



Simultaneously high-energy storage density and responsivity in quasi-hysteresis-free Mn-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-(Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1})\text{TiO}_3$ ergodic relaxor ceramics

Feng Li , Jiwei Zhai, Bo Shen, Xing Liu & Huarong Zeng

To cite this article: Feng Li , Jiwei Zhai, Bo Shen, Xing Liu & Huarong Zeng (2018) Simultaneously high-energy storage density and responsivity in quasi-hysteresis-free Mn-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-(Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1})\text{TiO}_3$ ergodic relaxor ceramics, Materials Research Letters, 6:7, 345-352, DOI: [10.1080/21663831.2018.1457095](https://doi.org/10.1080/21663831.2018.1457095)

To link to this article: <https://doi.org/10.1080/21663831.2018.1457095>



© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.



View supplementary material [↗](#)



Published online: 01 Apr 2018.



Submit your article to this journal [↗](#)



Article views: 4299



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 38 View citing articles [↗](#)



ORIGINAL REPORT



Simultaneously high-energy storage density and responsivity in quasi-hysteresis-free Mn-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-(Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1})\text{TiO}_3$ ergodic relaxor ceramics

Feng Li^{a,b,c}, Jiwei Zhai^a, Bo Shen^a, Xing Liu^a and Huarong Zeng^b

^aKey Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Functional Materials Research Laboratory, School of Materials Science & Engineering, Tongji University, Shanghai, People's Republic of China; ^bKey Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, People's Republic of China; ^cUniversity of Chinese Academy of Sciences, Beijing, People's Republic of China

ABSTRACT

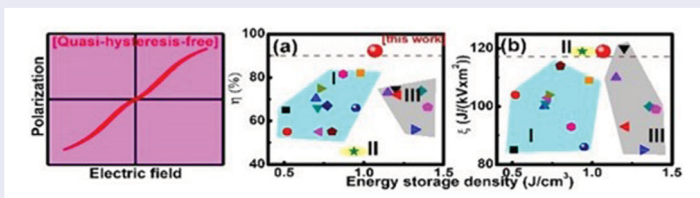
High-energy storage density, responsivity and efficiency, i.e. $W_R = 1.07 \text{ J/cm}^3$, $\xi = 119 \text{ J/(kV m}^2\text{)}$ and $\eta = 92\%$, were simultaneously obtained in Mn-doped $0.62\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}0.32(\text{Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1})\text{TiO}_3$ ergodic relaxor ceramics. Appropriate Mn doping was beneficial to enhance breakdown field strength. Moreover, temperature and different atmosphere-dependent impedance spectroscopy results indicated that oxygen vacancies were the conductivity mechanism for all samples. The valence state of Mn together with the conjugation between Mn ion and oxygen vacancies was confirmed by X-ray photoelectron spectra and electric paramagnetic resonance. The above results indicate that quasi-hysteresis-free loops with high-energy storage performances can be obtained by the induced defect complex.

ARTICLE HISTORY

Received 3 December 2017

KEYWORDS

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$; energy storage; defect complex; quasi-hysteresis-free



IMPACT STATEMENT

High-energy storage density $W_R = 1.07 \text{ J/cm}^3$, responsivity $\xi = 119 \text{ J/(kV m}^2\text{)}$ and efficiency $\eta = 92\%$ were simultaneously obtained in quasi-hysteresis-free ceramics by introducing defect complex.

1. Introduction

High performances of dielectric materials are desired to meet the ever-increasing consumer and industrial requirements for electronic components. The ubiquitous lead zirconium titanate (PZT)-based piezoelectric ceramics, though dominating the electronic markets, are gradually abandoned due to its contamination to the environment. Recently, lead-free perovskite-type ceramics have received a flurry of interests and much progress has been made [1,2]. Among them, lead-free

bismuth sodium titanate (BNT)-based ceramics has been extensively studied due to the giant electro-strain properties that were discovered in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (BNT-BT-KNN) ceramics [3]. Due to the slanted nature of P-E loops, Gao et al. initially investigated the energy storage properties in BNT-BT-KNN ceramics, and recoverable energy storage density $W_R \sim 0.59 \text{ J/cm}^3$ was obtained under 5.6 kV/mm . It also exhibited temperature-insensitive characteristics within the ergodic phase region, which predicted a promising

CONTACT Jiwei Zhai apzhai@tongji.edu.cn Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Functional Materials Research Laboratory, School of Materials Science & Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, People's Republic of China; Huarong Zeng huarongzeng@mail.sic.ac.cn Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

Supplemental data for this article can be accessed here. <https://doi.org/10.1080/21663831.2018.1457095>

© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.
This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

candidate to the application in energy storage capacitors [4]. Later, much attention has been paid to the energy storage properties in BNT-based ceramics [5–8]. As a matter of fact, apart from the advantage of the solid-state dielectric bulks that can operate at high temperature, BNT-based ceramics can also exhibit a good temperature stability because of their diffuse phase transition behavior due to the transformation between R3c and P4bm polar nanoregions (PNRs) [9,10].

The widespread application of power electronics demands high-energy storage/responsivity and efficiency material, the W_R and efficiency in BNT-based ceramics is limited yet so far. With respect to enhancing W_R ; generally, two routes are usually adopted to in the BNT-based material.

- (i) The coexistence of nonergodic and ergodic phase will result in large maximum polarization ($P_{\max}$) and low remnant polarization (P_r), thus enlarging the gap between $P_{\max}$ and P_r , which is beneficial to obtain large W_R (usually with pinched P–E loops). This can be usually realized via composition and temperature modulation [5,7].
- (ii) Another approach to enhance W_R is improving the breakdown field strength (BDS). The addition of ‘hard’ dopant (Fe, Mn, etc.) and complex-ion (such as $(\text{Ni}_{1/3}\text{Nb}_{2/3})^{4+}$) is believed to be an effective method to improve BDS [11,12].

For example, significant results have been obtained in $(1-x)\text{Bi}_{0.48}\text{La}_{0.02}\text{Na}_{0.48}\text{Li}_{0.02}\text{Ti}_{0.98}\text{Zr}_{0.02}\text{O}_{3-x}\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$ ceramics reported by Yang et al. The maximum energy storage density can be obtained for the sample with $x = 0.10$ at room temperature (RT), with an energy storage density of 2.04 J/cm^3 at 178 kV/cm , the performance of which is outstanding in lead-free ceramics. However, the energy storage efficiency is only around 55% [13]. Balancing of energy storage density and efficiency in the BNT-material has been a difficult problem. The transformation between the relaxor phase and long ferroelectric order is always accompanied by giant strain with large hysteresis in BNT-based materials. The charge–discharge time is within few micro-seconds, the exceptionally large strain in BNT-based ceramics will lead to large localized stress and may easily crack during repeated charge–discharge cycles, especially when high electric field is applied [5]. Moreover, due to hysteresis, a large portion of the energy will dissipate as heat during the discharging process, which inevitably results in high energy loss and reduce service life for electronic components. It is worthy to note that the pure ergodic relaxor phase can get rid of the above two shortcomings. However, the $P_{\max}$ for the pure ergodic phase is

usually low when far away from the nonergodic-ergodic phase region due to the enhanced local random field that impedes the appearance of long-range ferroelectric order, then low W_R will be obtained. So we envisaged whether a low hysteresis loops can be designed and large energy storage density/responsivity and efficiency can be obtained simultaneously under moderate electric field in BNT-based ceramics?

It is extensively reported that appropriate doping of transition metal ions with different valences (e.g. Mn, Fe ions) is beneficial for the enhancement of resistivity and piezoelectric properties [14,15]. In this letter, the energy storage properties and defect chemistry of Mn-doped $0.62\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3\text{--}0.32(\text{Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1})\text{TiO}_3$ ergodic relaxor ceramics have been studied in detail. The impedance spectroscopy, X-ray photoelectron spectra (XPS) and electric paramagnetic resonance (EPR) were also investigated to explore the role of the Mn dopant in modifying the defect microstructure and energy storage properties. The results indicated that quasi-hysteresis-free loops with high-energy storage performances can be obtained by inducing defect complex. The experimental details are shown in the supplemental data.

2. Results and discussions

Figure 1(a) shows the XRD patterns of the 0–2 Mn ceramics. It can be seen that the main perovskite phase can be formed for these ceramics and a high content of Mn addition will result in the appearance of second phase ($\text{Sr}_6\text{Bi}_2\text{O}_9$). Moreover, all single diffraction peaks signify the pseudocubic symmetry for the studied samples. The inset of Figure 1(a) shows the SEM microstructure for 1 Mn ceramic morphology as a representative. All compositions are well densified with pore-free microstructure. The Mn addition has a minor effect on the grain size and it is in the vicinity of $1.5 \mu\text{m}$.

The distribution of the BDS of ferroelectric ceramics is considered to follow the Weibull function [16]. According to the Weibull distributions, the BDS data of the 0–2 Mn ceramics are plotted in Figure 1(b). Twenty samples for each composition are measured to obtain the average BDS values. The results show that all the plots display a relatively good linearity and the Weibull modulus β is more than 8, indicating the reliability of the fitting [17]. Besides, β is correlated with the range of BDS, and the intercept determines the magnitude of BDS, as shown by the dashed line. Apparently, the BDS first increases from 0 Mn to 1 Mn sample, and gradually decreases with a further addition of the Mn content. It is well known that the BDS depends on a couple of factors, including porosity, grain size, conductivity mechanism

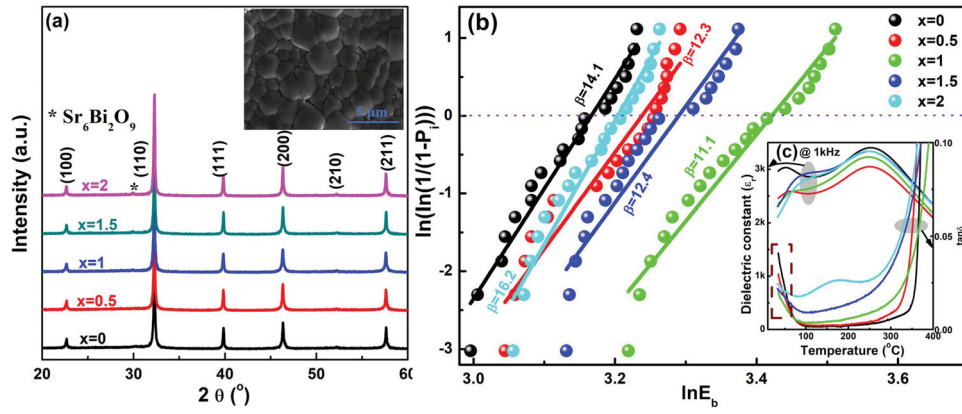


Figure 1. (a) XRD patterns of the 0–2 Mn ceramics, and the inset shows the SEM microstructure for 1 Mn ceramic morphology; (b) the Weibull plots of dielectric BDS of the 0–2 Mn ceramics and (c) temperature dependence of dielectric constant (ϵ_r) and loss ($\tan \delta$) at frequency of 1 kHz.

and extrinsic parameters such as sample thickness and electrode area. For the 0–2 Mn ceramics, the evolution of RT dielectric loss and the appearance of second phase may be a key factor to determine the BDS value. As shown in Figure 1(c), for low Mn doping with 0–1 Mn ceramics, the dielectric loss is gradually depressed. However, more Mn amount will enhance the dielectric loss, as indicated by the dashed rectangle in Figure 1(c), which may be due to the fact that excessive Mn content provides more pathways for the localized electron hopping process; at the same time, the appearance of the second phase will also make the ceramics leaky, so the ceramics will breakdown more easily with the application of electric field [18]. Therefore, the value of BDS is maximized for 1 Mn ceramic with the low dielectric loss at RT. Moreover, the dielectric constant of all samples exhibits a shoulder at T_s and a broad maximum at T_m , both of which are closely related with the evolution of PNRs and an indication of relaxor phase transition behavior [19].

In order to ascertain the conduction mechanism in the 0–2 Mn ceramics, impedance spectroscopy is adopted as it is known to be an effective technique to characterize the contribution of the grain, grain boundary and electrode interface to the electrical conduction behavior in ferroelectric ceramics [20]. Complex impedance spectra are measured in the selected temperature range of 470–580°C for 0–2 Mn ceramics, as shown in Figure 2(a–e) (dots). It is worth noting that the semicircles do not appear at a lower temperature because of the high resistivity. A single semicircle is observed from the complex impedance results indicating that a single relaxation mechanism dominates the impedance. The value of Z' decreases with an increase in the measuring temperature, demonstrating that all samples exhibit a negative temperature coefficient of resistance behavior that is analogous to the semiconductor [21]. Due to the non-Debye

relaxation behaviors, a parallel R-C circuit is simulated to fit the impedance data, as shown in Figure 2(f). By using the ZView software, the resistance (R_b) and capacitance (C_b) are simulated based on the fitting results and a close agreement between the experimental (dots) and fitting results (line) is obtained. The fitting results are listed in the supplementary material (Table 1). The conductivity of the bulk σ_b and activation energy E_a can be calculated by the formula [22]:

$$\sigma_b = \frac{h}{S \times R_b}, \quad (1)$$

$$\sigma_b = \sigma_0 \exp \left(-\frac{E_a}{k_B T} \right), \quad (2)$$

where h is the sample thickness, S is the electrode area, R_b is the bulk resistance, E_a is the activation energy of conduction, k_B is the Boltzmann constant and T is the absolute temperature. The variation of bulk conductivity with the temperature is plotted in Figure 2(g). It can be seen that the experimental data obey the Arrhenius law according to the fitting results. As seen from Figure 2(h), the E_a of all samples increases with a rise of the Mn content. It is estimated to be 0.4, 0.65, 0.7 eV, 0.85 and 0.85 and for 0–2 Mn ceramics, respectively. It has been demonstrated that E_a is in the range of 0.5–2 eV for oxygen vacancies and its value depends on the concentration [23]. On the one hand, the oxygen vacancies can be easily introduced because of the A-site deficiency component ($\text{Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1}\text{TiO}_3$). On the other hand, the substitution of Ti by the Mn element is expected to induce the formation of oxygen vacancies as charge compensation. Therefore, it is rational to speculate that oxygen vacancies dominate the conductivity since the value of E_a is determined to be around 0.4–0.85 eV in the studied compositions, which is also in line with other BNT-based

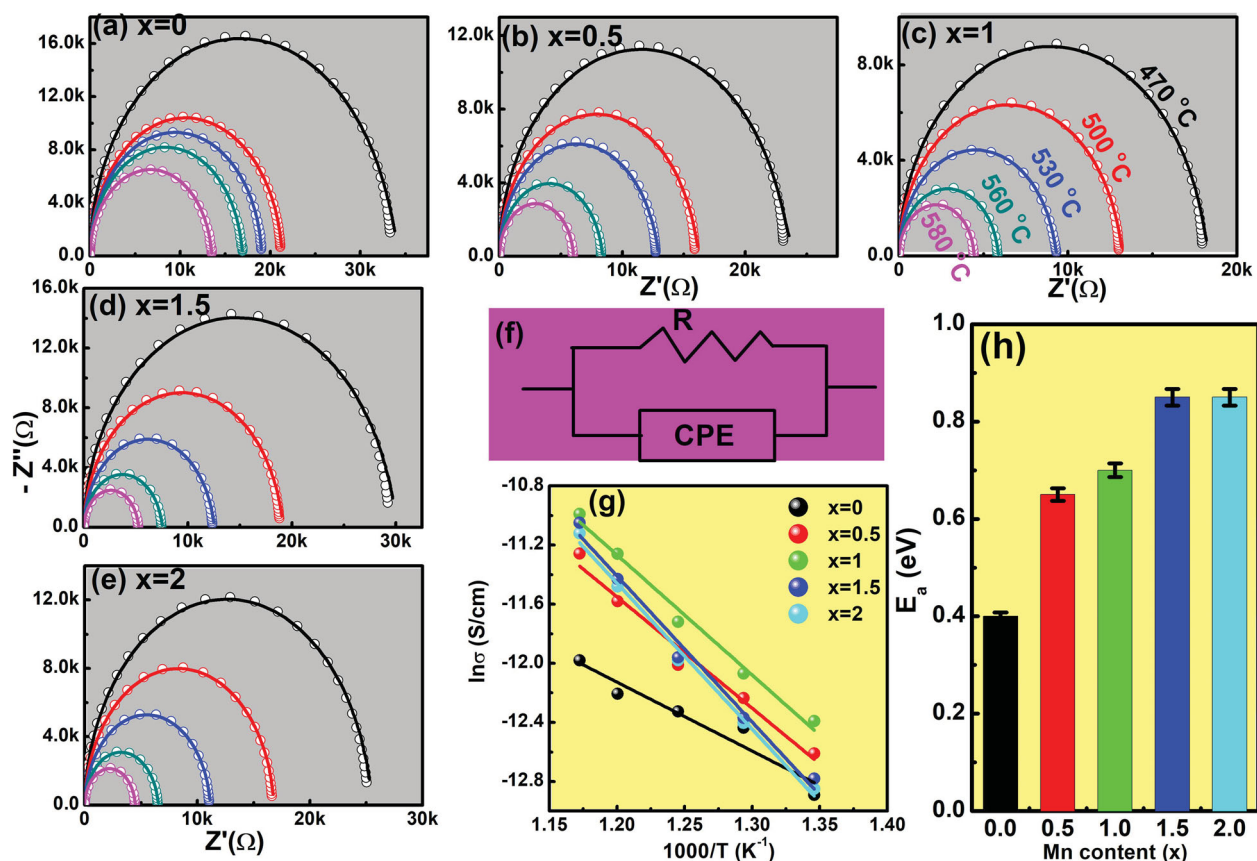


Figure 2. (a–e) Complex impedance plots for 0–2 Mn ceramics in the temperature range of 470–580 °C (the dots are experimental data and the solid lines represent the fitting results); (f) equivalent circuit proposed for impedance data fitting; (g) Arrhenius-type plots of the conductivity with temperature and (h) variation of activation energy E_a as a function of the Mn content.

materials [24]. The E_a refers to the dissociation of defect dipoles and corresponds to the ability of transition from constrained oxygen vacancies to the freely moved ones. The gradual enhancement of E_a with Mn addition is believed to be related to the reduction of free oxygen vacancies [25]. Therefore, appropriate Mn doping can hinder the migration of oxygen vacancies and the local electron hopping and then effectively enhance the BDS.

Figure 3(a,b) shows the $Z''(f)$ and $M''(f)$ spectra for $x = 1$ Mn ceramic over 470–580 °C as a representative. Impedance spectroscopy with a single peak indicates the absence of the grain-boundary component in $x = 1$ Mn ceramic as there is no additional arcs at a lower frequency range [26], which is also in agreement with the above discussions. Complex impedance plots measured in nitrogen, air and oxygen atmosphere are shown in Figure 3(c). It can be seen that the impedance plots in air and oxygen are nearly the same, which predicts that the resistivity remains unchanged when is 1 Mn ceramic is exposed to air and oxygen atmospheres. However, when the 1 Mn ceramic is exposed to nitrogen atmosphere, the resistivity is drastically reduced. A similar phenomenon has also been witnessed in other Mn-doped BNT-BT-SBT

ceramics. The obvious variation of resistivity in the inert nitrogen atmosphere indicates that ceramics exhibits an n-type semiconductor behavior, which is probably due to the loss of oxygen according to previous studies [27,28]. The normalized activation energies E_a for three different atmospheres are displayed in Figure 3(d). It can be obviously seen that the E_a increases with an increase in the oxygen partial pressure. It is known that exposure to nitrogen atmosphere for these ceramics is easily to be induced the oxygen vacancies. The enhancement of E_a indicates a decrease in the concentration of oxygen vacancies.

Figure S1 (a1–a5) shows the XPS profile of O 1s of the 0–2 Mn ceramics. It is found that the spectra are composed of two peaks by using Gaussian fitting. The first peak located at the low binding energy around 529.6 eV is assigned to be lattice oxygen. Another peak in the vicinity of 531.4 eV is attributed to the presence of oxygen vacancies in the 0–2 Mn ceramics, which confirms the existence of oxygen vacancies. Ti 2p_{3/2} and Ti 2p_{1/2} XPS peaks are displayed in Figure S1 (b1–b5). According to the fitting results, the peak position has not changed for the all compositions within the resolution of XPS

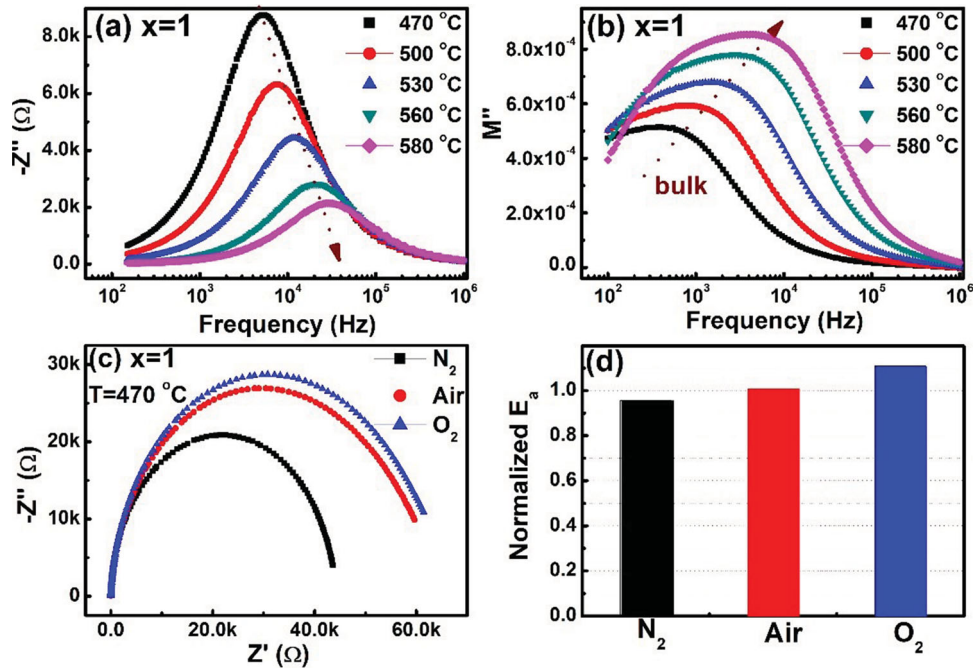


Figure 3. (a–b) Z'' and M'' spectrum for 1 Mn ceramics over 470–580 °C; comparison of (c) complex impedance plots at 470 °C and (d) normalized E_a for 1 Mn ceramics in nitrogen, air and oxygen atmospheres.

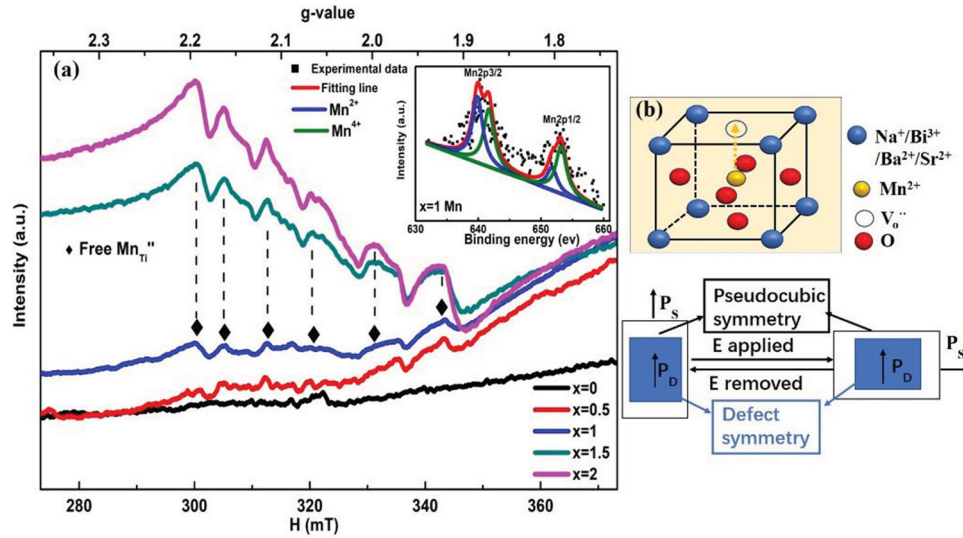


Figure 4. (a) RT X-band EPR spectra for 0–2 Mn ceramics, the inset shows the XPS of 1 Mn ceramic and (b and c) schematic illustration of defect structure of Mn-doped ceramics.

(shown by the dashed line), probably indicating the positive charge $V_o^{\bullet}$ is not compensated by the reduction of Ti^{4+} to Ti^{3+} state [29]. However, further systematic research is needed to clarify the valence of Ti under this condition.

To further give an insight into the role of Mn element in the BNT-BT-SBT ceramics, X-band EPR spectra are characterized for the all compositions, as shown in Figure 4(a). These spectra are analogous to other Mn-doped BNT-based ceramics and demonstrate that the Mn

element has been incorporated into the octahedral environment at the Ti positions [30]. The EPR signal of 0 Mn ceramic is absent because of its diamagnetic nature. The 0.5–2 Mn ceramics exhibit a hyperfine structure with typical six-line splitting but with different EPR intensities. This signal originates from the Mn^{2+} as a type of free Mn^{2+} . The EPR signal of Mn^{4+} lies below the detect limit for the EPR spectra in this study. In order to confirm the oxidation state of the Mn element, XPS of Mn 2p spectra for 1 Mn ceramic is presented in the inset of

Figure 4(a). The overlapped spectra are also fitted by the Gaussian function to determine the valent state of the Mn dopant. It can be seen that two peaks with different binding energies are observed, indicating the existence of two Mn valent states. The main peak around 641.3 and 653.4 eV can be assigned to $\text{Mn}2p_{3/2}$ and $\text{Mn}2p_{1/2}$, respectively. Specifically, the peak at the lower binding energy of 640.2 eV is assigned to Mn^{2+} , the peak at the higher binding energy of 641.9 eV is probably assigned to Mn^{4+} , which is in a good agreement with the literature [31]. Therefore, the mix $\text{Mn}^{2+}/\text{Mn}^{4+}$ valent states are obtained in Mn-doped BNT-BT-SBT ceramics, further suggesting that the Mn element has diffused into the perovskite B-site in the ceramics. It is obvious that the inhomogeneous EPR signals can be observed, which indicates the presence of the nearest-neighbor oxygen vacancies. With increasing Mn content, the intensity of

the EPR signal is enhanced, which is related with the increasing concentration of Mn^{2+} and corresponding oxygen vacancies. Moreover, the induced oxygen vacancies are expected to be easily trapped by the free Mn^{2+} ion since free Mn^{2+} has a strong force to attract $V_{\text{O}}^{\bullet\bullet}$, which is evidenced by the slight asymmetry of the EPR signal that indicates that oxygen vacancies have been trapped by the $\text{Mn}_{\text{Ti}}^{\prime\prime}$ defect center and form the $\text{Mn}_{\text{Ti}}^{\prime\prime} - V_{\text{O}}^{\bullet\bullet}$ complex [29]. Under this condition, incorporation of Mn will result in the presence of defect complexes $\text{Mn}_{\text{Ti}}^{\prime\prime} - V_{\text{O}}^{\bullet\bullet}$ in the ceramics, which is schematically illustrated in Figure 4(b). The conjugation between Mn^{2+} and oxygen will create a P_{D} , which is in parallel with spontaneous polarization (P_{S}). When the external electric field is applied to the ceramics, P_{S} switches instantaneously with the cycling of external electric field yet the P_{D} exhibits a much slower switching speed compared to P_{S} . So the P_{D}

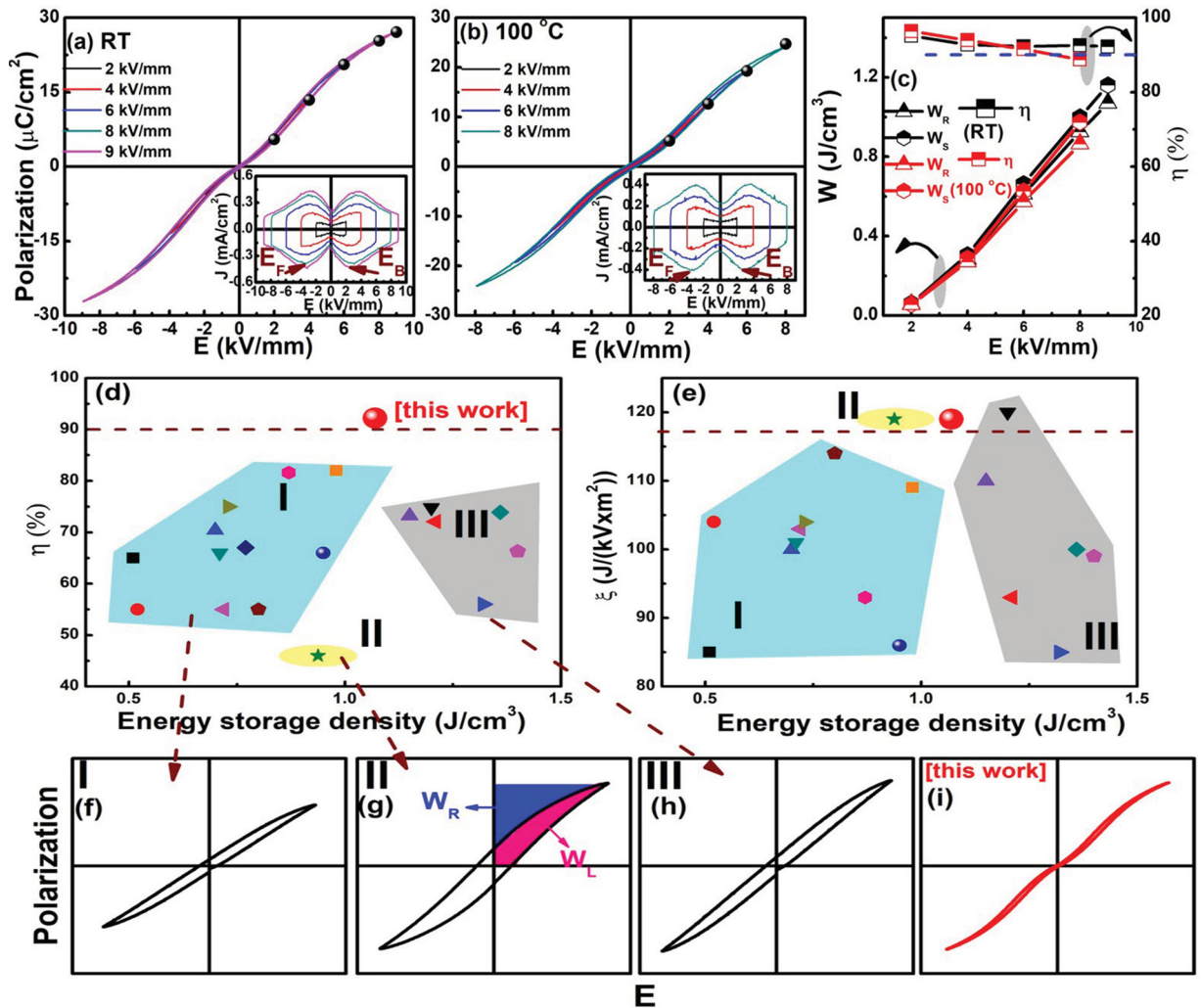


Figure 5. (a and b) P-E hysteresis loops for 1 Mn ceramics under different electric fields with corresponding J-E loops in their insets; (c) the electric field dependence of W_R , W_S and η at RT and 100 °C, respectively. (d and e) Comparison of W_R and ξ among previously reported BNT-based ceramics; (f-h) three kinds of P-E loops reported in the literature, the inset of (g) illustrates the definition of W_R and W_L in the P-E loop and (i) the quasi-hysteresis-free loop discovered in this work.

will act as an internal field to switch the domain back to its original state with the release of electric field [11].

The RT P–E loops of the all samples are shown in Figure S2. Only slim P–E loops are observed, which signal the pure ergodic phase for all ceramics [32]. Moreover, the addition of 0.5 Mn and 1 Mn is beneficial to reduce the energy loss for the ceramic, which is related to the appearance of $\text{Mn}_{\text{Ti}}'' - V_0^\bullet$, as shown in the inset of Figure S2. The 1 Mn ceramic is selected to study its energy storage behavior because of its enhanced theoretical BDS according to Weibull distributions. As shown in Figure 5(a,b), bipolar P–E hysteresis loops with current density J–E loops of 1 Mn ceramic are measured under different electric fields at RT and 100°C. Quasi-hysteresis-free loops are obtained and the P_{max} gradually increases with the increase in electric field. Generally, the recoverable energy storage density is calculated according to the formula $W_R = \int_{P_r}^{P_{\text{max}}} E dP$, the energy storage efficiency $\eta = W_R / (W_R + W_L)$ and $W_S = W_R + W_L$ [33], which is illustrated in Figure 5(g). It is obvious that both the stored and recoverable energy storage density W_S and W_R increase with augmenting electric field. As shown in the inset of Figure 5(a,b), the back-forward and forward E_B and E_F appear under high electric field strengths, indicating that the ferroelectric order is induced with the coherence of PNRs and then contributes to the large polarization. It is found that the W_R for 1 Mn ceramic could reach as high as 1.07 J/cm³ under moderate electric field of 9 kV/mm at RT and also maintains 0.86 J/cm³ under 8 kV/mm at 100°C. Interestingly, within various electric field strengths at RT and 100°C, the η is no less than 90%, indicating the ultra-low energy loss during domain switching. This may be the contribution of the dipole complex $\text{Mn}_{\text{Ti}}'' - V_0^\bullet$, as discussed above. It should be noted that the η becomes low under an electric field of 8 kV/mm at 100°C, probably due to the enhanced conductivity at high temperatures and it may be also the mechanism for the decreased BDS. A normalized parameter $\xi = W_R/E$ is introduced to characterize the energy storage ability. The ξ could reach 119 J/(kV m²) together with a large $\eta = 92\%$ under moderate electric field (9 kV/mm), which is much higher than other BNT-based ceramics, as shown in Figure 5(d,e).

According to literature survey, the relationship of $W_R \sim \eta$ and $W_R \sim \xi$ is plotted in Figure 5(a,b) among the reported BNT-based ceramics. Generally, there are three approaches to enhance W_R :

- (i) Modulating the phase portion of ferroelectric phase and ergodic phase to maximize the ΔP ($\Delta P = P_{\text{max}} - P_r$) and minimize the W_L at moderate electric field. Usually, both of W_R and η exhibit common performances.

- (ii) A large P_{max} accompanied by a large W_L under high electric field. Both of the W_R and W_L is quite large, however, the η is very low.
- (iii) Enhancing the measuring electric field for the ceramics within the ergodic phase. The W_R can be enhanced compared to I . However, η remains low still.

As a matter of fact, both the W_R and η are the two important parameters to measure the energy storage performance in the application of power electronics. What is more, the ceramics should not be repeatedly operated under high electric field, especially for BNT-based material with a large strain. Therefore, the parameter ξ instead of W_R is expected to be a benchmark for the energy storage ability in different BNT-based ceramics. The simultaneously high ξ and η is as a result of the quasi-hysteresis-free loops with high polarizations, as indicated in Figure 5(i).

3. Conclusions

Mn doping is beneficial to enhance BDS and $W_R = 1.07 \text{ J/cm}^3$, $\xi = 119 \text{ J/(kV m}^2\text{)}$ and $\eta > 90\%$ are simultaneously obtained in 1 Mn ceramics. The high performance of the ceramic originates from the quasi-hysteresis-free loops with high polarization as result of the appearance of the defect dipoles, which is confirmed by synergistic measurements, including the XPS, complex impedance and EPR analysis. This work may provide another avenue to design simultaneous high-energy storage density, responsivity and efficiency in BNT-based ceramics.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported the Ministry of Science and Technology of China through the 973-Project under grant [2015CB654601], National Key R&D Program of China [2016YFA0201103] and the Instrument Developing Project of Chinese Academy of Sciences [ZDKYYQ20180004].

ORCID

Feng Li  <http://orcid.org/0000-0002-4112-8604>

References

- [1] Rödel J, Jo W, Seifert KTP, et al. Perspective on the development of lead-free piezoceramics. *J Am Ceram Soc.* 2009;92:1153–1177.
- [2] Shrout TR, Zhang SJ. Lead-free piezoelectric ceramics: alternatives for PZT? *J Electroceram.* 2007;19:113–126.

- [3] Zhang ST, Kouna AB, Aulbach E, et al. Giant strain in lead-free piezoceramics $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ system. *Appl Phys Lett*. 2007;91:112906.
- [4] Gao F, Dong XL, Mao CL, et al. Energy-storage properties of $0.89\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}0.05\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ lead-free anti-ferroelectric ceramics. *J Am Ceram Soc*. 2011;94:4382–4386.
- [5] Li F, Zhai JW, Shen B, et al. Influence of structural evolution on energy storage properties in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-SrTiO}_3\text{-NaNbO}_3$ lead-free ferroelectric ceramics. *J Appl Phys*. 2017;121:054103.
- [6] Xu Q, Lanagan MT, Huang XC, et al. Dielectric behavior and impedance spectroscopy in lead-free BNT-BT-NBN perovskite ceramics for energy storage. *Ceram Int*. 2016;42:9728–9736.
- [7] Cao WP, Li WL, Zhang TD, et al. High-energy storage density and efficiency of $(1-x)[0.94\text{NBT-}0.06\text{BT}]\text{-}x\text{ST}$ lead-free ceramics. *Energy Technol*. 2015;3:1198–1204.
- [8] Pu YP, Yao MT, Zhang L, et al. High energy storage density of $0.55\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.45\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9-x}\text{Zr}_{0.1}\text{Sn}_x\text{O}_3$ ceramics. *J Alloys Compd*. 2016;687:689–695.
- [9] Jo W, Schaab S, Sapper E, et al. On the phase identity and its thermal evolution of lead free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}6\text{mol}\%\text{BaTiO}_3$. *J Appl Phys*. 2011;110:074106.
- [10] Dittmer R, Jo W, Damjanovic D, et al. Lead-free high-temperature dielectrics with wide operational range. *J Appl Phys*. 2011;109:034107.
- [11] Cao WP, Li WL, Feng Y, et al. Defect dipole induced large recoverable strain and high energy-storage density in lead free $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based systems. *Appl Phys Lett*. 2016;108:202902.
- [12] Zhou MX, Liang RH, Zhou ZY, et al. High energy storage properties of $(\text{Ni}_{1/3}\text{Nb}_{2/3})^{4+}$ complex-ion modified $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics. *Mater Res Bull*. 2018;98:166–172.
- [13] Yang HB, Yan F, Lin Y, et al. High energy storage density over a broad temperature range in sodium bismuth titanate-based lead-free ceramics. *Sci Rep*. 2017;7:8726.
- [14] Zhang HW, Chen C, Deng H, et al. Ultrahigh ferroelectric response in Fe modified $0.95(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-}0.05\text{BaTiO}_3$ single crystals. *J Mater Chem C*. 2014;2:10124–10128.
- [15] Sapper E, Dittmer R, Damjanovic D, et al. Aging in the relaxor and ferroelectric state of Fe-doped $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}x\text{BaTiO}_3$ piezoelectric ceramics. *J Appl Phys*. 2014;116:104102.
- [16] Wang GY, Huang XY, Jiang PK. Tailoring dielectric properties and energy density of ferroelectric polymer nanocomposites by high-k nanowires. *ACS Appl Mater Interfaces*. 2015;7:18017–18027.
- [17] Xue SX, Liu SH, Zhang WQ, et al. Dielectric properties and charge-discharge behaviors in niobate glass ceramics for energy-storage applications. *J Alloys Compd*. 2014;617:418–422.
- [18] Yang J, Meng XJ, Shen MR, et al. Effects of Mn doping on dielectric and ferroelectric properties of $(\text{Pb,Sr})\text{TiO}_3$ films on (111) Pt/Ti/SiO₂/Si substrates. *J Appl Phys*. 2009;106:094108.
- [19] Cross LE. Relaxor ferroelectrics: an overview. *Ferroelectrics*. 1994;151:305–320.
- [20] Xu Q, Li TM, Hao H, et al. Enhanced energy storage properties of NaNbO_3 modified $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ based ceramics. *J Eur Ceram Soc*. 2015;35:545–553.
- [21] Barick BK, Choudhary RNP, Pradhan DK. Dielectric and impedance spectroscopy of zirconium modified $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ ceramics. *Ceram Int*. 2013;39:5695–5704.
- [22] Chen PY, Chou CC, Tseng TY, et al. Correlation of microstructures and conductivities of ferroelectric ceramics using complex impedance spectroscopy. *Jpn J Appl Phys*. 2010;49:061505.
- [23] Steinsvik S, Bugge R, Gjønnes J, et al. The defect structure of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($x = 0\text{--}0.8$) investigated by electrical conductivity measurements and electron energy loss spectroscopy (EELS). *J Phys Chem Solids*. 1997;58:969–976.
- [24] Bai WF, Zheng P, Wen F, et al. Lead-free BNT-based composite materials: enhanced depolarization temperature and electromechanical behavior. *Dalton Trans*. 2017;46:15340–15353.
- [25] Zhang L, Hao H, Zhang SJ, et al. Defect structure-electrical property relationship in Mn-doped calcium strontium titanate dielectric ceramics. *J Am Ceram Soc*. 2017;100:4638–4648.
- [26] Li M, Pietrowski MJ, De Souza RA, et al. A family of oxide ion conductors based on the ferroelectric perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Nature Mater*. 2014;13:31–35.
- [27] Zang JD, Li M, Sinclair DC, et al. Impedance spectroscopy of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ based high-temperature dielectrics. *J Am Ceram Soc*. 2014;97:2825–2831.
- [28] Zang JD, Li M, Sinclair DC, et al. Impedance spectroscopy of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ceramics modified with $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$. *J Am Ceram Soc*. 2014;97:1523–1529.
- [29] Zhang HW, Deng H, Chen C, et al. Chemical nature of giant strain in Mn-doped $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ lead-free ferroelectric single crystals. *Scr Mater*. 2014;75:50–53.
- [30] Aksel E, Jakes P, Erdem E, et al. Processing of manganese-doped $[\text{Bi}_{0.5}\text{Na}_{0.5}]\text{TiO}_3$ ferroelectrics: reduction and oxidation reactions during calcination and sintering. *J Am Ceram Soc*. 2011;94:1363–1367.
- [31] Wang XF, Liang PF, Chao XL. Dielectric properties and impedance spectroscopy of MnCO_3 -modified $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free ceramics. *J Am Ceram Soc*. 2015;98:1506–1514.
- [32] Viola G, Ning H, Wei XJ, et al. Dielectric relaxation, lattice dynamics and polarization mechanisms in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based lead-free ceramics. *J Appl Phys*. 2013;114:014107.
- [33] Jin L, Li F, Zhang SJ, Green DJ. Decoding the fingerprint of ferroelectric loops: comprehension of the material properties and structures. *J Am Ceram Soc*. 2014;97:1–27.