

# Novel BiFeO<sub>3</sub>–BaTiO<sub>3</sub>–Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> Lead-Free Relaxor Ferroelectric Ceramics for Energy-Storage Capacitors

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A novel lead-free relaxor ferroelectric ceramic of (0.67–*x*)BiFeO<sub>3</sub>–0.33BaTiO<sub>3</sub>–*x*Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> [(0.67–*x*)BF–0.33BT–*x*BMN, *x* = 0–0.1] was prepared by a solid-state reaction method. A relatively high maximum polarization  $P_{\max}$  of 38  $\mu\text{C}/\text{cm}^2$  and a low remanent polarization  $P_r$  of 5.7  $\mu\text{C}/\text{cm}^2$  were attained under 12.5 kV/mm in the *x* = 0.06 sample, leading to an excellent energy-storage density of  $W \sim 1.56 \text{ J}/\text{cm}^3$  and a moderate energy-storage efficiency of  $\eta \sim 75\%$ . Moreover, a good temperature stability of the energy storage was obtained in the *x* = 0.06 sample from 25°C to 190°C. The achievement of these characteristics was basically attributed to an electric field induced reversible ergodic to ferroelectric phase transition owing to similar free energies near a critical freezing temperature. The results indicate that the (0.67–*x*)BF–0.33BT–*x*BMN lead-free relaxor ferroelectric ceramic could be a promising dielectric material for energy-storage capacitors.

## I. Introduction

INCREASING attention has been given to novel dielectric materials for energy-storage capacitors due to their widespread applications in the field of power electronics. High-energy storage density ( $W$ ) and energy-storage efficiency ( $\eta$ ) are basically required for advanced pulsed power capacitors, which of course need to be operated at elevated temperatures without sacrificing their energy-storage performances. Relatively large energy loss resulting from domain reorientation in ferroelectrics or from low-temperature antiferroelectric-ferroelectric phase transition in antiferroelectrics has restricted their practical applications. Alternatively, relaxor ferroelectrics are characteristic of slim polarization versus electric field ( $P$ – $E$ ) hysteresis loops, thus displaying relatively high maximum polarization ( $P_{\max}$ ) and low remanent polarization ( $P_r$ ).<sup>1</sup> Particularly, the polarization of relaxors can exhibit a good temperature stability because of their diffuse phase transition behavior around the dielectric maxima. Taking global environmental problems into account, these lead-containing material systems need to be replaced by environment-friendly materials. A lead-free BaTiO<sub>3</sub> (BT)–Bi(Mg<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub> relaxor ferroelectric thin film was reported to display a  $W$  value in excess of 37 J/cm<sup>3</sup> together with a good thermal stability from room temperature (RT) to 200°C.<sup>2</sup> However, their limited thickness has restricted the overall stored energy. In addition, some lead-free bulk ceramics have been also investigated, such as Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> (BNT)-based

and BT-based systems with  $W$  values of rarely larger than 1 J/cm<sup>3</sup>.<sup>3–7</sup> BiFeO<sub>3</sub> (BF) has been recognized as a potential lead-free ferroelectric material owing to its excellent intrinsic polarization ( $P > 100 \mu\text{C}/\text{cm}^2$ ),<sup>8</sup> which offers the greatest scope for enhancing energy-storage properties. It is known that undoped BF is not suitable for the energy-storage application due to its relatively high electrical leakage current.<sup>9</sup> Solid solutions of (1–*x*)BF–*x*BT exhibited a high  $P_{\max}$  at a rhombohedral to pseudocubic structural phase boundary (*x* = 0.33),<sup>10</sup> but their  $W$  values were very limited because of large energy loss from an obvious hysteresis and a large  $P_r$  value. Moreover, Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (BMN) is a typical B-site complex perovskite,<sup>11</sup> which has been used as a microwave dielectric material due to its high dielectric constant and very low dielectric loss.<sup>12</sup> The addition of BMN into BT was found to decrease  $P_r$  and slightly increase the dielectric breakdown strength ( $E_b$ ), both of which are beneficial to the improvement of energy-storage properties.<sup>13</sup>

In this communication, a new lead-free ferroelectric solid solution of (0.67–*x*)BF–0.33BT–*x*BMN was reported. The influence of the substitution of BMN for BF on the structure, dielectric, ferroelectric, and energy-storage properties was explored, concluding the mechanism of generating good energy-storage properties. An excellent energy-storage property ( $W = \sim 1.56 \text{ J}/\text{cm}^3$ ,  $\eta = \sim 75\%$ ) was attained in the *x* = 0.06 sample together with a desirable temperature stability from 25°C to 190°C.

## II. Experimental Procedures

The (0.67–*x*)BF–0.33BT–*x*BMN (*x* = 0–0.1) ceramics were synthesized by a conventional solid-state reaction route using high-purity powders of Bi<sub>2</sub>O<sub>3</sub> ( $\geq 99.0\%$ ), Fe<sub>2</sub>O<sub>3</sub> ( $\geq 99.0\%$ ), BaCO<sub>3</sub> ( $\geq 99.0\%$ ), TiO<sub>2</sub> ( $\geq 99.0\%$ ), 4MgCO<sub>3</sub>Mg(OH)<sub>2</sub>·5H<sub>2</sub>O ( $\geq 99.0\%$ ), and Nb<sub>2</sub>O<sub>5</sub> ( $\geq 99.0\%$ ). The stoichiometric powder mixtures were calcined at 700°C–800°C for 12 h. The synthesized powders were uniaxially pressed into pellets with 10 mm in diameter. Sintering was performed in the temperature range of 980°C–1020°C for 2 h in closed alumina crucibles at a heating rate of 5°C/min.

The grain morphology of the pellets was observed by a scanning electron microscope (SEM; JEOL JSM 6490LV, Tokyo, Japan). Electrical properties were measured after silver electrodes were fired on major surfaces of the samples at 550°C for 30 min. Dielectric properties were measured as a function of temperature (25°C–500°C) and frequency (10–1000 kHz) using an LCR meter (Agilent E4980A, Santa Clara, CA) for virgin samples. The  $P$ – $E$  loops and strain versus electric field curves ( $S$ – $E$ ) were measured using a ferroelectric measuring system (Precision multiferroelectric, Radiant Technologies Inc, Albuquerque, NM) connected with an accessory laser interferometer vibrometer (AE SP-S 120E, SIOS Meßtechnik, GmbH, Ilmenau, Germany).

X. Tan—contributing editor

Manuscript No. 36857. Received May 7, 2015; approved June 5, 2015.

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### III. Results and Discussion

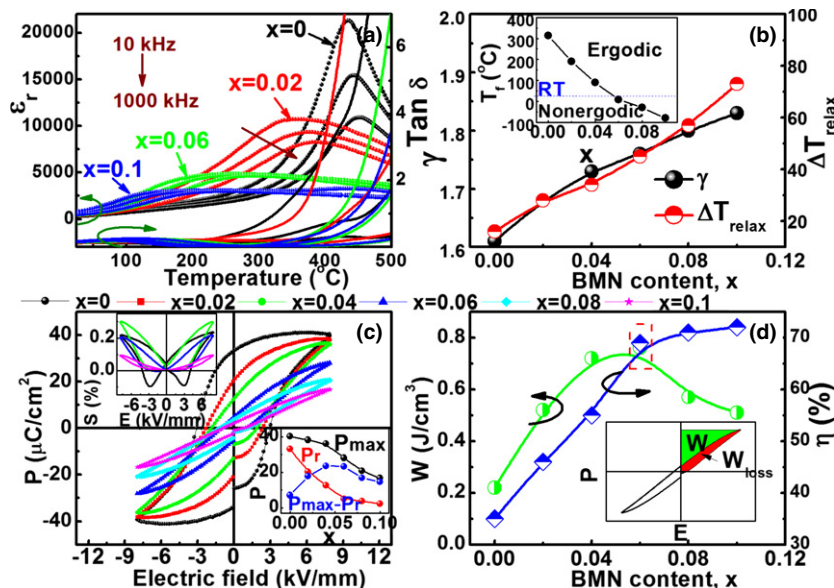
Figure 1(a) illustrates the temperature and frequency dependence of dielectric permittivity ( $\epsilon_r$ ) and loss tangent ( $\tan\delta$ ) for  $(0.67-x)\text{BF}-0.33\text{BT}-x\text{BMN}$  ceramics sintered at their optimal temperatures. Observably, all samples exhibited typical frequency dispersion and diffuse phase transition near the dielectric maximum temperature ( $T_m$ ). With increasing  $x$ , the maximum permittivity ( $\epsilon_m$ ) dramatically dropped and dielectric peaks became broader. Generally, the diffuseness degree of dielectric peaks can be calculated from a modified Curie-Weiss law  $1/\epsilon - 1/\epsilon_m = (T - T_m)/C$  at  $T > T_m$ , where  $\gamma$  is the indicator of the diffuseness degree.<sup>14</sup> In addition, the parameter  $\Delta T_{\text{relax}}$  defined as the difference between two  $T_m$  values measured at 1 MHz and 10 kHz is a rough estimation of the relaxation degree. It can be seen from Fig. 1(b) that with increasing  $x$ , a significant increase in these two parameters was observed, signifying the enhancement of dielectric relaxor behavior. The enhanced local random fields due to increased cation disorder leads to a gradual increase in the dynamics of polar nanoregions (PNRs) as well as a decrease in size of PNRs. A freezing temperature  $T_f$  can be obtained by fitting the measured dielectric permittivity versus temperature curves to the *Vogel-Fulcher* relationship,<sup>15</sup> as shown in the inset of Fig. 1(b), indicating that the relaxor phase at RT transformed from a nonergodic state to an ergodic state. In addition, the corresponding loss tangent was also found to decrease at elevated temperatures with increasing  $x$ , which should benefit to the energy-storage applications. This is partially attributed to a fine and dense microstructure (2–3  $\mu\text{m}$  in grain size, relative density of >96%) for BMN substituted compositions as confirmed by SEM.

As shown in Fig. 1(c), the  $0.67\text{BF}-0.33\text{BT}$  binary ceramics exhibited a saturated  $P$ - $E$  loop, which is typical of a nonergodic relaxor phase. It can be irreversibly transformed into a normal ferroelectric phase such that the  $x = 0$  sample has larger  $P_{\text{max}}$  and  $P_r$  simultaneously. With increasing  $x$ ,  $P_{\text{max}}$  exhibited only a gradual decrease but  $P_r$  decayed rapidly as a result of the reversibility of the ergodic to ferroelectric phase transition. As  $x$  was further increased, a long-range ferroelectric order would become difficult to be induced from an ergodic phase because of bigger energy barriers, leading to a quick drop of both  $P_{\text{max}}$  and  $P_r$  [see the lower right inset of Fig. 1(c)]. The achievement of the largest  $\Delta P = P_{\text{max}} - P_r$  ( $\sim 24 \mu\text{C}/\text{cm}^2$ ) at  $x = 0.06$  would be definitely beneficial to the

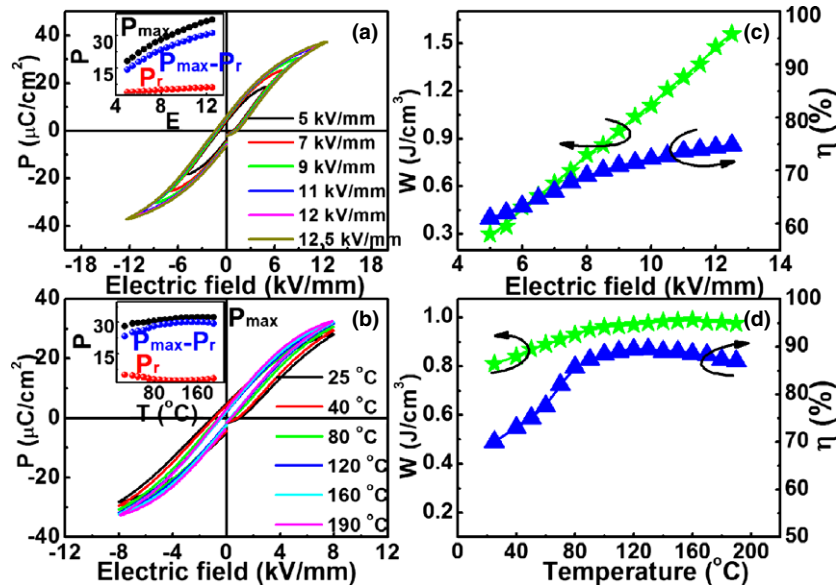
energy-storage density according to the integral formula:  $W = \int_{P_r}^{P_{\text{max}}} E \cdot dP$ . Figure 1(d) gives both  $W$  and  $\eta$  ( $\eta = W/(W + W_{\text{loss}})$ ,  $W_{\text{loss}}$  is the energy loss density) as a function of  $x$ , as also schematically displayed by the inset of Fig. 1(d). The  $W$  increased significantly with an increment of  $x$  and reached the maximum values of  $0.78\text{--}0.8 \text{ J}/\text{cm}^3$  at  $x = 0.04\text{--}0.06$ . Furthermore,  $\eta$  also increased sharply up to  $\sim 70\%$  at  $x \leq 0.06$ , and then rose slowly due to a dramatic decrease in the  $W$  value at  $x > 0.06$  in spite of a continuous decrease in the  $W_{\text{loss}}$  value. By comparison, excellent energy-storage properties ( $W \sim 0.8 \text{ J}/\text{cm}^3$  and  $\eta \sim 70\%$ ) under  $8 \text{ kV}/\text{mm}$  at RT) were obtained in the  $x = 0.06$  sample. For the same reason,<sup>16</sup> enhanced electrostrains were observed in the  $x = 0.04$  sample [see upper left inset of Fig. 1(c)]. However, bigger dynamic hysteresis of the ergodicity recovery during discharging for the  $x = 0.04$  sample led to smaller  $W$  values (larger  $P_r$ ) than the  $x = 0.06$  sample.

Figure 2 demonstrates the dependence of energy-storage properties of the  $x = 0.06$  sample on the electric field and temperature. With increasing the electric field,  $P_{\text{max}}$  was found to increase rapidly but  $P_r$  remained almost unchanged [Fig. 2(a)]. As a result, the  $\Delta P = P_{\text{max}} - P_r$  value increased linearly from  $14.4$  to  $32.3 \mu\text{C}/\text{cm}^2$  with increasing the field from  $2.5$  to  $12.5 \text{ kV}/\text{mm}$ . It can be, in principle, enhanced only if the applied electric field is below  $E_b$ . Therefore, both  $W$  and  $\eta$  increased with increasing the electric field, as shown in Fig. 2(c). As the electric field was  $12.5 \text{ kV}/\text{mm}$ ,  $W$  and  $\eta$  for the  $x = 0.6$  sample could reach as high as  $1.56 \text{ J}/\text{cm}^3$  and  $75\%$ , respectively, although its  $\eta$  value was still lower than that of linear dielectrics.<sup>17</sup> A comparison of ferroelectric and energy-storage properties among several lead-free ferroelectric ceramics was made in Table I. Although  $\text{BT}-\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$  was reported to have a much higher  $\eta$  value, yet its  $W$  value is relatively low. It can be seen that the  $\text{BF}-\text{BT}-\text{BMN}$  system ( $x = 0.06$ ) possessed a relatively high  $W$ , which is almost two times higher than that of  $\text{Nb}_2\text{O}_5$ -modified  $\text{BF}-\text{BT}$  ceramics.<sup>18</sup>

As we know, the size of PNRs becomes smaller and the dynamics of PNRs increases with increasing temperature. Moreover, the content of nonergodic phases in the sample will gradually decrease with increasing temperature until the sample enters into a complete ergodic phase zone at high temperatures. As shown in Fig. 2(b), a slow and slight increase in the  $P_{\text{max}}$  value with increasing temperature was



**Fig. 1.** (a) Dielectric properties with changing temperature and frequency for  $(0.67-x)\text{BF}-0.33\text{BT}-x\text{BMN}$  ceramics, (b) the variation in  $\Delta T_m$  and  $\gamma$  values as a function of  $x$ ; the inset shows the  $T_f$  value as a function of  $x$ , (c)  $P$ - $E$  loops of  $(0.67-x)\text{BF}-0.33\text{BT}-x\text{BMN}$  ceramics; the lower right inset shows characteristic values of polarization as a function of  $x$  and the upper left inset indicates bipolar  $S$ - $E$  loops, and (d) both  $W$  and  $\eta$  as a function of  $x$ ; the inset schematically displays the formation of  $W$  and  $W_{\text{loss}}$  in a  $P$ - $E$  loop.



**Fig. 2.**  $P$ - $E$  loops measured at RT under different (a) electric fields and (b) temperature for the  $x = 0.06$  sample, and both  $W$  and  $\eta$  values as a function of (c) electric field and (d) temperature. The insets in Figs. 2(a) and (b) show the  $P_{\max}$ ,  $P_r$ , and  $P_{\max}-P_r$  values under various electric fields and temperatures, respectively.

**Table I.** Comparison of Ferroelectric and Energy-Storage Properties Between  $(0.67-x)\text{BF}-0.33\text{BT}-x\text{BMN}$  ( $x = 0.06$ ) Ceramics and Other Lead-Free Ceramics

Compounds	$E$ (kV/mm)	$P_{\max}$ ( $\mu\text{C}/\text{cm}^2$ )	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$W$ ( $\text{J}/\text{cm}^3$ )	$\eta$ (%)	References
BNT-BT-KNN	5.6	~21	~8.9	0.59	/	[3]
BNT-BT-KN	10	~28	~2.6	0.89	~73	[4]
BNKT-KNN	10	~32	~4.7	1.2	/	[5]
BST	23	~6	~0.3	0.89	/	[6]
BT-Bi( $\text{Mg}_{2/3}\text{Nb}_{1/3}$ ) $\text{O}_3$	14	~14	~0.4	1.13	~93	[7]
BF-BT-Nb $_2\text{O}_5$	9	~25	~5.3	0.71	/	[18]
BF-BT-BMN	12.5	~38	~5.7	1.56	~75	This study

( $\text{K}_{0.5}\text{Na}_{0.5}$ ) $\text{NbO}_3$ , KNN;  $\text{KNbO}_3$ , KN; ( $\text{Bi}_{0.5}\text{Na}_{0.5-x}\text{K}_x$ ) $\text{TiO}_3$ , BNKT;  $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ , BST.

observed, meaning that ergodic and/or nonergodic relaxor states could be transformed into a long-range ferroelectric order. A gradual decrease in  $P_r$  with increasing temperature was attributed to both the decrease in the nonergodic phase content and the increase in PNR dynamics. As a result, the  $\Delta P = P_{\max} - P_r$  value varied slightly from 24 to 29  $\mu\text{C}/\text{cm}^2$  as measuring temperature increased from RT to 190°C [see the inset of Fig. 2(b)]. For the same reason, the calculated  $W$  values slightly fluctuated between 0.8 and 0.98  $\text{J}/\text{cm}^3$  within a broad temperature range, as shown in Fig. 2(d). However, the  $\eta$  values changed obviously from 75% to 90% with increasing temperature. On one hand, the decrease in the amount of nonergodic phases would lead to the lack of domain reorientation during the discharging process. On the other hand, the increased ergodic PNR dynamics should largely decrease the hysteresis effect of the field-induced ferroelectric phase back to ergodic phases.<sup>16,19</sup> When the temperature was above 160°C, the  $W$  and  $\eta$  values slightly decreased due to the increase in conductivity. BNT-BT-KNN ceramics were reported to own a temperature insensitive energy-storage characteristic as a result of the stable antiferroelectric-like phase (ergodic relaxor phase) over a wide temperature range.<sup>3</sup> According to our results, ergodic relaxor phases should be at least capable of being transformed into a long-range ferroelectric order within the required temperature range. An excellent temperature stability of energy-storage properties observed in the  $x = 0.06$  sample should largely benefit from both the diffuse phase transformation process

and the ergodic-nonergodic phase coexistence in a wide temperature range.<sup>16</sup>

#### IV. Conclusions

The lead-free  $(0.67-x)\text{BF}-0.33\text{BT}-x\text{BMN}$  solid solution ceramics were successfully prepared. The substitution of BMN for BF was found to induce a typical dielectric relaxor behavior, during which a relatively high  $P_{\max}$  of 38  $\mu\text{C}/\text{cm}^2$  and a low  $P_r$  of 5.7  $\mu\text{C}/\text{cm}^2$  were obtained under 12.5 kV/mm in the  $x = 0.06$  sample, leading to an energy-storage density of  $W \sim 1.56 \text{ J}/\text{cm}^3$  and energy-storage efficiency of  $\eta \sim 75\%$ . Moreover, a good temperature stability of the energy storage was obtained in the  $x = 0.06$  sample from 25°C to 190°C. The achievement of these characteristics was basically attributed to both a diffuse phase transformation process and an electric field induced reversible ergodic to ferroelectric phase transition.

#### Acknowledgments

Financial support from the National Natural Science Foundation of China (grant no. 51472069, U1432113, 51332002) and the Anhui Provincial Natural Science Foundation (1508085JGD04) is gratefully acknowledged.

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