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# Novel BaTiO<sub>3</sub>-Based, Ag/Pd-Compatible Lead-Free Relaxors with Superior Energy Storage Performance

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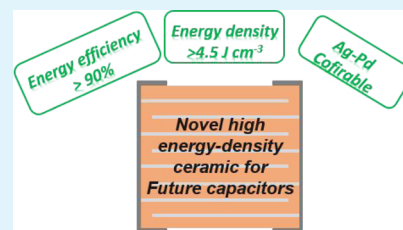
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Supporting Information

**ABSTRACT:** Ceramic dielectrics are reported with superior energy storage performance for applications, such as power electronics in electrical vehicles. A recoverable energy density ( $W_{\text{rec}}$ ) of  $\sim 4.55 \text{ J cm}^{-3}$  with  $\eta \sim 90\%$  is achieved in lead-free relaxor BaTiO<sub>3</sub>-0.06Bi<sub>2/3</sub>(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramics at  $\sim 520 \text{ kV cm}^{-1}$ . These ceramics may be co-fired with Ag/Pd, which constitutes a major step forward toward their potential use in the fabrication of commercial multilayer ceramic capacitors. Compared to stoichiometric Bi(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>-doped BaTiO<sub>3</sub> (BT), A-site deficient Bi<sub>2/3</sub>(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> reduces the electrical heterogeneity of BT. Bulk conductivity differs from the grain boundary only by 1 order of magnitude which, coupled with a smaller volume fraction of conducting cores due to enhanced diffusion of the dopant via A-site vacancies in the A-site sublattice, results in higher breakdown strength under an electric field. This strategy can be employed to develop new dielectrics with improved energy storage performance.

**KEYWORDS:** energy storage, capacitors, lead-free, BaTiO<sub>3</sub>, dielectric, ceramics



## 1. INTRODUCTION

Energy storage technologies such as lithium-ion batteries and electrolytic super-capacitors have been the focus of much recent research.<sup>1,2</sup> Batteries provide long-lasting energy/power through a continuous slow discharge rate whereas super-capacitors charge and discharge more rapidly and are primarily used in kinetic energy recovery systems.<sup>3–10</sup> However, their polymeric components mean that they have limited temperature stability.<sup>11</sup> In contrast, ceramic dielectric capacitors do not offer such high energy density but are stable above 100 °C and are finding applications in high temperature, high power electronics in electric vehicles, and in pulsed power and laser applications.<sup>12–15</sup>

The total energy density

$$W_{\text{total}} = \int E dP \quad (1)$$

recoverable energy density

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP \quad (2)$$

and energy conversion efficiency

$$\eta = \frac{W_{\text{rec}}}{W_{\text{total}}} \quad (3)$$

for nonlinear dielectric capacitors are obtained from the integration of polarization–electric field ( $P$ – $E$ ) loop, where  $P_{\text{max}}$  is maximum polarization and  $P_r$  is remanent polarization. Therefore, both large  $\Delta P$  ( $P_{\text{max}} - P_r$ ) and maximum applied electric field ( $E_{\text{max}}$ ) are desirable for achieving high  $W_{\text{rec}}$  and  $\eta$ .

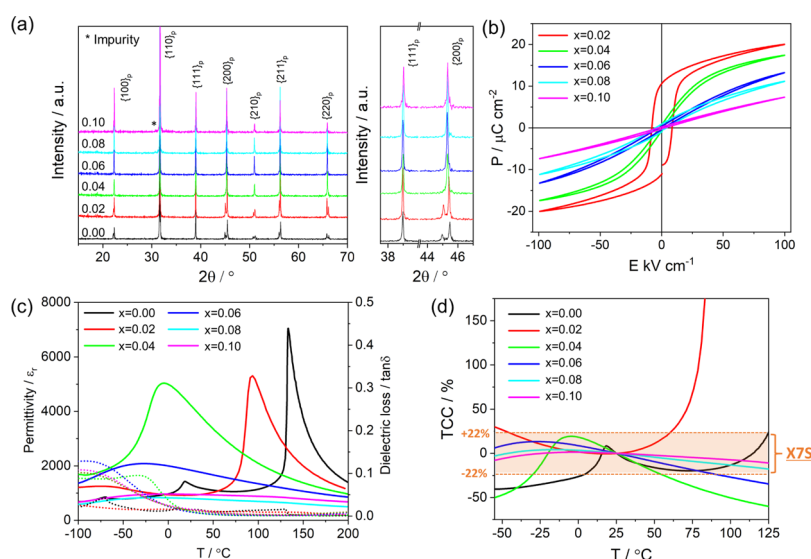
The  $W_{\text{rec}}$  and  $\eta$  for ferroelectrics (FEs) are restricted because of low  $\Delta P$  and  $E_{\text{max}}$ . Instead, weakly nonlinear relaxor-FEs (RFEs) and anti-FEs (AFEs) are generally proposed as potential candidates for high energy density ceramic capacitors, with compositions commonly based on BaTiO<sub>3</sub>(BT),<sup>16–25</sup> Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>(NBT),<sup>26–29</sup> BiFeO<sub>3</sub>(BF),<sup>30–37</sup> NaNbO<sub>3</sub>(NN),<sup>38–40</sup> K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>(KNN),<sup>41–44</sup> and AgNbO<sub>3</sub>(AN) ceramics.<sup>13,45,46</sup> Even though excellent  $E_{\text{max}}$  ( $> 400 \text{ kV cm}^{-1}$ ) and  $\eta$  ( $> 80\%$ ) have been achieved in RFE ceramics,  $W_{\text{rec}}$  is still limited by low  $P_{\text{max}}$  ( $< 45 \mu\text{C cm}^{-2}$ ) which requires further improvement to achieve  $W_{\text{rec}} > 4 \text{ J cm}^{-3}$ . AFEs possess larger  $P_{\text{max}}$  at an intermediate electric field ( $\sim 300 \text{ kV cm}^{-1}$ ) but saturation of the polarization restricts  $W_{\text{rec}}$  and they often exhibit low  $\eta$  ( $< 70\%$ ) because of the field induced transition to the FE state.

BT-based ceramics are commercially the most attractive candidates for high energy density storage since they are already utilized for consumer electronics at low fields as filters and de-couplers. The first example of improved  $W_{\text{rec}}$  ( $2.3 \text{ J cm}^{-3}$  at  $225 \text{ kV cm}^{-1}$ ) for BT-based compositions was 0.7BT-0.3BiScO<sub>3</sub> (0.7BT-0.3BS) bulk ceramics, whose properties

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**Figure 1.** (a) X-ray powder diffraction patterns in a  $2\theta$  range from 15 to  $70^\circ$  with representative  $\{111\}_p$  and  $\{200\}_p$  XRD reflections for  $x\text{B}_{2/3}\text{MN-BT}$ . (b) Bipolar  $P$ – $E$  loops and (c) temperature-dependent  $\epsilon_r$  (Solid line) and  $\tan \delta$  (Dashed line) data for  $x\text{B}_{2/3}\text{MN-BT}$  ceramics with  $x = 0.00$ – $0.10$ . (d) TCC value for  $x\text{B}_{2/3}\text{MN-BT}$  ceramics with  $x = 0.00$ – $0.10$  in a temperature range from  $-55$  to  $125^\circ\text{C}$ .

were enhanced to  $6.1\text{ J cm}^{-3}$  in multilayer ceramic capacitors (MLCCs).<sup>25</sup> The same research group reported 0.7BT-0.3BS MLCCs which exhibited much better temperature stability ( $<15\%$  from 0 to  $300^\circ\text{C}$ ) and  $W_{\text{rec}}$  compared with commercial X7R (poor temperature stabilities) and C0G (low  $W_{\text{rec}}$  and  $E_{\text{max}}$ ) capacitors.

Stoichiometric  $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$  (BMN) is a commonly reported third end-member or dopant in perovskite solid solutions and has been shown to optimize  $W_{\text{rec}}$  by promoting a weakly nonlinear relaxor state.<sup>25,47,48</sup> Solid solutions which incorporate a range of ion sizes and valences on the A and B sites of the perovskite structure disrupt coupling between polarisable species ( $\text{Bi}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{Nb}^{5+}$ ), reducing  $P_r$  but simultaneously creating an “active solid solution” of local disordered regions within a pseudocubic matrix, which can be addressed by an electric field leading to high  $P_{\text{max}}$ .<sup>49</sup>

This strategy has been adopted in many lead-free systems to effectively enhance  $\Delta P$  and  $W_{\text{rec}}$ , for example, 0.10 BMN-BT ( $1.18\text{ J cm}^{-3}$ ),<sup>50</sup> 0.06 BMN-BF-BT ( $1.56\text{ J cm}^{-3}$ ),<sup>51</sup> 0.15 BMN-NN ( $2.8\text{ J cm}^{-3}$ ),<sup>38</sup> and 0.10 BMN-KNN ( $4.08\text{ J cm}^{-3}$ ).<sup>41</sup> Such dopant strategies are often accompanied by an increase in electrical homogeneity and reduction of grain size/porosity, leading to enhanced  $E_{\text{max}}$ .<sup>33,36,43,52</sup> However, the role of A-site vacancies ( $V_A$ ) is rarely addressed in “active solid solutions”.

In this study, a solid solution of BT with A-site deficient  $\text{Bi}_{2/3}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  ( $\text{B}_{2/3}\text{MN}$ ) has been synthesized and the role of  $V_A$  in optimizing  $E_{\text{max}}$  and  $W_{\text{rec}}$  is investigated. Small concentrations of  $V_A$  have been reported previously to improve the conductivity of lead-free dielectrics, such as  $\text{SrTiO}_3$  (ST) and BT.<sup>53–55</sup> In addition, we postulate that  $V_A$  reduces the concentration of Bi based alloying addition required to induce a weakly nonlinear relaxor state, thereby enhancing compatibility with conventional Ag–Pd electrodes which react with Bi at high temperatures.

We demonstrate that A-site deficient  $x\text{B}_{2/3}\text{MN-BT}$  exhibits a bulk and grain boundary response similar to conventional BMN-BT ceramics but the total conductivity is at least one order of magnitude lower. The lower conductivity leads to an enhancement of  $E_{\text{max}} \sim 520\text{ kV cm}^{-1}$  ( $\sim 270\text{ kV cm}^{-1}$  for

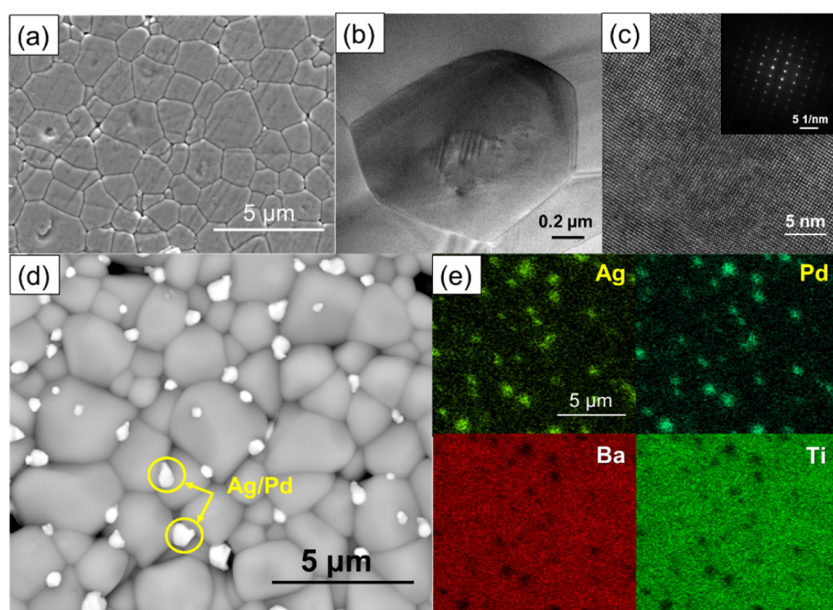
BMN-BT) and results in  $W_{\text{rec}} \sim 4.55\text{ J cm}^{-3}$  and  $\eta \sim 92\%$  in compositions with  $x = 0.06$ . Although several materials have similar  $W_{\text{rec}}$ ,<sup>17–19</sup> A-site deficient  $x\text{B}_{2/3}\text{MN-BT}$  compositions were also shown to be compatible with Ag–Pd metal, suggesting potential for commercialization as high-voltage, high-temperature MLCCs.

## 2. EXPERIMENTAL PROCEDURES

A-site deficient  $x\text{Bi}_{2/3}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-(1-x)\text{BaTiO}_3$  ( $x\text{B}_{2/3}\text{MN-BT}$ ) ceramics, with ( $x = 0.00, 0.02, 0.04, 0.06, 0.08, \text{ and } 0.10$ ) solid solution were synthesized using a conventional solid-state reaction with analytical-grade raw powders of  $\text{BaCO}_3$  ( $>99.5\%$ ),  $\text{TiO}_2$  ( $>99.9\%$ ),  $\text{MgO}$  ( $>99.9\%$ ),  $\text{Nb}_2\text{O}_5$  ( $>99.5\%$ ), and  $\text{Bi}_2\text{O}_3$  ( $>99.9\%$ ). Excess 0.5 mol %  $\text{Bi}_2\text{O}_3$  was added to compensate for Bi-loss during processing and  $\text{Li}_2\text{CO}_3$  was used as a fluxing agent to reduce the sintering temperature.<sup>56–58</sup> Mixed powders were ball milled for 16 h, dried, and calcined 2 h at  $900^\circ\text{C}$ . After calcination, the mixed powder was ball milled for 16 h, dried, and uniaxially pressed into 10 mm diameter pellets, followed by sintering 4 h from  $1050$ – $1200^\circ\text{C}$ . The density of sintered ceramic pellets was evaluated using the Archimedes principle, yielding relative densities  $>95\%$  of theoretical. To investigate the chemical compatibility of A-site deficient  $x\text{B}_{2/3}\text{MN-BT}$  with the Ag–Pd (70–30%) electrode, 20 wt % of Ag–Pd electrode ink was mixed with ceramic powders and co-fired 4 h in air at  $1100^\circ\text{C}$ .

X-ray diffraction (XRD) was performed using a D2 phaser X-ray diffractometer on crushed pellets, annealing for 5 h in air at  $550^\circ\text{C}$  to eliminate residual stress. Specimens for scanning electron microscopy (SEM) were ground, polished, thermally etched at  $1080^\circ\text{C}$  for 30 min, and carbon coated. Thermally etched ceramics were evaluated using an FEI Inspect F50 SEM, equipped with backscattered electron (BSE) and energy-dispersive X-ray spectroscopy (EDX) detectors. Samples for transmission electron microscopy (TEM) were ground manually to  $\sim 50\text{ }\mu\text{m}$ , followed by polishing to electron transparency using an Argon ion mill (PIPS II 69S, Gatan, USA). Samples were examined with a JEOL JEM 2100F (JEOL, Tokyo, Japan) operated at 200 kV.

Ceramic pellets for electrical measurements were ground to 0.2 mm, gold sputter-coated for 1 min. FE  $P$ – $E$  measurements were performed using an aixACCT TF2000E system with a 1 Hz triangular signal. Temperature-dependent permittivity and loss were examined using an Agilent 4184A precision LCR meter from  $-100$  to  $200^\circ\text{C}$  from 1 kHz to 1 MHz. The electrical microstructure was evaluated



**Figure 2.** (a) Thermal-etched SEM surface image for 0.06B<sub>2/3</sub>MN-BT ceramic. (b) Bright-field TEM image of grains in 0.06B<sub>2/3</sub>MN-BT ceramics. (c) High-resolution TEM images with  $\langle 110 \rangle$  diffraction patterns. (d) BSE surface micrographs of Ag–Pd co-fired 0.06B<sub>2/3</sub>MN-BT ceramics. (e) EDX mapping distribution of Ag, Pd, Ba, and Ti elements.

using an Agilent E4980A impedance AC analyzer from room temperature (RT) to 800 °C at 25 °C intervals on heating. Impedance data ( $Z''$  and  $M''$ ) were normalized by a geometric factor (thickness/surface area) and fitted using ZView software (Scribner Associates, Inc., Southern Pines, NC), as reported previously.<sup>59–61</sup>

### 3. RESULTS AND DISCUSSION

#### 3.1. Crystal Structure, Dielectric, and FE Properties.

The crystal structure of ceramic powders was examined using XRD data collected in 15–70°  $2\theta$  range, as shown Figure 1a. A single-phase perovskite is observed for compositions with  $x \leq 0.06$ . A secondary phase (peaks labelled in Figure 1a) is presented in  $x = 0.08$  and  $x = 0.10$ , indicating that the solubility limit of B<sub>2/3</sub>MN in BT has been reached. Doublets merge into single peaks as  $x$  increases, suggesting a transformation from tetragonal into pseudocubic symmetry, in which the correlation length of polar order decreases. Full-pattern refinement of the diffraction data for all single-phase compositions was carried out, Table S1 (Supporting Information), confirming a pseudocubic phase for  $x > 0.02$ , Figure S1 (Supporting Information).

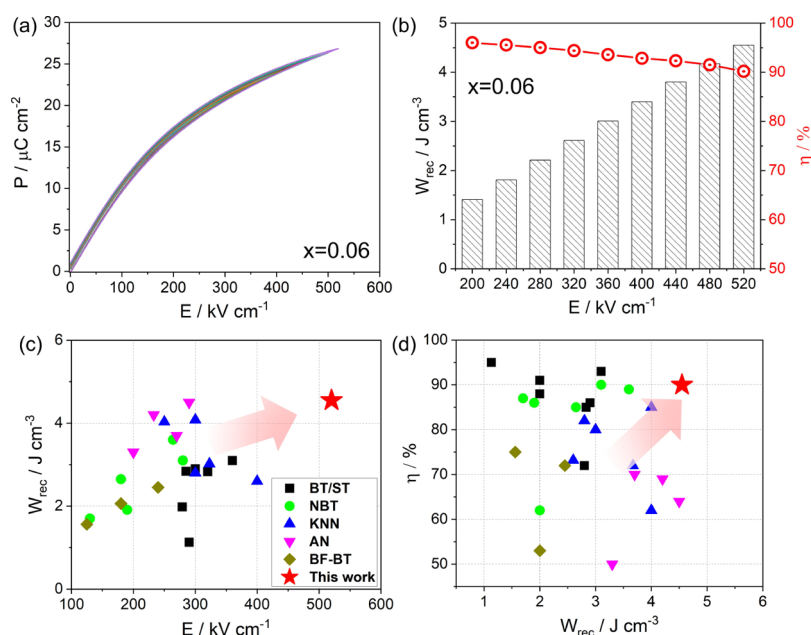
Bipolar P–E loops obtained at 100 kV cm<sup>−1</sup> for  $x$ B<sub>2/3</sub>MN-BT ceramics are displayed in Figures 1b and S2 (P–E loop for BT at 60 kV cm<sup>−1</sup>, Supporting Information). A FE P–E loop is observed for  $x = 0.00$  and 0.02, with  $P_{\max} \sim 20 \mu\text{C cm}^{-2}$  and  $P_r \sim 12 \mu\text{C cm}^{-2}$ . Both  $P_{\max}$  and  $P_r$  reduce gradually but  $\Delta P$  increases with  $x$ , indicating a FE to RFE transition. The temperature-dependent relative permittivity ( $\epsilon_r$ , solid line) and dielectric loss ( $\tan \delta$ , dashed line) at 100 kHz for  $x$ B<sub>2/3</sub>MN-BT ceramics are shown in Figure 1c. The sharp anomalies for BT at  $\sim 135$  °C ( $\epsilon_r \sim 7000$ ), 22 °C ( $\epsilon_r \sim 1750$ ), and  $-70$  °C ( $\epsilon_r \sim 950$ ) correspond to the cubic–tetragonal, tetragonal–orthorhombic, and orthorhombic–rhombohedral phase transitions, respectively.<sup>62</sup> As  $x$  increases, the maximum  $\epsilon_r$  decreases continuously reaching 1000 for  $x = 0.10$ , which shows a rather temperature independent  $\epsilon_r$ . Temperature-independent permittivity were reported for conventional BMN-BT solid solution by Reaney and co-workers with temperature

coefficient of capacitance (TCC)  $< \pm 15\%$ .<sup>63</sup> Here, TCC values for  $x$ B<sub>2/3</sub>MN-BT ( $x \geq 0.04$ ) at 100 Hz were calculated, as shown Figure 1d, with  $x = 0.08$  and  $x = 0.10$  exhibiting TCC  $< \pm 22\%$  from  $-55$  to 125 °C, corresponding to an X7S specification. Frequency-dependent dielectric properties for  $x$ B<sub>2/3</sub>MN-BT ceramics are shown in Figure S3 (Supporting Information). A frequency-independent dielectric peak occurs at  $\sim 135$  and 102 °C for  $x = 0.00$  and  $x = 0.02$ , respectively, corresponding to the Curie temperature ( $T_c$ ) but a frequency dispersion is observed in  $\epsilon_r - T$  curve for  $x > 0.02$ , indicating relaxor behavior.

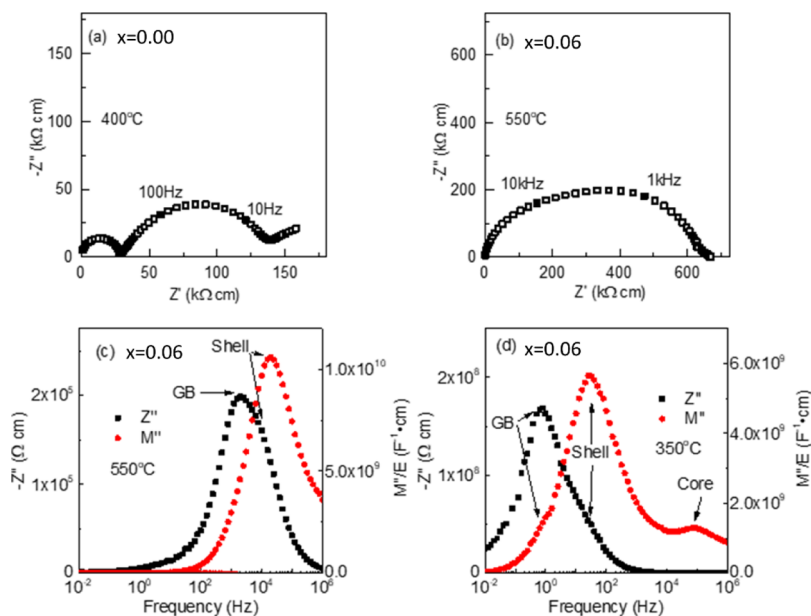
**3.2. Microstructure.** SEM images of thermal-etched surfaces for  $x$ B<sub>2/3</sub>MN-BT ceramics are shown in Figure 2a ( $x = 0.06$ ) and Figure S4 (Supporting Information). The average grain size reduces with increasing  $x$  from 25  $\mu\text{m}$  for  $x = 0.00$  to  $\sim 2.8 \mu\text{m}$  for  $x = 0.06$ , Table S2 (Supporting Information). Secondary phases are observed for  $x = 0.08$  and  $x = 0.10$  at the grain boundary. TEM images of a ceramic with  $x = 0.06$ , as shown in Figure 2b,c, revealed some cores with FE or tweed-like domains surrounded by a largely featureless pseudocubic shell (Figure 2b).

Most research into BT-based MLCCs with superior  $W_{\text{rec}}$  utilize Pt as inner electrodes; however, the use of such expensive noble metal precludes their commercial exploitation in mass production applications.<sup>17–19,24,64</sup> It is therefore, essential to evaluate compatibility of potential MLCCs dielectric layers against lower cost electrode systems such as Ni, Ag, or Ag–Pd. In the case of Bi-based or containing compounds, reaction with Ni is a well-known phenomenon, which is often accompanied by decomposition at the low  $p(\text{O}_2)$  required for co-firing with Ni internal electrodes.<sup>65,66</sup> The sintering of Bi-based compounds with pure Ag electrodes is also problematic and limited to co-firing at  $< 850$  °C because of melting of Ag. Even for systems which can co-fire at  $< 850$  °C, the reaction of Bi containing compounds with Ag is common depending on the thermodynamic stability of the Bi compound in the presence of Ag. This is exemplified by Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub> which reacts with Ag electrodes to form Ag-





**Figure 3.** (a) Unipolar P–E loops under  $E_{\text{max}}$  and (b) calculated  $W_{\text{rec}}$  and  $\eta$  at different electric field for  $0.06\text{B}_{2/3}\text{MN-BT}$  ceramics. (c) Comparisons of electric field vs  $W_{\text{rec}}$  and (d)  $W_{\text{rec}}$  vs  $\eta$  among lead-free dielectric ceramics, including BT-based,<sup>24,25,50</sup> NBT-based,<sup>26,27,29</sup> KNN-based,<sup>38,41,43,44</sup> AN-based,<sup>13</sup> and BF-based.<sup>30,31,36,51</sup> \*The author only used data points from the references to compare with our reported data and there is no any graphics that are reproduced from any other resource.



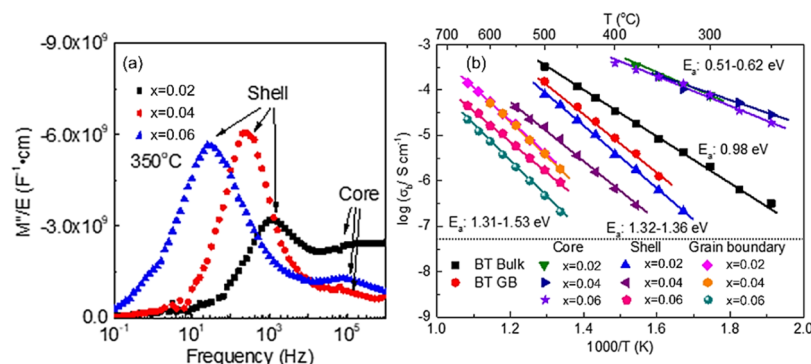
**Figure 4.**  $Z^*$  plots of  $x\text{B}_{2/3}\text{MN-BT}$  ceramics with (a)  $x = 0.00$  at 400 °C and (b)  $x = 0.06$  at 550 °C. Spectroscopic plots of  $Z''$  and  $M''$  for  $x = 0.06$  at (c) 550 and (d) 350 °C.

molybdate compounds.<sup>67</sup> The sintering temperature of compositions with  $x = 0.06$  is  $> 850$  °C, and therefore, the use of pure Ag can be ruled out but alternatively Ag–Pd alloys can be employed at higher temperatures.

In this study, we have therefore investigated the compatibility of  $0.06\text{B}_{2/3}\text{MN-BT}$  with Ag–Pd. SEM images and EDX mapping do not reveal chemical interaction between Ag–Pd particles and ceramic grains, as shown in Figure 2d,e, indicating that  $0.06\text{B}_{2/3}\text{MN-BT}$  is a promising material for the commercial fabrication of MLCCs.

**3.3. Energy Storage Performance.** The energy storage properties are obtained from unipolar P–E loops under the

$E_{\text{max}}$ . The low  $\Delta P$  and  $E_{\text{max}}$  ( $< 200$   $\text{kV cm}^{-1}$ ) of BT gave a poor response, as predicted, and the energy storage properties are not illustrated in this contribution. The unipolar P–E loops of  $x\text{B}_{2/3}\text{MN-BT}$  ( $0.02 \leq x \leq 0.08$ ) at  $E_{\text{max}}$  are shown in Figure S5a–d (Supporting Information), with corresponding  $E_{\text{max}}$  and  $\Delta P$  displayed in Figure S6a (Supporting Information). The highest  $E_{\text{max}} \sim 520$   $\text{kV cm}^{-1}$  and  $\Delta P \sim 25$   $\mu\text{C cm}^{-2}$  are both obtained for ceramics with  $x = 0.06$ , as shown Figure 3a. The  $W_{\text{rec}}$  and  $\eta$  for compositions with  $0.02 \leq x \leq 0.08$  are calculated and displayed in Figure S5e–h (Supporting Information). The highest  $W_{\text{rec}} \sim 4.55$   $\text{J cm}^{-3}$  and  $\eta \sim 90\%$  are obtained for  $0.06\text{B}_{2/3}\text{MN-BT}$  at  $E_{\text{max}} \sim 520$   $\text{kV cm}^{-1}$



**Figure 5.** (a) Spectroscopic plots of  $M''$  for  $x\text{B}_{2/3}\text{MN-BT}$  ceramics ( $0.02 \leq x \leq 0.06$ ) at  $350\text{ }^{\circ}\text{C}$ . (b) Arrhenius plot of conductivity of different components in  $x\text{B}_{2/3}\text{MN-BT}$  ( $0.00 \leq x \leq 0.06$ ).

(Figures 3b and S6b, Supporting Information), exhibiting the highest  $W_{\text{rec}}$  values compared to all reported BT-based lead-free ceramics to date (Figure 3c,d). Other systems have recently shown higher  $W_{\text{rec}}$  but this is accompanied by either poor efficiency ( $<70\%$ ) such as AN or cannot be co-fired with internal electrodes other than Pt, for example  $\text{BF}^{36}$  compounds.

**3.4. Electrical Microstructure.** Complex impedance plane plots and spectroscopic plots of  $Z''$  and  $M''$  data for  $x\text{B}_{2/3}\text{MN-BT}$  ceramics are given in Figure 4 for various temperatures. BT consisted of three components at  $400\text{ }^{\circ}\text{C}$ : two semicircles and a low-frequency spike, as shown in Figure 4a. These data were interpreted based on an equivalent circuit comprising three parallel resistor–capacitor elements connected in series.<sup>59–61</sup> The capacitance extracted from these three components from high to low frequency are 30 pF, 20 nF, and  $5\text{ }\mu\text{F}$  and are attributed to grain (bulk), grain boundary, and electrode responses, respectively. Contrary to BT, only one arc is observed in all  $x\text{B}_{2/3}\text{MN-BT}$  samples, for example,  $x = 0.06$  at  $550\text{ }^{\circ}\text{C}$ , as shown in Figure 4b. However, the inspection of the combined  $Z''$  and  $M''$  spectroscopic plots at  $550\text{ }^{\circ}\text{C}$  indicate this arc should consist of two semicircles representing two electroactive regions with similar resistivity, as shown in Figure 4c. The capacitances for high- and low-frequency arcs are 50 and 250 pF which correspond to grain and grain boundary contributions, respectively. In addition, one more  $M''$  peak is observed at lower temperatures ( $350\text{ }^{\circ}\text{C}$ ), as shown in Figure 4d. It has a corresponding capacitance of 200 pF which suggests it is also a bulk response. Therefore,  $x\text{B}_{2/3}\text{MN-BT}$  ceramics exhibit an electrical core–shell microstructure, in agreement with TEM images, as shown in Figure 2b. The change in capacitance ( $C = 1/2M''$ ) indicates a decreasing core and increasing shell volume fraction with increasing  $x$ , as shown in Figure 5a. Assuming the permittivity for the core and shell remains relatively similar for all  $x\text{B}_{2/3}\text{MN-BT}$  ceramics, the volume fraction of the core/shell region decreases from 40/60 to 20/80 for  $x = 0.02$  and  $x = 0.06$ , respectively. Similar bulk and grain boundary responses were also reported in conventional,  $y\text{BMN-BT}$  ( $y = 0.05\text{--}0.20$ ) ceramics but total resistivity obtained from  $Z''$ -plot for  $x\text{B}_{2/3}\text{MN-BT}$  is at least one order of magnitude larger, which explains the enhancement of  $E_{\text{max}}$ .<sup>50</sup>

The conductivity of different components in  $x\text{B}_{2/3}\text{MN-BT}$  are summarized in an Arrhenius plot, as shown in Figure 5b. The conductivity of the core,  $\sigma_{\text{b,core}}$ , of all three samples ( $x = 0.02, 0.04$ , and  $0.06$ ) are similar. However, with increasing  $x$ , the conductivity of the shell,  $\sigma_{\text{b,shell}}$ , and grain boundary,  $\sigma_{\text{gb}}$ ,

decreases by 2 and 1 order of magnitude, respectively. The activation energy,  $E_a$ , of both core and shell remains relatively unchanged at  $\sim 0.51\text{--}0.62\text{ eV}$  for  $\sigma_{\text{b,core}}$  and  $1.32\text{--}1.36\text{ eV}$  for  $\sigma_{\text{b,shell}}$ .  $\sigma_{\text{b}}$  and  $\sigma_{\text{gb}}$  of BT is lower than the  $\sigma_{\text{b,core}}$  of  $x\text{B}_{2/3}\text{MN-BT}$  ceramics but higher than the  $\sigma_{\text{b,shell}}$  with an  $E_a$  of 0.98 and 1.35 eV, respectively.

For BT ( $x = 0.00$ ),  $\sigma_{\text{gb}}$  is lower than  $\sigma_{\text{b}}$ , especially around RT because of the higher activation energy of  $\sigma_{\text{gb}}$  compared to  $\sigma_{\text{b}}$ . Under an electrical field, therefore, the voltage applied at the grain boundary is higher than the bulk which leads to a much higher local field. The enhancement of  $E_{\text{max}}$  in  $x\text{B}_{2/3}\text{MN-BT}$  (especially for  $x = 0.06$ ) is attributed to the following three facts: (i) the total conductivity,  $\sigma_{\text{total}}$ , decreases with increasing  $x$  doping level. The  $\sigma_{\text{total}}$  of composition with  $x = 0.06$  is  $\sim 3$  orders and  $>1$  order of magnitude lower than BT and BMN-BT ceramics, respectively, which leads to a reduction in leakage current under at a high field. (ii) The conductivity difference between bulk ( $\sigma_{\text{b,shell}}$  in  $x = 0.06$ ) and grain boundary response is higher in  $x = 0.00$  than  $x = 0.06$ . The difference in  $E_a$  is 0.32 and 0.22 eV compositions with  $x = 0.00$  and  $x = 0.06$ , respectively, which also means that the difference in  $\sigma_{\text{b,shell}}$  and  $\sigma_{\text{gb}}$  at RT is significantly smaller in  $0.06\text{B}_{2/3}\text{MN-BT}$  than BT. Despite the existence of some core–shell grains, the shell region constitutes  $\sim 80\%$  of the volume fraction of  $0.06\text{B}_{2/3}\text{MN-BT}$  and cannot be bypassed by the current. Thus, the voltage is more evenly distributed throughout the sample in  $0.06\text{B}_{2/3}\text{MN-BT}$  compare to BT which leads to a high  $E_{\text{max}}$ . (iii) the much smaller grain size of  $0.06\text{B}_{2/3}\text{MN-BT}$  ( $\sim 2.8\text{ }\mu\text{m}$ ) compared with BT ( $\sim 25\text{ }\mu\text{m}$ ) and BMN-BT ( $\sim 6\text{--}10\text{ }\mu\text{m}$ ) ceramics yields a higher volume fraction of the grain boundary and consequently reduces local electrical fields. We postulate that the lower volume fraction of cores in  $x\text{B}_{2/3}\text{MN-BT}$  is attributed to the greater diffusion rates of dopants through cubo-octahedral interstices in comparison with BMN-BT.

## 4. CONCLUSIONS

In summary, A-site deficient  $x\text{Bi}_{2/3}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-BT}$  ( $x\text{B}_{2/3}\text{MN-BT}$  with  $x = 0.00\text{--}0.10$ ) ceramics were successfully fabricated using the solid–state reaction. A phase transition from FE to RFE, associated with structural transformation from tetragonal to cubic, is observed in  $x\text{B}_{2/3}\text{MN-BT}$  ceramics with increasing  $x$ . A record high  $E_{\text{max}} \sim 520\text{ kV cm}^{-1}$  and  $W_{\text{rec}} \sim 4.55\text{ J cm}^{-3}$  for BT-based compositions were realized in ceramics with  $x = 0.06$  which may be co-fired with Ag–Pd without a chemical reaction. Impedance data revealed that the high  $E_{\text{max}}$  for  $0.06\text{B}_{2/3}\text{MN-BT}$  ceramics was because of a

reduction in the total electrical conductivity, with greater electrical homogeneity between different electrical components and an overall smaller volume fraction of cores. Compared to BMN-BT, the presence of  $V_A$  in  $x\text{B}_{2/3}\text{MN-BT}$  not only encouraged electrical homogeneity but also reduces the concentration of Bi on the A-site ensuring greater compatibility with Ag–Pd electrodes.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c13057>.

Full-pattern refinement of  $x\text{B}_{2/3}\text{MN-BT}$  ceramics with refined crystallography details; P–E loop for BT ceramics; frequency-dependent dielectric properties for  $x\text{B}_{2/3}\text{MN-BT}$  ( $x = 0.00 \leq x \leq 0.10$ ) ceramics; SEM image of thermal-etched surfaces for  $x\text{B}_{2/3}\text{MN-BT}$  ( $x = 0.00 \leq x \leq 0.10$ ) ceramics with average grain size information; and unipolar P–E loops under  $E_{\text{max}}$  and (e–h) calculated energy storage properties ( $W_{\text{rec}}$ ,  $\eta$ ,  $E_{\text{max}}$  and  $\Delta P$ ) at different electric fields for  $x\text{B}_{2/3}\text{MN-BT}$  ceramics (PDF)

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### Author Contributions

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### Notes

The authors declare no competing financial interest.

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## NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on September 21, 2020. Reference 47 was removed from the paper, and the subsequent references renumbered. The corrected version was reposted on September 21, 2020.