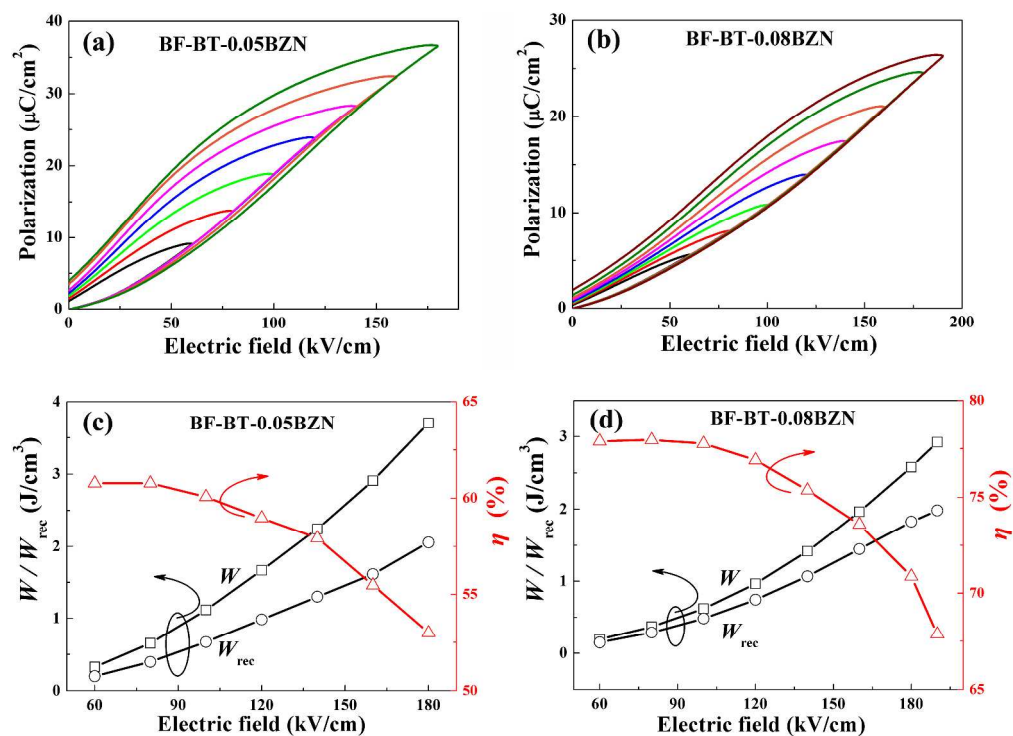


Fig. 5. Unipolar P-E loops under different electric fields for (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN. W , W_{rec} and η as a function of electric field for (c) BF-BT-0.05BZN and (d) BF-BT-0.08BZN.

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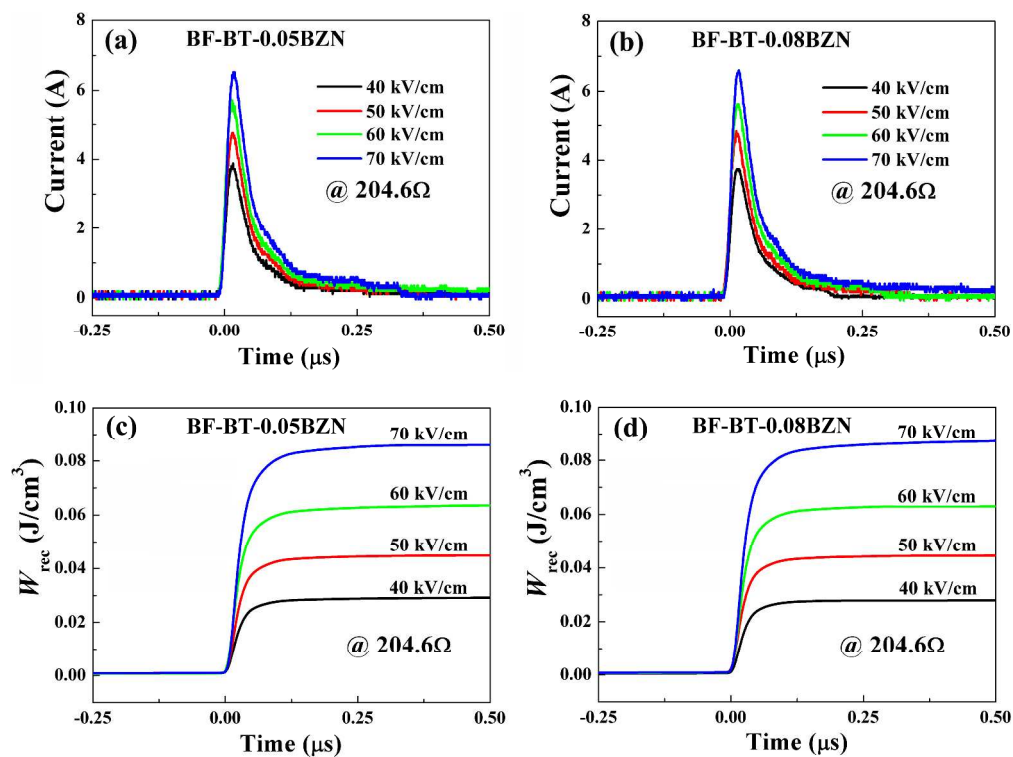


Fig. 6. Time dependence of the pulsed discharge current for (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN. Time dependence of W_{rec} for (c) BF-BT-0.05BZN and (d) BF-BT-0.08BZN.

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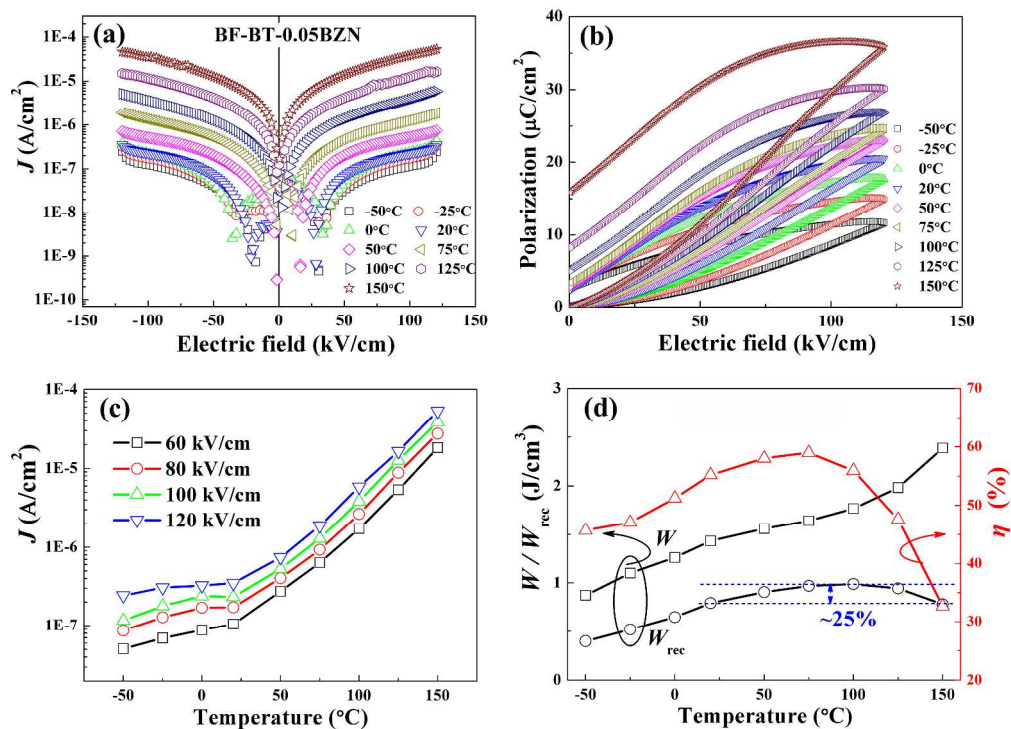


Fig. 7. In-situ temperature dependence of (a) J and (b) unipolar P-E loops for BF-BT-0.05BZN at an electric field of 120 kV/cm. (c) J as a function of temperature at different electric fields. (d) W , W_{rec} and η as a function of temperature.

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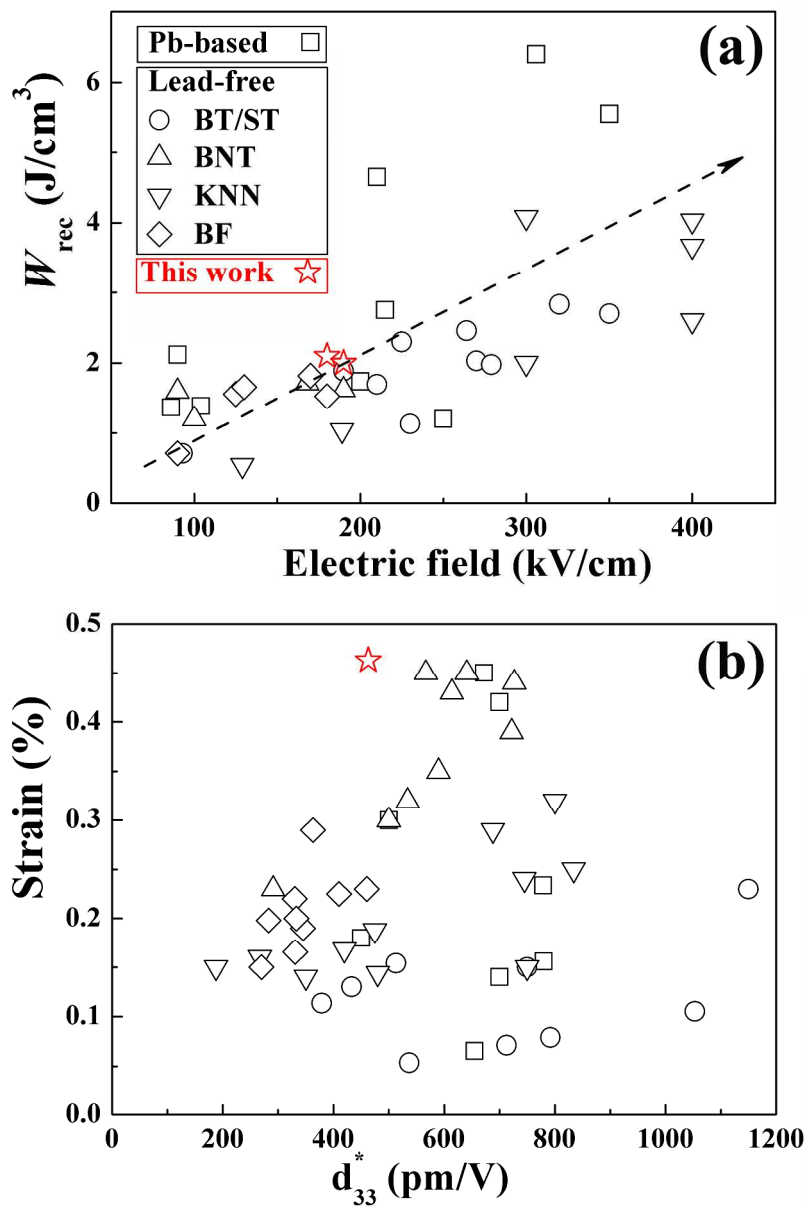
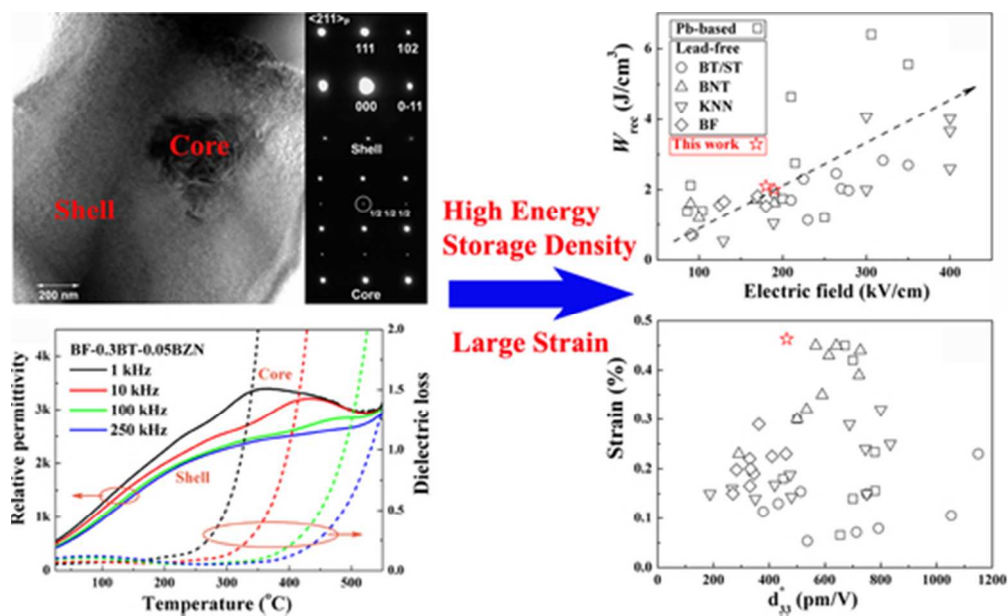


Fig. 8. Comparison of (a) W_{rec} vs electric field and (b) strain vs d_{33}^* among lead-based and lead-free ceramics.12-25, 26-36, 45-86

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