

# Enhanced electrical and energy storage properties of BNT-based ceramics by the nanocrystals-induced method

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## ABSTRACT

The effect of BT nanocrystals on phase structure and electrical characteristics of lead-free BNT ceramics was investigated in this study. The molten-salt method was used to make the BT nanocrystals. All ceramics showed a pure perovskite phase. The density values ranged from 5.87 to 5.91 g/cm<sup>3</sup>. The highest density value was obtained for the sample of BT seed = 5 mol%. With increasing BT seed content, the dielectric constant ( $\varepsilon_r$ ) at room temperature tended to increase. The sample of 10BTs (x = 10 mol%) had the highest dielectric constant ( $\varepsilon_r$  = 1652). For compositions of BT-added, the dielectric spectra showed a broad maximum around  $T_{\text{F-R}}$ . The sample of 5BTs (x = 5 mol%) had the highest d<sub>33</sub> value of 161 pC/N. Furthermore, a high energy storage density ( $W \sim 0.69 \text{ J/cm}^3$ ) with the highest energy storage efficiency ( $\eta = 70\%$ ) was obtained from the sample of BT nanocrystals added (BTs = 0.10 mol%).

## 1 Introduction

For many years,  $Pb(Zr_{1-x}Ti_x)O_3$  (PZT) has been reported to have outstanding dielectric and piezoelectric characteristics. These ceramics are very important for many electronic applications [1]. PZT ceramics, on the other hand, are not environmentally friendly due to the toxicity of lead oxide and, in particular, its high vapor pressure during the high temperature sintering process. In recent years, many researchers have been working on producing leadfree piezoelectric materials as alternatives to leadbased materials [2–7]. Sodium bismuth titanate (Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> or NBT) [3, 4, 8–13] is one of the leadfree ceramics that is considered to be an important ceramic for lead-free fabrication and a promising candidate for electronic applications. Because of its high remnant polarization (38  $\mu$ C/cm<sup>3</sup>) and high Curie temperature (340 °C). However, the pure BNT ceramic has a significant coercive field ( $E_c \sim 73$  kV/

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cm) [8] and high conductivity, resulting in a difficult poling process. Moreover, it was found that the data on piezoelectric properties especially d<sub>33</sub> values of the pure BNT ceramic are scarce and also showed low values. For application, pure BNT materials are unsuitable for the energy storage process because they show a high hysteresis with high  $P_r$  and  $E_c$ values. Several processing methods have been used to enhance the electrical characteristics of lead-free BNT ceramics for energy storage and other applications. One of the methods to enhance the electrical characteristics of BNT-based ceramics, is to dope other metal oxide and rare earth elements, such as La-doped BNT [14], Ce-doped BNT (Bi<sub>0.5</sub>Na<sub>0.44</sub>K<sub>0.06-</sub> TiO<sub>3</sub>) [15], Er-doped BNT [16] and Nd-doped BNT (Bi<sub>1-x</sub>Nd<sub>x</sub>Na<sub>0.5</sub>TiO<sub>3</sub>) [17], K-doped BNT (Bi<sub>0.5</sub>(- $Na_{1-x}K_x)_{0.5}TiO_3$  [18], Mn-doped BNT-ST (0.7BNT-0.3ST) [19]. Moreover, many researchers have carried out developing electrical properties of the BNT ceramics by the addition with other compound to improve their electrical properties, such as (Bi<sub>0.5-</sub> Na<sub>0.5</sub>)TiO<sub>3</sub>-BaTiO<sub>3</sub> (BNT-BT) [11, 20, 21], (Bi<sub>0.5</sub>Na<sub>0.5</sub>)- $TiO_3$ -Ba(Al<sub>0.5</sub>Ta<sub>0.5</sub>)O<sub>3</sub> (BNT-BAT) [22],  $(Bi_{0.51}Na_{0.47})TiO_3$ -Ba $(Zr_{0.3}Ti_{0.7})O_3$  (BNT-BZT) [23], Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub>-K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> (BNT-BT-KNN) [24], BiTi<sub>0.5</sub>Zn<sub>0.5</sub>O<sub>3</sub>-Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub> (BZT-BNT-BT) [25]. Nevertheless, the electrical properties of piezoelectric ceramics are widely known to be dependent not only on their composition but also on their texture, particularly the crystallographic grain (grain orientations) in the microstructure of the ceramics. The template-grain growth and seed-induced approach have been used in the fabrication of piezoelectric materials to produce texture in ceramics that can enhance electrical properties such as high dielectric constant and piezoelectric coefficient [26-34]. Those methods are applied using nanoparticles as a seed or template added to the base ceramic component. The use of the above processes to fabricate lead-free ceramics has been reported to improve their electrical properties [26–34]. Recently, W. Bai et al. [29] revealed that using plate-like SrTiO<sub>3</sub> increased the piezoelectric coefficient  $(d_{33}^*)$  of 0.72(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-0.28SrTiO<sub>3</sub> (BNT-ST) ceramics. When compared to the random ceramic sample, the textured ceramics demonstrated improved dielectric characteristics and high piezoelectric properties with a strain level of 0.39% at 70 kV/cm and strain  $d_{33}^*$  $(S_{\text{max}}/E_{\text{max}})$  of 557 pm/V. Moreover, textured (BNT-KN-ST) ceramics in the composition of 0.90(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-0.05KNbO<sub>3</sub>-0.05SrTiO<sub>3</sub> systems prepared by template-grain growth and using perovskite plate-like (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub> and SrTiO<sub>3</sub> particles as template have been reported by Bai et al. [30]. Shu et al. [31] investigated the electrical properties of (Ba<sub>0.85</sub>Ca<sub>0.15</sub>)(Ti<sub>0.9</sub>Zr<sub>0.1</sub>)O<sub>3</sub> (BCZT) ceramics induced by BNT powder (prepared by the molten-salt method and varied the calcine temperature). The excellent electrical properties with  $d_{33} = 450$  pC/N,  $k_p = 53\%$ , and  $\varepsilon_r = 4013$  were obtained for the BNT powder calcined at 820 °C.

In our initial attempts, we investigated the effect of nanometric seeds on the phase structure and electrical properties of BCZT ceramics [32] prepared by the seed-induced method while varying the seed amount (0.0-4.0 mol%). The pure perovskite phase was created at a low calcination temperature, according to the findings. Some electrical properties, particularly the  $d_{33}$  value, were improved using BCZT seed. The maximum phase transition temperature  $(T_c)$  was 93 °C, the highest  $d_{33}$  was 520 pC/N, and the highest  $k_{\rm t}$  was 48% in samples with 3.0 mol% seed. In addition, using the same technique as the nanocrystal seeds, we investigated the electrical characteristics of Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> ceramics [33] and Bi<sub>0.5</sub>(Na<sub>0.80</sub>K<sub>0.20</sub>)<sub>0.5-</sub> TiO<sub>3</sub> [34]. Results discovered that the seed-added samples had the highest piezoelectric charge coefficient  $(d_{33})$  and piezoelectric voltage coefficient  $(g_{33})$ . At room temperature, BNT seeds increased energy storage density [33].

The seeding process, also known as template-grain growth (TGG), has been shown to improve the electrical characteristics of piezoelectric ceramics in the literature. Thus, in this research, we applied the seedinduced technique to improve the electrical properties and energy storage properties of BNT-based ceramics using BT nanocrystals as seeds.

#### 2 **Experimental procedure**

In this work, lead-free Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> ceramic was produced by a seed-induced method using the nanoparticles of BaTiO<sub>3</sub> as seeds. The starting materials of the BaTiO<sub>3</sub> seed were synthesized by the molten-salt method. The seed starting powders were weighed and mixed with KCl–NaCl salt (1:1) before being heated at 750 °C for 2 h. They were then washed multiple times with hot deionized water until no trace of anion remained before being dried in an oven at 120 °C. The BT seed was then mixed with the raw materials of Bi<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich,  $\geq$  99.9%), NaCO<sub>3</sub> (Sigma-Aldrich, 99.95–100.5%), TiO<sub>2</sub> (Sigma-Aldrich, 99–105.5%) in the ratio of BNT: seed = (1– *x*):*x*, where BT seed content varied from 0 to 10 mol% (0, 3, 5, 7 and 10 mol%) and prepared by the mixed oxide method. The mixed powder was ball-milled for 24 h before being calcined for 2 h at 900 °C. The powder was then combined with an organic binder, pressed into pellets, and sintered for 2 h at 1100 °C. The ceramics preparation is illustrated schematically in Fig. 1.

X-ray diffraction technique (XRD) and scanning electron microscopy (SEM) were used to analyze the phase structure and microstructure of bulk ceramic materials. Ceramic samples were polished and covered with silver paste to make electrodes for testing electrical properties. An automatic dielectric measurement system (4980A, precision LCR meter) was used to determine the dielectric properties and ac conductivity of sintered ceramics as a function of frequency and temperature. Ferroelectric properties measurement, the electrode coated samples had an applied electric field of up to 1–7 kV/mm using a Sawyer-Tower circuit (Radiant Technology Inc.). The ferroelectric parameter, such as P-E loop, remnant polarization  $(P_r)$  and coercive fields  $(E_c)$ , were measured and investigated as a function of BT seed content. The coated ceramics were poled at room temperature for 30 min in a silicone oil bath with an electric field of 6-7 kV/mm to achieve piezoelectric characteristics. An S5865 d<sub>33</sub> meter (KCF Technologies) was used to determine the piezoelectric coefficient after 24 h. The strain-electrical field (S-E) at ambient temperature was investigated using an optical displacement sensor combined with the Radiant ferroelectric system. To determine the butterfly strain curve, a strong electric field of 70 kV/cm was used.

## 3 Results and discussion

The lead-free  $Bi_{0.5}Na_{0.5}TiO_3$  ceramic was successfully synthesized using the  $BaTiO_3$  powder as seeds. The  $BaTiO_3$  particles (BTs) was successfully synthesized using the molten-salt method. The phase structure of BTs was found to be a pure perovskite phase with particles of ~ 318 nm at a calcination temperature of 750 °C, as illustrated in Fig. 2. The XRD phase

matched to JC-file No.01-074-2491, which was the data of BaTiO<sub>3</sub>. After that, the BNT was mixed with BT seed (BNT-*x*BTs) and sintered for 2 h at 1100 °C, result can be noted that the BT-nano particle enhanced the densification process in BNT ceramic. Figure 3 displays the X-ray diffraction patterns of all ceramics. The XRD patterns revealed that all conditions exhibited a pure perovskite phase throughout the range investigated at  $2\theta = 20-60$ , with peaks corresponding to the perovskite peaks of (100), (110), (111), (002)(200), (210), and (211) (This is the JC-file standard). In BNT-based ceramic systems, the pure perovskite phase indicated that the BT seed had diffused successfully into the BNT lattice. From the expanded XRD patterns in the range of 39°-48° are shown in Fig. 3b, it was found that the position of the peak of BTs-added samples are slightly shifted towards the lower angles compared to the BNT sample without BTs. The results revealed that inserting BT seed particles into the lattices can produce lattice distortion, which results in a change in the crystal structure of the BNT ceramics. [20, 35, 36]. In the compositions of non-BTs sample and lower BTs content ( $x \le 5 \mod \%$ ), the XRD peaks presented a rhombohedral (R) phase, which is observed by the splitting peaks at around  $2\theta \sim 40^{\circ}-42^{\circ}$  of (111) reflections and the single peak at around  $2\theta \sim 46^{\circ}$ -48° of (200) reflections. When x = 7 mol%, the XRD peak presented a phase mixture of rhombohedral and tetragonal phases due to the splitting peak of the (111) and (200) reflections. With increasing BT seed (x = 10 mol%), the peaks merged into a single peak of (111) reflections. This indicated that the crystal structure is transformed into a tetragonal phase [18, 37, 38]. The values of bulk density, relative density, and grain size of the ceramic systems are shown in Table 1. Figure 4 shows SEM micrographs of BNT-BTs ceramics as well as the sintered surface distribution percentage. The Archimedes principle and the line intercept method were used to determine the density value and grain size, respectively. It was found that the ceramics have bulk density values in the range of 5.87 to 5.91 g/cm<sup>3</sup> with a theoretical density of 97.95-98.96%. The highest density value was obtained for the sample of BTs = 5.0 mol%. According to Fig. 4 and Table 1. It was found that as the BTs were increased from x = 0.0 to x = 7.0 mol%, the grain size tended to decrease, with only minor increases in the sample of BTs = 10.0 mol%. It is wellknown that the change in grain size of ceramics can



BT seed-750

20

seed) powder calcined at 750 °C

30

lated defects, 2. the difference in atomic radius, and 3.



the sintering process. The sintering process in terms Fig. 2 XRD patterns and surface morphology of BaTiO<sub>3</sub> (BT of lattice diffusion of vacancies (the vacancies introduced by doping) from the pore to the grain be attributed to; 1. the printing effect of vacancy-reboundaries. The doping ions lead to a decrease in

diffusion rate which results in the concentration near

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ntensity (a.u.)

Sample	Density (g/cm <sup>3</sup> )	Relative density (%)	Grain size (µm)	$\epsilon_r^{a}$	$ an\delta$ <sup>a</sup>	$\epsilon_r^{\ b}$	$ an \delta$ <sup>b</sup>	$T_{\text{R-F}}$ (°C)	$T_{\rm m}$ (°C)
0BTs	5.87	98	1.94	669	0.050	5827	0.895	~ 200	324
3BTs	5.88	98	1.07	832	0.038	3371	0.011	174	313
5BTs	5.91	99	0.99	1247	0.038	3141	0.011	100	309
7BTs	5.88	98	0.78	1597	0.052	3977	0.085	70	320
10BTs	5.89	98	0.84	1654	0.059	4022	0.025	70	313

Table 1 Density values and dielectric properties of BNT-BTs ceramics

<sup>a</sup>Dielectric data obtained at room temperature (RT) and a frequency of 1 kHz

<sup>b</sup>Dielectric data obtained at maximum temperature and a frequency of 1 kHz

the grain boundaries and reduces their mobility. The decreasing grain size of BT seed-added samples may be due to BT particles accumulating near the grain boundaries, leading to grain growth being interrupted and a decrease in density [39, 40]. The grains of the seed-free sample (0BNTs) had a square grain shape, however, this altered to a polygon shape after BT seed was introduced from 3.0 to 10.0 mol%. Seedadded samples revealed uniform grains and a homogeneous microstructure on the ceramic surface, with no significant pores. It is possible that the association between faceted microcrystal forms and high crystallinity is general in solids, as it has been found for several substances [41, 42]. The seeded samples had a very homogenous microstructure distribution, which could be due to the nanometric seed particles operating as a nucleus for homogeneous grain development in the BNT ceramics [27]. Furthermore, the uniform grain and homogenous grain size distribution in seed samples may be associated with a higher degree of densification. Figure 5 illustrates the dielectric ( $\varepsilon_r$ ) and dielectric loss (tan $\delta$ ) as a function of BT seed content (room temperature and 1 kHz). From the figure, it was compared to the dielectric constant and dielectric loss of the BNT with variation in BTs content. It can be seen that the dielectric constant increased with increasing BTs content, the highest dielectric constant of 1654 was obtained for the sample with 10 mol% BTs content. The result found that the BTs content enhances the dielectric constant at room temperature of BNT ceramics. In the dielectric loss case, it was decreased when adding 3 mol% of BTs content, while increased the BTs content at 5 to 10 mol% tended to increase. Generally, grain size has a significant effect on the dielectric constant of lead-free ceramics. The domain walls in fine grain ceramics ( $G \sim 1 \text{ mm}$ ) are more difficult to move than those in coarse grain ceramics ( $G \sim 10$  mm), and the high dielectric constant in the fine grain ceramics cannot describe in terms of increased domain wall contributions. To understand the dielectric constant behavior of fine-grain ceramics, different stresses were considered. In the present work, the increasing dielectric constant with increasing BT seed adding may be due to the decreasing grain size. Those results might also arise from the Ba<sup>2+</sup> ions substituted for the A site, oxygen or ion vacancies and inner stress in the lattice structure appeared. Increasing dielectric constant at room temperature may be the result of the oxygen or ion vacancies and inner stress [43, 44]. The lowest dielectric loss at the sample of  $x = 3 \mod \%$  may be due to the uniform grains (as seen in the SEM micrograph).

Figure 6 indicates the dielectric properties ( $\varepsilon_r$  and  $tan\delta$ ) as a function of temperatures ranging from 30 to 500 °C and a frequency range of 1 kHz–1 MHz. Also, the arrows indicate the direction of increasing frequency. The results revealed that the ceramics exhibited two dielectric peaks corresponding to the temperature of  $T_{\rm F-R}$ at lower temperatures ~ 50–150 °C ( $T_{\rm F-R}$  denotes the temperature of ferroelectric to ergodic relaxor phase transition) and phase transition temperature  $(T_m)$  (paraelectric phase transition) at the position of the maximum dielectric constant ( $\sim 300$  °C), which is clearly observed for the BTs-added samples. Usually, the  $T_{F-R}$  is referred to as a depolarization temperature  $(T_d)$  [45]. The  $T_{F-R}$  of ceramics shifted towards lower temperature which decreased from 200 °C for pure BNT to 70 °C for the BT-added samples ( $x = 7 \mod \%$  and 10 mol%) (as data listed in Table 1). Results should be noted that the addition of BTs had an effect on the phase formation of BNT ceramic from ferroelectric to ergodic



Fig. 4 SEM micrographs and distribution percentage of sintered BNT-xBTs ceramics

relaxor (ER) phase. In addition, this may be caused by the internal stress which originates from the BT seed particle. Moreover, the shifting  $T_{F-R}$  to low temperatures may be caused by the decreasing grain size. The broad peak and frequency dependence of  $\varepsilon_r$  and tan $\delta$ for the BTs-added specimens indicate that their ceramics exhibit relaxor behavior [46]. The broader peak for the BTs-added ceramics indicates that the diffused transition behavior emerges in BNT-BTs systems [47, 48]. The maximum value of  $\varepsilon_r$  decreased from 5827 to 3141 for the pure BNT ( $x = 0 \mod \%$ ) to BTs-added sample with  $x = 5.0 \mod \%$  and then increased to 4022 for the sample of BTs-added (x) = 10 mol%, as shown in Fig. 6 and as data listed in Table 1. The dielectric loss behavior of those ceramic systems (pure BNT and BTs-added BNT)



Fig. 5 Dielectric constant ( $\varepsilon_r$ ) and dielectric loss (tan $\delta$ ) as a BTs content measured at room temperature and 1 kHz

was similar to the report of Li et al. [27]. They reported that  $PbTiO_3$  seed leads to low dielectric loss at high temperatures for PZT ceramics.

Electric field-induced polarization of BNT-*x*BTs ceramic systems measured at RT under a maximum electric field of 70 kV/cm is displayed in Fig. 7a. It can be stated that the compositions of BNT-*x*BTs ( $x \le 5 \text{ mol}\%$ ) had a like-square ferroelectric loop (the behavior of normal ferroelectric) with the large remnant polarization ( $P_r$ ) as plots in Fig. 7c. With increasing BTs content from x = 7 mol% to 10 mol%, the *P*–*E* loops of the ceramics sample transform to the

"pinched" loop (the  $P_r$  is greatly dropped as seen in Fig. 7c). The  $P_r$  and  $E_c$  values tended to clearly decrease from 38.52 to 3.31  $\mu$ C/cm<sup>2</sup> and 56.15 to 5.73 kV/cm, respectively, with increasing the BTs content (as plots in Fig. 7c). This indicates that the long-range ferroelectric order of the BNT-based system is significantly disrupted by the addition of BT seed, leading to the increase in the degree of ergodicity (the presence of an ergodic relaxor (non-polar) phase at zero electric field) [49]. The decrease in  $P_{\text{max}}$ may be due to the effect of BT addition leading to the decreasing grain size. Also, the decreasing  $P_{\text{max}}$  is due to the complexity of the domain morphology decrease. In addition, the decreasing  $P_{max}$  for a sample of  $x = 10 \mod \%$  might be the large random fields in the ER state that could result in insufficient polarization switching (an inferior  $P_{\text{max}}$  if the E<sub>B</sub> is not sufficiently high) [44, 50].

The transformation of ferroelectric to ergodic relaxor phase for ceramics is also examined by bipolar strain behavior. Besides, it is well-known that changes of polarization are dependent on domain behavior. The bipolar strain-electric field (S–E loops) of BNT-BTs ceramics (measured at RT under an electric field of 70 kV/cm) are displayed in Fig. 7b. It can be seen that the S–E loops of BNT ceramic systems showed clearly change with BT seed content. The S–E hysteresis loops of BNT ceramics changes



Fig. 6 Dielectric constant ( $\varepsilon_r$ ) and dielectric loss (tan $\delta$ ) as a function of temperatures and frequency



Fig. 7 a P-E hysteresis loops, b S-E hysteresis loops, c plots of  $P_r$  and  $E_c$  and d plots of  $S_{max}$  and  $d^*_{33}$  values of BNT-BTs ceramic samples

from the "butterfly shape" (a common characteristic of normal ferroelectric; FE material) into the "sproutshaped" loop with the increasing of BTs content. Pure BNT and the sample of BTs addition ( $x \le 5 \mod \%$ ) indicate a "butterfly shape" with approximately negative strain (The difference between zero-field strain and the lower strain is denoted by  $S_{neg}$ ). For a ferroelectric, this is typical domain switching [51]. With increasing BTs content of  $x = 7 \mod \%$  indicates the sprout-shaped S-E loops with a small negative strain ( $S_{\text{neg}} \sim 0.015\%$ ) and the only positive strain was observed in the sample of BTs = 10 mol%. The decrease in negative strain (from  $\sim -0.03$  to  $\sim -0.015\%$ ) in BNT samples with increasing BTs content from the sample of  $x = 3 \mod \%$  to  $7 \mod \%$ may be due to the changes of ferroelectric domains to dynamically active nano-domains in the ergodic relaxor state [52]. This result is related to the P-*E* hysteresis behavior. The maximum strain  $(S_{max})$ and the normalized strain coefficient  $d_{33}$  ( $d_{33}$  can calculate according to the equation;  $S_{\text{max}}/E_{\text{max}}$ ) as

illustrated in Fig. 7d. Results can be stated that the  $S_{\text{max}}$  and  $d_{33}^{*}$  values increased (0.023% to 0.19% and 33–271 pm/V, respectively) with the further increase in BTs content from  $x = 0 \mod \%$  to 7 mol% and then decreased at the sample of 10 mol% BTs (0.11% and 152 pm/V). The intrinsic and extrinsic contributions to electric field-induced strain as well-known. In this present, results can be noted that the enhancement of strain for BTs (x = 7 mol%) addition ( $S_{\text{max}} = 0.19\%$ ) and = 271 pm/V) may be caused by the increase of the degree of ergodicity, evident by the appearance of the pinched P-E loop [53]. Furthermore, the highest  $S_{\text{max}}$  and low negative strain in the sample of BTs = 7 mol% may be due to the existence of a boundary between the nonergodic (ferroelectric) and an ergodic relaxor state [54].

Figure 8 illustrates the energy storage density (*W*) and energy storage efficiencies ( $\eta$ ) of ceramics. The energy storage density (*W*) and energy storage efficiencies ( $\eta$ ) were calculated from the *P*–*E* hysteresis loop using the following Eqs. (1) and (2) [55, 56];

$$W = \int_{P_r}^{P_{\max}} E dp \tag{1}$$

$$\eta = \frac{W}{W + W_{\text{loss}}} \tag{2}$$

where *W* is the energy storage density,  $P_{\text{max}}$  is maximum polarizations,  $P_{\text{r}}$  is remnant polarization, *E* is the applied external electric field and  $W_{\text{loss}}$  refer to the energy loss density.

The integration of the area of the *P*–*E* hysteresis loops was calculated to obtain the energy storage density (*W*) and energy loss density ( $W_{loss}$ ) of ceramics, as shown in Fig. 8a. A dielectric constant, dielectric loss, breakdown strength (DBS), and grain size had an effect on the energy storage properties. To achieve a high energy storage density (*W*), a high breakdown electric field ( $E_B$ ), a reduced remnant polarization ( $P_r$ ) and an increased maximum polarization ( $P_{max}$ ) (a large polarization difference,  $\Delta P = P_{max} - P_r$ ) were required [23, 55].

In this present, the *W* and  $\eta$  values of ceramics are displayed in Fig. 8b. The results can be observed as a 70 kV/cm applied electric field (measured at room temperature), the *W* and  $\eta$  values tended to increase with increasing BT seed content. The highest value of *W* was 0.68 J/cm<sup>3</sup> with the value of  $\eta = 58\%$  obtained at the sample of BT seed-added (x = 0.10 mol%). This value is similar to the value obtained from the ceramic system of BNKTZ-0.02La and BNKTT-0.02ST which Butnoi et al. [38] and Malik et al. [56] reported

on this. So, the enhanced energy storage density of the seed-added samples may have resulted from the pinched unipolar *P*–*E* loop with large differences in values of  $P_{\text{max}} - P_{\text{r}}$  and high breakdown electric field ( $E_{\text{b}}$ ). The  $E_{\text{B}}$  of dielectric ceramics is generally affected by a band gap, porosity, grain size, secondary phase, and space charge. According to the relationship between EB and grain size as a formula,  $E_{\text{B}} \propto \frac{1}{\sqrt{G}}$ where *G* is the grains size. The decreasing grain size with increasing BT seed content for these ceramic systems might be suggested that BNT doped with BT seed ceramics had a high EB value [39, 54, 57, 58]. Moreover, the results of energy storage density are related to the dielectric constant  $\varepsilon_{\text{r}}$  (as seen in Fig. 4).

Figure 9 illustrates the piezoelectric charge coefficient  $(d_{33})$  and piezoelectric voltage coefficient  $(g_{33})$  of studied ceramics. It can be found that the BTs-added BNT ceramics exhibited better values of  $d_{33}$  than pure BNT for the present work. The  $d_{33}$  values increased from 120 pC/N to 161 pC/N with increasing BT seed from x = 0 to x = 5 mol%, then dropped with further increasing BT seed content from  $x = 7 \mod \%$  to 10 mol%. The high  $d_{33}$  value was obtained for the samples of BTs-added (x = 5.0 mol%). The increasing d<sub>33</sub> value for seed-added ceramics may be related to the density value of studied ceramics. The  $d_{33}$  value was enhanced with seed (nano-crystals) adding, the result is close to the work reported by Ye et al. [28]. They reported that using a BT template can improve the  $d_{33}$  value of lead-free BCZT ceramics. In addition, an increase in piezoelectric coefficients can be



Fig. 8 a Schematics calculation of W and  $W_{\text{loss}}$  and b Plots of W and  $\eta$  as a function of BT seed content



**Fig. 9** Piezoelectric charge coefficient  $(d_{33})$  and piezoelectric voltage coefficient  $(g_{33})$  of BNT-BTs ceramics

obtained from ferroelectric ceramics with a twophase coexistence as well-known [20, 54, 59]. This may be correlated with XRD data which indicates the transition from the rhombohedral phase to the tetragonal phase for a sample of  $x \ge 5$ . Furthermore, the piezoelectric properties are known to be influenced by the extrinsic effect, which is related to the domain movement mechanism via domain wall motion and dipole displacement [60, 61]. For the  $g_{33}$ values as shown in Fig. 9, it was found that the value tended to decrease with increasing BTs content. The value of  $g_{33}$  was dependent on the piezoelectric coefficient  $(d_{33})$  and dielectric constant  $(\varepsilon_r)$ . This indicates that the decrease of  $g_{33}$  of studied ceramic is related to the increasing  $\varepsilon_r$  with increasing BTs content. The  $g_{33}$  values were in the range of  $3.05 \times 10^{-3}$ –  $20.30 \times 10^{-3} \text{ Vm/N}.$ 

It is well-known that the BNT-based system exhibits a more complex phase structure and phase transition, depending on composition, temperature, electrical field, and stress. In recent years, many researchers have described some of the electrical properties of BNT-based systems based on the concept of ergodicity. The optimized piezoelectric and large field-induced strain response of BNT-based systems can be expected at the phase boundary in a "nonergodic relaxor, NR" (normal ferroelectric) state and between "NR" (normal ferroelectric) and "ergodic relaxor, ER" (nonpolar) states, respectively. Conversely, in order to optimize the energy storage can be expected at the phase boundary in the ER (nonpolar) state [54]. It seems that the results of the piezoelectric response and energy storage of these ceramic systems relate to the above concept.

#### 4 Conclusion

A sample of lead-free BNT ceramics was prepared utilizing a seed-induced process using BT particles as a nanocrystal seed. All of the ceramics had a pure perovskite phase. The density values ranged from 5.87 to 5.91 g/cm<sup>3</sup>. The sample of 10BTs (x = 10 mol%) had the highest dielectric constant ( $\varepsilon_{r-} = 1652$ ). For the BTs composition ( $x \ge 3 \text{ mol}\%$ ), the dielectric spectra showed a broad maximum around  $T_{F-R}$ . A high recoverable energy storage density  $W_{rec} \sim 0.68 \text{ J/cm}^3$  was achieved in the sample with x = 10 mol% BT seeds. The highest  $d_{33}$  result was 161 pC/N in a sample of 5BTs (x = 5 mol%).

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#### **Author contributions**

Each author contributed significantly to the work's conception or design; data acquisition, analysis, and interpretation; the development of new software used in the work; drafted or substantially revised the work; and approved the submitted version.

## Data availability

The authors confirm that all data generated or analyzed during this study are included in this published article. The data supporting the findings of this study are available within the article.

#### Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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