Energy harvesting, electrical, and magnetic properties of potassium bismuth titanate-based lead-free ceramics

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1. Introduction

Perovskite-type ceramics ABO₃ are widely used in the electronics industry. Lead zirconate titanate (PZT) is an ABO₃ ceramic that is the most widely used piezoelectric ceramic owing to its excellent electrical properties [1–3]. However, since lead is hazardous and the toxicity of lead is recognized to be a serious problem, many lead-containing ceramics are banned [1, 4]. Among others, the European Union has passed legislations limiting the amount of lead in electronics, with the exception of piezoelectrics until lead-free alternatives are available [5, 6]. Thus, the development of lead-free piezoelectric ceramics has attained significant attention in recent years. There is an urgent need to explore lead-free high-performance piezoelectric ceramics that can replace PZT-based ceramics [5, 7].

Many investigations have focused on lead-free piezoelectric materials based on barium titanate (BaTiO₃, BT), bismuth sodium titanate (Bi₃.₅Na₆.₃Ti₅O₄, BNT), potassium sodium niobate (K₀.₃Na₀.₃NbO₃, KNN), and bismuth potassium titanate (Bi₅.₃K₀.₇Ti₅O₃, BKT) [8]. Among lead-free piezoelectric materials, BT-based materials were the first to be practically used in piezoelectric ceramics. However, BT has low piezoelectric charge constant (190 pC/N) and low Curie temperature (120°C), thus limiting its applications [8]. The BNT has been recognized as potential candidates for developing lead-free piezoelectric materials [9] due to exhibited strong ferroelectric properties with relatively large remnant polarization (Pₑ = 38 μC/cm²) and high Curie temperature (Tₑ = 320°C) [3, 4, 6, 7]. However, their piezoelectric properties degrade at around a depolarization temperature (T_d) of approximately 100–200°C [9], large coercive field and high conductivity, leading to poor poling treatments and under-developed piezoelectric performance [4]. The pure KNN ceramic is expected as one of candidate lead-free materials because these ceramics exhibit high Curie temperature (Tₑ = 420°C) and good ferroelectricity (Pₑ = 33 μC/cm²). However, they have poor piezoelectricity (d₃₃ = 80 pC/N) and low bulk density. The obstacle in the processing of KNN-based ceramics is largely due to instability of KNN phase and volatility of alkali oxides sintering at high temperatures, making it difficult to obtain high density [8].

Another promising group of lead-free piezoelectric ceramics are based on Bi₅.₃K₀.₇Ti₅O₃ or BKT ceramics. The BKT is a perovskite ferroelectric material with a relatively higher Curie temperature (Tₑ = 380°C) [10–12] than other perovskite-based materials such as...
BNT and BT [13]. Furthermore, BKT is one of the rare lead-free perovskites which crystallizes in a tetragonal symmetry at room temperature (RT) [14,15], while most of others are in rhombohedral phase. It has been reported that BKT can potentially form a rhombohedral-tetragonal MPB with many other lead-free compositions [13]. The BKT ceramic was first fabricated by Smolenskii et al. [16] in 1959. It can be developed for application in filters, resonators, and micro-electromechanical systems (MEMS) [10]. Ivanova et al. [17] reported that the lattice constants of BKT ceramics are $a = 0.3913$ nm, $c = 0.3993$ nm, which agree well with those reported by Hiruma et al. [11] ($a = 0.3913$ nm, $c = 0.3993$ nm). Moreover, BKT has also attracted interest because of its high depolarization temperature, $T_d \sim 250^\circ$C. This is good for the applications at high temperature such as in electromechanical devices which operate at high temperatures, for example in the fuel injection systems [1]. The BKT ceramic seems to be a candidate for lead-free piezoelectrics with a high $T_c$ and $T_d$ values. However, it is difficult to prepare a dense ceramic body by a conventional ceramic fabrication process [18]. This is due to the fact that secondary phases such as $K_2Ti_6O_{13}$ are easily formed during the sintering process at high temperatures (Supplementary Figures S1-S4 and Table S1) [19]. Based on the data in the supplementary information, it indicated that the ceramics sintered at lower temperature of $1000$–$1025^\circ$C showed a single perovskite structure, however, had a lower density value. While the ceramics sintered at higher temperature of $1075^\circ$C showed high densification, however, the secondary phases, i.e. $Bi_4Ti_3O_{12}$ and $K_2Ti_6O_{13}$, were observed in this sample (the details of which are shown in the supplementary information). Moreover, the volatilization of $Bi_2O_3$ and $K_2CO_3$ at high temperature hinders the highly dense pure BKT ceramics, which results in low electrical properties and poor understanding of its basic properties [20,21]. The piezoelectric properties of the pure BKT ceramic are not generally high enough for most applications. Thus, some modifications should be made to obtain high-density samples with improved electrical properties.

In order to further enhance the properties of BKT-related ceramics and to meet the requirements for typical applications, it is necessary to develop new BKT-based materials. The binary system of the BKT-BaNb$_2$O$_6$ ceramics have been synthesized by Pu et al. [10]. They reported that the optimum dielectric ($\varepsilon = 2960$) and piezoelectric properties ($d_{33} = 96$ pC/N, $k_p = 17.8\%$, $Q_m = 150$) were achieved in a morphotropic phase boundary (MPB) which separated the rhombohedral and tetragonal phases in the range of $x = 0.01$–$0.02$. Zuo et al. [22] reported that the addition of LiNbO$_3$ (LN) could improve the piezoelectric properties, i.e. $d_{33}$ and $k_p$ values, of the BKT ceramic. Structure-property relationships of the lead-free (1-x)BKT-xBMT system were investigated by Zeb et al. [1,23,24]. They reported that the BKT ceramic was modified by BMT, they obtained an improvement in the $d_{33}$ and room temperature electromechanical bipolar strains. The effect of Zr substitution for Ti on the ferroelectric and piezoelectric properties of lead-free BKT ceramic were reported by Ito et al. [25]. They found that the coercive electric field decreased monotonically with increasing $Zr$ content, while the largest remanent polarization of 26 $\mu$C/cm$^2$ was observed for the $x = 0.04$ ceramic. As a result, the ceramic with $x = 0.04$ showed an enhanced $d_{33}$ of 140 pC/N.

Recently, bismuth nickel titanate, Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$ or BNT has been an interesting lead-free piezoelectric material for next-generation ferroelectric memories and piezoelectric devices based on the fact that Bi$^{3+}$ takes the same electronic configuration (4$f^{14}$ 5d$^{10}$ 6$s^2$) as Pb$^{2+}$ [26]. The BNT has a perovskite structure with a pseudo-cubic phase when fabricated under high atmospheric pressures. It has a tetragonal symmetry with large tetragonality and low tolerance factor ($t = 0.9498$) [27]. In the previous work, it turns out that the addition of BNT into the BNT ceramic could decrease the temperature for the first dielectric anomaly, and thus enhance its piezoelectric properties [27]. The lead-free BNT-modified BNT-BT ceramics have been systematically investigated by Bai et al. [28]. The addition of BNT decreases the $T_d$, $T_{F/R}$, $P$, and $E_c$ values and can improve the piezoelectric properties of the BNT-BT ceramics. Some previous work reported that PZT ceramics doped by BNT possess good ferroelectric properties and high $T_c$ [29]. The 0.25BNT-0.75PZT ceramic possesses high density and rather homogenous microstructure morphology accompanied by a uniform distribution of elements, especially Bi and Pb, even in grains and grain boundaries, which contribute greatly to their best electrical performances, i.e. $T_c = 227^\circ$C and $\varepsilon_m = 18,011$ at 10 kHz, $d_{33} = 510$ pC/N and $K_p = 59.8\%$ poled at 25 kV/cm [29]. The effect of nickel titinate (NiTiO$_3$) on the electrical properties of the BNT ceramic was investigated by Chen et al. [30]. They reported that Ni doping can substantially reduce the band gap of $Bi_{0.5}Na_{0.5}TiO_3$ materials to $\sim 2$ eV. The novel BNT-NiTiO$_3$ system, which illustrates three narrow band gaps and relatively high polarization values, has broad application prospects for ferroelectric photovoltaic devices.

Since the BKT ceramic is an important lead-free material employed in actual applications [1,5,13], its modification is of considerable interest, and this ceramic is expected to exhibit better properties than those of the single phase. In the present research, the modification of the BKT ceramic by BNT was achieved with the aim of improving its properties. The role of the modifier concentration on the ceramic properties including phase formation, microstructure, and electrical properties (i.e. dielectric and piezoelectric) of the BKT ceramic was investigated. Since data of the
mechanical and magnetic properties for BKT-based ceramics are rare, the effect of the modifier concentration on the mechanical (i.e. hardness, Young’s Modulus and fracture toughness) and magnetic properties of the BKT ceramic was also discussed in details. Furthermore, much attention has been paid to energy problem aspects for the present day. Therefore, the piezoelectric voltage coefficient \(g_{33}\) and the off-resonance figure of merit (FoM) for energy harvesting were also determined and discussed in this work.

2. Experimental procedure

The conventional mixed oxide technique was used to synthesize the lead-free system of \((1-x)\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3\) or BKN,T ceramics (where \(x = 0, 5, 10, 15\) and \(20\) mol%). Analytical grade reagents of Bi$_2$O$_3$ (99.9%, Aldrich), K$_2$CO$_3$ (99%, Sigma-Aldrich), TiO$_2$ (99.9%, Sigma-Aldrich) and NiO (99.9%, Sigma-Aldrich) were used as starting materials. All carbonate powders were first dried at 120°C for 24 h in order to eliminate any moisture. The raw materials were stoichiometrically weighed according to the BKN,T formula, and then vibratory milled with yttrium stabilised zirconia media for 6 h in an ethanol solution. The slurry was then dried in an oven. After drying, the obtained powder was calcined at 900°C for 2 h at a heating/cooling rate of 5°C/min. Afterward, a few drops of 3 wt% polyvinyl alcohol (PVA) binders were added to the obtained powders before being uniaxially pressed into discs 10 mm in diameter. The green pellets were sintered at 1050°C for 4 h dwell time by using a heating and cooling rate of 5°C/min.

An X-ray diffractometer (Rigaku) was used to identify the phase of both powders and ceramics. The SmartLab Studio II program was used to analyze the phase structure. The tolerance factor \(t\), \(c/a - 1\), the average ionic radius of the A-site \((r_{\text{Asite}})\) and the average ionic radius of the B-site \((r_{\text{Bsite}})\) values were also calculated in this work. Bulk density was measured in accordance with the Archimedes’ method. Raman spectra were obtained on polished sintered pellets with a Raman spectrometer (T6400 JY, Horiba Jobin Yvon). A scanning electron microscope (SEM, JEOL JSM- 6335 F) was used to study microstructural features of the ceramics. Grain size was determined by the mean linear intercept method (ASTM E112-88). All samples were polished to a mirror finish before the mechanical measurement. The well-polished ceramics were then subjected to the microhardness tester (Vickers hardness, \(H_V\) and Knoop hardness, \(H_K\)). Young’s Modulus \((E)\) and fracture toughness \((K_{IC})\) were determined following the method as described by Marshall et al. [31] and Meredith et al. [32]. Before being subjected to electrical characterization, all samples were carefully polished to 1 mm thickness to obtain a parallel scratch-free surface. Silver paste was painted onto both sides of each sample and then the sample were fired at 700°C for 30 min to form electrodes. Dielectric properties at room temperature (RT) as a function of various frequencies and voltages were carried out by a 4192A LCR-meter. The temperature dependence of dielectric properties as a function of various voltages was also measured. The ferroelectric hysteresis data \((P-E)\) was examined by using a standard ferroelectric analyzer (Radiant Precision High Voltage Interface). An AC electric field of 10–50 kV/cm and a frequency of 1 Hz were used in the \(P-E\) measurements. Remanent polarization \((P_r)\) and coercive field \((E_c)\) values were determined from the hysteresis loops. The leakage current density-electric field \((J-E)\) curve was also measured. For the piezoelectric measurements, all samples were poled at 25°C in a stirred silicone oil bath by applying a DC electric field equal to 5 kV/mm for 15 min. The low-field piezoelectric coefficient \((d_{33})\) of each sample was measured using a \(d_{33}\)-meter (KCF Technologies, 55865) at a frequency of 50 Hz from samples aged 24 h. The piezoelectric voltage coefficient \((g_{33})\) was also calculated: 

\[ g_{33} = d_{33}/\varepsilon_{0}\varepsilon_{r}, \]

where \(\varepsilon_0\) is the permittivity of free space and \(\varepsilon_r\) is the dielectric constant [8,33,34]. In addition, the off-resonance figure of merit (FoM) for energy harvesting was calculated via the following equation: 

\[ \text{FoM} (\text{pm}^2/\text{N}) = d_{33} E_{33}^{1/2} \]

[8,35]. Lastly, the magnetic properties were obtained using the vibrating sample magnetometer or VSM (Model 7404, Lake Shore Cryotronics, Inc., Westerville, OH, USA) with the magnetic field of \(-10 \text{ kOe} \leq H \leq 10 \text{ kOe}.

3. Results and discussion

3.1. Phase evolution and raman analysis

The mixed calcined powders of the BKN,T were characterized using XRD analysis over a wide 28 range of 20–80° as shown in Figure 1. Within the detection limits of the XRD instrument, a single perovskite structure without any extra or secondary peaks was observed for pure BKT powder. After increasing the modifier content to \(x = 5–10\) mol%, a single perovskite structure was also obtained. However, a secondary peak of bismuth titanate oxide, Bi$_4$Ti$_3$O$_{12}$ (ICDD file no. 00–047-0398) was detected after increasing the modifier content up to \(x = 15–20\) mol%.

X-ray diffraction patterns with 28 = 20–80° of the BKN,T ceramics are displayed in Figure 2(a–e). Although the calcined powers showed some secondary phase, all ceramics exhibited a single perovskite structure with no trace of secondary phases. The formation of a secondary phase for the calcination state may be due to an insufficient energy of the calcination process to promote the diffusion process, which also influences the reaction kinetics of the complex system [2]. For the XRD result, it is believed that the modifier...
ions have successfully diffused into the BKT lattices and formed a solid solution during processing, where the reagents have already reacted to form the end compounds with a release of CO$_2$ from the carbonates. A detailed view of the XRD patterns at 2$\theta$ = 38.5–40.5° and 2$\theta$ = 44–48° are shown in the inset of Figure 2. The XRD parameters of the BKN,T ceramics analysis by SmartLab Studio II program are listed in Table 1. The XRD data revealed the pure BKT ceramic with a tetragonal structure (space group P4mm) [10,36] which was matched with ICDD file number 36–0339 for the (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ tetragonal phase. This can be evidenced by the splitting of (002)$_T$/2(000)$_T$ peaks at 2$\theta$ = 44–48° [10,12,22] and the existence of a single (111)$_T$ peak at 2$\theta$ = 38.5–40.5°. This result also agrees with the result observed earlier by Pu et al. [10] and Hiruma et al. [11]. However, with a further increase in the modifier content, the (200)$_T$-(002)$_T$ diffraction peaks gradually merged into a single peak. This suggested that there was a change from tetragonal to cubic phase as the modifier content was increasing. In this work, the c/a – 1 value, which can be linked with the tetragonality of all samples, was calculated from the XRD data as seen in Table 1. It can be seen that the c/a – 1 value decreased with increasing modifier content. This was consistent with the phase transition from tetragonal to cubic as the modifier was increasing.

![Figure 1](image1.png)  
**Figure 1.** X-ray diffraction patterns of the BKN,T mixed calcined powders where 2$\theta$ = 20–80°.

![Figure 2](image2.png)  
**Figure 2.** X-ray diffraction patterns of the BKN,T ceramics where (a) x = 0 mol%, (b) x = 5 mol%, (c) x = 10 mol%, (d) x = 15 mol%, and (e) x = 20 mol% (inset: XRD pattern of the BKN,T ceramics with 2$\theta$ = 38.5–40.5° and 2$\theta$ = 44–48°).
Moreover, the positions of all peaks slightly shifted toward higher 2θ angles in comparison with the pure BKT ceramic. This suggests that the modifier produces a lattice distortion which may be due to the diffusion of Ni$^{2+}$ ions into the lattices. Ni$^{2+}$ ions have diffused into the lattices where it is expected that ions of Ni$^{2+}$ should enter into the B-site (Ti$^{4+}$ site) of the ABO$_3$ lattices due to the fact that the radius of Ni$^{2+}$ (0.69 Å) is close to that of Ti$^{4+}$ (0.605 Å) [37].

A simple description of the geometric packing within perovskite structure can be characterized by the tolerance factor (t). This value is a simple geometric number which was worked out by Goldschmidt [38]. Normally, the t value describes the stability and relationship between cations and anions in the perovskite structure, which is defined by the following equation [39–41]:

\[
t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}
\]

where $r_A$, $r_B$, and $r_O$ are the ionic radii of cation A, cation B and oxygen for the ABO$_3$ perovskite structure, respectively. For a complex perovskite system, $r_A$ and $r_B$ are the ionic radii of composed ions normalized by the atomic ratio. The ionic radii refer to those reported by Shannon [37]. For the BKN$_x$T system, the average ionic radius of the A-site ($r_{A\text{-site}}$) and the average ionic radius of the B-site ($r_{B\text{-site}}$) can be calculated from the following equations [39,40,42]:

\[
r_{A\text{-site}} = x[r_B^{2+}] + (1-x)[1/2r_B^{3+} + 1/2r_K^{+}]
\]

\[
r_{B\text{-site}} = x[r_B^{2+}] + (1-x)[r_K^{+}]
\]

where $r_B^{2+}$ and $r_K^{+}$ are the ionic radii of Ni$^{2+}$ and Ti$^{4+}$, respectively. Normally, the t value also provides an indication of the degree to which the atoms can be displaced from their ideal packing positions and still be stabilized in the perovskite structure. It reflects structural modifications such as distortions, rotations, and tilting of the octahedra [38], where these factors consequently affect the electric properties of the perovskite structure. For the t values lower than 0.9 or higher than 1.1, typically, the perovskite structure is often unstable due to mismatch between preferred A-O and B-O bond lengths [38,40]. The calculated average A-site ionic radii ($r_{A\text{-site}}$) and the average B-site ionic radii ($r_{B\text{-site}}$) as a function of the modifier content are presented in Figure 3(a) and the related values are listed in Table 1. The $r_{A\text{-site}}$ decreased while the $r_{B\text{-site}}$ increased with increasing modifier content. This was also consistent with the additive that produced a lattice distortion as mentioned above. Plot of the $c/a - 1$ and t values as a function of the modifier content are shown in Figure 3(b). In the present work, the t values were calculated to be 0.9954–1.0111 for a composition with $x = 0–20$ mol\% ceramics. The t and $c/a - 1$ values decreased with increasing modifier content. This was consistent with the phase transition from tetragonal to cubic as the modifier was increasing as mentioned above. The $c/a - 1$ value had an exponential relation (first order) with the modifier which can be expressed as: $c/a - 1 = 0.025 \exp(x/1.68) + 0.00023$. While the t had a linear relation with the modifier (x content) which can be expressed as: $t = 1.011 - 7.84 \times 10^{-4}x$. In addition, plot of the t value as a function of $c/a - 1$ value are displayed in Figure 3.
Figure 4. Raman spectra of the BKN,T ceramics measured at room temperature (RT) in the wavenumber range of 100–1200 cm\(^{-1}\).

(c). It can be seen that the \( t \) had an exponential relation with first order with the \( c/a - 1 \) and can be expressed as: \( t = -0.0139 \exp ((-c/a-1)/0.0012) + 1.011 \).

To further understand the phase evolution, a Raman analysis was carried out. The Raman spectra of the BKN,T ceramics measured at room temperature (RT) in the wavenumber range of 100–1200 cm\(^{-1}\) are shown in Figure 4. The RT Raman spectrum is similar to that observed previously for the BKT ceramics [43,44]. In Figure 4, there are four main regions of the Raman spectra. The Raman modes below \( \sim 150 \) cm\(^{-1}\) are related to the Bi\(^{3+}\) vibrations [36]. The Raman modes between 200–380 cm\(^{-1}\) are thought to be contributed by the Ti-O vibration [15,44]. Raman modes between 500–650 cm\(^{-1}\) are dominated by Ti-O\(_6\) octahedral vibrations [44,45]. The high-wave number range above 700 cm\(^{-1}\) could be related to oxygen vibration and the existence of oxygen vacancies [44]. The high-frequency range has been linked to \( A_1(LO) \) and \( E(LO) \) overlapping bands [44,45]. As the modifier concentration was further increased, the intensity of the band at about 280–300 cm\(^{-1}\) gradually decreased. This evolution is evidently related to a gradual disappearance of the tetragonal phase [44]. The mode in the region between 500–650 cm\(^{-1}\) gradually broadened (especially at 650 cm\(^{-1}\)) with increasing modifier content. This evolution may be related to the gradual change of the tetragonal structure to the pseudo-cubic one in accordance with the X-ray results [44].

3.2. Densification, microstructure and mechanical properties

The FE-SEM micrographs with as sintered surfaces and their average grain size of the BKN,T ceramics are shown in Figure 5 and Table 2, respectively. The SEM result confirmed that all ceramics are dense with relatively high-density values of 5.71–6.12 g/cm\(^3\) which an increase in the density of samples was observed as the modifier content increased (see Figure 6(a)). Most grains of all ceramics show a clear grain boundary with a cubic-like shape. The additive seems to have a slight influence on the microstructure as well as the average grain size decreased with increasing modifier concentration. Using the linear intercept method, the average grain size was found to decrease from 1.13 \( \mu \)m for the pure BKT ceramic to around 0.83 \( \mu \)m for the 20 mol\% ceramic, indicating that the role of the modifier content in the pure BKT system is that of a grain growth inhibitor. This can be attributed to the fact that the modifier concentrates near grain boundaries.

Figure 5. The FE-SEM micrographs with as sintered surfaces of the BKN,T ceramics where (a) \( x = 0 \) mol\%, (b) \( x = 5 \) mol\%, (c) \( x = 10 \) mol\%, (d) \( x = 15 \) mol\%, (e) \( x = 20 \) mol\% and (f) plots of grain size as a function of \( x \) content.
Table 2. Microstructure, mechanical, electrical, and energy harvesting properties of the BKN₄T ceramics.

| x (mol%) | Grain size (µm) | Hᵥ (GPa) | Hₘ (GPa) | E (GPa) | Kₑ (MPa·m¹/₂) | tan δ (at 1 kHz) | d₈ (10⁻² Vm/N) | FoM (pm²/N) |
|----------|-----------------|-----------|-----------|----------|----------------|----------------|----------------|--------------|
| 0        | 1.13            | 4.09      | 4.00      | 60       | 0.69           | 1.02            | 1208           | 11.03        | 1.33         |
| 5        | 1.02            | 4.46      | 4.26      | 67       | 0.71           | 1.52            | 1252           | 123.0        | 6.64         |
| 10       | 0.93            | 4.66      | 4.49      | 70       | 0.75           | 1.76            | 1654           | 145.0        | 18.06        |
| 15       | 0.84            | 4.71      | 4.58      | 81       | 0.82           | 1.86            | 1536           | 162.0        | 15.82        |
| 20       | 0.83            | 4.97      | 4.78      | 89       | 0.83           | 1.54            | 1519           | 170.0        | 10.04        |

\[
Hₖ = \frac{14.23P}{d^2}
\]  

where \( P \) = load (N) and \( d \) = half-length of long diagonal (µm). Young’s modulus (E) was determined following the method described by Marshall et al. [31]. Fracture toughness (\( K_{IC} \)) was also determined from the length of the cracks that propagated from the four corners of indentation impression, following the method described by Meredith et al. [32]. The \( E \) and \( K_{IC} \) values were also calculated using the following formula [49–51]:

\[
E = \frac{aH_k}{[(b/a) - (b'/a')]}
\]

\[
K_{IC} = 0.016 \left( \frac{E}{H_v} \right)^{1/2} \left( \frac{P}{c^{3/2}} \right)
\]

where \( a \) = Marshall constant (~ 0.45), \( b = a \) = length of the \( H_k \) tip mark with short diagonal/length of the \( H_k \) tip mark with long diagonal (0.14), \( b' = a' \) = length of the \( H_k \) indentation with short diagonal/length of the \( H_k \) indentation with long diagonal, and \( c = \) crack length (m). Plots of grain size and density values as a function of the modifier content are shown in Figure 6(a). The related mechanical values are also summarized in Table 2. Based on Figure 6(b), the \( H_v \) and \( H_k \) values of the pure BKT ceramic were 4.09 GPa and 4.00 GPa, respectively. The \( H_v \) and \( H_k \) values initially increased with increasing modifier content, and then reached the maximum value of 4.97 GPa and 4.78 GPa, respectively, for the 20 mol% ceramic. It should be noted that the hardness values of the 20 mol% ceramic in this work were close to that of the Bi₀.⁴₈₅(Na₀.₃₈₈K₀.₀⁹₇)Ba₀.₀₂₁Sr₀.₀⁹⁹TiO₃ + 2 vol% Fe₂O₃ or BNBST + 2 vol% Fe₂O₃ ceramic reported by our previously work [52] which obtained the \( H_v \) and \( H_k \) values of 5.60 GPa and 4.90, respectively, the hardness properties comparison of which are shown in the supplementary Table S2. The hardness improvement for the BKN₄T system contributed to both improvements of densification and the reduction of grain size, where the higher density but lower grain size can give rise to better mechanical properties (Figure 6(a)) [53]. From the study of \( E \) and \( K_{IC} \) values in Figure 6(c), it was found that these values depended on composition and their trends followed that of the trend of hardness value. In the present work, the \( E \) and \( K_{IC} \) values increased with increasing modifier and reached the maximum value of 89 GPa.
3.3. Dielectric properties

Plots of room temperature dielectric constant ($\varepsilon'$), dielectric loss (tan $\delta$) and imaginary value of dielectric constant ($\varepsilon''$) as a function of frequency of the BKN$_x$T ceramics are presented in Figure 7(a-c). The $\varepsilon''$ value was calculated using the relation: $\varepsilon' = \varepsilon'' \tan \delta$. Based on Figure 7(a-c), it was found that both $\varepsilon'$ and $\varepsilon''$ decreased with an increasing of the measurement frequency for all samples, similarly observed in the previous work [56]. In the low-frequency range, the dielectric constant value of all synthesized ceramics was high [56]. Plots of room temperature of $\varepsilon'$ and tan $\delta$ as a function of the modifier content at a frequency of 1 kHz are shown in Figure 7(d). The $\varepsilon'$ initially increased with increasing modifier content and reached a maximum value of 1763 for the 10 mol% ceramic while the tan $\delta$ value showed a similar trend as compared to that of the $\varepsilon'$ value. The $\varepsilon'$ value in this work was higher than the $\varepsilon'$ value (~1689) of the BNKBST + 2 vol% Fe$_2$O$_3$ composition observed previously by Jaita et al. [52], the dielectric properties comparison of which are shown in the supplementary Table S3.

The effect of applied voltage on dielectric properties both at room temperature and high temperature was investigated. Plots of dielectric constant as a function of frequency at various applied voltages of the BKN$_x$T ceramics are shown in Figure 8. With an increase in the applied voltage from 0.2 V to 35 V, there was a slight change in the dielectric constant at both low and high frequency regions for all samples. Plots of dielectric constant as a function of temperature at various applied voltages (@10 kHz) of the BKN$_x$T ceramics are shown in Figure 9. The applied voltage was found to have no effect on the dielectric behavior for the $x = 0$–15 mol% ceramics. For the 20 mol% ceramic, there was no change in the dielectric constant.

![Figure 7](image-url)
in the low temperature region; however, at a high temperature (> 300°C), the dielectric constant plateau showed a slight increase in dielectric constant with an increase in the applied voltage.

The Lorentz-type relation has been proposed to describe the degree diffuseness of a phase transition, which is given by the following [57,58]:

$$\frac{\varepsilon_A}{\varepsilon} = 1 + \frac{(T - T_A)^2}{2\delta_A^2}$$  \hspace{1cm} (9)

where $\varepsilon_A$ is the parameters defining the temperature of the dielectric peak and the extrapolated value of $\varepsilon$ at $T = T_A$. The $\delta_A$ value was calculated from a plot of $\ln(\varepsilon_A/\varepsilon-1)$ versus the $\ln((T-T_A)^2$, and the value is listed in Table 2. It can be seen that the $\delta_A$ increased with an increase in the modifier content and reached a maximum value of 170 K for the 20 mol% ceramic. This confirms that the diffuse phase transition is stronger for the compositions with a higher modifier content.

3.4. Ferroelectric and leakage current density properties

The polarization-electric field ($P$-$E$) hysteresis loops of the BKN$_x$T ceramics, measured at RT under various electric fields of 10– 50 kV/cm and a frequency of 1 Hz is plotted in Figure 10. Plots of $P_r$ and $E_c$ values as functions of electric field are also shown in Figure 10. It was found that $P_r$ and $E_c$ values increased with increasing an electric field for all compositions. Unsaturated hysteresis loops were found at lower electric fields, while at an electric field of 50 kV/cm, more saturated hysteresis loops were found. At electric field of 50 kV/cm, the pure BKT ceramic exhibited a weak ferroelectric behavior with $P_r = 3.53 \mu C/cm^2$ and $E_c = 15.92$ kV/cm. However, the incorporation of the modifier had a significant influence on the ferroelectric hysteresis loop shape and polarization response. The $P_r$ initially increased with increasing the modifier content and reached a maximum value of 12.23 $\mu C/cm^2$ for the 5 mol% ceramic with a well-saturated
Figure 9. Plots of dielectric constant ($\varepsilon_r$) as a function of temperature at various applied voltages of the BKN,T ceramics, measured at $@10$ kHz where (a) $x = 0$ mol%, (b) $x = 5$ mol%, (c) $x = 10$ mol%, (d) $x = 15$ mol%, (e) $x = 20$ mol%.

$P$-$E$ hysteresis loop. This indicates that the modifier promoted a ferroelectric ordering. However, with further increasing the modifier up to $10$– $20$ mol%, the $P$, value then decreased. Furthermore, the $E_c$ value also decreased with increasing the modifier content.

Leakage current density ($J$) as a function of applied electric field ($E$) of the BKN,T ceramics was carried out, as seen in Figure 11. Resistivity was also calculated from the $J$-$E$ plot at an electric field of $30$ kV/cm, as seen in the inset of Figure 11. There was a sharp increase in the current with the applied electric field at low electric field, followed by nearly saturation at high electric field [59]. The pure BKT ceramic showed $J$ value of approximately $1.40 \times 10^{-6}$ A/cm$^2$. The $J$ value increased with increasing amount of the modifier and showed the maximum value of $3.64 \times 10^{-6}$ A/cm$^2$ for the $x = 5$ mol % ceramic (at high electric fields of $30$ kV/cm), then decreased with further increasing the modifier content. As expected, the resistivity (at $30$ kV/cm) tended to decrease with the modifier, and the lowest value of $8.24 \times 10^{11}$ $\Omega$.m was noted for the $x = 5$ mol % ceramic, and then increased with increasing the modifier content. This is in accordance with the result of ferroelectric properties.

3.5. Magnetic properties
Plots of magnetization ($M$) and magnetic field ($H$) of the BKN,T ceramics, measured at RT and under the magnetic field of $-10$ kOe $\leq H \leq 10$ kOe are presented in Figure 12. The $x = 0$ and $5$ mol% ceramics show non-magnetic behavior with slim and linear hysteresis loop. However, a slight improvement in magnetic behavior was observed for samples with $x = 10$– $20$ mol%. In this work, the improvement in magnetic behavior is may be due to many reasons. The contribution of magnetic clusters and paramagnetic host may be a reason for this improvement. The increase of number and size of magnetic region clusters (magnetic contribution) in paramagnetic host (paramagnetic contribution) can improve the magnetic behavior, which thus gives rise magnetically ordered clusters in
an overall paramagnetic host [60]. The formation of magnetically ordered clusters has also been reported in other systems [60–62]. Furthermore, the improvement in magnetic behavior is may be due to the formation of oxygen vacancies which caused by the Ni ions diffused into the BKT lattices. When the Ni$^{2+}$-substitution in the Ti$^{4+}$ site of the lattice, the oxygen vacancy can be generated to compensate the charge neutrality. The oxygen vacancies can locally trap electrons to occupy orbitals interacting with the 3d shell of Ni$^{2+}$, as a result in an electron-mediated ferromagnetism. This can the ferromagnetism coupling [63]. A similar improvement was also observed by Jarupoom et al. [55] in the Ba(Zr$_{0.7}$Ti$_{0.3}$)O$_3$/CoO or BZT/CoO composites, which suggested that the addition of CoO nanoparticles enhanced the magnetic properties of the BZT ceramic with a slight change in the ferroelectric properties, where the magnetocapacitance value (-MC) was also increased with increasing CoO concentration. Furthermore, Rawat et al. [64]

Figure 10. Polarization-electric field ($P$-$E$) hysteresis loop, and plots of $P_r$ and $E_c$ values as a function of electric field of the BKN, T ceramics, measured at RT under various electric fields of 10–50 kV/cm and a frequency of 1 Hz.
reported that the increase in remnant magnetization for the \((1-x)[0.65\text{BaTiO}_3-0.35\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3]-x\text{BiFeO}_3\) or BT-BNT-BFO, was linked with the increase in the concentration of magnetic ions \(\text{Fe}^{3+}\) with the increase of \(\text{BiFeO}_3\) concentration.

### 3.6. Piezoelectric and energy harvesting properties

Plots of low-field piezoelectric coefficients \(d_{33}\) as a function of the electric field \(E\) of the BKN\(x\) T ceramics are shown in Figure 13. The \(d_{33}\) value increased with increasing electric field from 0 kV/mm to 5 kV/mm. However, the \(x = 10\) mol % ceramic showed the better result with the highest value and rate of increasing (see Figure 13(f)).

Energy-harvesting utilizing piezoelectric materials has recently attracted extensive attention due to the strong demand of self-powered electronics \cite{65}. A key factor when evaluating piezoelectric energy harvester is the piezoelectric voltage coefficient \(g_{33}\) value \cite{8,42}, which was also calculated from the following equation \cite{8,33,34,42}:

\[
g_{33} = \frac{d_{33}}{\varepsilon_r \varepsilon_0} \tag{10}
\]

\(E_{\text{f}}\)

Figure 11. Plots of leakage current density \(J\) as a function of applied electric field \(E\) of the BKN\(x\) T ceramics (Inset show: resistivity as a function of \(x\) content at 20 kV/cm).

![Figure 11](image1.png)

Figure 12. Plots of magnetization \(M\) and magnetic field \(H\) of the BKN\(x\) T ceramics, measured at RT and under the magnetic field of \(-10\) kOe \(\leq H \leq 10\) kOe, where (a) \(x = 0\) mol\%, (b) \(x = 5\) mol\%, (c) \(x = 10\) mol\%, (d) \(x = 15\) mol\%, (e) \(x = 20\) mol\%.

![Figure 12](image2.png)
where $d_{33}$ is the measured piezoelectric coefficients and $\varepsilon_r$ is the dielectric constant of the piezoelectric material and $\varepsilon_0$ is the dielectric constant in a vacuum. The plot of the piezoelectric voltage coefficient ($g_{33}$) versus the modifier of the BKN$_x$T ceramics @ electric field of 5 kV/mm is presented in Figure 14 and its related values are also summarized in Table 2. The $g_{33}$ value can be improved by the modifier. The $g_{33}$ value increased from $11.03 \times 10^{-3}$ Vm/N for the pure BKT ceramic to the maximum value of $23.92 \times 10^{-3}$ Vm/N for the 5 mol% ceramic and then decreased with further increasing of the modifier content. The piezoelectric constant values of the 5 mol% ceramic in this work were higher previously works such as the BNKBST ceramics [52] which reported the $d_{33}$ and $g_{33}$ values were 172 pC/N and $1.20 \times 10^{-3}$ Vm/N, respectively. The piezoelectric properties comparison are shown in the supplementary Table S4. An improvement of the $g_{33}$ value for this work is due to an improvement of the $d_{33}$ value and to a lower room temperature dielectric constant in this composition. A similar observation was made by Liu et al. [34] in textured KNN-based ceramics which also reported the high $d_{33}$ and low $\varepsilon_r$ of textured ceramics, as a result in large $g_{33}$ value. The maximum $g_{33}$ value for this work is high for lead-free ceramics, and also texture ceramics [8,34].

Since the ceramics presented high $d_{33}$ and $g_{33}$ values at RT, it is interesting to determine the energy harvesting performance of the studied materials. The $g_{33}$ is important for evaluating material figure of merit for piezoelectric sensors [8]. Therefore, the off-resonance figure of merit (FoM) for energy harvesting was evaluated via the following equation [8,66]:

$$\text{FoM (pm}^2/\text{N}) = d_{33} \times g_{33} \quad (11)$$

Figure 13. Plots of low-field piezoelectric coefficients ($d_{33}$) as a function of electric field ($E$) of the BKN$_x$T ceramics where (a) $x = 0$ mol%, (b) $x = 5$ mol%, (c) $x = 10$ mol%, (d) $x = 15$ mol%, (e) $x = 20$ mol%, and (f) plots of $d_{33}$ as a function of $E$ for all samples.
where $d_{33}$ and $g_{33}$ are the low-field piezoelectric coefficient and the piezoelectric voltage constant of the device, respectively. Plots of the off-resonance figure of merit (FoM) as a function of the modifier content of the BKN$_x$T ceramics are presented in Figure 14 and related values are also summarized in Table 2. The pure BKT ceramic had the FoM value of 1.33 pm$^2$/N. With an increase of the modifier content, the FoM increased to the maximum value of 6.64 pm$^2$/N for the $x = 5$ mol% ceramic, which was more than 5.0 times (or 399%) as compared to the pure BKT ceramic, and then slightly decreased with a further increase of the modifier. It can be seen that the trend of the FoM value is similar to that of the trend of $g_{33}$ value [8]. A comparison of the $g_{33}$ and the FoM values with the previously lead-free piezoelectric ceramics is summarized in Table 3 [4,8,42,67–70]. It should be noted that the $g_{33}$ and the FoM value in this work ($x = 5$ mol% ceramic) is considered high when compared with many lead-free piezoelectric ceramics. Based on the obtained data, the energy harvesting behavior improvement was achieved in this system. The highest $g_{33}$ of 23.92 $\times 10^{-3}$ Vm/N and FoM of 6.64 pm$^2$/N as observed for the $x = 5$ mol% ceramic, suggests that this composition has a potential to be one of the promising lead-free piezoelectric candidates for further use in energy harvesting applications.

4. Conclusion

In summary, the lead-free BKN$_x$T ceramics (where $x = 0, 5, 10, 15$ and $20$ mol%) were successfully synthesized by a solid-state mixed oxide method. Phase evolution, microstructure, mechanical, dielectric, piezoelectric, magnetic and energy harvesting properties of all ceramics were examined. X-ray diffraction results showed that all ceramic samples exhibited a single phase with the perovskite structure. There was a change from tetragonal to cubic phase with an increase of the modifier content. The reduction of grain size was observed when the modifier was added. The densification, mechanical and electrical properties of the BKN$_x$T ceramics were also found to improve with an increase of the modifier. The highest hardness values ($H_{\text{v}} = 4.97$ GPa, $H_{\text{k}} = 4.78$, $E = 89$ GPa, $K_{\text{IC}} = 0.83$ MPa.m$^{1/2}$) were observed for the 20 mol% ceramic. The maximum dielectric ($\varepsilon' = 1763, \tan \delta = 0.0697$) was obtained for the 10 mol% ceramic. A slight improvement of magnetic behavior was also observed in this system. The highest piezoelectric voltage constant ($g_{33} = 23.92 \times 10^{-3}$ Vm/N) and the off-resonance figure of merit for energy harvesting (FoM = 6.64 pm$^2$/N) were obtained for the 5 mol% ceramic, which suggested that this ceramic has a potential to be one of the promising lead-free piezoelectric candidates for further use in energy harvesting applications.

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