Enhanced electrical properties of new lead-free 0.995Bi$_{0.5}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$-0.005LiNbO$_3$ ceramics by (Ba$_{0.99}$Nd$_{0.02}$)TiO$_3$ doping

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ABSTRACT

It is well known that the Bi$_{0.3}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$ or BNKT ceramic possesses quite high piezoelectric coefficient (i.e., $d_{33}$ ~ 151 pC/N). This research attempted to prepare (1-y)[0.995Bi$_{0.5}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$]+y[0.005LiNbO$_3$] or (1-y)[0.995BNKT-0.005Li]-yBaTiO$_3$ (where y = 0–0.05 mol fraction) lead-free ceramics by conventional sintering method. The optimum sintering condition was found to be 1100°C with a 2 h dwell time with a heating/cooling rate of 5°C/min. The XRD patterns of all samples showed pure perovskite phase. The optimized electrical properties were found in the sample having the composition of y = 0.03 mol fraction. Its dielectric constant was ~1980 with the dielectric loss of 0.0508 at room temperature and ~5987 with dielectric loss of 0.0540 at 268°C. The maximum $S_{max}$ value of 0.25% with $d_{33}$ = 491 pm/V, and the piezoelectric coefficient of 258 pC/N were also obtained. The polarization-electric field hysteresis loops of pure and lightly-doped samples indicated a normal ferroelectric behavior. The transition to anti-ferroelectric behavior was observed for the samples with high BNdT content. This showed that the electrical properties of BNKT-LN ceramics could be tuned by small addition of BNdT with the optimum FoM values of 3.80 pm$^2$/N. These lead-free compounds may be suitable for energy harvesting applications.

1. Introduction

Lead zirconate titanate (PZT) is a widely used perovskite material and about 60% of the commercially manufactured electronic products contain this compound. However, lead-based compounds are considered harmful for human body and surrounding environment due to the presence of lead and lead-oxide during the production process and usage of these devices [1,2]. The piezoelectric devices used in many applications still employ lead-based systems due to their outstanding piezoelectric properties [2]. Therefore, the search for lead-free piezoelectric ceramic systems, such as (Ba$_{0.85}$Ca$_{0.15}$)$_{1-x}$Ti$_2$O$_3$ (BCZT) [3], Bi$_{0.5}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$ (BNKT) [4], Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) [5] and BaTiO$_3$ (BT) [6] and attempts to improve their properties have currently attracted much interest and effort.

Peroxysite material with ABO$_3$ structure has a long history and plays an essential role in many electronic devices. Among the well-known lead-free perovskite systems, Bi based compound such as Bi$_{0.5}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$ (BNKT) is considered a potential replacement of PZT-based ceramics. The previous study in 1986 by Wang et al. [7] reported that the morphotropic phase boundary (MPB) between Na$_{0.5}$Bi$_{0.5}$TiO$_3$-K$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT–KBT) was located at 16–20 mol% of KBT. In addition, Sasaki et al. [8] reported the morphotropic phase boundary (MPB) between the rhombohedral (BNT) and tetragonal phases (BKT) near x = 0.16–0.20 (for Bi$_{0.5}$ (Na$_{1-x}$K$_x$)$_{0.5}$ TiO$_3$ composition) by X-ray diffraction. For the investigation of Bi$_{0.5}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$ (BNKT) doped with LiNbO$_3$ (LN), it was found that the addition of small amount of LN concentration into BNKT (x = 0.005) could significantly improve the electrical properties of BNKT in which the room temperature dielectric constant attained the relatively high value of 1654 and piezoelectric coefficient ($d_{33}$) of 162 pC/N [9]. Moreover, another previous study has demonstrated that addition of BNdT was found to improve the dielectric and piezoelectric properties of BNKT ceramic (i.e. $e_r$ = 1716, $T_c$ = 327°C and $d_{33}$ = 211 pC/N) [10].

This research intends to investigate a new lead-free ceramic system with the composition, (1-y)[0.995Bi$_{0.5}$ (Na$_{0.80}$K$_{0.20}$)$_{0.5}$ TiO$_3$-0.005LiNbO$_3$]+y[0.005BNKT] or (1-y)[0.995BNKT-0.005Li]-yBaTiO$_3$ (where y = 0–0.05 mol fraction). It is expected that the prominent peaks of 0.995BNKT-0.005LN and BNdT compounds may be combined and give the optimum properties. The effects of BNdT addition on phase, microstructure and electrical properties (i.e., dielectric, ferroelectric,
piezoelectric properties, and strain behavior) of 0.995BNKT-0.005LN lead-free ceramic systems were therefore investigated and discussed in detail.

2. Experimental procedures

Lead-free piezoelectric ceramics with the composition of (1-y)[0.995 Bi0.5(NA0,80KO0,20)0.5TiO3-0.005LiNbO3]y (Ba0.98Na0.02)TiO3, where y = 0–0.05 mol fraction, were synthesized by a conventional mixed oxide technique. The raw materials were commercial powders of Bi2O3 (98%, Fluka), Na2CO3 (99.5%, Carlo Erba), K2CO3 (99%, Sigma-Aldrich), TiO2 (98.5%, Sigma-Aldrich), Li2CO3 (99.0%, Sigma-Aldrich), Nb2O5 (99.0%, Sigma-Aldrich) for the synthesis of 0.995BNKT-0.005LN. BaCO3 (98.5%, Fluka), Nd2O3 (99.9%, Sigma-Aldrich) and TiO2 (98.5%, Sigma-Aldrich) were employed as the precursors for the preparation of BNdT powder. For the first step, all carbonate powders were dried in an oven at a temperature of 120°C for 24 h to remove the residual moisture. All raw materials were stoichiometrically weighed and mixed by ball milling for 24 h in 99% ethanol. The mixtures were dried again in an oven at 120°C for 24 h. The prepared powder mixture of 0.995BNKT-0.005LN was calcined at 900°C for 2 h while that of BNdT was separately calcined at 1100°C for 2 h with a heating/cooling rate of 5°C/min. After adding a few drops of 4 wt% PVA binder into the calcined powders, the cylindrical disks (10-mm in diameter) were formed using a uniaxial press. All green pellets were sintered at the maximum sintering temperature of 1100°C with 2 h dwell time and a heating/cooling rate of 5°C/min in an alumina crucible. Crystal structures of all sintered ceramics were examined in 2θ range of 20–70 degrees using an X-ray diffractometer (XRD-Phillip, X-pert). Theoretical densities of all samples were calculated based on the theoretical densities of BNKT (5.84 g/cm3) [11] and BT (6.01 g/cm3) [12]. Raman spectra were studied by a Raman spectroscopy (Raman Jobin Yvon Horiba, T64000). A scanning electron microscope (SEM, JEOL JSM-6335 F) was used to study microstructural features of all ceramics. The linear shrinkage was calculated using the ratio of the sample diameter before and after sintering process. The average grain size was estimated by counting the number of grains intercepted by one or more straight lines from SEM image.

For the measurement of the electrical properties, all samples were polished to 1 mm thickness to obtain parallel scratch-free surfaces. The silver paste was painted onto both surfaces of each sample before being heated at 500°C for 15 min to form conductive electrodes. Room temperature dielectric constant and dielectric loss were measured at a frequency of 1, 10, and 100 kHz using a 4263B LCR-meter. The dielectric constant as a function of temperature was investigated using a high precision LCR meter (LCR 821, GW INSTEK). Room temperature polarization-electric field (P-E) hysteresis loop was measured under 25 Hz frequency using a Sawyer-Tower circuit. Remanent polarization (Pr), maximum polarization (Pmax), and coercive field (Ec) values were obtained from the hysteresis loop. Room temperature strain-electric field (S-E) data were measured under 0.1 Hz frequency using an optical displacement sensor (Fotonic Sensor model MTI-2100). The bipolar strain curve at maximum electric field of 50 kV/cm was also carried out. The maximum strain (Smax) and the negative strain (Sneg) values were calculated from the bipolar curve. The normalized strain coefficient (d33) was also calculated using the following relationship: d33 = Smax/Emax. The samples for piezoelectric measurement were poled in silicone oil bath at 55°C under an applied DC electric field of 4 kV for 15 min. Piezoelectric coefficient (d33) was recorded from 1-day aged samples using d33 meter (KCF technologies, SS865). The piezoelectric voltage constant (g33) and the off-resonance figure of merit (FoM) for energy harvesting application were also calculated.

3. Results and discussion

All (1-y)[0.995BNKT-0.005LN]-yBNdT (where y = 0–0.05 mol fraction) samples possessed high relative densities of ~98% of their theoretical values with their corresponding linear shrinkage (see Table 1). Both the relative densities and linear shrinkage showed a slight increase with increasing BNdT concentration. Figure 1(a) shows X-ray diffraction patterns of all sintered samples. The data showed that a pure perovskite structure was obtained without any detectable impurity phase, indicating the complete ionic substitution during solid state sintering process. For the A-site position (with coordination number (CN) of 12), Li+ ion (no confirmed reported ionic radius value but the expectation value should be between rLi+(0.92 Å, CN = 8 [13] and rLi+(1.39 Å, CN = 12 [13])) and Ba2+(rBa2+ = 1.61 Å [13]) ions were likely distributed into Bi3+(rBi3+ = 1.40 Å [14]), Na+ (rNa+ = 1.39 Å [13]), K+ (rK+ = 1.64 Å [13]) and Nd3+(rNd3+ = 1.27 Å [13]) while Nb5+(rNb5+ = 0.64 Å [13]) entered into B-site (CN = 6) of Ti4+ position (rTi4+ = 0.61 Å [13]). From Figure 1(b) and (c), the 0.995BNKT-0.005LN ceramic shows a mixed phase of tetragonal and rhombohedral.

### Table 1. Physical properties of (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics.

| y     | Relative densities (%) | Linear shrinkage (%) | c/a   | Grain size (μm) |
|-------|------------------------|----------------------|-------|-----------------|
| 0     | 98.23 ± 0.03           | 18.32 ± 0.05         | 0.3300| 0.32 ± 0.11     |
| 0.01  | 98.33 ± 0.07           | 18.33 ± 0.03         | 0.1051| 0.38 ± 0.15     |
| 0.02  | 98.45 ± 0.08           | 18.54 ± 0.02         | 0.1080| 0.47 ± 0.17     |
| 0.03  | 98.99 ± 0.04           | 18.66 ± 0.05         | 1.1124| 0.55 ± 0.18     |
| 0.04  | 98.78 ± 0.03           | 18.68 ± 0.03         | 1.1111| 0.64 ± 0.19     |
| 0.05  | 98.67 ± 0.03           | 18.72 ± 0.08         | 1.1110| 0.78 ± 0.15     |
structure. The broad peak at 2θ ~ 40 degree indicated the overlapping of (111)_{(111)} and (111)_{h} peaks but the intensity of both rhombohedral and tetragonal peaks at this angle was rather weak. The presence of tetragonal phase was clearly seen near 2θ ~ 46 degree from the splitting of (002)_{T}/(200)_{T} peaks. The addition of 0.018BNdT into 0.995BNKT-0.005LN showed a higher intensity peak but still quite broad. Nevertheless, the split (002)_{T}/(200)_{T} peaks at this angle still showed the same feature and, with no apparent change in the peaks at other angles, mixed tetragonal and rhombohedral phases were still maintained. When the amount of added BNdT was further increased, the (111)_{(111)} and (111)_{h} peak became narrower and the intensity of rhombohedral peaks became weaker with the (111)_{T} peak became more prominent. Since the intensity of the tetragonal peaks at 2θ ~ 46 remained nearly the same, it was therefore expected that the addition of BNdT into 0.995BNKT-0.005LN favored the formation of tetragonal phase. From this BNdT substitution, a slight increase in anisotropy of the tetragonal phase could also be observed from the increased tetragonality (c/a), which was calculated from the split (002)_{T}/(200)_{T} peaks and their values are listed in Table 1. The variation in the tetragonality (c/a) from this study showed similar trend to that obtained in BNKT-BNdT system [10].

Raman spectroscopy was used to confirm the phase structure of all samples and complement the XRD data. The Raman spectra usually reflects the large length scale average structure of bulk materials [15,16]. The result of Raman spectroscopy observed at room temperature is shown in Figure 2. The spectra were described according to the eight Gaussian-Lorentzian mode following the previous literature reported [1,17]. Four main regions containing Raman peaks could be indicated. The first peak at around 100–200 cm\(^{-1}\) frequency range could be associated with the vibration of A-site cations such as Na, K, and Bi in the perovskite structure (Na-O, K-O, and Bi-O bonds). The second broad peak at 200–400 cm\(^{-1}\) range was assigned as Ti-O vibrations (A1 mode). The third frequency region at around 400–750 cm\(^{-1}\) modes was associated with the vibration of the TiO\(_6\) octahedra, possibly resulting from a superposition between longitudinal optical (LO) and transverse optical (TO) bands of A1 mode. The last region with frequency greater than 700 cm\(^{-1}\) has been reported to be linked to the A1 (longitudinal optical) and E (longitudinal optical) overlapping bands [18,19]. The Raman spectrum of 0.995BNKT-0.005LN in this study was in agreement with that of the previously reported BNKT ceramics [15,16,20] whose structure was determined to be consisted of rhombohedral (R3c) and tetragonal (P4bm) phases. With the addition of BNdT, no apparent change in Raman shift was observed for all four regions. This was likely due to the small amount of the BNdT used. However, it could be noticed that for the second region (200–400 cm\(^{-1}\)), there seemed to be a very small peak-splitting feature in \(y = 0.03–0.05\) samples. Based on our XRD analysis and the study by Jaita and Jarupoom [20], in which the splitting of peaks at this frequency region was clearly shown, this suggested that our BNdT-doped samples were consisted of tetragonal and rhombohedral phase, with a slightly decreasing amount of the latter.

![Figure 2](image)

**Figure 2.** Raman spectrum of BNKT-BNdT ceramics with (a) \(y = 0.00\), (b) \(y = 0.01\), and (c) \(y = 0.02\).
Figure 2. Raman spectra of the (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics at room temperature.

Figure 3. SEM images of (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics.

dopants in the form of solid solution as in our study, the presence of aliovalent ions could induce some defects (such as vacancies to compensate for charge imbalance) which could inhibit grain growth and change the local interfacial energy [23,24] such that the anisotropy of interfacial energy was reduced and the grain shape became more equiaxed as compared to that of the undoped one. Among the BNdT-added samples, the grain size slightly increased with increasing BNdT concentration. The values of the average grain sizes are listed in Table 1.

Room temperature (RT) dielectric constant ($\varepsilon_r$) and dielectric loss (tanδ) measured at 1 kHz frequency are listed in Table 2. At higher frequency, the polarization modes could not follow the applied electric field, $\varepsilon_r$ therefore decreased [25]. The undoped 0.995BNKT-0.005LN showed low $\varepsilon_r$ value of $\sim$1066 compared to the doped samples. The $\varepsilon_r$ tended to increase with increasing BNdT content up to 0.04 mol fraction. However, the $\varepsilon_r$ was slightly dropped when 0.05 mol fraction BNdT was doped. The addition of BNdT in 0.995BNKT-0.005LN was expected to act as a donor dopant, which facilitates the reorientation of PNRs and dipoles, causing an increase in the dielectric constant as often found in many donor-doped lead-free systems [26,27]. However, the further increase in donor concentration can lead to the presence of cation vacancies, which can inhibit the reorientation of PNRs and dipoles, causing a decrease in the dielectric constant [10]. This suggested the mechanism of induced
charge defects acting against donor-doped behavior [9]. This observed result is consistent with the previous work reported for the BNKT-BZT system [28]. However, the highest ε value observed in 0.97[0.995BNKT-0.005LN]-0.03BNdT sample of our present work was found to be higher than the ε value (~1745) of BNKT-BNdT system previously reported by Jaita et al. [10]. All samples showed low dielectric loss (tanδ) values ranging between 0.0485 and 0.0513.

Plots of temperature dependent dielectric constant (εr) and dielectric loss (tanδ) of (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics at various frequencies of 1, 10 and 100 kHz are presented in Figure 4. The maximum dielectric constant (εm) at high temperature of y = 0 mol fraction sample was found to be 5542 with tanδ of 0.0206. The highest εm value was obtained for 0.97[0.995BNKT-0.005LN]-0.03BNdT sample. The tanδ of all samples showed the values ranging between 0.0091 and 0.0782. For the 0.995BNKT-0.005LN sample, a dielectric peak (at higher temperature) together with a sudden drop of dielectric constant upon cooling (at lower temperature) were shown. It was proposed in a previous work studied by Wang et al. [29] that the sharp change in dielectric curve was due to a phase transition from ferroelectric to anti-ferroelectric phase upon heating. The temperature at which this transition occurred was called the depolarization temperature (Td). The εr reached the maximum value at Tm at which anti-ferroelectric-paraelectric phase transition was observed [30]. It can be found from our study that the BNdT-doped 0.995BNKT-0.005LN ceramics exhibited diffuse phase transition of εr at Td compared to the abrupt change observed in pure 0.995BNKT-0.005LN ceramic. It can be also seen from Figure 4 that Td and Tm values of BNdT-doped samples were frequency dependent, i.e. Td increased while Tm decreased with increasing measurement frequency. As shown in Figure 5, Td and Tm of pure 0.995BNKT-0.005LN ceramic were found to be 120°C and 215°C, respectively. The Td tended to decrease while Tm increased with BNdT concentration. The observed result was consistent with the previous work studied on the dielectric properties of CeO2-added (Bi0.5Na0.5)0.99Ba0.06TiO3 ceramics [31]. The dielectric result observed in this study was believed to be resulted from ionic substitutions. The substitution of Ba2+ ion for K+ ion was likely to be the key factor affecting the dielectric response of BNdT-doped ceramics. Due to the difference in oxidation number and ionic radii between Ba2+ and K+ ions, the ionic substitution could produce some A-site vacancies and lattice distortion. It was believed that besides the dipole moments, charged defects generated from A-site vacancies could also respond to the changes in temperature and frequency. Therefore, the broadening of the phase transition accompanying the frequency dependence of Td and Tm was observed in the ceramics. Moreover, the lattice distortion also contributed to the domain wall motion and, consequently, to the variation of Td and Tm values.

The measurement of polarization-electric field (P-E) hysteresis loops was conducted to determine the ferroelectric properties of (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics. Figure 6 presents the hysteresis loop of all

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**Table 2.** Electrical properties of (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics.

| y  | εr (RT) | tanδ (RT) | P0 (μC/cm²) | ε (kV/cm) | εmax (μC/cm²) | εm (kV/cm) | ρ0 (μs/cm) | Smax (%) | SNmax (%) | d33 (pm/V) | d33 (pm/NC) | q33 (10⁻⁶ V/mN) | FoM (pm²/N) |
|----|---------|-----------|-------------|-----------|---------------|-----------|------------|-----------|------------|-----------|-------------|---------------|-------------|
| 0  | 1.066   | 0.0507    | 22.29       | 17.94     | 30.64         | 50.09     | 0.09       | 0.08      | 0.14       | -0.07     | 279          | 156          | 12.98       | 2.02        |
| 0.01 | 1538    | 0.0502    | 15.93       | 17.34     | 28.98         | 50.21     | 0.01       | 0.17      | 0.05       | -0.03     | 338          | 160          | 11.76       | 1.88        |
| 0.02 | 1989    | 0.0513    | 13.74       | 13.33     | 31.48         | 50.40     | 0.04       | 0.22      | -0.07     | 436       | 176          | 9.99         | 1.76        |
| 0.03 | 1980    | 0.0508    | 11.63       | 12.42     | 28.88         | 50.90     | 0.03       | 0.25      | -0.05     | 491       | 258          | 14.71        | 3.80        |
| 0.04 | 1983    | 0.0485    | 9.38        | 8.65      | 30.39         | 50.39     | 0.05       | 0.16      | -0.06     | 317       | 220          | 12.25        | 2.69        |
| 0.05 | 1890    | 0.0510    | 7.19        | 7.72      | 30.89         | 50.39     | 0.05       | 0.15      | -0.06     | 297       | 197          | 11.77        | 2.31        |
samples obtained at room temperature. The normal well-saturated \( P-E \) loop was obtained for the 0.995BNKT-0.005LN ceramic, which indicated a typical ferroelectric behavior. The values of remnant polarization \( (P_r = 22.29 \, \mu C/cm^2) \), coercive field \( (E_c = 15.93 \, kV/cm) \) and loop squareness \( (R_{sq} = 0.98) \) were found to be similar to those of previous works \([1,32]\). The addition of BNdT into 0.995BNKT-0.005LN samples displayed the slimmer loops with softer ferroelectric character. At BNdT content of \( y = 0.04 \) and 0.05, the pinch-type loops showing the characteristics of anti-ferroelectric behavior started to form, in agreement with the lower ferroelectric-antiferroelectric transition temperature \( (T_d) \) observed in the dielectric constant data. The introduction of BNdT in the host perovskite unit cell of 0.995BNKT-0.005LN ceramic induced a structural distortion through defect dipole formation in the initial ferroelectric \( (FE) \) phase with co-existing nonpolar/ergodic relaxor \( (ER) \) phase, leading to the observed phase transition temperature \( (T_d) \) whose value could be tuned by compositional manipulation \([33]\). Since

![Figure 5](image1.png)

*Figure 5.* Plots of \( T_m \) and \( T_d \) as a function of BNdT concentration in \((1-y)[0.995BNKT-0.005LN]-yBNdT\) ceramics.

![Figure 6](image2.png)

*Figure 6.* Polarization-electric field \( (P-E) \) hysteresis loops of the \((1-y)[0.995BNKT-0.005LN]-yBNdT\) ceramics.

the free energy of the \( FE \) and \( ER \) phases are very close, the \( ER \) to \( FE \) phase transition could be induced by external electric field and the reverse transition occurred when the field was removed. Hence, the \( P-E \) loops in this study showed similar feature to those observed in nonpolar BNT- and BNKT-based materials \([32-36]\). Comparing to the 0.995BNKT-0.005LN ceramic, the values of \( P_r \) and \( E_c \) for \((1-y)[0.995BNKT-0.005LN]-yBNdT\) samples showed a decreasing trend with increasing BNdT content as shown in Table 2.

Figure 7 presents the bipolar electric field-induced strain curves of all samples recorded at room temperature. The maximum strain \( (S_{max}) \) and the negative strain \( (S_{neg}) \) obtained from the curve \([37]\) with the calculated normalized strain coefficient \( (d_{33}^* = S_{max}/E_{max}) \) \([38]\) are listed in Table II. The 0.995BNKT-0.005LN possessed the \( S_{max} \) value of 0.14% with \( d_{33}^* = 279 \, pm/V \). The addition of BNdT caused an increase in \( S_{max} \) and \( d_{33}^* \) value. The highest \( S_{max} \) was found in the 0.97 \([0.995BNKT-0.005LN]-0.03BNdT\) sample with the value of 0.25% and \( d_{33}^* = 491 \, pm/V \). The significant
enhancement in bipolar strain of BNdT-doped ceramics could be attributed to the reversible ER-FE phase transition induced by an applied field [36]. However, the $S_{\text{max}}$ and $d_{33}^*$ values starting to drop at the composition of $y = 0.04$ and 0.05 mol fractions.

The piezoelectric coefficient ($d_{33}$) recorded at room temperature is listed in Table 2. The $d_{33}$ value (i.e. 156 pC/N) of the 0.995BNKT-0.005LN sample was in agreement with the values previously reported for the BNKT-LN system [9]. The addition of BNdT caused an increase in $d_{33}$ with the maximum value (258 pC/N) obtained at the composition of $y = 0.03$ mol fraction. This value was higher than that reported in the previously investigated BNKT-BNdT system [10]. The piezoelectric voltage coefficient ($g_{33}$), which is the key evidence to determine the figure of merit for piezoelectric sensor application, can be calculated using the relation, $g_{33} = d_{33}/\varepsilon_0$, where $g_{33}$ is the piezoelectric voltage constant, $\varepsilon_0$ the dielectric constant of the piezoelectric material, $\varepsilon_0$ the dielectric constant in vacuum, and $d_{33}$ the piezoelectric charge constant [39,40]. The addition of BNdT contributed to the increasing trend of the $g_{33}$ value compared to that of the 0.995BNKT-0.005LN sample. The maximum $g_{33}$ value of $14.71 \times 10^{-3}$ V/mN was obtained for the $y = 0.03$ sample. The off-resonance figure of merit (FoM) for energy harvesting can be obtained from the multiplication between piezoelectric charge constant ($d_{33}$) and the piezoelectric voltage constant ($g_{33}$), i.e. $\text{FoM} = d_{33}g_{33}$ [41]. The 0.995BNKT-0.005LN sample had the FoM value of 2.02 pm²/N. The FoM of BNdT-doped samples showed the maximum value of 3.80 pm²/N for the $y = 0.03$ mol fraction sample. The maximum FoM value in this study compared to those reported in literature for several lead-free compounds are shown in Table 3. The comparative data showed that the addition of suitable amount of BNdT into 0.995BNKT-0.005LN ceramic could improve the performance of lead-free 0.995BNKT-0.005LN ceramics for energy harvesting applications.

![Figure 7. The bipolar electric field-induced strain curves of the \((1-y)[0.995\text{BNKT-0.005LN}]-y\text{BNdT}\) ceramics.](image)

| Table 3. The comparison table of FoM value. |
|-------------------------------------------|
| lead free ceramics system | FoM Value (pm²/N) | reference |
|---------------------------|------------------|-----------|
| $0.970[0.995\text{Bi}_{0.5}\text{Na}_{0.5}\text{K}_{0.25}\text{Li}_{0.25}]\text{TiO}_3$ | 3.80 | this work |
| $\text{Bi}_{1.7}\text{K}_{0.2}\text{TiO}_3$ | 1.33 | [42] |
| $0.94[\text{Bi}_{0.5}\text{Na}_{0.5}]\text{TiO}_3$ | 4.52 | [43] |
| $(\text{K}_{0.2}\text{Na}_{0.8})\text{TiO}_3$ | 4.60 | [44] |
| $\text{Ba}_{0.5}\text{Ca}_{0.5}\text{TiO}_3$ | 3.62 | [45] |
| $0.90\text{Ba}_{0.1}\text{Ca}_{0.9}\text{TiO}_3$ | 2.90 | [45] |

4. Conclusions

This research successfully fabricated the new lead-free (1-y)[0.995BNKT-0.005LN]-yBNdT ceramics system by the conventional solid state sintering method. The samples for this study were sintered at the optimum sintering condition of 1100°C for 2 h. All samples showed the mixed tetragonal and rhombohedral phases with the slight weakening concentration of the latter when the BNdT concentration increased. The electrical properties measurement indicated that the optimum dielectric constant (~5987 at 268°C), ferroelectric parameters ($P_r = 11.63$ μC/m², $E_c = 12.42$ kV/cm), piezoelectric coefficient (258 pC/N) and maximum FoM values of 3.80 pm²/N could be obtained for the 0.97 [0.995BNKT-0.005LN]-0.03BNdT sample. This sample may be further optimized and used for energy harvesting applications.

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