



# The effects of Ba<sup>2+</sup> content on depolarization temperature and pyroelectric properties of lead-free 0.94Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>–0.06Ba<sub>1+x</sub>TiO<sub>3</sub> ceramics

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**Abstract** Lead-free 0.94Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>–0.06Ba<sub>1+x</sub>TiO<sub>3</sub> (NBT–0.06B<sub>1+x</sub>T) ceramics (0.0 ≤ x ≤ 0.03) were synthesized by a conventional solid-state reaction process. X-ray diffraction shows that the compositions are at the morphotropic phase boundary where rhombohedral and tetragonal phase coexist. Grain size slightly changes with the increase of Ba<sup>2+</sup> content and reaches the minimum at x = 0.02. The depolarization temperature ( $T_d$ ) decreases with the extra Ba<sup>2+</sup> content but the lowest  $T_d$  was obtained at x = 0.01–0.02. The pyroelectric coefficient ( $p$ ) was measured as a function of Ba<sup>2+</sup> content, and increased from  $2.90 \times 10^{-4}$  to  $3.54 \times 10^{-4}$  C m<sup>-2</sup> °C<sup>-1</sup>, and from  $55.3 \times 10^{-4}$  to  $740.7 \times 10^{-4}$  C m<sup>-2</sup> °C<sup>-1</sup> for x = 0.00 and 0.02 at RT, and depolarization temperature ( $T_d$ ) respectively. The pyroelectric coefficient ( $p$ ) shows a large increase with rising the temperature and reaches the maximum value at the depolarization temperature ( $T_d$ ). The figures of merits of  $F_i$ ,  $F_v$  and  $F_D$  have all been improved with the addition of extra barium. These improved pyroelectric properties indicate that NBT–0.06B<sub>1+x</sub>T is a promising material for pyroelectric applications or a wide range of temperature.

## 1 Introduction

At present the most widely used ferroelectric materials are lead-based ceramics such as PZT and PZT-based multi-component ceramics due to their superior piezoelectric and electrical properties, but there are two serious

environmental problems arising from the fabrication of lead-containing materials: atmospheric pollution caused by PbO vapour during ceramic fabrication, and the difficulty in removing lead during component recycling. Lead-containing electronic products have been banned in WEEE (waste electrical and electronic equipment) and ROHS (restriction of use of certain hazardous substances) legislation [1]. Therefore there is a need to develop lead-free materials with properties comparable to lead-based ceramics. Among the lead-free materials, sodium bismuth titanate (Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>, (NBT)) and NBT-based materials are considered to be an important material for the fabrication of lead-free material [2–5] due to their excellent ferroelectric and dielectric properties [5]. Large efforts of investigation on NBT-based materials for their piezoelectric applications have been made while there have been limited reports on their pyroelectric properties.

Pyroelectric ceramic materials are becoming increasingly on high demand in variety of industrial applications such as sensors, infrared detectors, thermal cameras, gas detectors, microelectronic devices, as well as actuators, transducers, medical devices, airplanes and spacecraft [6]. These materials could have a large pyroelectric coefficient (polarization change vs temperature change) at a phase transition temperature. NBT exhibits two structural phase transitions: the first one ( $T_d$ ) from a ferroelectric rhombohedral to a tetragonal phase (~260–350 °C) and the second one ( $T_c$ ) from a tetragonal phase to a paraelectric cubic phase (520–540 °C). These phase transition temperatures are well above room temperature. Hence it is necessary to bring the phase transition temperature down to near room temperature (RT) for many applications, and that can be achieved by using various dopants [7]. In NBT-based systems, there is a weakly polar intermediate phase [8],

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which occurs between the depolarization temperature  $T_d$  and the temperature of maximum permittivity ( $T_m$ ) [9–12].

$(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x\text{BaTiO}_3$  has a morphotropic phase boundary at  $x = 0.06\text{--}0.07$  [13] and its depolarization temperature ( $T_d$ ) is  $\sim 123$  °C and well below its phase transition temperature ( $T_m$ ) which is around 300 °C. Jo et al. [14] reported that  $T_d$  could be the phase transition temperature from ferroelectric to relaxor or from rhombohedral ferroelectric to tetragonal ferroelectric [12]. This phase transition at  $T_d$  may induce a large pyroelectric effect. Guo et al. [15] studied the pyroelectric properties of  $(1-x)\text{NBT}-x\text{Ba}(\text{ZrTi})\text{O}_3$  ( $0 \leq x \leq 0.12$ ) ceramics and found that the pyroelectric coefficient was enhanced from  $0.057 \mu\text{C cm}^{-2} \text{ }^\circ\text{C}^{-1}$  at  $RT$  to  $2.21 \mu\text{C cm}^{-2} \text{ }^\circ\text{C}^{-1}$  at  $T_d$  (87 °C). In this work, we aim to bring down the  $T_d$  by varying the  $\text{Ba}^{2+}$  content in  $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.06\text{Ba}_{1+x}\text{TiO}_3$  ( $\text{NBT}-0.06\text{B}_{1+x}\text{T}$ ) ceramics and to investigate the effect of  $\text{Ba}^{2+}$  content on the depolarization temperature, and the subsequent dielectric and pyroelectric properties at  $T_d$ .

## 1.1 Experimental

A solid state synthesis route was used to prepare  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$  composition. The raw materials used in this project were powders, bismuth oxide ( $\text{Bi}_2\text{O}_3$ , 99.999 %), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99.5 %), barium carbonate ( $\text{BaCO}_3$ , 99.98 %), and Titanium dioxide ( $\text{TiO}_2$ , >99.8 %). All chemicals were purchased from Sigma-Aldrich, UK.

The amounts of powders were calculated according to the chemical formula of  $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{Ba}_{1+x}\text{TiO}_3$  with  $x = 0.00, 0.01, 0.02$ , and  $0.03$ . The raw materials were ball-milled in acetone for 24 h. in order to mix and mill the powders. The resultant slurries were dried at 50 °C for 8 h. The dried powder cakes were ground in a mortar for 10 min. and sieved through a 250  $\mu\text{m}$  mesh in order to aid the calcination. The powders were calcined at 850 °C for 180 min at a heating ramp rate of 1 °C per min and cooling rate 5 °C per min in a furnace. After calcination, powders were re-milled for 24 h. in acetone, and 2 % of poly vinyl alcohol (PVA) was added as an organic binder to the dried powders to enhance the mechanical strength of the particles. After that the powders were dried in oven at 80 °C until fully dried. The dried powders were ground and sieved and subsequently pressed into green pellets with a diameter of 10 mm under an uniaxial compaction with load  $\sim 78$  MPa for 5 min at  $RT$ . The pellets were sintered at temperatures up to 1150 °C in closed crucibles in order to minimize the loss of volatile  $\text{Na}^+$  and  $\text{Bi}^{3+}$ . The pellets were manually wet polished on both sides using silicon carbide paper to improve uniformity

and dried at 100 °C overnight to remove the moisture. Silver conductive paint (RS limited) was used to electrode the pellets, and electrical poling at 5.5–6 kV/mm for 10 min at  $RT$  in silicone oil was carried out using a Keithley (6517 Electrometer/high resistance) dc power supply.

SEM (FEI XL30 SFEG) was used to look at the surface morphology of the sintered samples and X-Ray Diffraction (XRD) (Siemens Ltd Model: D500) was used to investigate microstructure. As part of the electrical characterisation of the materials, dielectric measurements were made using an impedance analyser (Wayne kerr Electronics Ltd. Model 3245 and Hewlett Packard HP4092A). Dielectric data was collected over a temperature range from  $RT$  to 150 °C using a temperature controlled hotplate in the frequency range of 0.1–10 kHz. Pyroelectric measurements were made using the Byer-Roundy [16] method at the temperature between 20 and 90 °C (equipment up limitation) under vacuum and the pyroelectric current was collected by a Keithley electrometer (Model 6217). Dielectric and pyroelectric data was then used to study the phase changes such as depolarization temperatures ( $T_d$ ), and to determine figure of merit values  $F_i$ ,  $F_v$  and  $F_D$ .

Sample compositions are listed in Table 1.

## 2 Results and discussion

### 2.1 Effects of extra barium on microstructure

Figure 1 shows the XRD patterns of  $0.94\text{NBT}-0.06\text{B}_{1+x}\text{T}$  ( $\text{NBT}-0.06\text{B}_{1+x}\text{T}$ ) ceramic powders calcined at 850 °C for 3 h. Figure 1a showed that all ceramic samples have a pure perovskite structure ( $\text{ABO}_3$ ) and no second phase was observed. The absence of other phase indicates that  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$  lattices have either absorbed the extra amount of Barium ( $\text{Ba}^{2+}$ ), and formed the  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$  ceramic solid solutions [17, 18] or the amount of the second phase is too small to be tested by XRD. Figure 1 shows, in all the samples, a splitting in the peak [111] into [003] and [021] at  $39.0^\circ\text{--}41.0^\circ$ , indicating the existence of rhombohedral phase (Fig. 1b) and a splitting in the peak [200] into [200] and [002] at  $45.0^\circ\text{--}48.0^\circ$ , indicating the existence of tetragonal phase (Fig. 1c). The coexistence of both rhombohedral and tetragonal phases in  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$  ceramics proves that the sample structures are at morphotropic phase boundary (MPB), which was consistent with what was reported in literature [12, 14, 19]. Figure 1c shows that the splitting in peak [200] became quite pronounced for the sample at  $x = 0.02$  as shown in Fig. 1b. It seems that the composition of  $\text{NBT}-0.06\text{B}_{1+x}\text{Ti}$  with  $x = 0\text{--}0.03$  is still within MPB.

**Table 1** The NBT–0.06B<sub>1+x</sub>T<sub>1-x</sub>T, composition (sample) depending on the extra concentrations of Ba<sup>2+</sup> from A, x = 0.00 to D, x = 0.03; samples density (gm cm<sup>-3</sup>), comparing with the theoretical density (%) which is (ρ = 6 gm cm<sup>-3</sup>), and the relative permittivity (ε<sub>r</sub>),

Composition (sample name)	Lattice parameters (Å)			Density (ρ) gm cm <sup>-3</sup>	Compare with theoretical density%	Depolarization temperature (T <sub>d</sub> ) (°C)	Relative permittivity (ε <sub>r</sub> ) at RT	Dielectric loss (tanδ) at RT
	a = b	c						
NBT–0.06BT (A, x = 0.0)	5.488	13.505	5.697	94.95	125	1178	0.042	
NBT–0.06B <sub>1+0.01</sub> T (B, x = 0.01)	5.487	13.437	5.661	94.35	85	1468	0.046	
NBT–0.06B <sub>1+0.02</sub> T (C, x = 0.02)	5.494	13.505	5.718	95.55	85	1472	0.045	
NBT–0.06B <sub>1+0.03</sub> T (D, x = 0.03)	5.493	13.505	5.678	94.63	115	1266	0.040	

dielectric loss (tanδ) both at 1 kHz and RT the depolarization temperature (T<sub>d</sub>) values 0.0 ≤ x ≤ 0.03 in present work and from the literatures

The measurement of the lattice parameters (a, b and c) reveals that the extra Ba content has slightly changed a, b and c from a = b = 5.488 Å, c = 13.505 Å to a = b = 5.493 Å, c = 13.505 Å for Samples A to D respectively (Table 1). Sample C presents the biggest lattice parameters (a = b = 5.494 Å, c = 13.505 Å).

Comparing the ionic radii of the A-site cations of Na<sup>+</sup> (1.39 Å), Bi<sup>3+</sup> (1.31 Å) and Ba<sup>2+</sup> (1.61 Å) (coordination No. 12) according to Hume-Rothery rules, Ba<sup>2+</sup> in NBT–0.06B<sub>1+x</sub>Ti could replace Na<sup>+</sup> but seems to be difficult to replace Bi<sup>3+</sup> because the radius difference between Bi<sup>3+</sup> and Ba<sup>2+</sup> is more than 15 % [19]. Yoon et al. [19] reported that the c/a ratio increased with adding more extra Ba content and reached the maximum at x = 0.02. Thus the increase in Ba<sup>2+</sup> content would lead to the improvement of the tetragonality of BT in NBT–0.06B<sub>1+x</sub>T by compensating for the loss in Ba during the sintering stage. However, any extra Ba<sup>2+</sup> content more than x = 0.02 would not go to increase the c/a ratio because the c/a ratio was saturated at 0.02, and therefore consequently the extra Ba would precipitate into a secondary phase [19], but in this study the second phase was not identified up to x = 0.03, probably due to the amount of the secondary phase being too small to be tested by XRD.

Figure 2 shows the surface morphology of the NBT–0.06B<sub>1+x</sub>T ceramics by SEM. The average grain size was reduced from 1.7 μm at x = 0.00 to 1.61, 1.31, 1.52 at x = 0.01, 0.02 and 0.03, respectively. Increasing Ba<sup>2+</sup> led to a sharp reduction in the grain size and reached the lowest value at x = 0.02. In general, Ba<sup>2+</sup> behaves as an inhibitor of the grain growth in NBT system. In lead-based ceramics, such as PZT and PLZT (La-containing PZT), similar effect was also observed when lead was substituted with barium [17, 19, 20]. All the samples showed a density 94.63 ± 0.333 g/cm<sup>3</sup> as shown in Table 1. Density measurements revealed that Sample A, B and D at x = 0.0,

0.01 and 0.03 have a similar density value; however, Sample C, at x = 0.02 has a higher density.

### 2.2 Effects of extra barium on dielectric properties

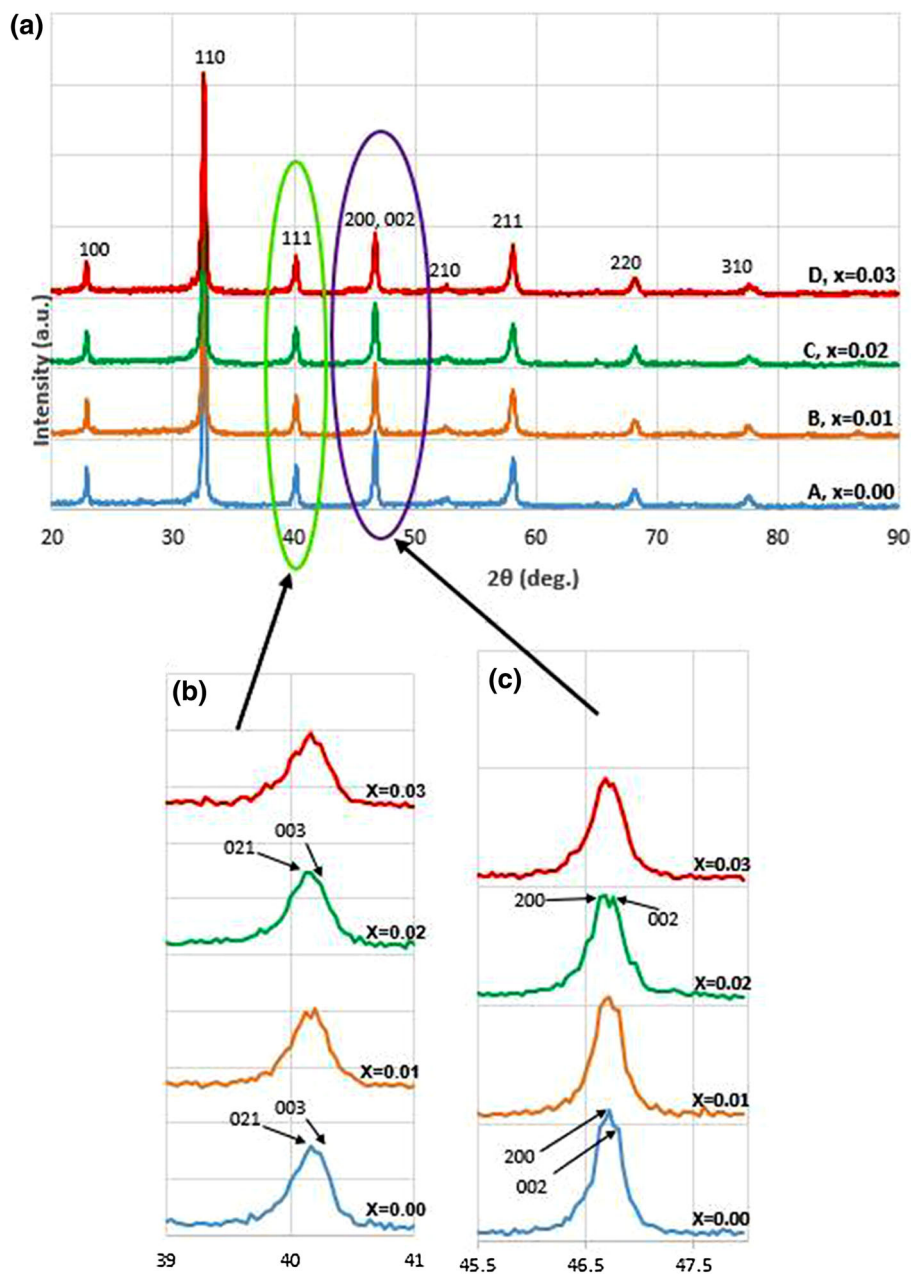
Figure 3 shows the temperature dependence of the dielectric properties of poled NBT–0.06B<sub>1+x</sub>T from RT up to 150 °C at different frequencies (1, 10 and 100 kHz). The relative dielectric permittivity (ε<sub>r</sub>) and the dielectric loss tangent (tanδ) show a strong dependence upon Ba content and temperature. The ε<sub>r</sub> increased with temperature for all samples; however, the ε<sub>r</sub> showed increasing at x = 0.01, and 0.02 at room temperature and this can be related to extra Ba<sup>2+</sup>. The extra Ba at x = 0.01 compensated the deficiency in Ba in BT side and rectified the tetragonality in NBT. The excess Ba up to 0.02 can then replace cations in the A-site of the NBT–0.06B<sub>1+x</sub>T perovskite structure, so Ba<sup>2+</sup> will replace Na<sup>+</sup> according to the radius matching rules and the donor behaviour of Ba will make the domain wall motion easier resulting in the increase of the dielectric properties of NBT–0.06B<sub>1+0.02</sub>T [12].

The ε<sub>r</sub> values at x = 0.01 and 0.02 were close to 1500 for both compositions whereas the ε<sub>r</sub> values at x = 0.0 and 0.03 at RT were near 1225. However, at T<sub>d</sub>, and 150 °C, the ε<sub>r</sub> for the samples at x = 0.01 and 0.02 increased to around 2000 and 2150 (T<sub>d</sub>), and above for both compositions 2500 (150 °C) respectively. However, the ε<sub>r</sub> values for the samples at x = 0.00 and 0.03 were relatively low, which are around 2250.

### 2.3 Effects of extra barium on depolarization temperature

Depolarization temperature (T<sub>d</sub>) is a parameter that has not clearly been defined [10], but the European standard on piezoelectric properties has defined it as the reduction of

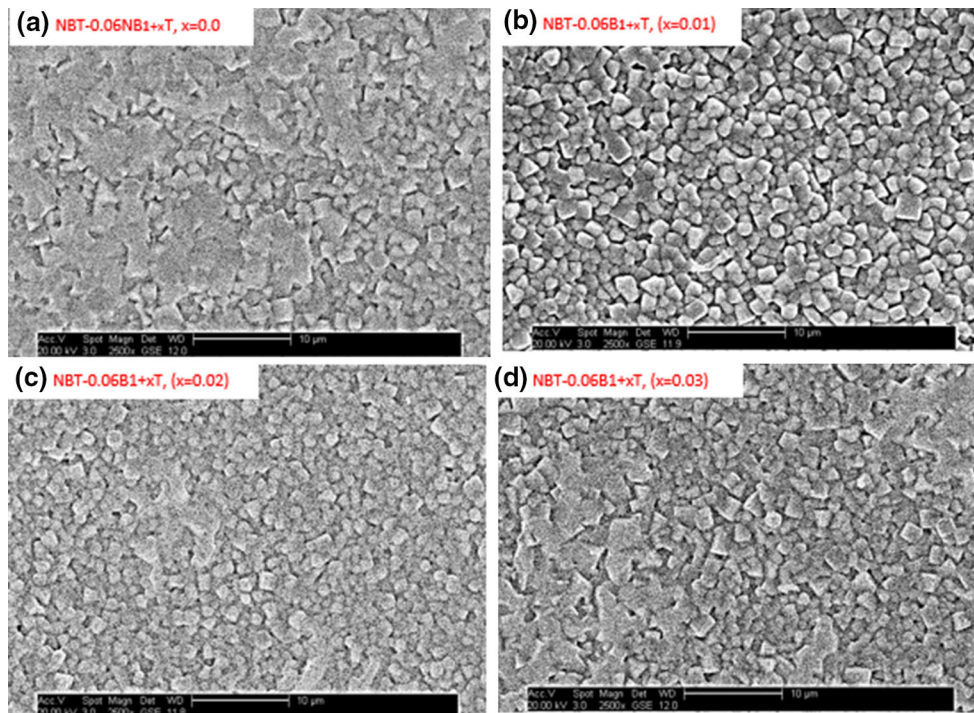
**Fig. 1** XRD patterns of NBT–0.06B<sub>1+x</sub>TiO<sub>3</sub> ceramics where, **a**  $x = 0.00, 0.01, 0.02$  and  $0.03$ ; **b** expansion at  $2\theta$  from  $39.6^\circ$  to  $40.6^\circ$  and **c** expansion at  $2\theta$  from  $45.0^\circ$  to  $48.0^\circ$



remnant polarization because of temperature and other influences [21]. However, there are other definitions of  $T_d$  such as the steep reduction of remnant polarization [7], or the phase transition temperature from ferroelectric (*FE*) to anti-ferroelectric (*AFE*) or to relaxor anti-ferroelectric or to relaxor [8, 22–25].

In this study,  $T_d$  was identified from the measurement of the dielectric loss ( $\tan\delta$ ) versus temperature. Figure 3 shows that the  $T_d$  of the NBT–0.06B<sub>1+0.00</sub>T was at  $\sim 125^\circ\text{C}$  and decreased to  $\sim 85^\circ\text{C}$  at  $x = 0.01$  and  $0.02$ , and then rises to  $\sim 115^\circ\text{C}$  at  $x = 0.03$ . The reduction in  $T_d$  is probably due to the formation of A-site vacancies with increasing Ba content in NBT–0.06B<sub>1+x</sub>T structures. In

ferroelectric NBT–BT perovskite structure, the ferroelectric domain stability is affected by the coupling between ferroelectric ( $\text{BO}_6$ ) and A-site cations, and the stability of the ferroelectric domains will be reduced when vacancies are generated between the octahedral ( $\text{BO}_6$ ) ferroelectric and A-site cations. In this study,  $\text{Ba}^{2+}$  content at  $x = 0.01$ – $0.02$  created A-site vacancies so the stability of the ferroelectric domain reduced as a result inducing the phase change from ferroelectric (*FE*) to relaxor anti-ferroelectric (*relaxor AFE*) and fast reduction by  $40^\circ\text{C}$  in depolarization temperature ( $T_d$ ) [14, 18, 21]. With a further increase of  $\text{Ba}^{2+}$  to  $x = 0.03$ , which is more than  $\text{Ba}^{2+}$  saturation content ( $x = 0.02$ ), the  $T_d$  was decreased by only



**Fig. 2** The SEM surface morphology, NBT–0.06B<sub>1+x</sub>T where, x = 0.00 (a); x = 0.01 (b); x = 0.02 (c); x = 0.03 (d)

about 10 °C, because there were less vacancies in A-site due to minimal (Ba<sup>2+</sup>/Na<sup>+</sup>) replacement and more ferroelectric domain wall stability [9, 14, 26]. The value of the  $T_d$  of NBT–0.06BT in this work is close to that reported in the literature (~123 °C) but the depolarization temperature of the NBT–0.06B<sub>1+x</sub>T, (0.01 ≤ x ≤ 0.02) is lower than 123 °C [27]. Table 1 lists the values of relative dielectric permittivity ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) at RT and depolarization temperatures ( $T_d$ ) at 1 kHz achieved in this work.

**2.4 Effects of extra barium on the pyroelectric properties**

The calculation of the figure of merits (*FOMs*) is based on the values of pyroelectric coefficient ( $p$ ), relative dielectric permittivity ( $\epsilon_r$ ), the dielectric loss tangent ( $\tan\delta$ ) and the specific heat ( $C_v$ ). There are several numbers of *FOMs* which are more appropriate to certain pyroelectric materials applications [6, 27] and are derived from these application requirements.

Pyroelectric coefficient ( $p$ ) and the *FOMs* were analysed by using the following equations: [5, 15, 28]

$$I_p = pA \frac{dT}{dt} \tag{1}$$

$$F_i = \frac{p}{C_v} \tag{2}$$

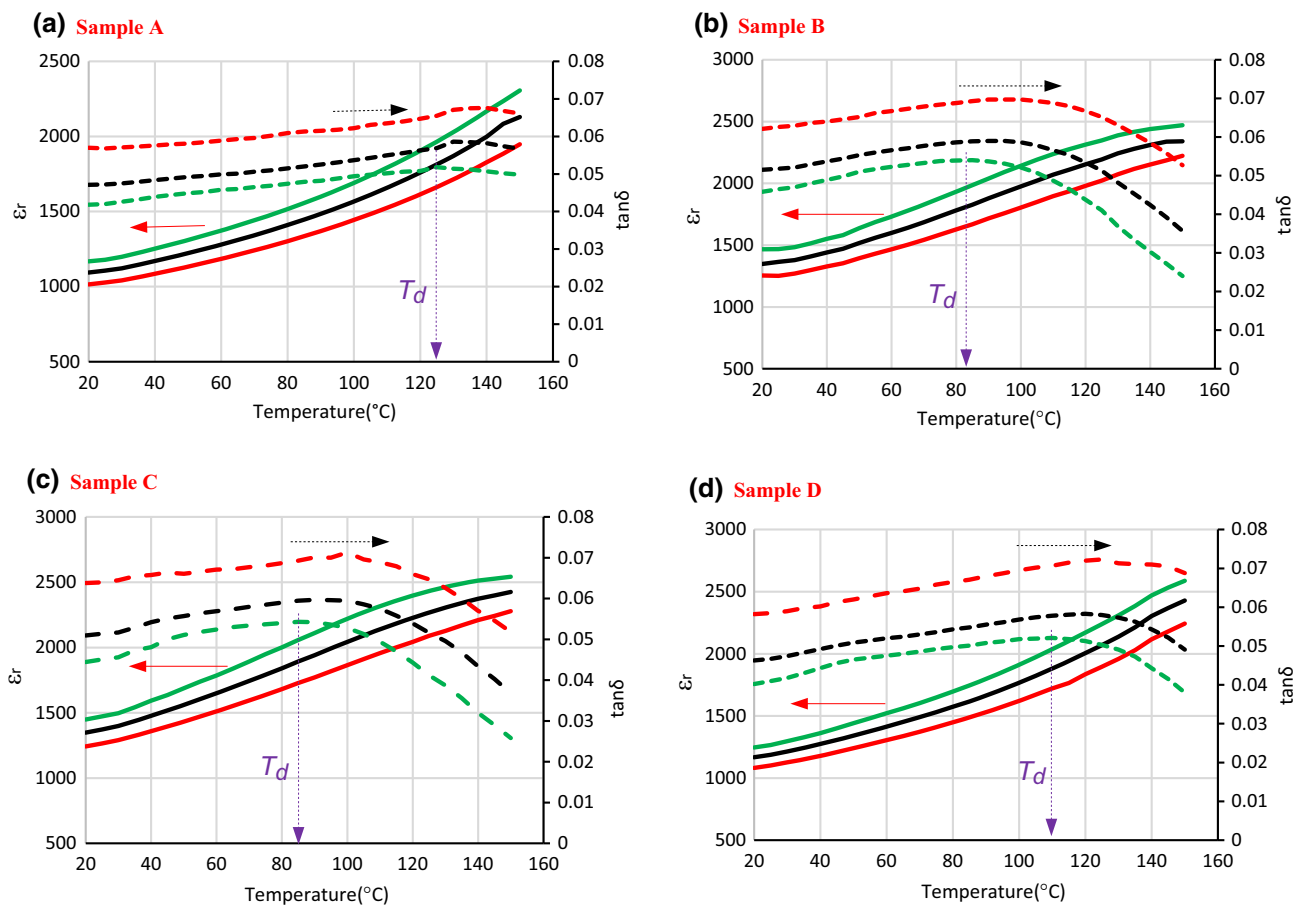
$$F_v = \frac{p}{C_v \epsilon_o \epsilon_r} \tag{3}$$

$$F_D = \frac{p}{C_v \sqrt{\epsilon_o \epsilon_r \tan\delta}} \tag{4}$$

where  $T$  is absolute temperature,  $t$  the time,  $I_p$  the pyroelectric current,  $F_i$  the high current ( $i$ ) detectivity figure of merit,  $F_v$  the high voltage ( $V$ ) detectivity figure of merit,  $F_D$  high detectivity figure of merit, and  $C_v$  the specific heat (2.8 JK<sup>-1</sup> cm<sup>-3</sup>, quoted fm [29]).

The pyroelectric current of NBT–0.06B<sub>1+x</sub>T, (0.00 ≤ x ≤ 0.03) ceramics was measured from RT to  $T_d$  or 90 °C that is our equipment upper limit.

Table 2 shows the pyroelectric coefficient ( $p$ ) and the figures of merit (*FOMs*) values of the NBT–0.06B<sub>1+x</sub>T, (0.00 ≤ x ≤ 0.03) at RT,  $T_d$  or 90 °C. The  $p$  values varied with the Ba<sup>2+</sup> content, and increased from 2.9 × 10<sup>-4</sup> (C m<sup>-2</sup> °C<sup>-1</sup>) to 3.54 × 10<sup>-4</sup> (C m<sup>-2</sup> °C<sup>-1</sup>) when x increased from 0.00 to 0.02 at RT. All the samples showed a great increase in  $p$  when the measurement temperature increased from 20 °C to  $T_d$  or 90 °C. This great increase in  $p$  at  $T_d$  or 90 °C was caused by the increase of  $I_p$  induced by the reorientation of ferroelectric domain and phase transition in MPB. When the temperature rises from RT to  $T_d$ , the phase transition from ferroelectric (*FR*) to relaxor antiferroelectric (relaxor *AFR*) started, and thus a sharp change in polarization resulted in a significant increase in  $p$  at  $T_d$  [15].



**Fig. 3** The change of the relative permittivity ( $\epsilon_r$ ) and loss tangent ( $\tan\delta$ ) with changing temperature ( $^{\circ}\text{C}$ ) from RT up to  $150^{\circ}\text{C}$ , for the  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$ , where  $0.0 \leq x \leq 0.03$  from **a-d** in three different

The  $T_d$  for Sample B ( $x = 0.01$ ) and C ( $x = 0.02$ ) is below  $90^{\circ}\text{C}$  and for Sample A ( $x = 0.00$ ) and D ( $x = 0.03$ ) above  $90^{\circ}\text{C}$ , which explained why Sample B and C had a greater increase in  $p$  than Sample A and D. According to Anton et al. [7], the  $T_d$  determination depends on the highest value of the dielectric loss tangent, which may consistently generate higher  $T_d$  than other methods such as the thermally stimulated depolarization current; therefore the  $T_d$  for Sample A and D might actually be less than  $\sim 125$  and  $\sim 110^{\circ}\text{C}$ , as a result that the observed increase in  $p$  for Sample A and D could be related to the beginning of the phase transition in these samples.

The increase of Ba content up to  $x = 0.02$  reduces the distortion in the perovskite structure due to the replacement of  $\text{Na}^+$  ( $1.39 \text{ \AA}$ ) by  $\text{Ba}^{2+}$  ( $1.61 \text{ \AA}$ ), which can shift the  $T_d$  to lower temperature [28]. Further increase in Ba content to  $x = 0.03$  would lead to the appearance of a secondary phase or the replacement of  $\text{Na}^+$ . Thus, the depolarization temperature at  $x = 0.03$  shows a slight increase than that at  $x = 0.01-0.02$  [14, 28, 30]. Table 2 also lists the  $p$  value ( $4.14 \times 10^{-4} \text{ C m}^{-2} \text{ }^{\circ}\text{C}^{-1}$ ) of a typical PZT ceramic

frequencies (1, 10 and 100) kHz. The identified of the depolarization temperature ( $T_d$ ) from the dielectric loss lines at 1 kHz

measured at RT as a reference. The prepared  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$  at  $x = 0.01-0.03$  in this research show the comparable pyroelectric coefficients ( $3.30-3.5 \times 10^{-4} \text{ C m}^{-2} \text{ }^{\circ}\text{C}^{-1}$ ) [5, 6, 9].

The values of  $F_i$ ,  $F_v$  and  $F_D$  of the  $\text{NBT}-0.06\text{B}_{1+x}\text{T}$  samples ( $0.00 \leq x \leq 0.03$ ) at RT,  $T_d$  or  $90^{\circ}\text{C}$  are also shown in Table 2. The  $F_i$  value increased from  $1.04 \times 10^{-10} \text{ (m/V)}$  ( $x = 0.00$ ) to  $1.24 \times 10^{-10} \text{ (m/V)}$  ( $x = 0.02$ ) at RT and from  $1.24 \times 10^{-10} \text{ (m/V)}$  ( $x = 0.02$ ) to  $260 \times 10^{-10} \text{ (m/V)}$  ( $x = 0.02$ ) at  $T_d$  ( $85^{\circ}\text{C}$ ). The  $F_i$  of Sample C ( $x = 0.02$ ) at RT is very close to that for PZT [ $1.415 \times 10^{-10} \text{ (m/V)}$ ] [3]. However, at  $T_d$  ( $85^{\circ}\text{C}$ ) this sample ( $x = 0.02$ ) shows a much higher  $p$  value [ $260 \times 10^{-10} \text{ (m/V)}$ ] than the best value ( $\sim 7.33 \times 10^{-10} \text{ (m/V)}$ ) at  $T_d$  ( $50^{\circ}\text{C}$ ) reported by Gue et al. [15].

The  $F_v$  values at RT and  $T_d$  or  $90^{\circ}\text{C}$  increased from  $0.99 \times 10^{-2} \text{ (m}^2 \text{ }^{\circ}\text{C}^{-1}\text{)}$  at  $x = 0.00$  to  $1.05 \times 10^{-2} \text{ (m}^2 \text{ }^{\circ}\text{C}^{-1}\text{)}$  at  $x = 0.03$ . All these  $F_v$  values exceed the value for PZT [5, 15, 29, 30].  $F_v$  values increased at  $T_d$  from  $0.95 \times 10^{-2}$  to  $164 \times 10^{-2} \text{ m}^2/\text{C}$  for Sample C ( $x = 0.02$ ).

**Table 2** Comparing the pyroelectric coefficients and the figures of merit ( $F_i$ ,  $F_v$ , and  $F_D$ ) of the NBT–0.06B<sub>1+x</sub>T(0.00 ≤ x ≤ 0.03) ceramic at frequency 1 kHz, at two different temperatures RT,  $T_d$  or 90 °C (due to equipment upper limit) with the other lead-free compositions and PZT

Composition	$p$ ( $\times 10^{-4}$ C m <sup>-2</sup> °C <sup>-1</sup> ) at RT or $T_d$	$F_i$ ( $\times 10^{-10}$ m V <sup>-1</sup> )	$F_v$ ( $\times 10^{-2}$ m <sup>2</sup> C <sup>-1</sup> ) at f. 1 kHz	$F_D$ ( $\times 10^{-6}$ Pa <sup>-1/2</sup> ) at f. 1 kHz	References
<b>NBT–0.06BT</b>	2.90 at RT	1.04 at RT	0.99 at RT	8.6 at RT	This study
<b>NBT–0.06BT</b>	55.3 at 90 °C	<b>19.7</b> at <b>90 °C</b>	<b>14</b> at <b>90 °C</b>	75.6 at 90 °C	This study
<b>NBT–0.06Ba<sub>1.01</sub>T</b>	3.47 at RT	1.238 at RT	0.95 at RT	7.7 at RT	This study
<b>NBT–0.06Ba<sub>1.01</sub>T</b>	<b>601</b> at <b>85 °C</b>	<b>215</b> at <b>85 °C</b>	<b>115</b> at <b>90 °C</b>	<b>674</b> at <b>90 °C</b>	This study
<b>NBT–0.06Ba<sub>1.02</sub>T</b>	<b>3.54</b> at RT	<b>1.244</b> at RT	0.95 at RT	8.3 at RT	This study
<b>NBT–0.06Ba<sub>1.02</sub>T</b>	<b>741</b> at <b>85 °C</b>	<b>260</b> at <b>85 °C</b>	<b>164</b> at <b>85 °C</b>	<b>915</b> at <b>85 °C</b>	This study
<b>NBT–0.06Ba<sub>1.03</sub>T</b>	3.30 at RT	1.177 at RT	<b>1.05</b> at RT	<b>9.1</b> at RT	This study
<b>NBT–0.06Ba<sub>1.03</sub>T</b>	73.1 at 90 °C	<b>26.12</b> at <b>90 °C</b>	<b>15</b> at <b>90 °C</b>	83.9 at 90 °C	This study
PZT	4.14 at RT	1.415 at RT	0.8 at RT	9.01	[5, 18]
NBT–0.07BZT	5.7 at RT	2.03 at RT	2.18 at RT	10.5	[5, 18]
NBT–0.07BZT	20.0 at 50 °C	7.33 at 50 °C	6.60 at 50 °C	33.6 at 50 °C	[5, 18]
NBT–0.07BZT	221 at 87 °C	–	–	–	[5, 18]
BNKBT	3.25 at RT	1.95 at RT	2.6 at RT	13.43	[5, 18]
KNLNTS	1.9 at RT	0.931 at RT	0.7 at RT	11.5	[5, 18]

The samples made in this study are given in bold

The values of  $F_D$  at RT,  $T_d$  or 90 °C are shown in Table 2. The  $F_D$  values increased with extra Ba<sup>2+</sup> content at RT from  $8.6 \times 10^{-6}$  Pa<sup>-1/2</sup> (x = 0.00) to  $9.2 \times 10^{-6}$  Pa<sup>-1/2</sup> (x = 0.03). Giant values for  $F_D$  achieved at  $T_d$  for Samples B and C were 674 and 915( $\times 10^{-6}$  Pa<sup>-1/2</sup>) respectively.  $F_D$  for PZT [5, 15, 29, 30] at RT is  $9.01 \times 10^{-6}$  Pa<sup>-1/2</sup> and Sample D showed a higher  $F_D$  value than PZT (Table 2).

### 3 Conclusion

The NBT–0.06B<sub>1+x</sub>T ceramics with extra Ba content were prepared by using conventional solid state synthesis route. The microstructure, dielectric, depolarization temperature and pyroelectric properties of these ceramics were dependent upon the Ba<sup>2+</sup> content. The depolarization temperature shifted to around 85 °C with increasing the Ba<sup>2+</sup> content up to x = 0.02. The pyroelectric coefficient and figures of merits ( $F_i$ ,  $F_v$ , and  $F_D$ ) all increase at RT when Ba<sup>2+</sup> content increases to x = 0.02. The giant pyroelectric coefficient,  $741 \times 10^{-4}$  (C m<sup>-2</sup> °C<sup>-1</sup>), was obtained at  $T_d$  when Ba<sup>2+</sup> content increases to x = 0.02. The results for NBT–0.06B<sub>1+x</sub>T obtained in this study indicate that NBT–0.06B<sub>1+x</sub>T are promising candidates for pyroelectric applications in a wide temperature range.

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### References

1. Sustainable development and Environment EC Directive on WEEE and ROHS in electrical and electronic equipment. [www.dti.gov.uk](http://www.dti.gov.uk)
2. T. Takenaka, K. Maruyama, K. Sakata, (Bi<sub>1/2</sub>Na<sub>1/2</sub>) TiO<sub>3</sub>–BaTiO<sub>3</sub> system for lead-free piezoelectric ceramics. *Jap. J. Appl. Phys.* **30**, 2236 (1991). doi:10.1143/JJAP.30.2236
3. X. Wang, X. Tang, H. Chan, Electromechanical and ferroelectric properties of (Bi<sub>1/2</sub> Na<sub>1/2</sub>) TiO<sub>3</sub>–(Bi<sub>1/2</sub> K<sub>1/2</sub>) TiO<sub>3</sub>–BaTiO<sub>3</sub> lead-free piezoelectric ceramics. *Appl. Phys. Lett.* **85**, 91 (2004). doi:10.1063/1.1767592
4. X. Ma, L. Xue, L. Wan, S. Yin, Q. Zhou, Y. Yan, Synthesis, sintering, and characterization of BNT perovskite powders prepared by the solution combustion method. *Ceram. Int.* **39**, 8147–8152 (2013). doi:10.1016/j.ceramint.2013.03.088
5. S.T. Lau, C.H. Cheng, S.H. Choy, D.M. Lin, K.W. Kwok, H.L.W. Chan, Lead-free ceramics for pyroelectric applications. *J. Appl. Phys.* **103**, 10–13 (2008). doi:10.1063/1.2927252
6. S. Patel, A. Chauhan, S. Kundu, N.A. Madhar, B. Ilahi, R. Vaish, K.B.R. Varma, Tuning of dielectric, pyroelectric and ferroelectric properties of 0.715Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>–0.065BaTiO<sub>3</sub>–0.22SrTiO<sub>3</sub> ceramic by internal clamping. *AIP Adv.* **5**, 087145 (2015). doi:10.1063/1.4929328
7. E.M. Anton, W. Jo, D. Damjanovic, J. Rdel, Determination of depolarization temperature of (Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub>-based lead-free piezoceramics. *J. Appl. Phys.* **110**, 1–14 (2011). doi:10.1063/1.3660253
8. Y. Guo, M. Gu, H. Luo, Antiferroelectric phase and pyroelectric response in (Na<sub>x</sub>Bi<sub>2</sub>)Ti<sub>1-x</sub>O<sub>3(1-x)</sub>–xBaTiO<sub>3</sub> ceramics. *J. Am. Ceram. Soc.* **94**, 1350–1353 (2011). doi:10.1111/j.1551-2916.2011.04509.x

9. X.J. Li, Z.Z. Xi, W. Long, P.Y. Fang, Synthesis of antiferroelectric  $(\text{Bi}_{0.534}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$  ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chin. Sci. Bull.* **58**, 2893–2897 (2013). doi:[10.1007/s11434-013-5972-2](https://doi.org/10.1007/s11434-013-5972-2)
10. J.-H. Cho, Y.-H. Jeong, J.-H. Nam, J.-S. Yun, Y.-J. Park, Phase transition and piezoelectric properties of lead-free  $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $\text{BaTiO}_3$  ceramics. *Ceram. Int.* **40**, 8419–8425 (2014). doi:[10.1016/j.ceramint.2014.01.051](https://doi.org/10.1016/j.ceramint.2014.01.051)
11. J. Suchanicz, U. Lewczuk, Effect of Ba addition on the structural, dielectric and ferroelectric properties of  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ceramics. *Mater. Sci Poland* **33**, 414–417 (2015). doi:[10.1515/msp-2015-0056](https://doi.org/10.1515/msp-2015-0056)
12. M. Chen, Q. Xu, B.H. Kim, B.K. Ahn, J.H. Ko, W.J. Kang, O.J. Nam, Structure and electrical properties of  $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$  piezoelectric ceramics. *J. Eur. Ceram. Soc.* **28**, 843–849 (2008). doi:[10.1016/j.jeurceramsoc.2007.08.007](https://doi.org/10.1016/j.jeurceramsoc.2007.08.007)
13. C. Ma, X. Tan, Phase diagram of unpoled lead-free—ceramics. *Solid State Commun.* **150**, 1497–1500 (2010). doi:[10.1016/j.ssc.2010.06.006](https://doi.org/10.1016/j.ssc.2010.06.006)
14. Q. Li, J. Wang, L. Ma, H. Fan, Z. Li, Large electrocaloric effect in  $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$  lead-free ferroelectric ceramics by  $\text{La}_2\text{O}_3$  addition. *Mater. Res. Bull.* **74**, 57–61 (2016). doi:[10.1016/j.materresbull.2015.10.010](https://doi.org/10.1016/j.materresbull.2015.10.010)
15. F. Guo, B. Yang, S. Zhang, F. Wu, D. Liu, P. Hu, Y. Sun, D. Wang, W. Cao, Enhanced pyroelectric property in  $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$ : role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Appl. Phys. Lett.* **103**, 182906 (2013). doi:[10.1063/1.4828675](https://doi.org/10.1063/1.4828675)
16. R.L. Byer, C.B. Roundy, Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *IEEE Trans. Sonics Ultrason.* **19**, 333–338 (1972). doi:[10.1109/T-SU.1972.29679](https://doi.org/10.1109/T-SU.1972.29679)
17. C. Xu, D. Lin, K.W. Kwok, Structure, electrical properties and depolarization temperature of  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $\text{BaTiO}_3$  lead-free piezoelectric ceramics. *Solid State Sci.* **10**, 934–940 (2008). doi:[10.1016/j.solidstatesciences.2007.11.003](https://doi.org/10.1016/j.solidstatesciences.2007.11.003)
18. M. Rawat, K.L. Yadav, A. Kumar, P.K. Patel, N. Adhlakha, J. Rani, Structural, dielectric and conductivity properties of  $\text{Ba}^{2+}$  doped  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  ceramic, advanced. *Mater. Lett.* **3**, 286–292 (2012). doi:[10.5185/amlett.2012.2322](https://doi.org/10.5185/amlett.2012.2322)
19. M.S. Yoon, N.H. Khansur, S.C. Ur, The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized  $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]$ – $0.06[\text{Ba}_{(1+x)}\text{TiO}_3]$ . *Ceram. Int.* **36**, 1265–1275 (2010). doi:[10.1016/j.ceramint.2010.01.011](https://doi.org/10.1016/j.ceramint.2010.01.011)
20. Y. Hiruma, K. Yoshii, H. Nagata, T. Takenaka, Investigation of phase transition temperatures on  $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$  and  $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $\text{BaTiO}_3$  lead-free piezoelectric ceramics by electrical measurements. *Ferroelectrics* **346**, 114–119 (2007). doi:[10.1080/00150190601180471](https://doi.org/10.1080/00150190601180471)
21. R. Ranjan, A. Dviwedi, Structure and dielectric properties of  $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ :  $0 \leq x \leq 0.10$ . *Solid State Commun.* **135**, 394–399 (2005). doi:[10.1016/j.ssc.2005.03.053](https://doi.org/10.1016/j.ssc.2005.03.053)
22. E. Sapper, S. Schaab, W. Jo, T. Granzow, J. Rödel, Influence of electric fields on the depolarization temperature of Mn-doped  $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ – $x\text{BaTiO}_3$ . *J. Appl. Phys.* **111**, 014105 (2012). doi:[10.1063/1.3674275](https://doi.org/10.1063/1.3674275)
23. S. Zhang, A.B. Kounga, E. Aulbach, W. Jo, T. Granzow, H. Ehrenberg, J. Rödel, Lead-free piezoceramics with giant strain in the system  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – $\text{BaTiO}_3$ – $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ . II. Temperature dependent properties. *J. Appl. Phys.* **103**, 034108 (2008). doi:[10.1063/1.2838476](https://doi.org/10.1063/1.2838476)
24. W. Jo, J.E. Daniels, J.L. Jones, X. Tan, P.A. Thomas, D. Damjanovic, J. Rödel, Evolving morphotropic phase boundary in lead-free  $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $\text{BaTiO}_3$  piezoceramics. *J. Appl. Phys.* **109**, 014110 (2011). doi:[10.1063/1.3530737](https://doi.org/10.1063/1.3530737)
25. W. Jo, J. Daniels, D. Damjanovic, W. Kleemann, J. Rdel, Two-stage processes of electrically induced-ferroelectric to relaxor transition in  $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $0.06\text{BaTiO}_3$ . *Appl. Phys. Lett.* **102**, 4 (2013). doi:[10.1063/1.4805360](https://doi.org/10.1063/1.4805360)
26. X. Li, P. Liu, Z. Xi, P. Fang, W. Long, X. Zhao, Effects of doping Bi and Nd on the phase transition and electric properties of  $(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$  ceramics. *J. Electroceram.* **32**, 86–91 (2014). doi:[10.1007/s10832-013-9881-1](https://doi.org/10.1007/s10832-013-9881-1)
27. Q. Xu, D.P. Huang, M. Chen, W. Chen, H.X. Liu, B.H. Kim, Effect of bismuth excess on ferroelectric and piezoelectric properties of a  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ – $\text{BaTiO}_3$  composition near the morphotropic phase boundary. *J. Alloys Compd.* **471**, 310–316 (2009). doi:[10.1016/j.jallcom.2008.03.078](https://doi.org/10.1016/j.jallcom.2008.03.078)
28. S.R. Shannigrahi, F.E.H. Tay, K. Yao, R.N.P. Choudhary, Effect of rare earth (La, Nd, Sm, Eu, Gd, Dy, Er and Yb) ion substitutions on the microstructural and electrical properties of sol-gel grown PZT ceramics. *J. Eur. Ceram. Soc.* **24**, 163–170 (2004). doi:[10.1016/S0955-2219\(03\)00316-9](https://doi.org/10.1016/S0955-2219(03)00316-9)
29. Y.Z. Zhu, S.P. Lin, Y. Zheng, D.C. Ma, B. Wang, Improvement of pyroelectric figures of merit in zirconia-doped congruent lithium niobate single crystals. *J. Mater. Sci.* **51**, 3155–3161 (2016). doi:[10.1007/s10853-015-9625-5](https://doi.org/10.1007/s10853-015-9625-5)
30. J. Abe, M. Kobume, T. Nishimura, T. Yazaw, Y. Nakai, Effects of manganese addition on pyroelectric properties of  $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$  ceramics. *Integr. Ferroelectr.* **80**, 87–95 (2006). doi:[10.1080/10584580600656502](https://doi.org/10.1080/10584580600656502)