

INFLUENCE OF Pr₆O₁₁-DOPING ON THE CRYSTAL STRUCTURE AND ELECTRICAL PROPERTIES OF BNBT PIEZOELECTRIC CERAMICS

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Abstract

In this work, a series of lead-free 0.97(Bi_{0.5}Na_{0.5})TiO₃-0.03BaTiO₃-xPr₆O₁₁ (BNBT-xPr) piezoelectric materials with x=0, 0.1, 0.3, 0.5, and 0.7 wt.% were created by the solid-state combustion route, to enhance their electric properties. The investigation on the phase evolution, microstructure, and electrical behavior of the specimens were carried out. The powders and ceramics were calcined and sintered for two hours at 800°C and 1180°C, correspondingly. All examples displayed a perfect perovskite lattice and no detectable impurity phase. XRD pattern examination for the ceramics disclosed the existence of rhombohedral and tetragonal phases in all examples. The rhombohedral phase was boosted by rising the doping levels, as established by the Rietveld refinement study. As the x content rose, the average grain size and measured density began to decrease from 0.90±0.10 to 0.73±0.07 μm and 6.13 to 6.05 g/cm³, correspondingly. It was noticed that Pr₆O₁₁ doping, decreased dielectric properties. The remnant polarization (P_r) of the samples rises from 22.2 to 27.7 μC/cm² with x rises from 0 to 0.3 and then dropped. The coercive field (E_c) of the ceramics rises significantly when Pr₆O₁₁ was incorporated. The BNBT lead-free ceramics doped with 0.3wt%Pr₆O₁₁, with a high P_r value, could be a promising candidate for memory applications to replace Pb-based ceramics.

Keywords: BNBT; Pr₆O₁₁; Perovskite; Solid-state combustion; Dielectric

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Introduction

As a result of their outstanding piezoelectric coefficient ($d_{33} > 400$ pC/N), lead zirconate titanate Pb(Zr_{1-x}Ti_x)O₃ (PZT)-based piezoelectric materials have been broadly utilized in industries like actuators, transducers, sensors and various electromechanical applications (Gao *et al.*, 2020; Huang *et al.*, 2020; Chen *et al.*, 2021; Li *et al.*, 2021). Unfortunately, most PZT ceramics cause severe environmental problems due to lead oxide toxicity. In the past several years, lead-free piezoelectric ceramics have been one of the most favored alternatives to replace lead-based ceramics owing to their environmental friendliness, like the frequently mentioned Bi_{0.5}Na_{0.5}TiO₃ (BNT)-based, BaTiO₃ (BT)-based, and (K_{0.5}Na_{0.5})NbO₃ (KNN)-based ceramics (Rodel *et al.*, 2009; Chatterjee *et al.*, 2018; Tan *et al.*, 2021). Due to its elevated Curie temperature and favorable ferroelectric features, BNT shows promise for utilization in piezoelectric applications (Smolenskii, 1961). However, the major drawback of pure BNT ceramics is a high coercive field (E_c) remains a problem during the poling process, degrading the piezoelectric coefficient (Chen *et al.*, 2016). The 0.97(Bi_{0.5}Na_{0.5})TiO₃-0.03BaTiO₃ (0.97BNT-0.03BT) solid solution has been given great interest in many research studies because of its increased piezoelectric coefficient and a lessening in E_c has been observed in compositions near the morphotropic phase boundary (MPB) (Xu *et al.*, 2008; Chatterjee *et al.*, 2018).

A number of investigations have demonstrated that the densification and electrical properties of piezoelectric materials can be enhanced by the addition of rare-earth elements such as Gd₂O₃, Er₂O₃, CeO₂, Nd₂O₃, Sm₂O₃, Yb₂O₃, and Pr₆O₁₁. (Shi *et al.*, 2009; Coondoo *et al.*, 2015; Chalfouh *et al.*, 2016; Han *et al.*, 2017; Pattipaka *et al.*, 2020; Kuang *et al.*, 2023). Recently, Pattipaka *et al.* reported that 0.04 mol% of Gd₂O₃ doped into (K_{0.5}Na_{0.5})_{0.96}Li_{0.04}(Nb_{0.8}Ta_{0.2})O₃ (KNLNT) ceramics modified the dielectric behaviors at room temperature ($\epsilon_r \sim 1025$), ferroelectric behavior ($P_r \sim 23.14$ μ C/cm², $E_c \sim 8.70$ kV/cm at 1 Hz), piezoelectric coefficient ($d_{33} \sim 128$ pC/N), and planar coupling factor ($k_p \sim 53\%$) (Pattipaka *et al.*, 2020). A high $d_{33} \sim 128$ pC/N, high $k_p \sim 0.283$, large mechanical quality factor ($Q_m \sim 216$), high thick coupling factor ($k_t \sim 0.54$), high $\epsilon_r \sim 891$, and a low dissipation factor ($\tan\delta \sim 0.018$) at 1 kHz were among the impressive results of doping (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ (BNBT) ceramics at 0.4 wt%CeO₂ (Shi *et al.*, 2009). Sm₂O₃-doped at 0.03% mol% in 0.94Bi_{0.5}Na_{0.5}TiO₃-0.06BaTiO₃

(BNT-BT) ceramics showed a maximum electric field-induced strain (S_{max}) of 0.35% and a normalized strain (d_{33}^*) of 446 pm/V (Kuang *et al.*, 2023). Chalfouh *et al.* revealed that doping BaTi_{0.925}(Yb_{0.5}Nb_{0.5})_{0.075}O₃ (BTYN) ceramics with the appropriate amount of Pr₆O₁₁ (0.006 mol%) enhanced the d_{33} value (Chalfouh *et al.*, 2016). Doping Pr₆O₁₁ at 0.04 wt.% resulted in a larger $d_{33} \sim 425$ pC/N and a maximum $P_r \sim 8$ μ C/cm² in (Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O₃ (BCTZ) ceramics (Coondoo *et al.*, 2015). Hence, the notion of using Pr₆O₁₁ doping to boost the densification and electrical behaviors of BNBT ceramics is very interesting and not resolved.

For the synthesis of superior lead-free piezoelectric materials, the solid-state combustion route has received a lot of interest (Chootin and Bongkarn, 2017; Kornphom *et al.*, 2018; Yotthuan *et al.*, 2020). The solid-state combustion process uses energy emitted from fuel to speed up the chemical interaction among the initial substances and helps reduce the temperature of the synthesis. This method produces powders with ultrafine, homogeneous particles that are highly pure. The ceramics also demonstrate a high density and good electrical performance.

Hence, we study the influence of Pr₆O₁₁ doping (0, 0.1, 0.3, 0.5 and 0.7 wt.%) on the phases evolution, microstructure and electrical properties of 0.97(Bi_{0.5}Na_{0.5})TiO₃-0.03BaTiO₃ ceramics synthesized using the solid-state combustion approach.

Experimental

0.97(Bi_{0.5}Na_{0.5})TiO₃-0.03BaTiO₃-xPr₆O₁₁ (BNBT-xPr; x=0, 0.1, 0.3, 0.5 and 0.7 wt.%) lead-free ceramics were synthesized by the solid-state combustion route. High-purity powders of Bi₂O₃ (99-101%, Himedia, IN), Na₂CO₃ (99%, Carol erba, TH), TiO₂ (99.9%, Acros organics, BEL), and Ba(NO₃)₂ (99.9%, Sigma-Aldrich, DEU) were utilized as initiating chemicals. After weighing the starting powders to the appropriate stoichiometry, they were combined and ball milled for 24 h in ethanol with zirconia balls. Subsequently, the suspensions were dried for 10 h at a temperature of around 100°C, or until the ethanol evaporated entirely. Next, the mixed powder and glycine were combined in a 1:2 ratio in an agate mortar, calcined for two hours at 800°C in normal air at a rate of 5°C/min, and then let to cool down freely. The pure BNT-BT calcined powders were mixed with Pr₆O₁₁

powder (99.9%, Carlo erba, TH) at various compositions and a 3 wt% polyvinyl alcohol (PVA) binder solution and then ball milled for 12 h. After the second ball milling, the BNBT-xPr powders were dried and ground. Using a hydraulic press, the obtained powders were compressed into pellets with a diameter of approximately 15 mm and a thickness of approximately 1.5 mm at a pressure of 80 MPa. The pellets were heated at 400°C for 3 h to burn away the binder before being sintered in air at 1180°C for two hours (heating rate of 5°C/min and let to cool down freely).

The phase structure of the materials was determined by X-ray diffraction (XRD, BRUKER, D8 ADVANCE). To verify the crystal structure and measure each phase, Rietveld refinement study was employed. The observation of the morphology of the specimens was inspected by scanning electron microscopy (SEM, JEOL, JSM-6610LV). The surfaces of the examples were polished using emery paper and an alumina polish to prepare the SEM specimens. To disclose their grain boundaries, the surfaces of ceramics were thermally etched at a temperature 1080°C for 30 min (with a heating rate of 5°C/min and let to cool down freely). The Archimedes approach was adopted to examine the density of the ceramics, and the linear interception route on the SEM picture was utilized to determine the mean grain size of the specimens. To make an electrode, silver paint was applied to both surfaces of the samples, and they were then burned at 500°C for 30 min (at a heating rate of 5°C/min and let to cool down freely). The dielectric behavior was described utilizing an LCR meter (HP, 4284A) operating at 1-100 kHz throughout a temperature range of around 30 to 400°C. The ferroelectric hysteresis (P-E) loops were examined utilizing a computer-controlled modified Sawyer-Tower circuit (Radiant, PLC2-The P-E loop) running at 1 Hz and 70 kV/cm.

Results and Discussion

The XRD patterns obtained in the 2θ range of 10–80° at room temperature for the BNBT-xPr ceramics manufactured with various Pr_6O_{11} quantities are displayed in Figure 1(a-c). All compositions displayed a perfect perovskite form with without trace of any secondary phase, which means Pr ions can diffuse into the BNBT lattice completely. As illustrated in Figure 1(b, c), the XRD patterns of all examples were zoomed at the 2θ range of approximately 39 to 41° and approximately 45 to 48° to ascertain the phase progression. The rhombohedral phase (R), which is represented by JCPDS file no. 36-0340, is indicated by the presence of two (003)/(021)_R peaks at a lower angle ($\sim 40^\circ$) and one (202)_R peak at a higher angle ($\sim 46^\circ$). The tetragonal phase (T) is identified by an individual (111)_T peak at a lower angle and two split peaks of (002)/(200)_T at a higher angle. This matches to JCPDS file no. 05-0626. The ceramics showed two peaks at a lower angle ($\sim 40^\circ$) in all compositions. All samples had non-symmetric and broad dual diffraction peaks at the higher angle ($\sim 46^\circ$), indicates the presence of R and T phases. Moreover, as illustrated in Figure 1(c), the shift of the diffraction peak is not clearly visible. So, we assumed that during the sintering process of the BNBT-xPr ceramics, Pr_6O_{11} may have disassociated and released Pr^{3+} ($\sim 0.99 \text{ \AA}$) and Pr^{4+} ($\sim 0.89 \text{ \AA}$) ions, which have an equal probability of replacing either $[\text{Bi}^{3+} (\sim 1.03 \text{ \AA}) / \text{Na}^+ (\sim 1.39 \text{ \AA}) / \text{Ba}^{2+} (\sim 1.61 \text{ \AA})]$ -sites or $[\text{Ti}^{4+} (\sim 0.605 \text{ \AA})]$ -site as the $\text{Pr}^{3+} / \text{Pr}^{4+}$ ionic sizes are in between these pairs, which is consistent with earlier studies (Coondoo *et al.*, 2015).

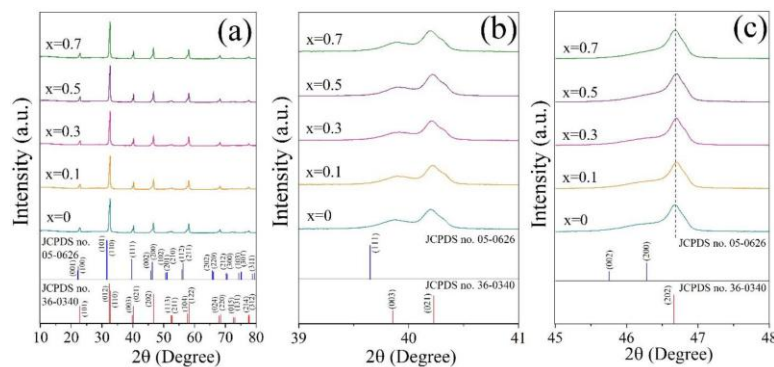


Figure 1. XRD patterns at room temperature of BNBT-xPr ceramics with different x in the 2θ range of (a) 10–80°, (b) 39–41°, and (c) 45–48°

In order to match the XRD data for verification and perfect the XRD study, each ceramic underwent Rietveld refinement utilizing Fullprof software. The Crystallography Open Database (COD) is the standard information source for the initial values of the space groups, lattice constants and atom functional positions (Sindhu *et al.*, 2012; Guerra *et al.*, 2017). The XRD data of the BNBT-xPr ceramics were refined using a structural model based on $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ with a rhombohedral phase (*R*), with a $R3c:H$ space group, and BaTiO_3 with a tetragonal phase (*T*), with an $P4bm$ space group. To modify the background, a Chebyshev polynomial function was employed. This pseudo-Voigt function describes the peak profiles. The quality of the refining was evaluated using a variety of parameters, like: R_p is the profile reliability, R_{wp} is the weighed pattern reliability, and χ^2 is the goodness of fit. Figure 2(a-c) displays the ultimate result from the Rietveld refinement. The quality values and phase proportion of the ceramics are presented in Figure 2. The estimated quality of

the fits proved to be $R_p \leq 9.47\%$, $R_{wp} \leq 7.07\%$ and $\chi^2 \leq 3.92$ (Figure 2), demonstrating a high degree of agreement between the computed and observed intensity profiles for all examples. According to the fitting results, *T* and *R* coexisted in all samples, and the amount of *R* increased as Pr_6O_{11} increased (Figure 2(a-c)).

SEM images of the surface morphology of BNBT-xPr ceramics are illustrated in Figure 3(a-e). All specimens were observed to have a polyhedral microstructure with clearly defined grain boundaries, a dense microstructure, and few pores. As the Pr_6O_{11} level rose, the average grain size of the ceramics began to reduce from 0.90 ± 0.10 to $0.73 \pm 0.07 \mu\text{m}$, implying that Pr_6O_{11} doping may hinder grain growth in BNBT ceramics (Ramovatar *et al.*, 2018). The measured density began to decline from 6.13 to 6.05 g/cm^3 upon *x* amount rose, as illustrated in Figure 3(f). The SEM pictures and the measured density data of the BNBT-xPr ceramics were in agreement.

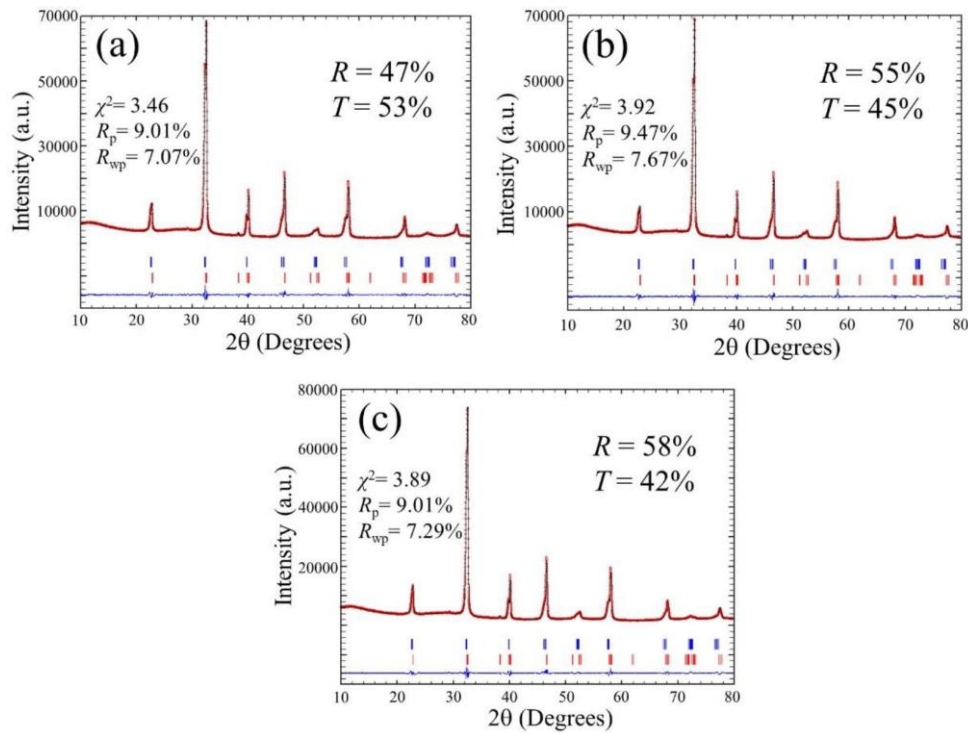


Figure 2. Typical Rietveld refinement analysis for BNBT-xPr ceramics with (a) $x=0$, (b) $x=0.3$, and (c) $x=0.7$, experimental (red hollow symbol), calculated (black solid line), Bragg reflection (blue vertical bar lines for $P4bm$ space group and red vertical bar lines for $R3c:H$ space group) and difference (Blue solid line) between experimental and calculated data are presented

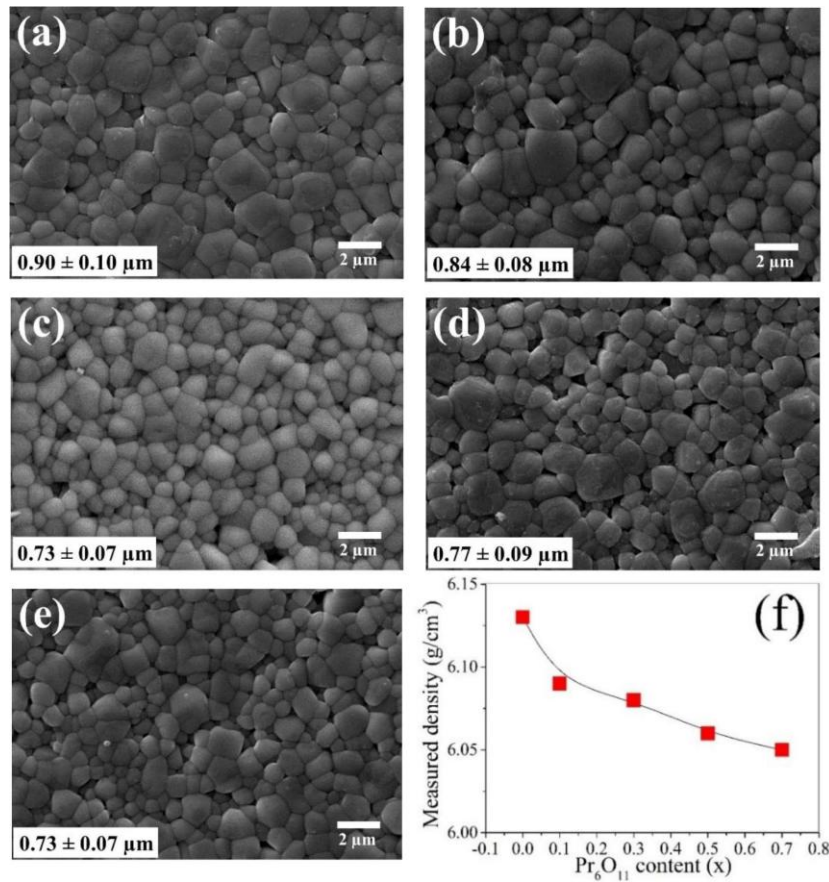


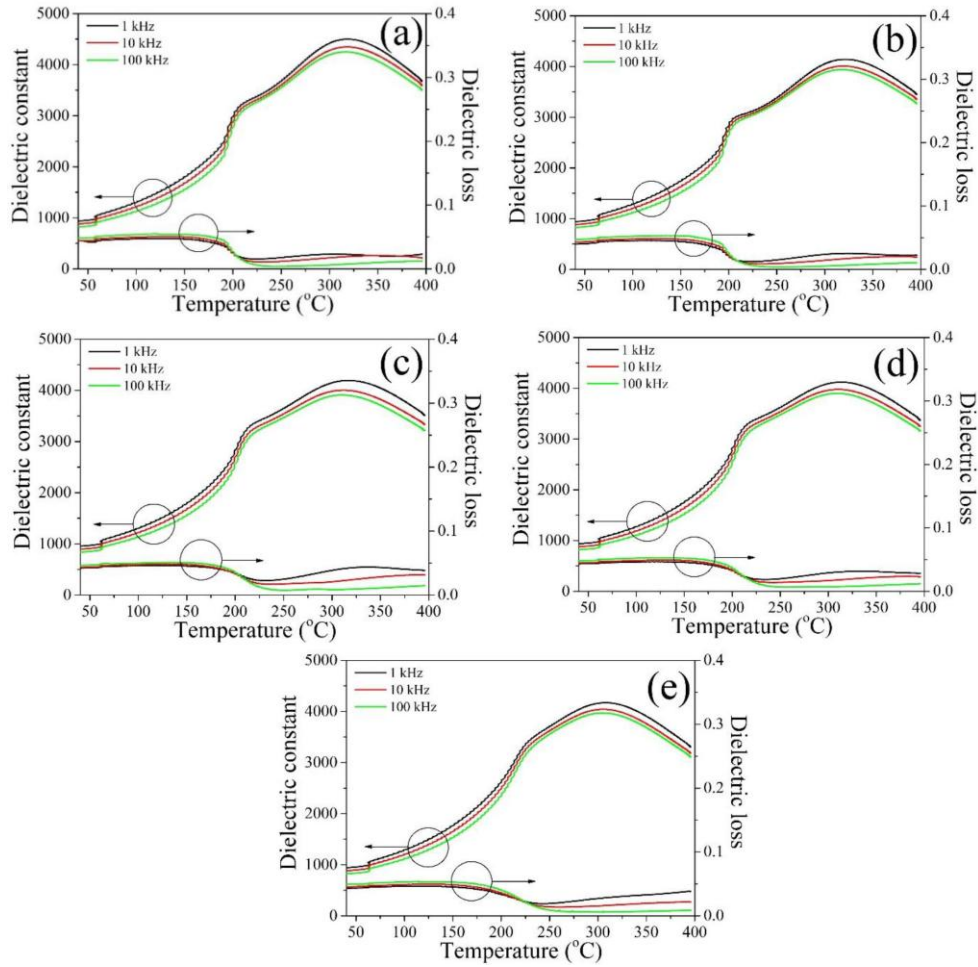
Figure 3. The SEM images of BNBT-xPr ceramics with (a) $x=0$, (b) $x=0.1$, (c) $x=0.3$, (d) $x=0.5$ and (e) $x=0.7$, and (f) measured density of the ceramics

Figure 4(a-e) illustrates the dielectric loss ($\tan \delta$) and relative permittivity (ϵ_r) of unpoled BNBT-xPr ceramics, determined at 1, 10, and 100 kHz from room temperature (RT) to 400°C. In all compositions, two dielectric anomalies were found throughout the entire temperature and frequency range investigated. The first curve was observed at a low temperature ($\sim 200^\circ\text{C}$), which is identified as the depolarization temperature (T_d). The second curve was observed at a higher temperature ($\sim 300^\circ\text{C}$), which corresponds to the maximum dielectric constant temperature (T_m). It is commonly accepted that T_d is linked to the relaxation of rhombohedral polar nanoregions (PNRs), whereas T_m is implicated with the relaxation of tetragonal PNRs, which originate from rhombohedral PNRs (Qiao *et al.*, 2019). Table 1 shows that as the x content rises from 0 to 0.7, the T_d rises from 202 to 221°C. On the contrary, T_m continuously decreased

from 322 to 308°C when the x content increased. Based on these results, we forecast that an important rise in T_d was associated with a rise in rhombohedral distortions (Bhupaijit *et al.*, 2020). The ϵ_r increased from 925 to 943 upon the x amount rising from 0 to 0.3 and then decreased when x rose further. The unmodified ceramic showed the highest maximum dielectric constant (ϵ_m) ~ 4514 and the lowest $\tan \delta$ at T_m (0.02). Compared with undoped ceramics, the dielectric properties of Pr₆O₁₁ doped BNBT ceramics deteriorated. This outcome could be explained by the low density and small grain sizes, which decreased the number of domain variations while enhancing the volume fraction of grain boundaries and the space charge trap at the boundaries, making domain reorientation difficult (Bongkarn *et al.*, 2016). The $\tan \delta$ at RT and T_m of the ceramics, are also included in Table 1.

Table 1. Dielectric and ferroelectric properties of BNBT-xPr ceramics as a function of x

x	T_d (°C)	T_m (°C)	ϵ_r at RT	ϵ_m at T_m	$\tan\delta$ at RT	$\tan\delta$ at T_m	P_r ($\mu\text{C}/\text{cm}^2$)	E_C (kV/cm)	R_{sq}
0	202	322	925	4514	0.04	0.02	22.2	40.7	1.20
0.1	204	320	931	4142	0.04	0.02	23.6	46.9	1.12
0.3	212	318	943	4196	0.04	0.04	27.7	45.7	1.11
0.5	212	314	924	4128	0.04	0.03	17.8	45.4	1.04
0.7	221	308	929	4171	0.03	0.03	18.7	46.4	1.06

**Figure 4. Temperature dependence of the relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) for unpoled BNBT ceramics with (a) $x=0$, (b) $x=0.1$, (c) $x=0.3$, (d) $x=0.5$, and (e) $x=0.7$**

The polarization-electric field (P - E) hysteresis loops for the BNBT-xPr ceramics are plotted for various x in Figure 5, which were tested utilizing an electrical field of 70 kV/cm. All the ceramics showed typical square ferroelectric and saturated P - E loops. The remanent polarization (P_r) value rose from 22.2 to 27.7 $\mu\text{C}/\text{cm}^2$ when the x amount rises from 0 to 0.3 (Table 1). As the x content increased to 0.5 and 0.7, the P_r value decreased, which can be explained by the low density and porous microstructure. The undoped BNBT

ceramic showed the lowest coercive field (E_C) value of 40.7 kV/cm. While the E_C value of the samples increased dramatically after Pr was doped into the BNBT ceramics (45.4 - 46.9 kV/cm), as shown in Table 1. Normally, compositional adaptation, microstructural variation, and lattice defects like oxygen vacancies can all affect changes in the E_C value. (Noguchi *et al.*, 2000; Wang *et al.*, 2016). In this case, the substitution of Pr^{3+} ions at Ti^{4+} sites in the form of acceptors may be the reason of the incremental change of E_C ; this leads to the building

of oxygen vacancies, which impedes the movement of the domain walls (Prasertpalichat *et al.*, 2016).

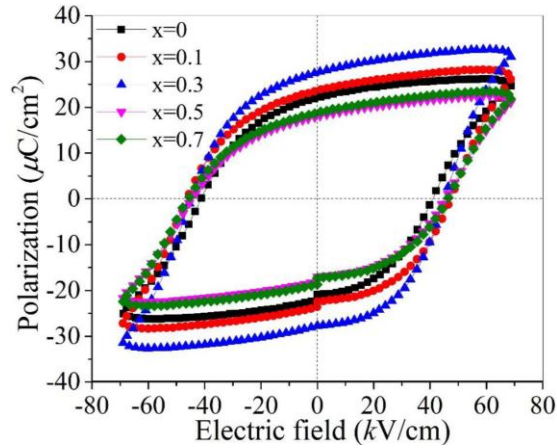


Figure 4. Polarization versus electric field of BNBT-xPr ceramics as a function of x

To examine the ferroelectric features of BNBT-xPr ceramics, the level of squareness (R_{sq}) of the P - E loops (Coondoo *et al.*, 2015; Haertling *et al.*, 1999) can be obtained by applying using the following formula:

$$R_{sq} = \frac{P_r}{P_s} + \frac{P_{1.1E_C}}{P_r}$$

Where the polarization corresponding to $1.1E_C$ is denoted by $P_{1.1E_C}$ and the saturation polarization by P_s . In principle, R_{sq} ought to equal 2. The perfect R_{sq} denotes greater homogeneity, consistency in grain size, and favorable switching characteristics of the ceramics (Haertling *et al.*, 1999; Coondoo *et al.*, 2015). Table 1 provides the R_{sq} values for each sample. The highest R_{sq} value was 1.20 for the undoped BNBT. While the R_{sq} values of Pr-doped BNBT ceramics were lower than the undoped ceramic.

Conclusions

Environmentally friendly, lead-free solid solutions of $0.97(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}0.03\text{BaTiO}_3\text{-}x\text{Pr}_6\text{O}_{11}$; BNBT-xPr ($x=0, 0.1, 0.3, 0.5$, and 0.7 wt.%) were manufactured using the solid-state combustion route. The impact of Pr_6O_{11} on the crystal structure, microstructure, dielectric, and ferroelectric behaviors of the specimens was

inspected. The structure of pure perovskite was seen in all samples, which means Pr ions can diffuse into the BNBT lattice completely. All examples display the combination of the tetragonal and rhombohedral phases. The Rietveld refining process confirmed that the fraction of the rhombohedral phase tended to rise with higher x . Pr_6O_{11} doping may restrict the grain growth of BNBT ceramics, as evidenced by the average grain size declining from 0.90 ± 0.10 to $0.73\pm0.07 \mu\text{m}$ as x rose. The measured density tended to decrease from 6.13 to 6.05 g/cm^3 with increased x . The dielectric behavior followed the same trend, diminishing with the addition of Pr_6O_{11} . The undoped BNBT ceramic showed good ferroelectric features ($P_r \sim 22.2 \mu\text{C/cm}^2$ and $E_C \sim 40.7 \text{ kV/cm}$). The maximum $P_r \sim 27.7 \mu\text{C/cm}^2$ of the BNBT ceramics was induced by Pr_6O_{11} doping at 0.3 . When Pr_6O_{11} was added, the E_C value increased significantly. This may be attributed to acceptor substitution of Pr^{3+} ions at Ti^{4+} sites, which resulted in the creation of oxygen vacancies that restricted the motion of the domain walls. Variations in density, microstructure, electrical characteristics, and phase evolution are all interrelated.

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