

STRUCTURAL, DIELECTRIC, AND ENERGY STORAGE PROPERTIES OF Ba²⁺ DOPED LEAD-FREE NaNbO₃-BASED CERAMICS

Pathit Premwichit¹ and Sasipohn Prasertpalichat^{1, 2,*}

Received: February 27, 2024; Revised: June 27, 2024; Accepted: November 20, 2024

Abstract

NaNbO₃-based antiferroelectric ceramics have recently attracted significant attention due to their potential in energy storage applications. This study explores the effect of barium (Ba²⁺) doping on the dielectric and energy storage properties of 0.88NaNbO₃-0.12Sr_{0.7}Bi_{0.2}TiO₃ (0.88Na_{1-2x}Ba_xNbO₃-0.12Sr_{0.7}Bi_{0.2}TiO₃, where $x = 0.0-0.025$) ceramics synthesized via the solid-state reaction method. The XRD results indicated that all samples possessed an orthorhombic structure. The transition temperature from the antiferroelectric *P* phase to *R* phase (T_{P-R}) significantly increased from 141°C at $x = 0.0$ to approximately 160°C for $x \geq 0.01$. Additionally, the dielectric loss ($\tan\delta$) within the temperature range of 32°C to 130°C for the 100xBa ceramic exhibited a notable reduction, decreasing from 0.012 ($x = 0.0$) to 0.002 ($x = 0.025$). As the Ba²⁺ doping content increased, the remnant polarization significantly decreased, leading to a narrower *P-E* hysteresis loop with enhanced energy storage density and efficiency. Consequently, the $x = 0.015$ composition achieved a maximum recoverable energy storage density of 0.28 J/cm³ and an energy storage efficiency of 76% under an applied electric field of 125 kV/cm. These findings guide the development of NaNbO₃-based antiferroelectric materials with enhanced energy storage.

Keywords: Lead-free ceramics; NaNbO₃-based compound; Dielectric properties; Energy storage performance

Introduction

Nowadays, the rapid advancement of science and technology has brought many benefits to daily lives. Concurrently, this advancement leads to the depletion of the world's non-renewable energy sources (i.e., oil, gas, and coal), making the development and deployment of renewable energy of great importance (Yao *et al.*, 2017;

Yang *et al.*, 2019a). In particular, the development of efficient energy storage devices can play a crucial role in mitigating this issue. Current energy storage devices are divided into four main types: batteries, dielectric capacitors, supercapacitors, and fuel cells (Bruce *et al.*, 2012; Li *et al.*, 2014; Wang *et al.*, 2016). Among these four types, dielectric

¹ Department of Physics, Faculty of Science, Naresuan University, Phitsanulok, Thailand. E-mail: pathitp64@nu.ac.th

² Research Center for Academic Excellent in Applied Physics, Faculty of Science, Naresuan University, Phitsanulok, Thailand. E-mail: sasipohnp@nu.ac.th

* Corresponding author

capacitors have been identified as a feasible option for energy storage systems, owing to their high energy density, rapid charge/discharge capabilities, and outstanding temperature stability, all of which enhance energy storage performance. (Hao, 2013; Liu *et al.*, 2018; Zhang *et al.*, 2020). For the current available dielectric materials, antiferroelectric (AFE) materials have been found to exhibit excellent energy storage performance due to their lower remnant polarization (P_r) and high maximum polarization (P_{max}), which arise from the phase transition between the antiferroelectric and ferroelectric phases (AFE–FE) (Hao *et al.*, 2009; Patel *et al.*, 2014). Consequently, AFE materials typically exhibit greater energy density than other dielectric materials. In the past, PbZrO₃ ceramics have been widely studied for ceramic capacitors due to their excellent dielectric energy storage characteristics (Yang *et al.*, 2019b). However, lead oxide toxicity poses environmental and health risks (Ellabban *et al.*, 2014). Therefore, researchers are increasing their efforts to accelerate the development and research of lead-free materials.

Lead-free AFE materials based on AgNbO₃ (AN) and NaNbO₃ (NN) ceramics have recently been identified as promising alternatives for energy storage, with the potential to substitute lead-based materials in the future (Megaw *et al.*, 1974; Chauhan *et al.*, 2015; Tian *et al.*, 2016). AgNbO₃-based ceramics have been observed to exhibit a typical dual hysteresis loop with large polarization under strong electric fields. Generally, AgNbO₃ ceramics have been extensively recognized for their relatively high recoverable energy storage density (W_{rec}), ranging from about 1.6–6.5 J/cm³ and an efficiency (η) of approximately 30–75% (Tian *et al.*, 2016; Zhao *et al.*, 2016; Gao *et al.*, 2019; Han *et al.*, 2019a; Han *et al.*, 2019b; Luo *et al.*, 2019; Lu *et al.*, 2021). However, the high cost of Ag₂O and the need for sintering in the oxygen (O₂) atmosphere are major hindrances for the mass production process (Tian *et al.*, 2016; Zhao *et al.*, 2017; 2018a; Han *et al.*, 2019a; Han *et al.*, 2019b). For this reason, researchers have focused their attention on another group of similar antiferroelectric materials.

NaNbO₃-based ceramics are another class of antiferroelectric perovskite compounds that have received great attention due to their easy preparation, low cost, and non-toxicity (Lanfredi *et al.*, 2002). Normally, pure NaNbO₃ ceramics mainly exhibit the AFE P phase ($Pbma$) with a coexistence of the ferroelectric Q phase ($P2_1ma$) at room temperature. Upon applying an external electric field, the AFE P phase readily converts into the ferroelectric Q phase due to a similar free energy profile (Shimizu *et al.*, 2014; Guo *et al.*, 2015), resulting in a characteristic ferroelectric P - E loop

with significant remnant polarization, which greatly limits its use as an energy storage dielectric (Mishra *et al.*, 2007). Recently, progress has been made in stabilizing the AFE phase by doping in NaNbO₃-based ceramics. For instance, Qi *et al.* (Qi *et al.*, 2019a) doped both BaZrO₃ and CaZrO₃ into an NaNbO₃-based ceramic system. They observed stabilized AFE phase at ambient temperature, featuring a double hysteresis P - E loop, which resulted in a relatively high W_{rec} of approximately 1.59 J/cm³ but a low $\eta = \sim 30\%$ in 0.9NaNbO₃-0.06BaZrO₃-0.04CaZrO₃ ceramics. However, despite having the double hysteresis loop with large P_m and small P_r , NaNbO₃-based ceramics still show relatively low W_{rec} and low η values due to large hysteresis during the reversible AFE-FE phase transition (Kittel *et al.*, 1951; Chauhan *et al.*, 2015). These limitations have hindered the progress of NaNbO₃-based energy storage properties. One potential solution is to introduce a local random field that can induce relaxation behavior, thereby disrupting the ferroelectric order and ultimately leading to higher energy storage performance (Zuo *et al.*, 2016). For instance, Qi *et al.* (Qi *et al.*, 2019a) discovered that introducing Bi_{0.5}Na_{0.5}TiO₃ into NaNbO₃ ceramics led to relaxor AFE characteristics, leading to a high W_{rec} (12.2 J/cm³) and η (69 %). The above research found that NaNbO₃ ceramics modified with ABO₃ still have a relatively low efficiency (< 80%) (Zhou *et al.*, 2018; Zuo *et al.*, 2018; Qi *et al.*, 2019a; Fan *et al.*, 2020; Shi *et al.*, 2020; Tian *et al.*, 2020; Xie *et al.*, 2020; Ye *et al.*, 2021). Recent studies show that incorporating A or B-site elements into the NaNbO₃-ABO₃ system contributes to improving energy storage efficiency. For example, Wang *et al.* (Wang *et al.*, 2021) doped Sm³⁺ at the A-site into the NaNbO₃-0.12Sr_{0.7}Bi_{0.2}TiO₃ system. They chose to add 0.12Sr_{0.7}Bi_{0.2}TiO₃, which enhances the antiferroelectricity in NaNbO₃ ceramics. Moreover, the addition of Sm³⁺ led to a significant phase transition from the antiferroelectric P phase to the antiferroelectric R phase, reducing P_r and increasing P_m , leading to a large W_{rec} (3.58 J/cm³) and a high η (82%) at 200 kV/cm for NN-SBT-2Sm. However, there are few reports on the energy storage properties of doped elements in NaNbO₃-ABO₃ ceramics (Wang *et al.*, 2021; Cheng *et al.*, 2022c; Premwicht *et al.*, 2023). Therefore, further development of NaNbO₃-ABO₃ ceramics is crucial to achieving high energy storage performance.

Recently, barium carbonate (BaCO₃) has been utilized to enhance the energy storage performance of dielectric materials. For example, Han *et al.* (Han *et al.*, 2019c) studied the influence of BaCO₃ doping on AgNbO₃-based ceramic systems. It was found

that W_{rec} was as high as 2.3 J/cm^3 with the energy-storage efficiency of 46% for the $\text{Ag}_{0.96}\text{Ba}_{0.02}\text{NbO}_3$, which was attributed to the improved AFE stability, decreased P_r , and increased P_m . Meanwhile, the optimal composition demonstrated outstanding temperature stability between 20°C and 120°C . Similarly, a small amount of Ba^{2+} doping into the BiFeO_3 ceramic system resulted in a reduction of P_r (Das *et al.*, 2012). Therefore, it is reasonable to hypothesize that Ba^{2+} doping might be promising for enhancing the energy storage performance of perovskite compounds. For this reason, this research is interested in studying the effect of Ba^{2+} doping in $0.88\text{Na}_{1-2x}\text{Ba}_x\text{NbO}_3-0.12\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ ($x=0.0-0.025$) ceramics on structural and morphological characteristics, dielectric properties, and energy storage performance. The findings obtained from this study will serve as guidelines for further application of energy storage materials.

Experimental procedure

The $0.88\text{Na}_{1-2x}\text{Ba}_x\text{NbO}_3-0.12\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (denoted as $100x\text{Ba}$, where x is 0.0, 0.005, 0.01, 0.015, 0.02 and 0.025) were synthesized using the conventional solid-state reaction method. Powders of Na_2CO_3 (99.95–100.05%, Alfa Aesar), Nb_2O_5 (99.9%, Alfa Aesar), BaCO_3 (99.8%, Alfa Aesar), SrCO_3 ($\geq 99.9\%$, Sigma-Aldrich), Bi_2O_3 (99.9% Sigma-Aldrich), and TiO_2 ($\geq 99.9\%$ Sigma-Aldrich) were used as starting materials. These powders were weighed according to their stoichiometric ratios and ball-milled in anhydrous ethanol with zirconia balls for 24 h. The powder mixture was then calcined at 910°C for 5 h. The resulting calcined powders were milled again for 24 h, dried, and mixed with a binder containing 3 wt% polyvinyl butyral (PVB) resin. Subsequently, the mixture was then compacted into green pellets ($\sim 1 \text{ cm}$ in diameter) and sintered at $1,180-1,225^\circ\text{C}$ for 2 h in air, following a PVB burnout step at 400°C for 3 h. To minimize the loss of volatile Bi and Na, all samples were enclosed in powders of their respective compositions.

The phase composition was analyzed using X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer. The sample's surface morphology was analyzed with a Field Emission Scanning Electron Microscope (FE-SEM, Thermo Scientific Apreo S). The analysis was conducted on a mirror-like surface that were thermally etched at approximately 100°C below the sintering temperature, with a gold coating applied on the ceramics' surface. For electrical characterization, the sintered ceramics were polished to a thickness of 0.03–0.06 cm, then silver

electrodes were applied to both surfaces and fired at 700°C for 30 minutes. The temperature-dependent dielectric properties were measured using an LCR meter (HP, 4284A) at frequencies of 1, 10, and 100 kHz. The P - E hysteresis loops were recorded using a ferroelectric test system (Premier II, Radiant Technologies Inc, USA) at a measurement frequency of 1 Hz.

Results and Discussion

Figure 1(a) presents the XRD patterns of powdered $100x\text{Ba}$ ($x = 0-0.025$) sintered ceramics within the 2θ range of $20^\circ-70^\circ$. The detection of a pure perovskite phase in the samples with $x = 0-0.025$ suggests the formation of a complete solid solution within the resolution limit of the XRD instrument. However, for the composition with $x = 0.03$, the second phase was observed, as shown in Figure 1(a). This suggests that the solubility limit of Ba in NN-SBT ceramics is approximately 3 mol%. Figure 1(b) and Figure 1(c) shows the enlarged view of the XRD patterns in the 2θ range of $31^\circ-34^\circ$ and $45^\circ-48^\circ$, respectively. At a 2θ angle around 32.5° , the splitting of the (200)/(114) peaks was observed, while around 42° , an asymmetric single (200) peak was evident, confirming that all $100x\text{Ba}$ ceramics have an orthorhombic structure. The result obtained is consistent with the data reported in previous studies of $(\text{Na}_{1-3/2x}\text{Bi}_{3/2x})(\text{Nb}_{1-x}\text{Mg}_x)\text{O}_3$ (Jiang *et al.*, 2021) and $(1-x)\text{NaNbO}_3-x(\text{Bi}_{0.8}\text{Sr}_{0.2})(\text{Fe}_{0.9}\text{Nb}_{0.1})\text{O}_3$ (Jiang *et al.*, 2022) ceramics. Additionally, as the Ba content increased, the position of the diffraction peak shifted towards the lower 2θ angle, indicating lattice volume expansion, as shown in Figure 1(b). This expansion could be attributed to the larger ionic radius of Ba^{2+} ($r_{\text{Ba}} = 1.61\text{\AA}$) compared to that of Na^+ ($r_{\text{Na}} = 1.39\text{\AA}$) on the A-site (Shannon, 1976).

Figure 2(a)–(f) shows the FESEM images of the mirror-like surfaces of $100x\text{Ba}$ ($x = 0-0.025$) ceramics after thermal etching. The inset in each figure illustrates the grain-size distribution. All compositions exhibited a dense microstructure with low porosity. The average grain size was analyzed by the linear intercept method. The mean grain size decreased significantly from $3.57 \mu\text{m}$ (for $x = 0.0$) to $1.41 \mu\text{m}$ (for $x = 0.010$). With a further increase of x to 0.015, 0.02, and 0.025, it slightly increased to $1.48 \mu\text{m}$, $1.55 \mu\text{m}$, and $1.62 \mu\text{m}$, respectively, which are still smaller than that of the undoped composition. The results are in line with previous studies by Han *et al.* (Han *et al.*, 2019c) which found that doping Ba^{2+} into AgNbO_3 ceramics could inhibit grain growth. The fluctuation in grain size with Ba^{2+} doping content could be explained as follows: initially, the doping of Ba^{2+} may suppress

grain growth, resulting in a smaller grain size (Dechakupt *et al.*, 2011; Balakt *et al.*, 2016). However, as the amount of Ba²⁺ continues to increase, a liquid phase forms, adversely affecting the microstructure and leading to larger grain sizes. The findings align with prior studies (Huang *et al.*, 2019; Chen *et al.*, 2020a; Chen *et al.*, 2020b). In addition, the densities of all compositions were determined by Archimedes' method. With an increase in Ba²⁺ content, the density slightly increased from 4.40 g/cm³ (for $x = 0.0$) to 4.41 g/cm³

(for $x = 0.005$) before gradually decreasing to 4.39, 4.37, 4.37, and 4.35 g/cm³ for $x = 0.01, 0.015, 0.02$, and 0.025, respectively. The theoretical density of 4.55 g/cm³ for pure NaNbO₃ was used for the calculation of the relative density (Lanfredi *et al.*, 2002). In this study, it was found that the minimum density of 4.35 g/cm³ corresponds to a relative density above 94%. The elevated relative density signifies that all the synthesized ceramics possess outstanding properties (Wang *et al.*, 2021).

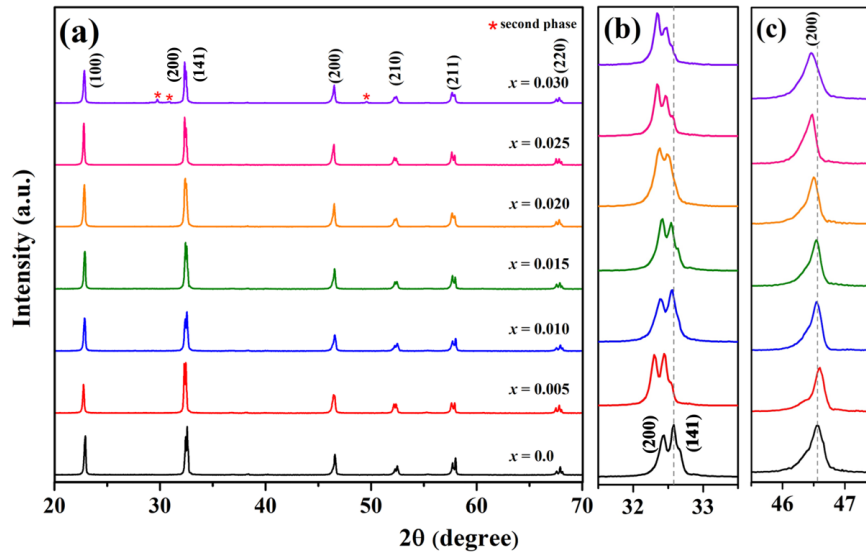


Figure 1. (a) X-Ray diffraction spectra of 100xBa ($x = 0–0.03$) crushed sintered ceramics at 2θ range of 20° – 70° and (b) 31° – 34° and (c) 45° – 48°

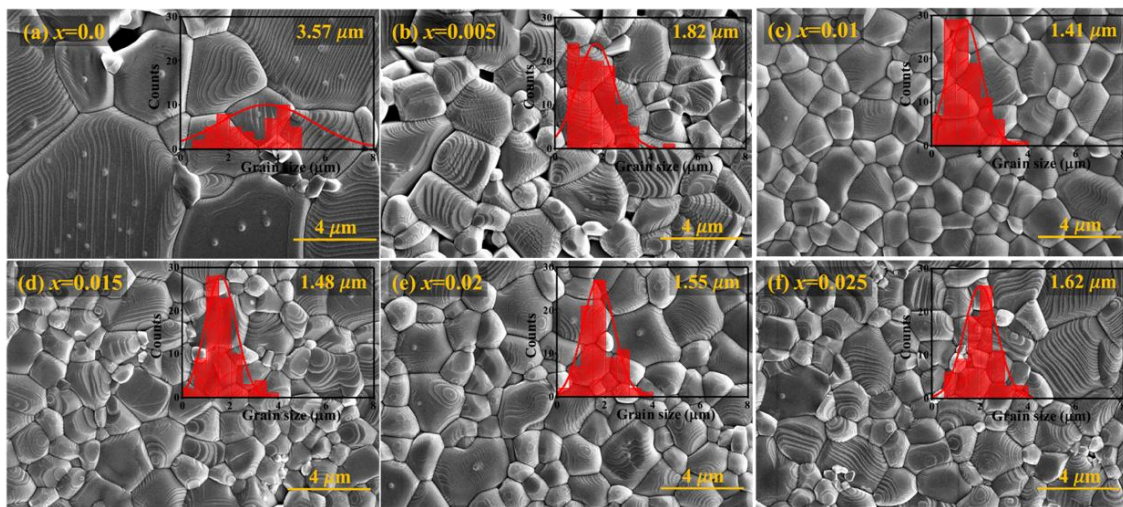


Figure 2. (a)–(f) FESEM images of the mirror-like surfaces of 100xBa ($x = 0–0.025$) ceramics after thermal etching, and the insets represent grain-size distribution

Figures 3(a)-(f) illustrate the temperature-dependent dielectric constant and loss curves for 100xBa ($x = 0-0.025$) ceramics, measured from 30°C to 450°C. For $x = 0.0$, the dielectric constant peak was observed at 141°C, which corresponds to the phase transition from the antiferroelectric P phase to the antiferroelectric R phase (abbreviated T_{P-R}). As x content increases, the T_{P-R} peak slightly increased from 141°C (for $x = 0.0$) to 145°C (for $x = 0.005$). When x further increased from 0.01 to 0.025, the peak of T_{P-R} increased significantly to around 160°C, as shown in Fig.3(c)-(f) and Table 1. The observed increase in T_{P-R} may arise from the higher valence Ba^{2+} cation compared to the substituted Na^+ ion. The replacement of Ba^{2+} for Na^+ causes the formation of cation vacancies on the A-site, resulting in a distortion of the structure and subsequently leading to a higher T_{P-R} (Noguchi *et al.*, 2001; Cai *et al.*, 2011). The shift of T_{P-R} to a higher

temperature also led to a significant reduction of the room temperature dielectric constant (ϵ_r) from 1,456 (for $x = 0.0$) to 665 (for $x = 0.025$), as shown in Table 1. With an increasing amount of x , the maximum dielectric constant (ϵ_m) initially decreased from 1,470 at $x = 0.0$ to 1,220 at $x = 0.01$, before sharply rising to around 1,600 for $x \geq 0.015$ (see Table 1). Furthermore, the dielectric loss ($\tan\delta$) at 1 kHz for 100xBa ceramics decreased significantly with increasing x content from 0.012 (for $x = 0.0$) to 0.002 (for $x = 0.025$). This low $\tan\delta$ value persisted within the temperature range of 32°C to 130°C. The decrease in dielectric loss generally results in reducing heat build-up in the ceramics during the application of an electric field, which may contribute to the improved dielectric breakdown strength (E_b) (Yang *et al.*, 2019a; Jiang *et al.*, 2022).

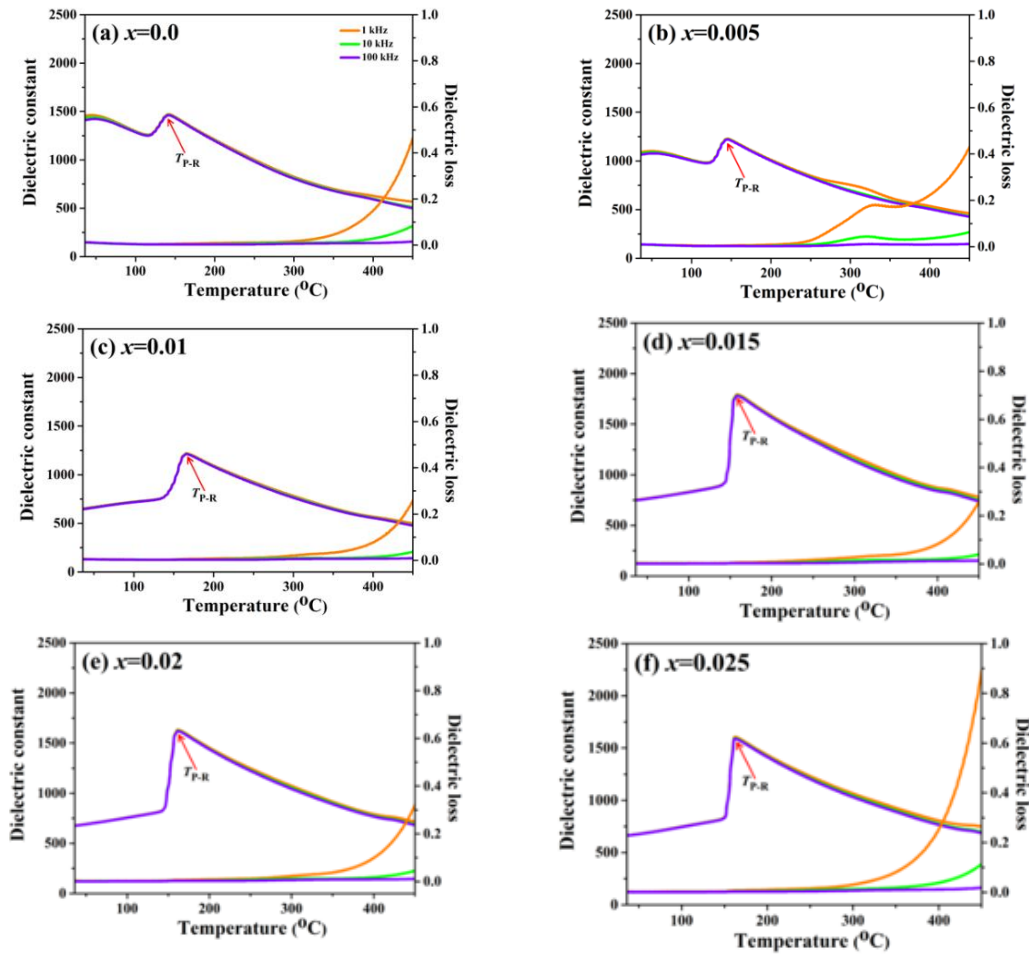


Figure 3. (a)-(f) The temperature dependence of the dielectric constant and dielectric loss for 100xBa ($x = 0-0.025$) ceramics, measured over a temperature range of 30°C-450°C

Table 1. The dielectric-property parameters (T_{P-R} , ϵ_r , ϵ_m , $\tan\delta_r$, $\tan\delta_m$) of 100xBa ($x = 0-0.025$) ceramics at 1 kHz.

Compositions	T_{P-R} (°C)	ϵ_r	$\tan\delta_r$	ϵ_m	$\tan\delta_m$
$x=0.0$	141	1,456	0.012	1,470	0.005
$x=0.005$	145	1,091	0.009	1,227	0.004
$x=0.01$	166	653	0.007	1,220	0.005
$x=0.015$	162	751	0.003	1,795	0.005
$x=0.02$	161	677	0.003	1,633	0.005
$x=0.025$	160	665	0.002	1,604	0.007

The unipolar P - E loops of 100xBa ($x = 0-0.025$) ceramics under the maximum electric field of each composition at a frequency of 1 Hz are shown in Figure 3(a) and Table 2. For $x = 0.0, 0.005$, and 0.01 compositions, the unipolar P - E loops data showed an open loop (see Figure 4(a)) with a relatively large remnant polarization (P_r) $\sim 1.5 \mu\text{C}/\text{cm}^2$, as shown in Table 2. As x increased to $0.015, 0.02$, and 0.025 , thin P - E loop with decreasing of P_r to near zero was observed. At the same time, as x increased, the maximum polarization ($P_{\max}$) also reduced from $7.05 \mu\text{C}/\text{cm}^2$ at $x = 0.0$ to $4.99 \mu\text{C}/\text{cm}^2$ at $x = 0.025$, as shown in Table 2. The observed slim P - E loop with a decrease in P_r and $P_{\max}$ could be attributed to the substitution of Ba²⁺ onto Na⁺. This substitution generates random electric fields that could break the ferroelectric long-range orders, resulting in formation of polar nanoregions (PNRs). Consequently, thin P - E loops are obtained, indicating a relaxation behavior (Qi *et al.*, 2019b; Qu *et al.*, 2019). The results are consistent with previous research on other NaNbO₃-based ceramics (Jiang *et al.*, 2022; Qu *et al.*, 2019; Qi *et al.*, 2021).

The energy storage performance were determined from the P - E hysteresis loops of each sample to calculate the energy-storage density (W), recoverable energy-storage density (W_{rec}), and energy-storage efficiency (η), as shown in equations (1)-(3) below (Zhao *et al.*, 2018b; Li *et al.*, 2020; Cheng *et al.*, 2022c).

$$W = \int_0^{P_{\max}} E dP \quad (1)$$

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

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

Where $P_{\max}$, P_r , and E are maximum polarization, remnant polarization, and electric field, respectively. The W_{rec} values of each composition under different electric fields are shown in Figure 4(a)-(b) and Table 2. The W_{rec} value was observed to decrease slightly from

$0.22 \text{ J}/\text{cm}^3$ to $0.20 \text{ J}/\text{cm}^3$ as x increased from 0.00 to 0.005 . With increasing x , the W_{rec} values increased to $0.24 \text{ J}/\text{cm}^3$ at $x = 0.01$, and peaked at $0.28 \text{ J}/\text{cm}^3$ at $x = 0.015$, before decreasing to $0.23 \text{ J}/\text{cm}^3$ and $0.22 \text{ J}/\text{cm}^3$ at $x=0.02$ and 0.025 , respectively. In contrast, with increasing x content, a significant increase in η value was observed from 47% (for $x = 0.0$) to 78% (for $x = 0.025$) under the maximum electric field of each composition as shown in Table 2. Among all compositions, the $x = 0.015$ sample exhibited the best energy storage performance, achieving a maximum $W_{\text{rec}} = 0.28 \text{ J}/\text{cm}^3$ and an efficiency (η) = 76% at $125 \text{ kV}/\text{cm}$, as presented in Table 2. Notably, Ba doping significantly enhances W_{rec} and η , aligning with previous findings on Ba-modified AgNbO₃ ceramics (Han *et al.*, 2019c).

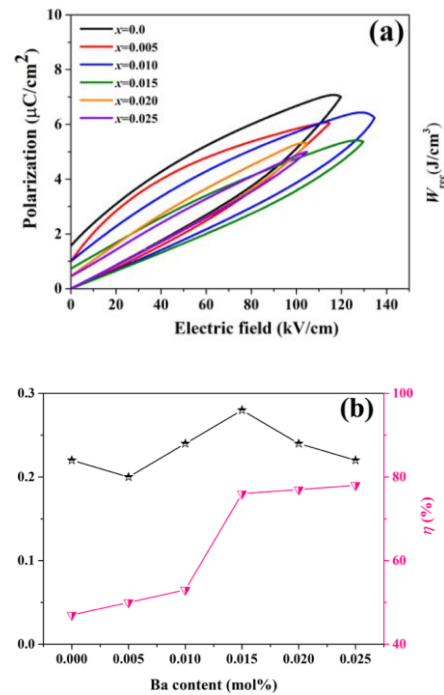
**Figure 4. (a) Unipolar P - E loops, (b) W_{rec} and η of 100xBa ($x = 0-0.025$) ceramics under different electric fields**

Table 2. Energy storage characteristics of 100xBa ($x = 0-0.025$) ceramics measured at 1 Hz.

Compositions	P_r ($\mu\text{C}/\text{cm}^2$)	$P_{\max}$ ($\mu\text{C}/\text{cm}^2$)	W (J/cm^3)	E_{applied} (kV/cm)	W_{rec} (J/cm^3)	η (%)
$x=0.0$	1.58	7.05	0.49	120	0.22	47
$x=0.005$	1.02	6.06	0.40	115	0.20	50
$x=0.01$	1.01	6.43	0.45	135	0.24	53
$x=0.015$	0.64	5.72	0.37	125	0.28	76
$x=0.02$	0.47	5.33	0.31	110	0.24	77
$x=0.025$	0.45	4.99	0.28	110	0.22	78

Conclusions

In this study, lead-free $0.88\text{Na}_{1-2x}\text{Ba}_x\text{NbO}_3-0.12\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (where x is 0.0, 0.005, 0.01, 0.015, 0.02 and 0.025) ceramics were synthesized via the solid-state reaction method. The XRD results confirmed a single-phase perovskite structure with an orthorhombic symmetry for $0 \leq x \leq 0.025$. As the Ba^{2+} content increased, the average grain size initially decreased but showed a slight rise at ($x = 0.015$), while the relative density remained above 94% for all samples. Additionally, the $T_{\text{P-R}}$ peak significantly shifted upward from 141°C at $x = 0.0$ to approximately 160°C for $x \geq 0.01$. Meanwhile, the dielectric loss ($\tan\delta$) exhibited a significant reduction, decreasing from 0.012 at $x = 0.0$ to 0.002 at $x = 0.025$ between 32°C and 130°C . Furthermore, an increase in Ba^{2+} content led to reductions in both P_r and $P_{\max}$, producing thinner P - E hysteresis loops with enhanced energy storage density and efficiency. Among all doping levels, the $x = 0.015$ composition exhibited the highest energy storage performance, achieving a maximum recoverable energy storage density of $0.28 \text{ J}/\text{cm}^3$ and an energy storage efficiency of 76% under an electric field of $125 \text{ kV}/\text{cm}$. These findings offer valuable insights for designing NaNbO_3 -based antiferroelectric materials for energy storage applications.

Acknowledgment

This work was financially supported by The National Science, Research, and Innovation Fund (NSRF) through Naresuan University (RB2566B018).

References

Balakt, A.M., Shaw, C.P., and Zhang, Q. (2016). The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{Ba}_{1-x}\text{TiO}_3$ ceramics. *Journal of Materials Science: Materials in Electronics*, 27:12,947-12,954. <https://doi.org/10.1007/s10854-016-5433-1>

Bruce, P.G., Freunberger, S.A., Hardwick, L.J., and Tarascon, J.M. (2012). Li- O_2 and Li-S batteries with high energy storage. *Nature Materials*, 11(1):19-29. <https://doi.org/10.1038/nmat3191>

Cai, W., Fu, C., Lin, Z., and Deng, X. (2011). Vanadium doping effects on microstructure and dielectric properties of barium titanate ceramics. *Ceramics International*, 37(8):3,643-3,650. <https://doi.org/10.1016/j.ceramint.2011.06.024>

Chauhan, A., Patel, S., Vaish, R., and Bowen, C.R. (2015). Antiferroelectric ceramics for high energy density capacitors. *Materials*, 8(12):8,009-8,031. <https://doi.org/10.3390/ma8125439>

Chen, H., Chen, X., Shi, J., Sun, C., Dong, X., Pang, F., and Zhou, H. (2020a). Achieving ultrahigh energy storage density in $\text{NaNbO}_3\text{-Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$ solid solution by enhancing the breakdown electric field. *Ceramics International*, 46(18):28,407-28,413. <https://doi.org/10.1016/j.ceramint.2020.07.345>

Chen, X., Li, X., Sun, J., Sun, C., Shi, J., Pang, F., and Zhou, H. (2020b). Simultaneously achieving ultrahigh energy storage density and energy efficiency in barium titanate-based ceramics. *Ceramics International*, 46(3):2,764-2,771. <https://doi.org/10.1016/j.ceramint.2019.09.265>

Cheng, X., Chen, X., and Fan, P. (2022c). Excellent energy storage performance in NaNbO_3 -based relaxor antiferroelectric ceramics under a low electric field. *Journal of Electroceramics*, 1-9. <https://doi.org/10.21203/rs.3.rs-812278/v1>

Das, R. and Mandal, K. (2012). Magnetic, ferroelectric and magnetoelectric properties of Ba-doped BiFeO_3 . *Journal of Magnetism and Magnetic Materials*, 324(11):1,913-1,918. <https://doi.org/10.1016/j.jmmm.2012.01.022>

Dechakupt, T., Tangsritrakul, J., Ketsuwan, P., and Yimmirun, R. (2011). Microstructure and electrical properties of niobium-doped barium titanate ceramics. *Ferroelectrics*, 415(1):141-148. <https://doi.org/10.1080/00150193.2011.577386>

Ellabban, O., Abu-Rub, H., and Blaabjerg, F. (2014). Renewable energy resources: Current status, future prospects and their enabling technology. *Renewable and Sustainable Energy Reviews*, 39:748-764. <https://doi.org/10.1016/j.rser.2014.07.113>

Fan, P., Zhang, S.T., Xu, J., Zang, J., Samart, C., Zhang, T., Tan, H., Salamon, D., Zhang, H., and Liu, G. (2020). Relaxor/antiferroelectric composites: A solution to achieve high energy storage performance in lead-free dielectric ceramics. *Journal of Materials Chemistry C*, 8(17):5,681-5,691. <https://doi.org/10.1039/D0TC00589D>

Gao, J., Zhang, Y., Zhao, L., Lee, K.Y., Liu, Q., Studer, A., Hinterstein, M., Zhang, S., and Li, J.F. (2019). Enhanced antiferroelectric phase stability in La-doped AgNbO_3 : Perspectives from the microstructure to energy storage properties. *Journal of Materials Chemistry A*, 7(5):2,225-2,232. <https://doi.org/10.1039/C8TA09353A>

- Guo, H., Shimizu, H., and Randall, C. A. (2015). Direct evidence of an incommensurate phase in NaNbO₃ and its implication in NaNbO₃-based lead-free antiferroelectrics. *Applied Physics Letters*, 107(11):112904. <https://doi.org/10.1063/1.4930067>
- Han, K., Luo, N., Jing, Y., Wang, X., Peng, B., Liu, L., Hu, C., Zhou, H., Wei, Y., and Chen, X. (2019a). Structure and energy storage performance of Ba-modified AgNbO₃ lead-free antiferroelectric ceramics. *Ceramics International*, 45(5):5,559-5,565. <https://doi.org/10.1016/j.ceramint.2018.12.014>
- Han, K., Luo, N., Mao, S., Zhuo, F., Chen, X., Liu, L., Hu, C., Zhou, H., Wang, X., and Wei, Y. (2019b). Realizing high low-electric-field energy storage performance in AgNbO₃ ceramics by introducing relaxor behaviour. *Journal of Materials*, 5(4):597-605. <https://doi.org/10.1016/j.jmat.2019.07.006>
- Han, K., Luo, N., Mao, S., Zhuo, F., Liu, L., Peng, B., Chen, X., Hu, C., Zhou, H., and Wei, Y. (2019). Ultrahigh energy-storage density in A-/B-site co-doped AgNbO₃ lead-free antiferroelectric ceramics: Insight into the origin of antiferroelectricity. *Journal of Materials Chemistry A*, 7(46):26,293-26,301. <https://doi.org/10.1039/C9TA06457E>
- Hao, X. (2013). A review on the dielectric materials for high energy-storage application. *Journal of Advanced Dielectrics*, 3(1):1330001. <https://doi.org/10.1142/S2010135X13300016>
- Hao, X., Zhai, J., and Yao, X. (2009). Improved energy storage performance and fatigue endurance of Sr-doped PbZrO₃ antiferroelectric thin films. *Journal of the American Ceramic Society*, 92(5):1,133-1,135. <https://doi.org/10.1111/j.1551-2916.2009.03015.x>
- Huang, Y., Li, F., Hao, H., Xia, F., Liu, H., and Zhang, S. (2019). (Bi_{0.51}Na_{0.47})TiO₃ based lead free ceramics with high energy density and efficiency. *Journal of Materials*, 5(3):385-393. <https://doi.org/10.1016/j.jmat.2019.03.006>
- Jiang, J., Li, X., Li, L., Guo, S., Zhang, J., Wang, J., Zhu, H., Wang, Y., and Zhang, S.T. (2022). Novel lead-free NaNbO₃-based relaxor antiferroelectric ceramics with ultrahigh energy storage density and high efficiency. *Journal of Materials*, 8(2):295-301. <https://doi.org/10.1016/j.jmat.2021.09.007>
- Jiang, J., Meng, X., Li, L., Zhang, J., Guo, S., Wang, J., Hao, X., Zhu, H., and Zhang, S.T. (2021). Enhanced energy storage properties of lead-free NaNbO₃-based ceramics via A/B-site substitution. *Chemical Engineering Journal*, 422:130130. <https://doi.org/10.1016/j.cej.2021.130130>
- Kittel, C. (1951). Theory of antiferroelectric crystals. *Physical Review*, 82(5):729. <https://doi.org/10.1103/PhysRev.82.729>
- Lanfredi, S., Lente, M.H., and Eiras, J.A. (2002). Phase transition at low temperature in NaNbO₃ ceramic. *Applied Physics Letters*, 80(15):2,731-2,733. <https://doi.org/10.1063/1.1470260>
- Li, Q., Han, K., Gadinski, M.R., Zhang, G., and Wang, Q. (2014). High energy and power density capacitors from solution-processed ternary ferroelectric polymer nanocomposites. *Advanced Materials*, 26(36):6,244-6,249. <https://doi.org/10.1002/adma.201402106>
- Li, Y., Zhen, Y., Wang, W., Fang, Z., Jia, Z., Zhang, J., Zhong, H., Wu, J., Yan, Y., and Xue, Q. (2020). Enhanced energy storage density and discharge efficiency in potassium sodium niobate-based ceramics prepared using a new scheme. *Journal of the European Ceramic Society*, 40(6):2,357-2,365. <https://doi.org/10.1016/j.jeurceramsoc.2020.01.050>
- Liu, Z., Lu, T., Ye, J., Wang, G., Dong, X., Withers, R., and Liu, Y. (2018). Antiferroelectrics for energy storage applications. *Advanced Materials Technologies*, 3(9):1800111. <https://doi.org/10.1002/admt.201800111>
- Lu, Z., Bao, W., Wang, G., Sun, S. K., Li, L., Li, J., Yang, H., Ji, H., Feteira, A., and Li, D. (2021). Mechanism of enhanced energy storage density in AgNbO₃-based lead-free antiferroelectrics. *Nano Energy*, 79:105423. <https://doi.org/10.1016/j.nanoen.2020.105423>
- Luo, N., Han, K., Zhuo, F., Xu, C., Zhang, G., Liu, L., Chen, X., Hu, C., Zhou, H., and Wei, Y. (2019). Aliovalent A-site engineered AgNbO₃ lead-free antiferroelectric ceramics toward superior energy storage density. *Journal of Materials Chemistry A*, 7(23):14,118-14,128. <https://doi.org/10.1039/C9TA02053E>
- Megaw, H.D. (1974). The seven phases of sodium niobate. *Ferroelectrics*, 7(1):87-89. <https://doi.org/10.1080/00150197408237956>
- Mishra, S.K., Choudhury, N., Chaplot, S.L., Krishna, P. S.R., and Mittal, R. (2007). Competing antiferroelectric and ferroelectric interactions in NaNbO₃: Neutron diffraction and theoretical studies. *Physical Review B*, 76(2):024110. <https://doi.org/10.1103/PhysRevB.76.024110>
- Noguchi, Y., Miyayama, M., and Kudo, T. (2001). Direct evidence of A-site-deficient strontium bismuth tantalate and its enhanced ferroelectric properties. *Physical Review B*, 63(21):214102. <https://doi.org/10.1103/PhysRevB.63.214102>
- Patel, S., Chauhan, A., and Vaish, R. (2014). Enhancing electrical energy storage density in anti-ferroelectric ceramics using ferroelastic domain switching. *Materials Research Express*, 1(4):045502. <https://doi.org/10.1088/2053-1591/1/4/045502>
- Premwicheit, P., Jaitha, N., Gupta, S.K., Cann, D.P., and Prasertpalichat, S. (2023). Dielectric and improved energy-storage properties in A-site Nd³⁺ doped lead-free 0.88NaNbO₃-0.12Sr_{0.7}Bi_{0.2}TiO₃ ceramics. *Integrated Ferroelectrics*, 238(1):160-172. <https://doi.org/10.1080/10584587.2023.2234564>
- Qi, H., Xie, A., Fu, J., and Zuo, R. (2021). Emerging antiferroelectric phases with fascinating dielectric, polarization, and strain response in NaNbO₃-(Bi_{0.5}Na_{0.5})TiO₃ lead-free binary system. *Acta Materialia*, 208:116710. <https://doi.org/10.1016/j.actamat.2021.116710>
- Qi, H., Zuo, R., Xie, A., Fu, J., and Zhang, D. (2019a). Excellent energy-storage properties of NaNbO₃-based lead-free antiferroelectric orthorhombic P-phase (Pbma) ceramics with repeatable double polarization-field loops. *Journal of the European Ceramic Society*, 39(13):3,703-3,709. <https://doi.org/10.1016/j.jeurceramsoc.2019.04.049>
- Qi, H., Zuo, R., Xie, A., Tian, A., Fu, J., Zhang, Y., and Zhang, S. (2019b). Ultrahigh energy-storage density in NaNbO₃-based lead-free relaxor antiferroelectric ceramics with nanoscale domains. *Advanced Functional Materials*, 29(35):1903877. <https://doi.org/10.1002/adfm.201903877>
- Qu, N., Du, H., and Hao, X. (2019). A new strategy to realize high comprehensive energy storage properties in lead-free bulk ceramics. *Journal of Materials Chemistry C*, 7(26):7,993-8,002. <https://doi.org/10.1039/C9TC02088H>
- Shannon, R.D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 32(5):751-767. <https://doi.org/10.1107/S0567739476001551>
- Shi, R., Pu, Y., Wang, W., Guo, X., Li, J., Yang, M., and Zhou, S. (2020). A novel lead-free NaNbO₃-Bi(Zn_{0.5}Ti_{0.5})O₃ ceramics system for energy storage application with excellent stability. *Journal of Alloys and Compounds*, 815:152356. <https://doi.org/10.1016/j.jallcom.2019.152356>

- Shimizu, H., Kobayashi, K., Mizuno, Y., and Randall, C.A. (2014). Advantages of low partial pressure of oxygen processing of alkali niobate: NaNbO_3 . *Journal of the American Ceramic Society*, 97(6):1,791-1,796. <https://doi.org/10.1111/jace.12815>
- Tian, A., Zuo, R., Qi, H., and Shi, M. (2020). Large energy-storage density in transition-metal oxide modified $\text{NaNbO}_3\text{-Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ lead-free ceramics through regulating the antiferroelectric phase structure. *Journal of Materials Chemistry A*, 8(17):8,352-8,359. <https://doi.org/10.1039/D0TA02285C>
- Tian, Y., Jin, L., Zhang, H., Xu, Z., Wei, X., Politova, E.D., Stefanovich, S.Y., Tarakina, N.V., Abrahams, I., and Yan, H. (2016). High energy density in silver niobate ceramics. *Journal of Materials Chemistry A*, 4(44):17,279-17,287. <https://doi.org/10.1039/C6TA06353E>
- Wang, J., Fan, H., Wang, M., and Fan, P. (2021). Significantly enhanced energy storage performance in Sm-doped $0.88\text{NaNbO}_3\text{-}0.12\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ lead-free ceramics. *Ceramics International*, 47(13):17,964-17,970. <https://doi.org/10.1016/j.ceramint.2021.03.249>
- Wang, Y., Song, Y., and Xia, Y. (2016). Electrochemical capacitors: Mechanism, materials, systems, characterization, and applications. *Chemical Society Reviews*, 45(21):5,925-5,950. <https://doi.org/10.1039/C5CS00580A>
- Xie, A., Qi, H., and Zuo, R. (2020). Achieving remarkable amplification of energy-storage density in two-step sintered $\text{NaNbO}_3\text{-SrTiO}_3$ antiferroelectric capacitors through dual adjustment of local heterogeneity and grain scale. *ACS Applied Materials and Interfaces*, 12(17):19,467-19,475. <https://doi.org/10.1021/acsami.0c00831>
- Yang, L., Kong, X., Li, F., Hao, H., Cheng, Z., Liu, H., Li, J. F., and Zhang, S. (2019a). Perovskite lead-free dielectrics for energy storage applications. *Progress in Materials Science*, 102:72-108. <https://doi.org/10.1016/j.pmatsci.2018.12.004>
- Yang, X., Zhuo, F., Wang, C., Liu, Y., Wang, Z., Tailor, H., He, C., and Long, X. (2019b). High energy storage density and ultrafast discharge in lead lutetium niobate based ceramics. *Journal of Materials Chemistry A*, 7(14):8,414-8,422. <https://doi.org/10.1039/C9TA00463G>
- Yao, Z., Song, Z., Hao, H., Yu, Z., Cao, M., Zhang, S., Lanagan, M.T., and Liu, H. (2017). Homogeneous/inhomogeneous-structured dielectrics and their energy-storage performances. *Advanced Materials*, 29(20):1601727. <https://doi.org/10.1002/adma.201601727>
- Ye, J., Wang, G., Chen, X., and Dong, X. (2021). Effect of rare-earth doping on the dielectric property and polarization behavior of antiferroelectric sodium niobate-based ceramics. *Journal of Materials*, 7(2):339-346. <https://doi.org/10.1016/j.jmat.2020.10.004>
- Zhang, H., Wei, T., Zhang, Q., Ma, W., Fan, P., Salamon, D., Zhang, S. T., Nan, B., Tan, H., and Ye, Z.G. (2020). A review on the development of lead-free ferroelectric energy-storage ceramics and multilayer capacitors. *Journal of Materials Chemistry C*, 8(47):16,648-16,667. <https://doi.org/10.1039/D0TC04381H>
- Zhao, L., Gao, J., Liu, Q., Zhang, S., and Li, J.F. (2018a). Silver niobate lead-free antiferroelectric ceramics: Enhancing energy storage density by B-site doping. *ACS Applied Materials and Interfaces*, 10(1):819-826. <https://doi.org/10.1021/acsami.7b17382>
- Zhao, L., Liu, Q., Gao, J., Zhang, S., and Li, J.F. (2017). Lead-free antiferroelectric silver niobate tantalate with high energy storage performance. *Advanced Materials*, 29(31):1701824. <https://doi.org/10.1002/adma.201701824>
- Zhao, L., Liu, Q., Zhang, S., and Li, J.F. (2016). Lead-free AgNbO_3 anti-ferroelectric ceramics with an enhanced energy storage performance using MnO_2 modification. *Journal of Materials Chemistry C*, 4(36):8,380-8,384. <https://doi.org/10.1039/C6TC03289C>
- Zhao, N., Fan, H., Ning, L., Ma, J., and Zhou, Y. (2018b). Temperature-stable dielectric and energy storage properties of $\text{La}(\text{Ti}_{0.5}\text{Mg}_{0.5})\text{O}_3$ -doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-(Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ lead-free ceramics. *Journal of the American Ceramic Society*, 101(12):5,578-5,585. <https://doi.org/10.1111/jace.15727>
- Zhou, M., Liang, R., Zhou, Z., and Dong, X. (2018). Superior energy storage properties and excellent stability of novel NaNbO_3 -based lead-free ceramics with A-site vacancy obtained via a Bi_2O_3 substitution strategy. *Journal of Materials Chemistry A*, 6(37):17,896-17,904. <https://doi.org/10.1039/C8TA07303A>
- Zuo, R., Fu, J., and Qi, H. (2018). Stable antiferroelectricity with incompletely reversible phase transition and low volume-strain contribution in BaZrO_3 and CaZrO_3 substituted NaNbO_3 ceramics. *Acta Materialia*, 161:352-359. <https://doi.org/10.1016/j.actamat.2018.09.010>
- Zuo, R., Qi, H., Fu, J., Li, J., Shi, M., and Xu, Y. (2016). Giant electrostrictive effects of $\text{NaNbO}_3\text{-BaTiO}_3$ lead-free relaxor ferroelectrics. *Applied Physics Letters*, 108(23):232904. <https://doi.org/10.1063/1.4953417>