

Article

Improving the Energy Storage Performance in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -Based Ceramics by Combining Relaxor and Antiferroelectric Properties

Srinivas Pattipaka ¹, Yeseul Lim ¹, Yundong Jeong ¹, Mahesh Peddigari ², Yuho Min ³, Jae Won Jeong ⁴, Jongmoon Jang ⁵, Sung-Dae Kim ¹ and Geon-Tae Hwang ^{1,*}

¹ Department of Materials Science and Engineering, Pukyong National University, 45, Yongso-ro, Nam-Gu, Busan 48513, Republic of Korea; cnuphy444@gmail.com (S.P.); imyeseul21@pukyong.ac.kr (Y.L.); yd3998@pukyong.ac.kr (Y.J.); sdkim@pknu.ac.kr (S.-D.K.)

² Department of Physics, Indian Institute of Technology Hyderabad, Kandi 502284, Telangana, India; mahesh.p@phy.iith.ac.in

³ School of Materials Science and Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu 41566, Republic of Korea; yuhomin@knu.ac.kr

⁴ Korea Institute of Materials Science (KIMS), 797 Changwondaero, Seongsan-gu, Changwon 51508, Republic of Korea; jeongjw1204@kims.re.kr

⁵ Department of Electronic Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea; jongmoon@yu.ac.kr

* Correspondence: gthwang@pknu.ac.kr

Abstract: Ceramic capacitors have received great attention for use in pulse power systems owing to their ultra-fast charge–discharge rate, good temperature stability, and excellent fatigue resistance. However, the low energy storage density and low breakdown strength (BDS) of ceramic capacitors limit the practical applications of energy storage technologies. In this work, we present a series of relaxor ferroelectric ceramics $(1-x) [0.94 \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.06\text{BaTiO}_3] - x \text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ ($1-x$ BNT-BT- x SBT; $x = 0, 0.20, 0.225, 0.25, 0.275$ and 0.30) with improved energy storage performances by combining relaxor and antiferroelectric properties. XRD, Raman spectra, and SEM characterizations of BNT-BT-SBT ceramics revealed a rhombohedral–tetragonal phase, highly dynamic polar nanoregions, and a reduction in grain size with a homogeneous and dense microstructure, respectively. A high dielectric constant of 1654 at 1 kHz and low remnant polarization of $1.39 \mu\text{C}/\text{cm}^2$ were obtained with the addition of SBT for $x = 0.275$; these are beneficial for improving energy storage performance. The diffuse phase transition of these ceramics displays relaxor behavior, which is improved with SBT and confirmed by modified the Curie–Weiss law. The combining relaxor and antiferroelectric properties with fine grain size by the incorporation of SBT enables an enhanced maximum polarization of a minimized P - E loop, leading to an improved BDS. As a result, a high recoverable energy density W_{rec} of $1.02 \text{ J}/\text{cm}^3$ and a high energy efficiency η of 75.98% at $89 \text{ kV}/\text{cm}$ were achieved for an optimum composition of $0.725 [0.94\text{BNT}-0.06\text{BT}]-0.275 \text{ SBT}$. These results demonstrate that BNT-based relaxor ferroelectric ceramics are good candidates for next-generation ceramic capacitors and offer a potential strategy for exploiting novel high-performance ceramic materials.

Keywords: ceramic capacitors; lead-free ceramics; relaxor and antiferroelectrics; energy storage density; energy efficiency



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1. Introduction

Dielectric materials have received great attention for energy storage applications in microwaves, pulse power systems, electric vehicles, and high-frequency inverters owing to their ultra-fast charge–discharge rate and better temperature stability than batteries, electrochemical capacitors, and dielectric polymers [1–6]. However, dielectric capacitors have a lower energy storage density and efficiency than batteries and polymers because

of their low dielectric breakdown strength (BDS), limiting their practical applications. Therefore, novel high-performance dielectric capacitors with high energy storage density and efficiency are needed for energy storage capacitor applications.

In general, the recoverable energy density (W_{rec}) and energy efficiency (η) of a dielectric capacitor can be calculated from the polarization (P)–electric field (E) loop using the following equations [6–10]:

$$W_{rec} = \int_{P_r}^{P_{max}} E dP \quad (1)$$

$$\eta = \frac{W_{rec}}{W_{rec} + W_{loss}} \quad (2)$$

where P_{max} is the maximum polarization, P_r is the remnant polarization, and W_{loss} is the energy loss. According to the above equations, the energy storage performance can be significantly improved by enhancing the difference between P_r and P_{max} (ΔP). The BDS is also an important parameter for energy storage, which means a higher BDS is required for a high W_{rec} .

Dielectric materials, such as linear dielectric (LDE), ferroelectric (FE), anti-ferroelectric (AFE), and relaxor ferroelectric (RFE) materials, have been extensively used in energy storage capacitors [5,6]. Among these materials, the RFE materials (for example, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT)-, BaTiO_3 (BT)-, and BiFeO_3 (BFO)-composition-based materials) show high maximum polarization, small remnant polarization, and slim P - E loops due to the creation of polar nanoregions (PNRs). Additionally, they mostly display highly dynamic short-range FE orders. Nevertheless, the PNRs can transform into long-range FE orders with the increasing electric field, leading to high maximum polarization. After the field is removed, the induced FE orders can simply convert into PNRs, resulting in a small remnant polarization [11–14]. Thus, the RFEs typically exhibit high W_{rec} and η . Therefore, lead-based RFEs have been extensively reported for applications in energy storage capacitors [15,16]. However, the toxicity of lead poses a risk to both human health and the environment, which has encouraged the development of alternative lead-free ceramic materials. Over the past few years, lead-free RFEs, including BT [17–21]-, BNT [3,22–27]-, NaNbO_3 (NN)/ $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) [28,29]-, and AgNbO_3 (AN) [30,31]-based materials, have been discovered and used in energy storage capacitor applications.

BNT-based materials display a strong ferroelectric response due to their large-electric-field-induced polarization and strain [32,33]. Hybridization between the Bi^{3+} $6s^2$ and oxygen $2p$ orbitals can result in weak Bi-O covalency with off-center Bi^{3+} , enabling substantial lattice relaxation and generating massive saturated polarization with high remnant polarization [34]. Additionally, the creation of PNRs is assisted by the local random fields caused by valency differences and chemical inhomogeneity [35,36]. In addition, the relaxor characteristics of the material can be enhanced by adding another phase (for example, tetragonal/orthorhombic) and modifying it with a suitable dopant/binary/ternary composition, enabling slim hysteresis loops [37]. Among these lead-free ceramics, the BNT-BT binary composition is a very popular system; it has a morphotropic phase boundary (MPB) between a rhombohedral and a tetragonal phase and also has a high maximum polarization; these features are responsible for higher energy storage density and efficiency [38]. Interestingly, the incorporation of SrTiO_3 (ST) into the BNT-BT system plays a significant role in enhancing dielectric and ferroelectric properties [26,39,40].

In this paper, we improved the energy storage performance in BNT-BT ceramics with the incorporation of SBT by combining relaxor and antiferroelectric properties. Relaxor ferroelectric materials exhibit a heterogeneous polar state at the nanoscale, and long-range domains are destroyed due to the cation order-disorder and random fields, resulting in a slim P - E loop [41–43]. The BT-BNT combination exhibits an AFE/FE response with relaxor characteristics, which makes them interesting for energy storage applications [44,45]. $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (SBT) is a relaxor ferroelectric with a small coercive field, small remnant polarization, and diffused dielectric maxima over a wide temperature range. It was utilized to make a solid solution with BNT-BT to achieve a relaxor nature [46]. Combining relaxor

and antiferroelectric properties with a fine grain size by the incorporation of SBT into BNT-BT enables an enhanced maximum polarization and a minimized P - E loop, leading to improved breakdown strength. An improvement in recoverable energy density of 1.02 J/cm^3 and a high energy efficiency of 75.98% at a BDS of 89 kV/cm are achieved using $0.725 [0.94\text{BNT}-0.06\text{BT}]-0.275 \text{ SBT}$ ceramics.

2. Materials and Methods

A conventional solid-state reaction method was used to prepare $(1-x) [0.94 \text{ Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.06\text{BaTiO}_3] - x \text{ Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ ($1-x \text{ BNT-BT} - x \text{ SBT}$; $x = 0, 0.20, 0.225, 0.25, 0.275$ and 0.30) ceramic powders. Raw materials were used, including Bi_2O_3 , Na_2CO_3 , BaCO_3 , TiO_2 , and SrCO_3 . They weighed as per a stoichiometric ratio and ball-milled for 24 h with ZrO_2 balls in an ethanol solution. Further, BNT, BT, and SBT slurries were dried at 120°C and calcined individually at temperatures of 800°C , 900°C , and 950°C for 2 h and 3 h, respectively, for the formation of their phases. These calcined BNT, BT and SBT powders were well mixed and ball-milled again for 12 h for the preparation of a BNT-BT-SBT composition. Furthermore, 5 wt.% of polyvinyl alcohol was added to the obtained powders before the product was pressed at 10 MPa into disks with 10 mm diameters and a thickness of about 0.5 mm. These pellets were sintered at 1100°C for 3 h with a heating and cooling rate of 5°C/min . Lastly, Ag paste was applied on the surface of sintered samples to measure electrical characterizations.

The phase evolution of the BNT-BT-SBT ceramic samples was investigated using an X-ray Diffractometer (Rigaku/Ultima IV) with a $\text{Cu-K}\alpha$ wavelength of $1.5406 \text{ \AA}$ and sweeping rate of 0.02039 degrees per minute at a voltage of 40 kV and current of 30 mA. Raman spectra were measured by a Raman spectrometer (JASCO, NRS-5100) with a laser wavelength of 532 nm. Surface morphology and elemental composition were investigated by a scanning electron microscope (SEM) (TESCAN/VEGA II LSU) equipped with an energy-dispersive spectrometer (EDS). Temperature- and frequency-dependent dielectric properties were assessed from room temperature (RT) to 400°C and 100 Hz–1000 kHz using an impedance analyzer (Hewlett Packard, 4284A). P - E hysteresis loops were performed from RT to 200°C using a ferroelectric tester (Aix ACCT Systems GmbH, TF Analyzer 2000).

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of $(1-x) \text{ BNT-BT} - x \text{ SBT}$ ceramic samples for $x = 0-0.30$. The XRD peaks clearly indicate that all the samples of BNT-BT-SBT display the formation of rhombohedral (R) and tetragonal (T) phases, demonstrating that the SBT diffused into BNT-BT lattices to form a homogeneous solid solution. It is well known that the $(1-x) \text{ BNT} - x \text{ BT}$ system possesses rhombohedral (Joint Committee on Powder Diffraction Standards (JCPDS) card No. 36-0340, 46-0001, Crystallography Open Database (COD) No. 2103295 for $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$) and tetragonal crystal structures (JCPDS card No. 89-1428, COD No. 1507756 and 2100858 for BaTiO_3) at MPB for $x = 0.06$ [47–54]. The coexistence of both rhombohedral and tetragonal phases in $(1-x) \text{ BNT-BT} - x \text{ SBT}$ ceramic samples for $x = 0-0.30$ was confirmed by the splitting of the $(111)/(-111)$ and $(002)/(200)$ peaks at 2θ about 40° and 46° , respectively, as shown in Figure 1b. However, no significant change in R and T phases was observed with the incorporation of the SBT composition. These results are in good agreement with the earlier reports on BNT-BT-based ceramic compositions [54,55]. In addition, these diffraction peaks shifted slightly to the lower-angle side with the addition of SBT into BNT-BT, indicating increased lattice parameters. The increased lattice parameters were responsible for Sr^{2+} ($1.44 \text{ \AA}$) having a larger ionic radius than Bi^{3+} ($1.36 \text{ \AA}$), Na^+ ($1.39 \text{ \AA}$), and Ba^{2+} ($1.35 \text{ \AA}$) at the A-site [56–58].

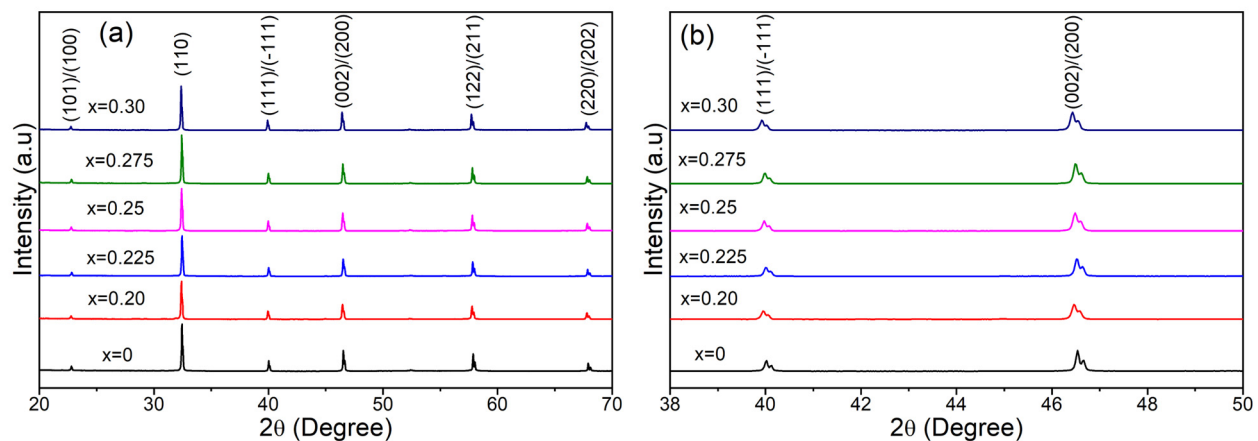


Figure 1. (a) X-ray diffraction patterns of the $(1-x)$ BNT-BT- x SBT ceramic samples for $x = 0$ – 0.30 in the 2θ range of 20° – 70° , and (b) enlarged XRD patterns in the range of 38° – 50° .

Figure 2 shows the Raman spectra of BNT-BT-SBT ceramic samples with spectral de-convolution. The Raman spectra of all the sintered samples are similar to those in the earlier reports on BNT-based ceramics [59,60]. The Raman modes separated into four regions, as illustrated at the top of Figure 2. (i) The Raman modes below 200 cm^{-1} were associated with the A-site (Bi-O, Na-O, Ba-O, and Sr-O) vibrations, (ii) the Raman modes between 200 and 420 cm^{-1} related to the B-O (Ti-O) vibrations, (iii) the modes between 420 and 690 cm^{-1} were associated with the BO_6 (TiO_6)–octahedra vibrations, and (iv) the Raman modes above 690 cm^{-1} corresponded to the A_1 and E overlapping modes [59]. The modes at 135 – 174 cm^{-1} were shifted to the higher wavenumbers of 159 – 218 cm^{-1} with SBT, related to the vibrations of A-site due to the A-site disorder. This disorder is produced by the addition of SBT (Bi^{3+} and Sr^{2+}) into the BNT-BT (Bi^{3+} , Na^+ , and Ba^{2+}) system [61]. Additionally, a significant shift occurred at 312 and 530 cm^{-1} to lower wavenumbers of 296 and 524 cm^{-1} with the addition of SBT, which was attributed to the enhancement of B-site disorder in the BNT-BT-SBT [57]. Besides, these Raman active modes became broadened, indicating the disturbance of the long-range FE order and the creation of highly dynamic polar nanoregions and improving the relaxor characteristics of BNT-BT-SBT ceramics [62]. These findings are in good agreement with the X-ray diffraction, dielectric and ferroelectric properties.

Figure 3 shows SEM images of the surface of BNT-BT-SBT ceramic samples. All the sintered ceramic samples show rectangular-shaped grains, which are uniformly distributed. Figure 3a clearly shows that the $x = 0$ sample displays a low-density microstructure, which gradually improves with the incorporation of SBT. The composition at higher concentrations shows a more compact and denser microstructure with smaller grains than other samples of $(1-x)$ BNT-BT- x SBT, where $x = 0.275$ and $x = 0.30$. In order to prove that all the sintered ceramic samples have uniform microstructures and are highly dense, the density of BNT-BT-SBT ceramics was estimated using the Archimedes principle. The density was found to be enhanced from $5.62 \pm 0.24\text{ g/cm}^3$ to $5.81 \pm 0.28\text{ g/cm}^3$ with SBT from $x = 0$ to 0.30 . The estimated relative density of BNT-BT-SBT was found to be 95.64% to 98.85% of the theoretical density [63], proving that these ceramic samples are highly dense and have homogeneous microstructures. Moreover, the average grain size of BNT-BT-SBT ceramic samples was calculated using Image-J 1.31 software using the linear intercept method. The average grain size was found to be $1.30 \pm 0.41\text{ }\mu\text{m}$ for the $x = 0$ sample (pure BNT-BT), and further; it was slightly reduced to $0.81 \pm 0.26\text{ }\mu\text{m}$ with the addition of SBT ($x = 0.30$). The reduction in grain size was ascribed to the larger radii of Sr^{2+} ($1.44\text{ }\text{\AA}$) than Bi^{3+} ($1.36\text{ }\text{\AA}$), Na^+ ($1.39\text{ }\text{\AA}$), and Ba^{2+} ($1.35\text{ }\text{\AA}$) at the A-site, which enhanced the lattice strain energy (ΔG_{strain}) [64,65]. The SEM results suggest that the sample with a fine grain size and a homogeneity and dense microstructure can sustain higher voltages, leading to improved BDS and energy storage properties [66,67]. Further, energy-dispersive X-ray

spectroscopy (EDS) was performed to analyze the elemental composition of BNT-BT-SBT ceramics for $x = 0$ –0.30. As seen in Figure 4, we assessed every element with the required composition and determined its atomic ratio. Moreover, A-site (Bi^{3+} , Na^{1+} , Ba^{2+} , and Sr^{2+}), B-site (Ti^{4+}) and oxygen atomic and molecular proportions were nearly in line with the stoichiometric ratio of the BNT-BT-SBT compositions (Table 1). It is noticed that there was a small reduction in the ratio of Bi and Na elements due to their volatile nature during high sintering temperatures [68].

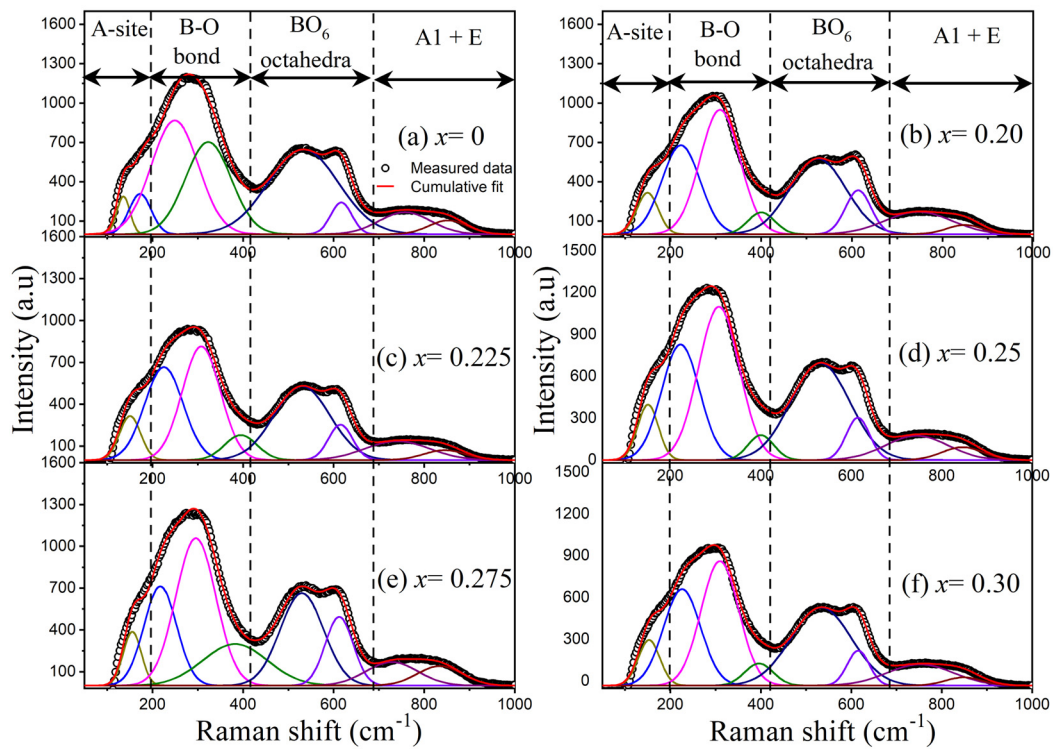


Figure 2. Raman spectra along with spectral deconvolution of $(1-x)$ BNT-BT- x SBT ceramic samples for (a) $x = 0$, (b) $x = 0.20$, (c) $x = 0.225$, (d) $x = 0.25$, (e) $x = 0.275$, and (f) $x = 0.30$.

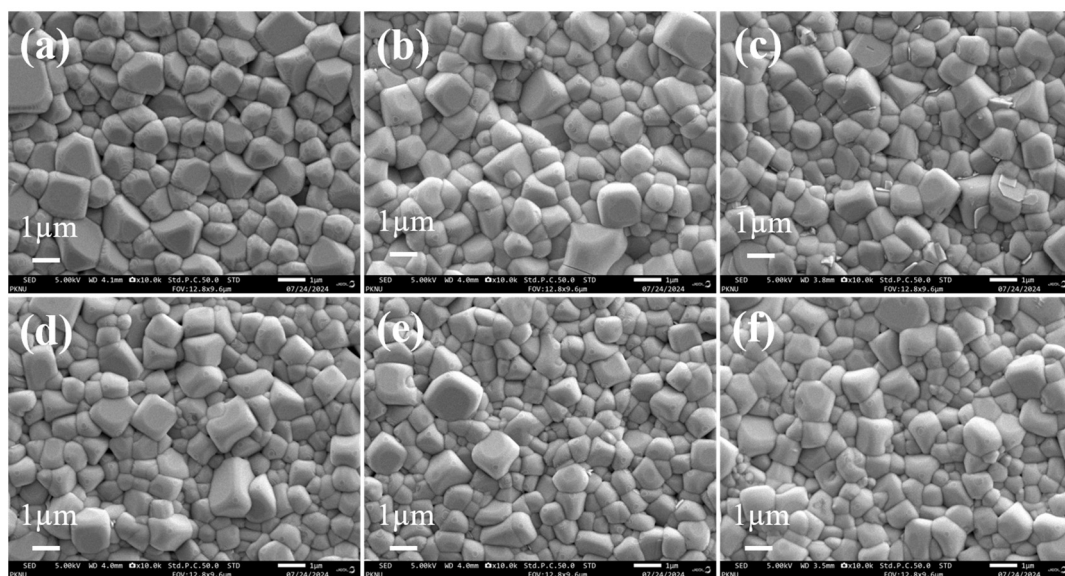


Figure 3. SEM images of $(1-x)$ BNT-BT- x SBT ceramic samples for (a) $x = 0$, (b) $x = 0.20$, (c) $x = 0.225$, (d) $x = 0.25$, (e) $x = 0.275$, and (f) $x = 0.30$.

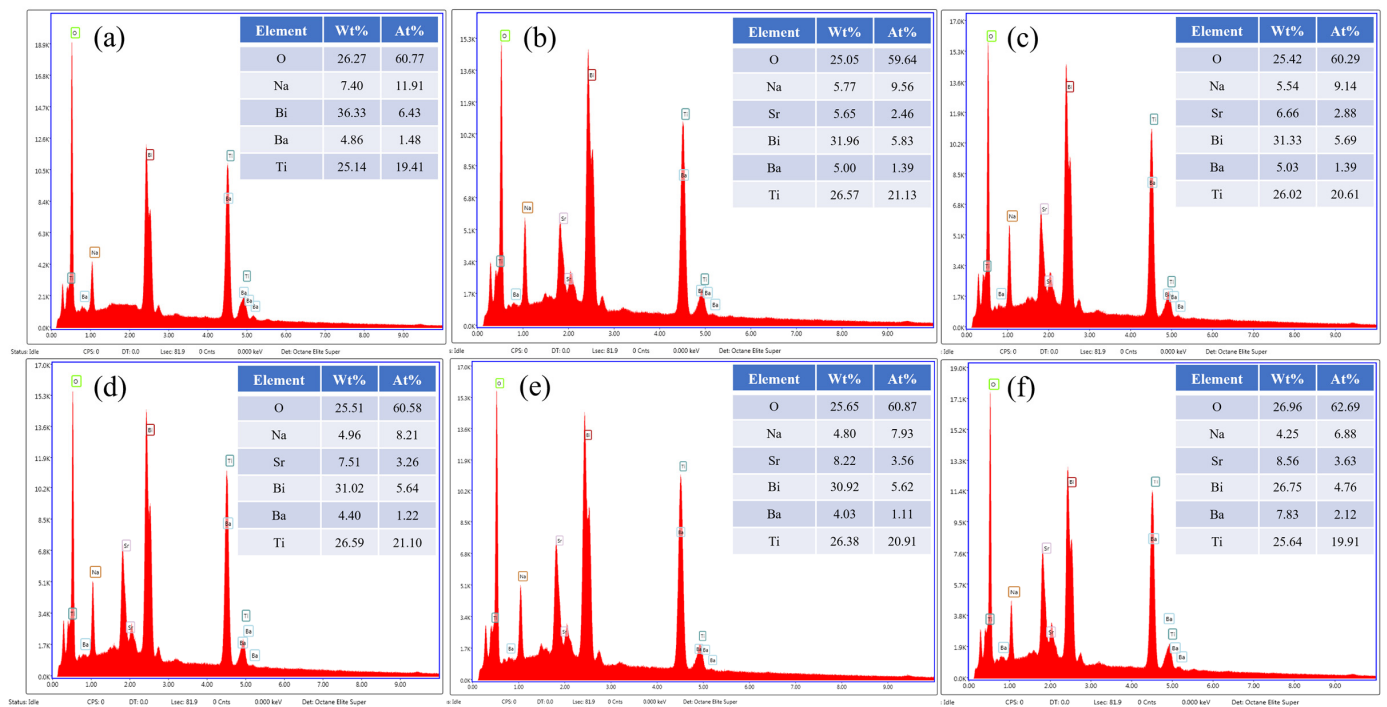


Figure 4. EDS spectra for the elemental analysis of $(1-x)$ BNT-BT- x SBT ceramics: (a) $x = 0$, (b) $x = 0.20$, (c) $x = 0.225$, (d) $x = 0.25$, (e) $x = 0.275$, and (f) $x = 0.30$.

Table 1. Elemental composition of $(1-x)$ BNT-BT- x SBT ceramic samples for $x = 0-0.30$.

Samples	Composition	
	Measured Atomic %	Theoretical Atomic %
$X = 0$	O = 60.77, Na = 11.91, Bi = 6.43, Ba = 1.48 and Ti = 19.41	A-site (Na = 9.4, Bi = 9.4 and Ba = 1.2), B-site (Ti = 20) and O = 60
$X = 0.20$	O = 59.64, Na = 9.56, Sr = 2.46, Bi = 5.83, Ba = 1.39 and Ti = 21.13	A-site (Na = 7.52, Bi = 8.32, Ba = 0.96 and Sr = 2.24), B-site (Ti = 20) and O = 60
$X = 0.225$	O = 60.29, Na = 9.14, Sr = 2.88, Bi = 5.69, Ba = 1.39 and Ti = 20.61	A-site (Na = 7.285, Bi = 8.185, Ba = 0.93 and Sr = 2.52), B-site (Ti = 20) and O = 60
$X = 0.25$	O = 60.58, Na = 8.21, Sr = 3.26, Bi = 5.64, Ba = 1.22 and Ti = 21.10	A-site (Na = 7.05, Bi = 8.05, Ba = 0.9 and Sr = 2.8), B-site (Ti = 20) and O = 60
$X = 0.275$	O = 60.87, Na = 7.93, Sr = 3.56, Bi = 5.62, Ba = 1.11 and Ti = 20.91	A-site (Na = 6.815, Bi = 7.915, Ba = 0.87 and Sr = 3.08), B-site (Ti = 20) and O = 60
$X = 0.30$	O = 62.69, Na = 6.88, Sr = 3.63, Bi = 4.76, Ba = 2.12 and Ti = 19.91	A-site (Na = 6.58, Bi = 7.78, Ba = 0.84 and Sr = 3.36), B-site (Ti = 20) and O = 60

Figure 5a illustrates dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) as functions of frequency for BNT-BT-SBT ceramics measured at RT from 100 Hz to 100 kHz. The sample $x = 0$ (BNT-BT) showed a lower ϵ_r of 1276 and lower $\tan\delta$ of 0.043 at 1 kHz as compared to pure BNT ceramics ($\epsilon_r = 692$ and $\tan\delta = 0.045$ at 1 kHz) [57,69]. The ϵ_r and $\tan\delta$ values were gradually enhanced to 1654 and 0.061 with the incorporation of SBT into BNT-BT for the $x = 0.275$ composition (as shown in Figure 5b). The improvement of the dielectric properties was attributed to the substitution of SBT into BNT-BT, a dense and homogeneous microstructure. Figure 5c,d show the temperature variation in ϵ_r and $\tan\delta$ of BNT-BT-SBT ceramics for lower and optimized compositions of $x = 0.20$ and 0.275 , which are measured at different frequencies of 0.1, 1, 10, 100, 1000 kHz. It is noticed that the dielectric maximum temperature (T_m) was shifted to a lower temperature with the addition of SBT for the composition of $x = 0.275$ than $x = 0.20$, as can be seen in Figure 5c,d. The addition of

SBT into BNT-BT can disrupt the long-range FE order, and lower the dielectric maximum temperature. As a result, PNRs form owing to the difference in ionic radius at the *A*-site of BNT-BT-SBT ceramics. Moreover, the dielectric maximum temperature peaks are shifted to higher temperatures, and gradually become diffuse with frequency, which indicates the typical relaxor ferroelectric behavior [70,71]. The degree of the relaxor behavior of these samples was calculated using a modified version of the Curie–Weiss law [56,72]:

$$\left(\frac{1}{\varepsilon_r}\right) - \left(\frac{1}{\varepsilon_r^m}\right) = \frac{(T - T_m)^\gamma}{C} \quad (3)$$

where ε_r^m is maximum dielectric constant at a maximum temperature T_m , T is absolute temperature, C is Curie constant, and γ is degree of relaxation. The value of γ is 1 for normal ferroelectrics and in between 1 and 2 for relaxor ferroelectrics [72]. Figure 5e,f display the log–log plots of $(1/\varepsilon_r - 1/\varepsilon_r^m)$ vs. $(T - T_m)$ of BNT-BT-SBT ceramics for the compositions of $x = 0.20$ and 0.275 , which were performed at 1 kHz. The γ value slightly enhanced from 1.88 ± 0.00311 to 1.92 ± 0.00315 , confirming the improved relaxor properties with the incorporation of SBT, resulting in high energy storage density and energy efficiency. These results are in good agreement with earlier reports [1–3].

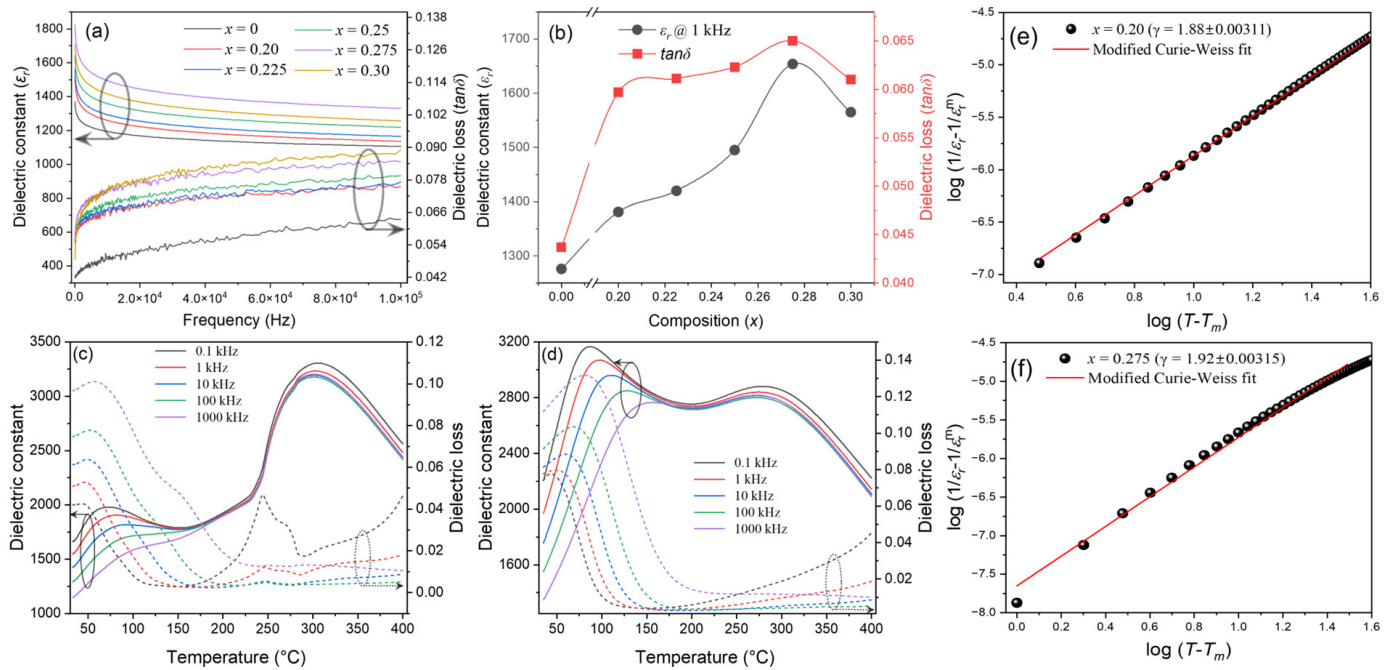


Figure 5. (a) Frequency variation in dielectric constant and dielectric loss of $(1-x)$ BNT-BT- x SBT ceramic capacitors for $x = 0$ – 0.30 . (b) Composition versus dielectric constant and dielectric loss. (c,d) Temperature dependency of dielectric constant and dielectric loss. (e,f) represent $\log(T - T_m)$ versus $\log\left[\left(\frac{1}{\varepsilon_r}\right) - \left(\frac{1}{\varepsilon_r^m}\right)\right]$ of $(1-x)$ BNT-BT- x SBT ceramic for $x = 0.20$ and 0.275 at 1 kHz.

Figure 6 shows the RT *P*-*E* loops of BNT-BT-SBT ceramic capacitors measured at 10 Hz. The BNT-BT-SBT sample ($x = 0$) displays typical FE characteristics. It shows a P_r of $17.06 \mu\text{C}/\text{cm}^2$, P_{max} of $29.29 \mu\text{C}/\text{cm}^2$, and coercive field (E_c) of $13.03 \text{ kV}/\text{cm}$. These values initially decreased for $x = 0.20$ and further increased with SBT, whereas the E_{BD} increased from $48.75 \text{ kV}/\text{cm}$ to $89.73 \text{ kV}/\text{cm}$ from $x = 0$ to 0.275 , which provides a high energy storage density (inset of Figure 6a). The *P*-*E* loops are slim as compared with the ferroelectric sample with a composition of $x = 0$; their shape is actually a pinched ferroelectric loop. The “pinched” hysteresis loop in ferroelectric materials can result from two key mechanisms: defect pinning or intrinsic phase transitions. In the first case, defects like impurities or grain boundaries pin domain walls, preventing full polarization switching

and creating a pinched loop. However, in defect-free systems, pinched loops can also arise from intermediate modulated phases that combine FE/AFE and RFE orders [73,74]. In this work, these phases form in $(1-x)$ BNT-BT- x SBT as the composition changes, leading to incomplete polarization switching. The material undergoes a transition between these modulated states by the application of an electric field, but the polarization does not completely revert to its original state after the field is removed. This results in a “pinched” loop due to the coexistence of AFE and RFE orders, preventing total polarization reversal. Therefore, the observed behavior can be understood by intrinsic phase transitions.

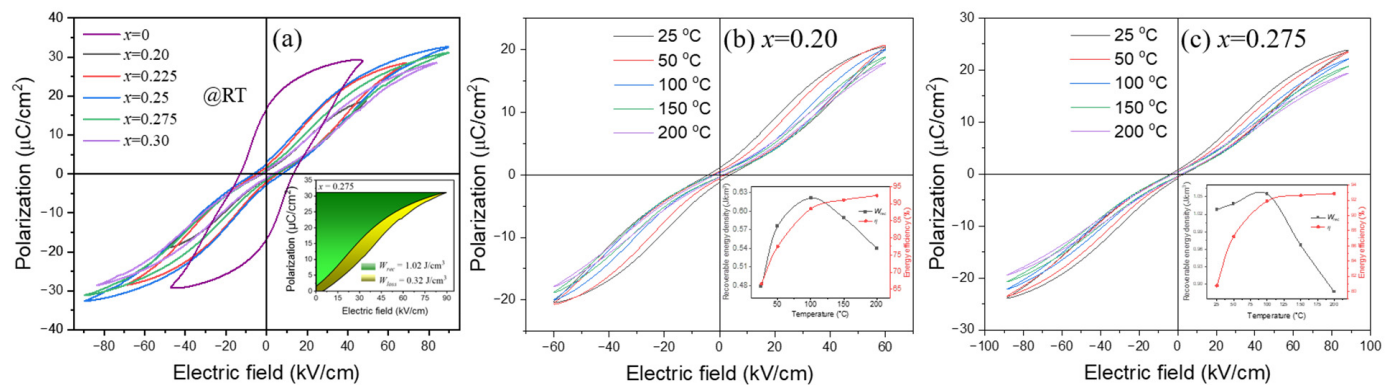


Figure 6. (a) RT bipolar P - E hysteresis loops of $(1-x)$ BNT-BT- x SBT ceramic capacitors for all compositions from $x = 0$ to 0.30. The inset of Figure 6a shows the unipolar P - E loop with energy storage density and energy loss for the optimized sample ($x = 0.275$). (b,c) bipolar P - E hysteresis loops. Insets of (b,c) show W_{rec} and η at different temperatures for $x = 0.20$ to 0.275.

Figure 6b,c show the bipolar P - E loops of BNT-BT-SBT ceramics measured at different temperatures and at 10 Hz. The energy storage density was increased with the temperature up to 100 °C, and further decreased due to diffusive FE to AFE transition (depolarization temperature). Dielectric and P - E hysteresis loop studies show that the T_d is mostly dependent on BNT-BT-SBT concentrations. Moreover, the energy storage properties in terms of W_{rec} , W_{loss} , and η were estimated by Equations (1) and (2) from unipolar P - E loops and shown in Table 2. The W_{rec} values gradually improved with the incorporation of SBT for $x = 0$ and 0.275. The sample $x = 0.275$ shows a high recoverable energy density of 1.02 J/cm³ at E_{BD} of 89.73 kV/cm and an energy efficiency of 75.83%. The improvement in the energy storage performance is achieved by combining relaxor and antiferroelectric properties. The combining relaxor and antiferroelectric properties by incorporation of SBT into BNT-BT produced an enhanced maximum polarization and a slim P - E loop, leading to an improved BDS, an improved recoverable energy density of 1.02 J/cm³, and a high energy efficiency of 75.98% at a BDS of 89 kV/cm using 0.725 [0.94BNT-0.06BT]-0.275 SBT lead-free ceramics. The values of W_{rec} and η of 0.725 (0.94 BNT-0.06 BT)-0.275 SBT ceramic capacitors are almost superior to, and comparable to, those of other lead-free ceramic materials, which are good candidates for energy storage capacitor applications [32,75–80].

Table 2. The values of ferroelectric (P_r , P_{max} , E_c , and E_{BD}) and energy storage properties (W_{rec} , W_{loss} , and η) of $(1-x)$ BNT-BT- x SBT ceramic capacitors for $x = 0$ –0.30.

Composition	P_r ($\mu\text{C}/\text{cm}^2$)	P_{max} ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	E_{BD} (kV/cm)	W_{rec} (J/cm ³)	W_{rec} (J/cm ³)	η (%)
$x = 0$	17.06	29.29	13.03	43.99	0.16	0.80	17.45
$x = 0.20$	0.79	18.76	2.19	48.75	0.39	0.14	73.58
$x = 0.225$	2.09	28.38	4.77	68.99	0.68	0.37	64.76
$x = 0.25$	2.95	32.82	6.47	89.38	0.93	0.50	65.03
$x = 0.275$	1.39	31.39	2.97	89.73	1.02	0.32	75.83
$x = 0.30$	1.00	28.54	2.33	83.53	0.96	0.22	81.35

4. Conclusions

A series of BNT-BT-SBT relaxor ferroelectric ceramics were fabricated using a conventional solid-state reaction method and we determined their energy storage properties by combining relaxor and antiferroelectric properties. XRD, Raman spectra, and SEM characterizations confirmed the formation of a rhombohedral–tetragonal phase, the presence of highly dynamic polar nanoregions, and reductions in grain size with homogeneous and dense microstructures. The dielectric and ferroelectric properties were enhanced. A high dielectric constant, low dielectric loss, and low remnant polarization were found with the incorporation of SBT into BNT-BT for $x = 0.275$ composition, which was beneficial for improving energy storage performance. Combining relaxor and antiferroelectric properties with fine grain size contributes a large breakdown strength. There is also large difference between P_{max} and P_r with the substitution of SBT, leading to high energy storage density and a high energy efficiency being obtained for the 0.725 [0.94BNT-0.06BT]-0.275 SBT composition. Our results demonstrate that combining relaxor and antiferroelectric properties is an effective approach and that BNT-BT-SBT ceramics are promising for energy storage capacitor applications.

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References

- Li, Q.; Chen, L.; Gadinski, M.R.; Zhang, S.; Zhang, G.; Li, H.U.; Iagodkine, E.; Haque, A.; Chen, L.-Q.; Jackson, T.N.; et al. Flexible High-Temperature Dielectric Materials from Polymer Nanocomposites. *Nature* **2015**, *523*, 576–579. [\[CrossRef\]](#) [\[PubMed\]](#)
- Kumar, N.; Ionin, A.; Ansell, T.; Kwon, S.; Hackenberger, W.; Cann, D. Multilayer Ceramic Capacitors Based on Relaxor BaTiO₃-Bi(Zn_{1/2}Ti_{1/2})O₃ for Temperature Stable and High Energy Density Capacitor Applications. *Appl. Phys. Lett.* **2015**, *106*, 252901. [\[CrossRef\]](#)
- Li, J.; Li, F.; Xu, Z.; Zhang, S. Multilayer Lead-Free Ceramic Capacitors with Ultrahigh Energy Density and Efficiency. *Adv. Mater.* **2018**, *30*, 1802155. [\[CrossRef\]](#) [\[PubMed\]](#)
- He, J.; Liu, X.; Zhao, Y.; Du, H.; Zhang, T.; Shi, J. Dielectric Stability and Energy-Storage Performance of BNT-Based Relaxor Ferroelectrics through Nb⁵⁺ and Its Excess Modification. *ACS Appl. Electron. Mater.* **2022**, *4*, 735–743. [\[CrossRef\]](#)
- Yang, Z.; Du, H.; Jin, L.; Poelman, D. High-Performance Lead-Free Bulk Ceramics for Electrical Energy Storage Applications: Design Strategies and Challenges. *J. Mater. Chem. A Mater.* **2021**, *9*, 18026–18085. [\[CrossRef\]](#)
- Wang, G.; Lu, Z.; Li, Y.; Li, L.; Ji, H.; Feteira, A.; Zhou, D.; Wang, D.; Zhang, S.; Reaney, I.M. Electroceramics for High-Energy Density Capacitors: Current Status and Future Perspectives. *Chem. Rev.* **2021**, *121*, 6124–6172. [\[CrossRef\]](#)
- Chen, Q.; Shen, Y.; Zhang, S.; Zhang, Q.M. Polymer-Based Dielectrics with High Energy Storage Density. *Annu. Rev. Mater. Res.* **2015**, *45*, 433–458. [\[CrossRef\]](#)
- Xie, A.; Zuo, R.; Qiao, Z.; Fu, Z.; Hu, T.; Fei, L. NaNbO₃-(Bi_{0.5}Li_{0.5})TiO₃ Lead-Free Relaxor Ferroelectric Capacitors with Superior Energy-Storage Performances via Multiple Synergistic Design. *Adv. Energy Mater.* **2021**, *11*, 2101378. [\[CrossRef\]](#)
- Li, T.; Jiang, X.; Li, J.; Xie, A.; Fu, J.; Zuo, R. Ultrahigh Energy-Storage Performances in Lead-Free Na_{0.5}Bi_{0.5}TiO₃-Based Relaxor Antiferroelectric Ceramics through a Synergistic Design Strategy. *ACS Appl. Mater. Interfaces* **2022**, *14*, 22263–22269. [\[CrossRef\]](#)
- Li, B.; Yan, Z.; Zhou, X.; Qi, H.; Koval, V.; Luo, X.; Luo, H.; Yan, H.; Zhang, D. Achieving Ultrahigh Energy Storage Density of La and Ta Codoped AgNbO₃ Ceramics by Optimizing the Field-Induced Phase Transitions. *ACS Appl. Mater. Interfaces* **2023**, *15*, 4246–4256. [\[CrossRef\]](#)

11. Yang, L.; Kong, X.; Li, F.; Hao, H.; Cheng, Z.; Liu, H.; Li, J.-F.; Zhang, S. Perovskite Lead-Free Dielectrics for Energy Storage Applications. *Prog. Mater. Sci.* **2019**, *102*, 72–108. [\[CrossRef\]](#)
12. Gui, D.-Y.; Ma, X.-Y.; Yuan, H.-D.; Wang, C.-H. Mn- and Yb-Doped BaTiO₃-(Na_{0.5}Bi_{0.5})TiO₃ Ferroelectric Relaxor with Low Dielectric Loss. *Materials* **2023**, *16*, 2229. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Shi, H.; Li, K.; Li, F.; Ma, J.; Tu, Y.; Long, M.; Lu, Y.; Gong, W.; Wang, C.; Shan, L. Enhanced Piezoelectricity and Thermal Stability of Electrostrain Performance in BiFeO₃-Based Lead-Free Ceramics. *Nanomaterials* **2023**, *13*, 942. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Ji, H.; Wang, D.; Bao, W.; Lu, Z.; Wang, G.; Yang, H.; Mostaed, A.; Li, L.; Feteira, A.; Sun, S.; et al. Ultrahigh Energy Density in Short-Range Tilted NBT-Based Lead-Free Multilayer Ceramic Capacitors by Nanodomain Percolation. *Energy Storage Mater.* **2021**, *38*, 113–120. [\[CrossRef\]](#)
15. Zhang, G.; Zhu, D.; Zhang, X.; Zhang, L.; Yi, J.; Xie, B.; Zeng, Y.; Li, Q.; Wang, Q.; Jiang, S. High-Energy Storage Performance of (Pb_{0.87}Ba_{0.1}La_{0.02})(Zr_{0.68}Sn_{0.24}Ti_{0.08})O₃ Antiferroelectric Ceramics Fabricated by the Hot-Press Sintering Method. *J. Am. Ceram. Soc.* **2015**, *98*, 1175–1181. [\[CrossRef\]](#)
16. Liu, Z.; Chen, X.; Peng, W.; Xu, C.; Dong, X.; Cao, F.; Wang, G. Temperature-Dependent Stability of Energy Storage Properties of Pb_{0.97}La_{0.02}(Zr_{0.58}Sn_{0.335}Ti_{0.085})O₃ Antiferroelectric Ceramics for Pulse Power Capacitors. *Appl. Phys. Lett.* **2015**, *106*, 262901. [\[CrossRef\]](#)
17. Yuan, Q.; Li, G.; Yao, F.-Z.; Cheng, S.-D.; Wang, Y.; Ma, R.; Mi, S.-B.; Gu, M.; Wang, K.; Li, J.-F.; et al. Simultaneously Achieved Temperature-Insensitive High Energy Density and Efficiency in Domain Engineered BaTiO₃-Bi(Mg_{0.5}Zr_{0.5})O₃ Lead-Free Relaxor Ferroelectrics. *Nano Energy* **2018**, *52*, 203–210. [\[CrossRef\]](#)
18. Zhao, P.; Wang, H.; Wu, L.; Chen, L.; Cai, Z.; Li, L.; Wang, X. High-Performance Relaxor Ferroelectric Materials for Energy Storage Applications. *Adv. Energy Mater.* **2019**, *9*, 1803048. [\[CrossRef\]](#)
19. Asbani, B.; Gagou, Y.; Ben Moumen, S.; Dellis, J.-L.; Lahmar, A.; Amjoud, M.; Mezzane, D.; El Marssi, M.; Rozic, B.; Kutnjak, Z. Large Electrocaloric Responsivity and Energy Storage Response in the Lead-Free Ba(Ge_xTi_{1-x})O₃ Ceramics. *Materials* **2022**, *15*, 5227. [\[CrossRef\]](#)
20. Yuan, Q.; Yao, F.; Wang, Y.; Ma, R.; Wang, H. Relaxor Ferroelectric 0.9BaTiO₃-0.1Bi(Zn_{0.5}Zr_{0.5})O₃ Ceramic Capacitors with High Energy Density and Temperature Stable Energy Storage Properties. *J. Mater. Chem. C Mater.* **2017**, *5*, 9552–9558. [\[CrossRef\]](#)
21. Suchanicz, J.; Sitko, D.; Stanuch, K.; Świerczek, K.; Jagło, G.; Kruk, A.; Kluczevska-Chmielarz, K.; Konieczny, K.; Czaja, P.; Aleksandrowicz, J.; et al. Temperature and E-Poling Evolution of Structural, Vibrational, Dielectric, and Ferroelectric Properties of Ba_{1-x}Sr_xTiO₃ Ceramics (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.45). *Materials* **2023**, *16*, 6316. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Yin, J.; Zhang, Y.; Lv, X.; Wu, J. Ultrahigh Energy-Storage Potential under Low Electric Field in Bismuth Sodium Titanate-Based Perovskite Ferroelectrics. *J. Mater. Chem. A Mater.* **2018**, *6*, 9823–9832. [\[CrossRef\]](#)
23. Qi, H.; Zuo, R. Linear-like Lead-Free Relaxor Antiferroelectric (Bi_{0.5}Na_{0.5})TiO₃-NaNbO₃ with Giant Energy-Storage Density/Efficiency and Super Stability against Temperature and Frequency. *J. Mater. Chem. A Mater.* **2019**, *7*, 3971–3978. [\[CrossRef\]](#)
24. Lu, Y.; Zhang, H.; Yang, H.; Fan, P.; Samart, C.; Takesue, N.; Tan, H. SPS-Prepared High-Entropy (Bi_{0.2}Na_{0.2}Sr_{0.2}Ba_{0.2}Ca_{0.2})TiO₃ Lead-Free Relaxor-Ferroelectric Ceramics with High Energy Storage Density. *Crystals* **2023**, *13*, 445. [\[CrossRef\]](#)
25. Jiang, Y.; Niu, X.; Liang, W.; Jian, X.; Shi, H.; Li, F.; Zhang, Y.; Wang, T.; Gong, W.; Zhao, X.; et al. Enhanced Energy Storage Performance in Na_{0.5}Bi_{0.5}TiO₃-Based Relaxor Ferroelectric Ceramics via Compositional Tailoring. *Materials* **2022**, *15*, 5881. [\[CrossRef\]](#)
26. Liu, X.; Shi, J.; Zhu, F.; Du, H.; Li, T.; Liu, X.; Lu, H. Ultrahigh Energy Density and Improved Discharged Efficiency in Bismuth Sodium Titanate Based Relaxor Ferroelectrics with A-Site Vacancy. *J. Mater.* **2018**, *4*, 202–207. [\[CrossRef\]](#)
27. Zhang, Y.; Jia, Y.; Yang, J.; Feng, Z.; Sun, S.; Zhu, X.; Wang, H.; Yan, S.; Zheng, M. Enhancing Energy Storage Performance of 0.85Bi_{0.5}Na_{0.5}TiO₃-0.15LaFeO₃ Lead-Free Ferroelectric Ceramics via Buried Sintering. *Materials* **2024**, *17*, 4019. [\[CrossRef\]](#)
28. Zhou, M.; Liang, R.; Zhou, Z.; Dong, X. Superior Energy Storage Properties and Excellent Stability of Novel NaNbO₃-Based Lead-Free Ceramics with A-Site Vacancy Obtained via a Bi₂O₃ Substitution Strategy. *J. Mater. Chem. A Mater.* **2018**, *6*, 17896–17904. [\[CrossRef\]](#)
29. Lubszczyk, M.; Brylewski, T.; Rutkowski, P.; Świerczek, K.; Kruk, A. Preparation and Physicochemical Properties of K_{0.5}Na_{0.5}NbO₃ Ceramics Obtained Using a Modified Wet Chemistry Method. *Mater. Sci. Eng. B* **2023**, *288*, 116135. [\[CrossRef\]](#)
30. Tian, Y.; Jin, L.; Zhang, H.; Xu, Z.; Wei, X.; Viola, G.; Abrahams, I.; Yan, H. Phase Transitions in Bismuth-Modified Silver Niobate Ceramics for High Power Energy Storage. *J. Mater. Chem. A Mater.* **2017**, *5*, 17525–17531. [\[CrossRef\]](#)
31. Xu, Y.; Guo, Y.; Liu, Q.; Bai, J.; Huang, J.; Lin, L.; Lu, S. Antiferroelectricity in New Silver Niobate Lead-Free Antiferroelectric Ceramics (1-x)AgNbO₃-xCaZrO₃ (x = 0.00–0.01). *J. Alloys Compd.* **2019**, *782*, 469–476. [\[CrossRef\]](#)
32. Liu, X.; Zhao, Y.; Shi, J.; Du, H.; Xu, X.; Lu, H.; Che, J.; Li, X. Improvement of Dielectric and Ferroelectric Properties in Bismuth Sodium Titanate Based Relaxors through Bi Non-Stoichiometry. *J. Alloys Compd.* **2019**, *799*, 231–238. [\[CrossRef\]](#)
33. Shi, J.; Fan, H.; Liu, X.; Li, Q. Giant Strain Response and Structure Evolution in (Bi_{0.5}Na_{0.5})_{0.945-x}(Bi_{0.2}Sr_{0.7}□_{0.1})_xBa_{0.055}TiO₃ Ceramics. *J. Eur. Ceram. Soc.* **2014**, *34*, 3675–3683. [\[CrossRef\]](#)
34. Li, F.; Hou, X.; Wang, J.; Zeng, H.; Shen, B.; Zhai, J. Structure-Design Strategy of 0–3 Type (Bi_{0.32}Sr_{0.42}Na_{0.20})TiO₃/MgO Composite to Boost Energy Storage Density, Efficiency and Charge-Discharge Performance. *J. Eur. Ceram. Soc.* **2019**, *39*, 2889–2898. [\[CrossRef\]](#)
35. Liu, N.; Liang, R.; Zhou, Z.; Dong, X. Designing Lead-Free Bismuth Ferrite-Based Ceramics Learning from Relaxor Ferroelectric Behavior for Simultaneous High Energy Density and Efficiency under Low Electric Field. *J. Mater. Chem. C Mater.* **2018**, *6*, 10211–10217. [\[CrossRef\]](#)

36. Wu, Y.; Fan, Y.; Liu, N.; Peng, P.; Zhou, M.; Yan, S.; Cao, F.; Dong, X.; Wang, G. Enhanced Energy Storage Properties in Sodium Bismuth Titanate-Based Ceramics for Dielectric Capacitor Applications. *J. Mater. Chem. C Mater.* **2019**, *7*, 6222–6230. [\[CrossRef\]](#)
37. Hu, Q.; Tian, Y.; Zhu, Q.; Bian, J.; Jin, L.; Du, H.; Alikin, D.O.; Shur, V.Y.; Feng, Y.; Xu, Z.; et al. Achieve Ultrahigh Energy Storage Performance in BaTiO₃–Bi(Mg^{1/2}Ti^{1/2})O₃ Relaxor Ferroelectric Ceramics via Nano-Scale Polarization Mismatch and Reconstruction. *Nano Energy* **2020**, *67*, 104264. [\[CrossRef\]](#)
38. Wang, H.; Jiang, X.; Liu, X.; Yang, R.; Yang, Y.; Zheng, Q.; Kwok, K.W.; Lin, D. An Effective Approach to Achieve High Energy Storage Density and Efficiency in BNT-Based Ceramics by Doping AgNbO₃. *Dalton Trans.* **2019**, *48*, 17864–17873. [\[CrossRef\]](#)
39. Shi, P.; Zhu, L.; Gao, W.; Yu, Z.; Lou, X.; Wang, X.; Yang, Z.; Yang, S. Large Energy Storage Properties of Lead-Free (1-x)(0.72Bi_{0.5}Na_{0.5}TiO₃–0.28SrTiO₃)-xBiAlO₃ Ceramics at Broad Temperature Range. *J. Alloys Compd.* **2019**, *784*, 788–793. [\[CrossRef\]](#)
40. Pan, Z.; Hu, D.; Zhang, Y.; Liu, J.; Shen, B.; Zhai, J. Achieving High Discharge Energy Density and Efficiency with NBT-Based Ceramics for Application in Capacitors. *J. Mater. Chem. C Mater.* **2019**, *7*, 4072–4078. [\[CrossRef\]](#)
41. Cross, L.E. Relaxor Ferroelectrics. *Ferroelectrics* **1987**, *76*, 241–267. [\[CrossRef\]](#)
42. Cowley, R.A.; Gvasaliya, S.N.; Lushnikov, S.G.; Roessli, B.; Rotaru, G.M. Relaxing with Relaxors: A Review of Relaxor Ferroelectrics. *Adv. Phys.* **2011**, *60*, 229–327. [\[CrossRef\]](#)
43. Kleemann, W. Relaxor Ferroelectrics: Cluster Glass Ground State via Random Fields and Random Bonds. *Phys. Status Solidi* **2014**, *251*, 1993–2002. [\[CrossRef\]](#)
44. Zhang, Z.; Tan, R.; Wang, F.; Yan, K. Core–Shell Grain Structure and High Energy Storage Performance of BNT-Based Relaxor Ferroelectric Ceramics. *Electron. Mater. Lett.* **2023**, *19*, 161–171. [\[CrossRef\]](#)
45. Glaum, J.; Heo, Y.; Acosta, M.; Sharma, P.; Seidel, J.; Hinterstein, M. Revealing the Role of Local Stress on the Depolarization of BNT-BT-Based Relaxors. *Phys. Rev. Mater.* **2019**, *3*, 054406. [\[CrossRef\]](#)
46. Lv, J.; Li, Q.; Li, Y.; Tang, M.; Jin, D.; Yan, Y.; Fan, B.; Jin, L.; Liu, G. Significantly Improved Energy Storage Performance of NBT-BT Based Ceramics through Domain Control and Preparation Optimization. *Chem. Eng. J.* **2021**, *420*, 129900. [\[CrossRef\]](#)
47. Xu, C.; Lin, D.; Kwok, K.W. Structure, Electrical Properties and Depolarization Temperature of (Bi_{0.5}Na_{0.5})TiO₃–BaTiO₃ Lead-Free Piezoelectric Ceramics. *Solid. State Sci.* **2008**, *10*, 934–940. [\[CrossRef\]](#)
48. Takenaka, T.; Kei-ichi Maruyama, K.M.; Koichiro Sakata, K.S. (Bi_{1/2}Na_{1/2})TiO₃–BaTiO₃ System for Lead-Free Piezoelectric Ceramics. *Jpn. J. Appl. Phys.* **1991**, *30*, 2236. [\[CrossRef\]](#)
49. Jones, G.O.; Thomas, P.A. Investigation of the Structure and Phase Transitions in the Novel A-Site Substituted Distorted Perovskite Compound Na_{0.5}Bi_{0.5}TiO₃. *Acta Crystallogr. B* **2002**, *58*, 168–178. [\[CrossRef\]](#)
50. Buttner, R.H.; Maslen, E.N. Structural Parameters and Electron Difference Density in BaTiO₃. *Acta Crystallogr. B* **1992**, *48*, 764–769. [\[CrossRef\]](#)
51. Al-Shakarchi, E.K.; Mahmood, N.B. Three Techniques Used to Produce BaTiO₃ Fine Powder. *J. Mod. Phys.* **2011**, *2*, 1420–1428. [\[CrossRef\]](#)
52. Mahmood, N.B.; Al-Shakarchi, E.K. Dielectric Properties of BNT-xBT Prepared by Hydrothermal Process. *J. Adv. Dielectr.* **2017**, *07*, 1750019. [\[CrossRef\]](#)
53. Nesterović, A.; Vukmirović, J.; Stijepović, I.; Milanović, M.; Bajac, B.; Tóth, E.; Cvejić, Ž.; Srdić, V.V. Structure and Dielectric Properties of (1-x)Bi_{0.5}Na_{0.5}TiO₃–xBaTiO₃ Piezoceramics Prepared Using Hydrothermally Synthesized Powders. *R. Soc. Open Sci.* **2021**, *8*, 202365. [\[CrossRef\]](#)
54. Craciun, F.; Galassi, C.; Birjega, R. Electric-Field-Induced and Spontaneous Relaxor-Ferroelectric Phase Transitions in (Na_{1/2}Bi_{1/2})_{1-x}Ba_xTiO₃. *J. Appl. Phys.* **2012**, *112*, 124106. [\[CrossRef\]](#)
55. Jaita, P.; Manotham, S.; Rujijanagul, G. Influence of Al₂O₃ Nanoparticle Doping on Depolarization Temperature, and Electrical and Energy Harvesting Properties of Lead-Free 0.94(Bi_{0.5}Na_{0.5})TiO₃–0.06BaTiO₃ Ceramics. *RSC Adv.* **2020**, *10*, 32078–32087. [\[CrossRef\]](#)
56. Gupta, S.K.; McQuade, R.; Gibbons, B.; Mardilovich, P.; Cann, D.P. Electric Field-Induced Strain in Sr(Hf_{0.5}Zr_{0.5})O₃-Modified Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO₃ Piezoelectric Ceramics. *J. Appl. Phys.* **2020**, *127*, 074104. [\[CrossRef\]](#)
57. Pattipaka, S.; James, A.R.; Dobbidi, P. Enhanced Dielectric and Piezoelectric Properties of BNT-KNNG Piezoelectric Ceramics. *J. Alloys Compd.* **2018**, *765*, 1195–1208. [\[CrossRef\]](#)
58. Tong, X.-Y.; Song, M.-W.; Zhou, J.-J.; Wang, K.; Guan, C.-L.; Liu, H.; Fang, J.-Z. Enhanced Energy Storage Properties in Nb-Modified Bi_{0.5}Na_{0.5}TiO₃–SrTiO₃ Lead-Free Electroceramics. *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 5780–5790. [\[CrossRef\]](#)
59. Jaita, P.; Saenkam, K.; Rujijanagul, G. Improvements in Piezoelectric and Energy Harvesting Properties with a Slight Change in Depolarization Temperature in Modified BNKT Ceramics by a Simple Technique. *RSC Adv.* **2023**, *13*, 3743–3758. [\[CrossRef\]](#)
60. Fernandez-Benavides, D.; Gutierrez-Perez, A.; Benitez-Castro, A.; Ayala-Ayala, M.; Moreno-Murguía, B.; Muñoz-Saldaña, J. Comparative Study of Ferroelectric and Piezoelectric Properties of BNT-BKT-BT Ceramics near the Phase Transition Zone. *Materials* **2018**, *11*, 361. [\[CrossRef\]](#)
61. Chu, B.; Hao, J.; Li, P.; Li, Y.; Li, W.; Zheng, L.; Zeng, H. High-Energy Storage Properties over a Broad Temperature Range in La-Modified BNT-Based Lead-Free Ceramics. *ACS Appl. Mater. Interfaces* **2022**, *14*, 19683–19696. [\[CrossRef\]](#) [\[PubMed\]](#)
62. Shi, L.N.; Wang, Y.G.; Ren, Z.H.; Jain, A.; Jiang, S.S.; Chen, F.G. Significant Improvement in Electrical Characteristics and Energy Storage Performance of NBT-Based Ceramics. *Ceram. Int.* **2022**, *48*, 26973–26983. [\[CrossRef\]](#)

63. Jaita, P.; Watcharapasorn, A.; Cann, D.P.; Jiansirisomboon, S. Dielectric, Ferroelectric and Electric Field-Induced Strain Behavior of Ba(Ti_{0.90}Sn_{0.10})O₃-Modified Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO₃ Lead-Free Piezoelectrics. *J. Alloys Compd.* **2014**, *596*, 98–106. [\[CrossRef\]](#)
64. Shannon, R.D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767. [\[CrossRef\]](#)
65. Boonlakhorn, J.; Thongbai, P.; Putasaeng, B.; Yamwong, T.; Maensiri, S. Very High-Performance Dielectric Properties of Ca_{1–3x/2}Yb_xCu₃Ti₄O₁₂ Ceramics. *J. Alloys Compd.* **2014**, *612*, 103–109. [\[CrossRef\]](#)
66. Sun, Z.; Wang, Z.; Tian, Y.; Wang, G.; Wang, W.; Yang, M.; Wang, X.; Zhang, F.; Pu, Y. Progress, Outlook, and Challenges in Lead-Free Energy-Storage Ferroelectrics. *Adv. Electron. Mater.* **2020**, *6*, 1900698. [\[CrossRef\]](#)
67. Choi, H.; Pattipaka, S.; Son, Y.H.; Bae, Y.M.; Park, J.H.; Jeong, C.K.; Lee, H.E.; Kim, S.-D.; Ryu, J.; Hwang, G.-T. Improved Energy Storage Density and Efficiency of Nd and Mn Co-Doped Ba_{0.7}Sr_{0.3}TiO₃ Ceramic Capacitors Via Defect Dipole Engineering. *Materials* **2023**, *16*, 6753. [\[CrossRef\]](#)
68. Maqbool, A.; Hussain, A.; Malik, R.A.; Rahman, J.U.; Zaman, A.; Song, T.K.; Kim, W.-J.; Kim, M.-H. Evolution of Phase Structure and Giant Strain at Low Driving Fields in Bi-Based Lead-Free Incipient Piezoelectrics. *Mater. Sci. Eng. B* **2015**, *199*, 105–112. [\[CrossRef\]](#)
69. Hiruma, Y.; Nagata, H.; Takenaka, T. Phase Diagrams and Electrical Properties of (Bi_{1/2}Na_{1/2})TiO₃-Based Solid Solutions. *J. Appl. Phys.* **2008**, *104*, 124106. [\[CrossRef\]](#)
70. Shvartsman, V.V.; Lupascu, D.C. Lead-Free Relaxor Ferroelectrics. *J. Am. Ceram. Soc.* **2012**, *95*, 1–26. [\[CrossRef\]](#)
71. Liu, G.; Wang, Y.; Han, G.; Gao, J.; Yu, L.; Tang, M.; Li, Y.; Hu, J.; Jin, L.; Yan, Y. Enhanced Electrical Properties and Energy Storage Performances of NBT-ST Pb-Free Ceramics through Glass Modification. *J. Alloys Compd.* **2020**, *836*, 154961. [\[CrossRef\]](#)
72. Uchino, K.; Nomura, S.; Cross, L.E.; Jang, S.J.; Newnham, R.E. Electrostrictive Effect in Lead Magnesium Niobate Single Crystals. *J. Appl. Phys.* **1980**, *51*, 1142–1145. [\[CrossRef\]](#)
73. Xu, B.; Paillard, C.; Dkhil, B.; Bellaiche, L. Pinched Hysteresis Loop in Defect-Free Ferroelectric Materials. *Phys. Rev. B* **2016**, *94*, 140101. [\[CrossRef\]](#)
74. Fan, P.; Zhang, Y.; Xie, B.; Zhu, Y.; Ma, W.; Wang, C.; Yang, B.; Xu, J.; Xiao, J.; Zhang, H. Large Electric-Field-Induced Strain in B-Site Complex-Ion (Fe_{0.5}Nb_{0.5})⁴⁺-Doped Bi_{1/2}(Na_{0.82}K_{0.12})_{1/2}TiO₃ Lead-Free Piezoceramics. *Ceram. Int.* **2018**, *44*, 3211–3217. [\[CrossRef\]](#)
75. Wu, J.; Mahajan, A.; Riekehr, L.; Zhang, H.; Yang, B.; Meng, N.; Zhang, Z.; Yan, H. Perovskite Sr_x(Bi_{1–x}Na_{0.97–x}Li_{0.03})_{0.5}TiO₃ Ceramics with Polar Nano Regions for High Power Energy Storage. *Nano Energy* **2018**, *50*, 723–732. [\[CrossRef\]](#)
76. Yan, Y.; Zeng, X.; Deng, T.; Chen, F.; Yang, L.; He, Z.; Jin, L.; Liu, G. Rheological, Mechanical, and Electrical Properties of Sr_{0.7}Bi_{0.2}TiO₃ Modified BaTiO₃ Ceramic and Its Composites. *J. Am. Ceram. Soc.* **2023**, *106*, 3052–3065. [\[CrossRef\]](#)
77. Li, Q.; Wang, C.; Yadav, A.K.; Fan, H. Large Electrostrictive Effect and Energy Storage Density in MnCO₃ Modified Na_{0.325}Bi_{0.395}Sr_{0.245}□_{0.035}TiO₃ Lead-Free Ceramics. *Ceram. Int.* **2020**, *46*, 3374–3381. [\[CrossRef\]](#)
78. Nayak, S.; Venkateshwarlu, S.; Budisuharto, A.S.; Jørgensen, M.R.V.; Borkiewicz, O.; Beyer, K.A.; Pramanick, A. Effect of A-site Substitutions on Energy Storage Properties of BaTiO₃-BiScO₃ Weakly Coupled Relaxor Ferroelectrics. *J. Am. Ceram. Soc.* **2019**, *102*, 5919–5933. [\[CrossRef\]](#)
79. Cao, W.P.; Li, W.L.; Dai, X.F.; Zhang, T.D.; Sheng, J.; Hou, Y.F.; Fei, W.D. Large Electrocaloric Response and High Energy-Storage Properties over a Broad Temperature Range in Lead-Free NBT-ST Ceramics. *J. Eur. Ceram. Soc.* **2016**, *36*, 593–600. [\[CrossRef\]](#)
80. Jabeen, N.; Hussain, A.; Qaiser, M.A.; Ali, J.; Rehman, A.; Sfina, N.; Ali, G.A.; Tirth, V. Enhanced Energy Storage Performance by Relaxor Highly Entropic (Ba_{0.2}Na_{0.2}K_{0.2}La_{0.2}Bi_{0.2})TiO₃ and (Ba_{0.2}Na_{0.2}K_{0.2}Mg_{0.2}Bi_{0.2})TiO₃ Ferroelectric Ceramics. *Appl. Sci.* **2022**, *12*, 12933. [\[CrossRef\]](#)

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