

The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics

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Abstract

Ta-doped lead-free 0.94NBT-0.06BT-xTa ($x = 0.0 - 1.0$ %) ceramics were synthesized by a conventional solid-state route. XRD shows that the compositions are at a morphotropic phase boundary where rhombohedral and tetragonal phases coexist. The depolarization temperature (T_d) shifted to lower temperature with the increase of Ta content. The pyroelectric coefficient (p) of doped ceramics greatly enhanced compared with undoped material and reached a maximum of $7.14 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at room temperature (RT) and $146.1 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at T_d at $x = 0.2\%$. The figure of merits, F_i and F_v , also showed a great improvement from $1.12 \times 10^{-10} \text{ m.v}^{-1}$ and $0.021 \text{ m}^2.\text{C}^{-1}$ at $x = 0.0$ to $2.55 \times 10^{-10} \text{ m.v}^{-1}$ and $0.033 \text{ m}^2.\text{C}^{-1}$ at $x = 0.2\%$ at RT . Furthermore, F_i and F_v show the huge improvement to $52.2 \times 10^{-10} \text{ m.v}^{-1}$ and $0.48 \times 10^{-10} \text{ m.v}^{-1}$ respectively at T_d at $x = 0.2\%$. F_C shows a value between 2.26 to $2.76 \times 10^{-9} \text{ C.cm}^{-2} \cdot ^\circ\text{C}^{-1}$ at RT at $x = 0.2\%$. The improved pyroelectric properties make NBT-0.06BT-0.002Ta ceramics a promising infrared detector material.

Keywords: Lead free ceramics; Lanthanum doping NBT-BT; Morphotropic phase boundary (MPB); Depolarization temperature; Pyroelectric properties; Figure of merits.

1. Introduction

Lead-free ceramics have been investigated heavily as a response to the legislations of the RoHS (restriction of use of certain hazardous substances) and the WEEE (waste electrical and electronic equipment) systems in the European Union and many other countries [1]. Among the investigated compositions, sodium bismuth titanate $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) is considered a promising lead-free material. The NBT is a perovskite ceramic material discovered by Smolenskii et al. in 1960 [2], and presents high ferroelectric properties such as a large remnant polarization ($P_r = 38 \mu\text{C}\cdot\text{cm}^{-2}$) in addition to high Curie temperature ($T_c = 325^\circ\text{C}$) [2]. The NBT structural phase diagram shows two transitions, firstly from rhombohedral (ferroelectric) to tetragonal (antiferroelectric) phases at depolarization temperature (T_d) around $180 - 220^\circ\text{C}$, and secondly from a tetragonal (antiferroelectric) phase to cubic (paraelectric) phases at Curie temperature (T_c) [2–6] around $300 - 350^\circ\text{C}$. However, the high value of both the coercive field ($E_c = 73 \text{ kV}\cdot\text{cm}$) and the leakage current at room temperature (RT) make the full poling of the NBT difficult [2–7]. To improve the NBT performance and to make it more suitable for various applications two ways have been utilized to achieve this goal: First, NBT were combined with another ceramic composition such as BaTiO_3 , NaNbO_3 , $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$, and SrTiO_3 [2,6,7] forming a new composition. Second, doping with other elements such as Mn, Eu, La, Zr, Al, Co, and many other elements [8]. These two approaches have been used to improving its properties.

Among these compositions, $(1-x) \text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - x\text{BaTiO}_3$ (NBT-xBT) have been attracted the attention of numerous researchers due to a paramount potential and considered as an alternative candidate to the lead-contain materials such as PZT in industrial fields such as a manufacturing the electronic device and sensors or in other diverse applications. Because at $x = 0.06-0.07$, NBT-xBT are at a Morphotropic Phase Boundary (MPB), at which the material shows a high ferroelectric, piezoelectric and pyroelectric properties. Although the MPB of

NBT-xBT exists at $x = 0.06-0.07$ which rhombohedral and tetragonal phases coexist [8,9], the majority of researches take $x=0.06$ as the reference for MPB composition [7]. In addition to its improved ferroelectric properties at MPB, poling of NBT-xBT is much easier than it is at other compositions due to a lower coercive field [8]. Its phase diagram of NBT-0.06BT is complex and presents various phase states such as ferroelectric (*FE*), antiferroelectric (*AFE*) or relaxor and paraelectric (nonpolar) (*PE*) and the phase diagram is not fully understood [2–6]. These phase transitions occur at different temperatures. Firstly, from ferroelectric (*FE*) to antiferroelectric (*AFE*), this transition could be from ferroelectric to relaxor [10] at depolarization temperature (T_d) at around 100 to ~ 165 °C [11,12]. Secondly, from antiferroelectric (*AFE*) to nonpolar (*PE*) phases, this transition happens at temperature around 225 °C to 292 °C, at either Curie temperature (T_c) [2–6] or the temperature at the maximum dielectric permittivity (T_m) [12]. The NBT-0.06BT phase transitions are also accompanying with structural transition from rhombohedral and tetragonal if the composition is at the MPB or rhombohedral to tetragonal or to relaxor if the composition is out of the MPB [5,11,12] and from tetragonal to cubic. These structural phase changes are very important to the pyroelectric applications because the large pyroelectric effect could be induced at these transitions.

NBT-0.06BT has been extensively investigated for its ferroelectric, dielectric and piezoelectric properties whereas, there are few publications of its pyroelectric properties [4]. Abe *et al.* studied the pyroelectric properties of MnO₂-doped NBT-0.06BT ceramics and reported the pyroelectric coefficient (p) (3.5×10^{-4} C.m⁻². °C⁻¹) at RT [13]. Ruiz *et al.* studied the pyroelectric properties of the NBT-0.065BT and reported the p (4.6×10^{-4} C.m⁻². °C⁻¹) and the figure of merit of F_C (1.44×10^{-9} C.m⁻². °C⁻¹) at RT [14]. Felix *et al.* investigated the pyroelectric behavior of NBT-xBT ($0.04 \leq x \leq 0.06$) and concluded that the pyroelectric properties of the NBT-0.06BT were better than that of NBT-0.04BT because it is in MPB and

reported a p value comparable to the PZT material [5]. Guo *et al.* reported the pyroelectric properties of Zr-doped NBT-xBaTO₃ ($0.0 \leq x \leq 0.12$) ceramics and found that p enhanced from $0.057 \mu\text{C}\cdot\text{cm}^{-2}\cdot^\circ\text{C}^{-1}$ at RT to $2.21 \text{ C}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$ at T_d (87°C) [4].

Pyroelectric properties usually reach a peak value at phase transition temperature, such as depolarization and Curie temperatures. Because these two phase transition temperatures of NBT-xBT is far too high, it would be beneficial if the phase transition temperature could be lowered to near room temperature. The main objective of this contribution is, by doping Ta₂O₃, to bring the depolarization temperature of NBT-0.06BT down and to observe the pyroelectric properties of these compositions in both room and depolarization temperatures.

2. Experimental

Ta⁵⁺-doped 0.94NBT-0.06BT ceramics were prepared by a solid-state synthesis route. The raw materials used in this project were powders, lanthanum oxide (Ta₂O₃), 99.0%, bismuth oxide (Bi₂O₃), 99.999%, sodium carbonate (Na₂CO₃), 99.5%, barium carbonate (BaCO₃), 99.98%, and Titanium dioxide (TiO₂), > 99.8% (all Sigma- Aldrich).

The amounts of powders were calculated according to the chemical formula of 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃-xTa, with $x = 0.0, 0.02, 0.05$, and 1.0 (%). The raw materials were ball-milled (zirconia milling media) in acetone in polyethylene pots for 24 hrs. in order to mix and mill the powders. The resultant slurries were dried overnight at 50°C . 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 step. The powders were calcined at 850°C for 180 min. in a closed alumina crucible at a heating ramp rate of 1°C per minute and cooling rate 5°C per minute in a furnace (Pyro Therm, ITEMP 14/6). After calcination, the powders were re-milled in acetone for 24 hrs., and then 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 fully dried in oven at 80°C . The dried powders were ground and

sieved and subsequently pressed into green pellets with a diameter of 10 mm under an uniaxial compaction with a load of ~ 78 MPs for 5 min at RT. The pellets were sintered at temperatures up to 1150°C for 120 min in closed crucibles in order to minimize the loss of volatile Na^{+} and 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 6.5 kV/mm for 10 min at RT in silicone oil was carried out using a Kiethley (6517 Electrometer/high resistance) dc power supply. Afterwards, the poled samples were washed thoroughly by using isopropanol in order to remove the silicone oil and then left in air for 3 hrs. to naturally dry. The poled samples are placed in short-circuit condition to eliminate any unwanted trapped charges.

SEM (FEI XL30 SFEG) was used to look at the grain morphology of the sintered samples and X-Ray Diffraction (XRD) (Siemens Ltd Model: D500) was used to investigate crystallisation and phase. Dielectric measurements were performed by an impedance analyser (Wayne kerr Electronics Ltd. Model 3245 and Hewlett Packard HP4092A)) over a temperature range from RT to 150°C using a custom-built temperature controlled hotplate in the frequency range of 0.1 - 10 kHz. Pyroelectric measurements were made using the Byer-Roundy [15] method on a custom-built computer controlled rig which used thermoelectric heaters to ramp the temperature between 20°C and 90°C whilst under vacuum and collect the pyroelectric current response from a Kiethley electrometer (Model 6217). Dielectric and pyroelectric data was then used to studying the phase changes such as depolarization temperatures (T_d), and to determine figure of merit values F_i , F_v , F_D and F_C .

3. Results and discussion

3-1. Effects of T_a on Microstructure

Fig. 1 (a) depicts XRD patterns of the Ta-doped NBT-0.06BT ceramics powders calcined at 850 °C for 3 hrs. All samples (A to D) showed a single crystalline perovskite phase without any detectable secondary phase, demonstrating that the Ta⁵⁺ diffused into NBT-0.06BT lattice and formed new NBT-0.06BT-xTa solid solutions. The different contents of the dopant did not cause a significant change to the phase structure of NBT-0.06BT.

The enlargement of the X-ray diffraction spectra of all samples illustrates the splitting in the peak [111] into [003] and [021] at 39.0° - 41.0° (fig.1 (b)), indicating the existence of the rhombohedral phase. The XRD spectra of a pure NBT presented a rhombohedral symmetry with splitting of the [111] peak into [003]/[021] at 38.0° - 42.0° at room temperature (RT) [11,16].

Another splitting was spotted in all samples in the peak [200] into [200] and [002] at 46°-48°, which refers to the existence of tetragonal phase in the NBT lattice [5,16–20] (Fig. 1(c)). The coexistence of rhombohedral and tetragonal phases in the NBT-0.06BT-xTa ceramics confirms that all sample structures are at the MPB area. Furthermore, Fig. 1(c) shows that the splitting in the peak [200] becomes quite pronounced for Sample C similar to Sample B (Fig.1 (b)). The position of the MPB of perovskite structure, such as NBT-0.06BT, can be determined according to Hiruma et al. [21] by calculating Goldsmith tolerance factor (*t*) of the second part (BaTiO₃) of this composition, and for our Ta-doped sample, by calculating the (*X*_{MPB}) value of the (BaTaTiO₃) using the equations 1 and 2 [21–23]:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

$$x_{MPB} = \frac{t_{MPB} - t_{NBT}}{t_{BT} - t_{NBT}} \quad (2)$$

Therefore, the result reveals that the MPB position moves from *x* = 0.0600 in Sample A to *x* = 0.0619 in Sample D, (Table 1). In addition, the *X*_{MPB} value of Sample C is 0.0609. Thus,

these results indicate that Samples C and D may slightly move away from the X_{MPB} value, which indicates that the high concentration of the Ta^{5+} shifts the MPB position towards Ba-rich (Table 1).

Table 1 shows the lattice parameters ($\text{\AA}$), the c/a ratio and the tolerance factors of undoped and doped samples (A-D). The lattice parameters “ $a = b$ ” and “ c ” have been affected by Ta^{5+} dopant. The c parameter shows an obvious increase from 13.4744 in Sample A to 13.5114 in Sample D. The calculations of the c/a ratio reveal that Samples B, C, and D have higher ratio than Sample A, indicating that the doped samples are more tetragonal in the structure than the undoped sample.

Comparing the ionic radius of Ta^{5+} with the A- and B-sites ionic radii according to the Shannon effective radii and the ionic radius relations [24], the ionic radius of A-site ions are Na^+ (1.39 $\text{\AA}$, CN12) (CN=coordination number), Bi^{3+} (1.31 $\text{\AA}$, CN12) and Ba^{2+} (1.61 $\text{\AA}$, CN12) [6-9]. And the B-site ion is Ti^{4+} (0.605 $\text{\AA}$, CN6), therefore, it can assume that the Ta^{5+} (0.64 $\text{\AA}$, CN6) ions [6, 18-20] substitute the B-site ions of the NBT-0.06BT lattice but not entering A-site because the big radius difference between A-site ions and the Ta^{5+} . The t value for stable perovskite structure is in the range of 0.77 - 0.99 [25]. The calculation of t value for all samples in this study shows that the value is between 0.97543 - 0.97518. Therefore, the results confirm that the all samples have a stable perovskite structure. Moreover, the tolerance factors of all samples show a clear decrease with the increase of the dopant content due to the replacement of the different contents of Ta^{5+} (Table 1).

Fig.2 shows the scanning electron microscope (SEM) images of the sample surfaces of the NBT-0.06BT- $x\text{Ta}$ ceramics. All samples display a dense microstructure with an average density around $97.16 \pm 0.25 \text{ g/cm}^3$. The Samples B, C, and D show a quite similar density value but higher than Sample (A), in addition, Sample C presents the highest density value among all other samples (Table 2). The average grain size of all samples decreases from

~1.82 μm in Sample A to ~1.62 μm in Sample D. The microstructures of Samples B, C, and D become slightly inhomogeneous with increasing the dopant content [26]. The small grains aggregated and surrounded by large grains.

The reduction of the grain size in doped samples is due to the creation of cation vacancies in A-site. Ta^{5+} replaces Ti^{4+} due to the radius analogy. However, there is a valence difference between them. Thus, the Ta^{5+} behaves as a donor, and in order to maintain the charge balance in the system, A-site vacancies form. These A-site vacancies may locate at the grain boundaries due to the thermodynamic stability of the system. The grain growth is restricted by these A-site vacancies. Thus, the Ta^{5+} can act as an inhibitor. As a result doping NBT-BT system with donor elements prevents the growth of the grains [27,28].

3-2. Effects of Ta on dielectric properties

Fig. 3 (a, to d) depicts the temperature dependence of the dielectric properties of poled NBT-0.06BT-xTa samples from RT up to 150 $^{\circ}\text{C}$ at three different frequencies of 1, 10, and 100 kHz. The relative permittivity (ϵ_r) of all samples increases with temperature, which behaves like a typical ferroelectric material [29].

The undoped sample shows a relative permittivity (ϵ_r) value of ~ 396 at RT and at 1 kHz (Fig. 3a). However, the doped samples illustrate much higher ϵ_r values than undoped sample and they are around 870, 1082 and 1006 for Sample B, C and D respectively. (Fig. 3 b to d). The ϵ_r shows a steady increase with the excess of the dopant content; however, Sample C presents the highest value than other samples.

Samples B, C, and D show a sharp increase in ϵ_r value with temperature but it was not identified in Sample A. This sudden rising in ϵ_r starts at ~100 $^{\circ}\text{C}$, ~60 $^{\circ}\text{C}$, and ~70 $^{\circ}\text{C}$ for Samples B, C, and D respectively. The ϵ_r values at these temperatures for the doped samples are around 1487, 1424, and 1367 respectively (Table 3).

The dielectric loss ($\tan\delta$) of undoped sample is ~ 0.044 at RT and 1 kHz and increases with dopant content to around 0.051, 0.057, and 0.056 for Samples B, C, and D respectively. Although, all doped samples show a close $\tan\delta$ value but Sample C presents the highest $\tan\delta$ value than all other samples due to its highest density among all samples (Table 2). With the increase of temperature, the $\tan\delta$ value increases to the maximum at the temperature widely known as the depolarization temperature (T_d) [10,17,30]. The T_d for Sample A is $\sim 115^\circ\text{C}$ while it is around 90°C , 50°C and 50°C for Samples B, C, and D respectively. The dielectric loss values of Samples A, B, C, and D at T_d are ~ 0.051 , 0.067, 0.065, and 0.064 respectively (Table 3). The doped samples show higher $\tan\delta$ value than undoped sample at T_d .

The temperatures that the ϵ_r value shows a sudden increasing (~ 100 , ~ 60 , and $\sim 70^\circ\text{C}$) in Samples B, C, and D are close to the T_d , (90 , 50 and 50°C), which were identified from the $\tan\delta$ peaks. Thus, these temperatures can also be considered as T_d .

3-3. Effects of Ta on depolarization temperature

Depolarization temperature (T_d) is an important parameter in pyroelectric study. Its origin has not been fully understood for NBT-xBT [17,31], and it has a few definitions [22].

The European standard on piezoelectric properties has defined the T_d as the reduction of remnant polarization because the temperature and other influences [32]. Another definition is the steep reduction of remnant polarization [19]. Also the phase transition temperature from ferroelectric (FE) to anti-ferroelectric (AFE) or to relaxor anti-ferroelectric phases [30,31,33,34]. However, Jo et al. reported that the T_d could be the phase transition temperature from ferroelectric to relaxor [34].

In this study, the T_d could be identified by two methods: (1) Dielectric method, the temperature at dielectric peak (Fig. 4 a, and b); (2) Pyroelectric method, the temperature at pyroelectric coefficient (p) peak (Table 4) [13].

The dielectric vs temperature plots in Fig.4 reveal that T_d decreased after doping Ta^{5+} from 115 °C (Sample A) to around 70 °C or 50 °C (Sample D) (Fig. 4 a, and b). The ϵ_r curves for doped samples show the T_d values at 100 °C, 60 °C and 70 °C in Samples B, C and D respectively; however, it was not identified in Sample A as shown in Fig.4 (a). These depolarization temperature values are slightly higher than the T_d identified from the dielectric loss ($\tan\delta$) curves for the same samples (Fig.4 (b)). Sample D shows an abnormal depolarization temperature, which is more than 10 °C higher than the T_d for Sample C whereas it should shift to lower temperature with increasing the dopant content.

The second method to obtain the T_d is from the maximum pyroelectric coefficient values. It is widely known that the maximum p can be achieved at the phase transition temperature [35–38]. NBT-0.06BT shows two phase-transition temperatures. First: at depolarization temperature (T_d) which is between 100 °C - 165 °C [17,25,39]. Second: at T_m which is between 225 °C – 292 °C [17,25,39]. In this study, the low phase transition temperature was utilised to identify the T_d and they are 78.8 °C, 49.1 °C, and 56.9 °C for Samples B, C, and D, respectively. However, T_d could not be identified for Sample A by pyroelectric method due to the upper temperature limit of equipment being at 90 °C (Table 3). In addition, Sample D shows an abnormal T_d , which is more than 7.8 °C higher than the T_d of Sample C whereas, it should shift toward low temperature with increasing the Ta content.

T_d of Sample D is at higher temperature than it expected. This can link to the position of the MPB area in this sample, which is move to 0.0619 (Ba-rich). Thus, the lack in the Ba^{2+} content could be responsible for the shift in T_d value toward higher temperature. Although the MPB of Sample C moves to the Ba-rich due to the same reason, the MPB position is closer to 0.0600 (Table 1).

Comparing the depolarization temperature results obtained by the two methods, the pyroelectric method shows T_d values lower than the dielectric method, which is in agreement with the results reported by Anton et al. [17].

Doping the B-site of the NBT-0.06BT with elements which have a bigger ionic radius than Ti^{4+} may be responsible for the decrease of the T_d to lower temperature. These elements consumed a larger space in oxygen octahedral than the elements with smaller ionic radii. Therefore, it may reduce the degree of freedom for B-site ion moving in the TiO_6 octahedra. As a result, it weakens the ferroelectric properties [40] of the NBT-0.06BT, and shifting the phase transition from ferroelectric (FE) to antiferroelectric (AFE) [18,30–32,33,34] or intermediate phase [17,25,39] at lower temperature. Thus, undoped NBT-0.06BT [38] showed T_d at higher temperature than B-site doped with bigger radii elements such as NBT-0.06BT-Nd [41]; NBT-0.06Ba(ZrTi)O₃ [33]; NBT-0.06Ba(MnTi)O₃ [42].

3-4. Effects of Ta on pyroelectric properties

Pyroelectric coefficient (p) is defined as the change in the spontaneous polarization by fluctuations in temperature [43]. In addition, its value at certain temperature is considered as one of the important parameters while selecting the material for pyroelectric applications. However, the efficient way for evaluating the pyroelectric material performance can be achieved by calculating the figure of merits (FOMs) that represent the essential parameters for the pyroelectric applications [17].

The calculation of the FOMs is based on the values of the pyroelectric coefficient, relative dielectric permittivity, dielectric loss and the specific heat [43]. There are several types of FOMs depending on special types of the pyroelectric applications such as infrared or thermal imaging [20, 41].

The types of FOMs depend on the input of thermal or electrical circuits, current or voltage. Therefore, for infrared applications that rely on the current responsivity, F_i is the relevant

FOM. Similarly, to enlarge the pyroelectric voltage, the more suitable FOM is F_v that characterizes to the high voltage (v) detectivity. Likewise, F_D is the FOM of the high and specific detectivity. F_C is a FOM of the infrared detector materials. These figure-of-merits have been used to characterize and select the materials for thermal and infrared applications as sensors or transducers [2,13,17]

In this study, the pyroelectric coefficient (p) of NBT-0.06BT-xTa was measured from RT to T_d for doped samples (B, C, and D) or 90 °C for undoped Sample (A).

The measurements of the pyroelectric coefficient (p) and FOMs were carried out using the Equations 3 - 7 [5,14,15].

$$I_p = pA \frac{dT}{dt} \quad (3)$$

$$F_i = \frac{p}{Cv} \quad (4)$$

$$F_v = \frac{p}{Cv\epsilon_o\epsilon_r} \quad (5)$$

$$F_D = \frac{p}{Cv\sqrt{\epsilon_o\epsilon_r} \tan\delta} \quad (6)$$

$$F_c = \frac{p}{\sqrt{\epsilon_r}} \quad (7)$$

where T is absolute temperature, t the time, p is the pyroelectric coefficient and I_p the pyroelectric current, F_i the high current (i) detectivity, F_v the high voltage (v) detectivity, F_D high detectivity, F_C the pyroelectric figure of merit. C_v^* the specific heat (2.8 JK⁻¹cm⁻³, quoted from [13]), ϵ_r the relative dielectric permittivity and ϵ_o the permittivity of free space.

Fig. 5 shows the change of p vs. temperature for NBT-0.06BT-xTa at a wide temperature range from RT to 90 °C. Sample B (x=0.2 %) shows the highest p at RT (Table 4). At a temperature range from 30 °C to 52 °C, Sample C (x=0.5 %) presents the highest pyroelectric

coefficient of $\sim 109.0 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at T_d ($\sim 49.1^\circ\text{C}$). At temperature range between 53°C to 60°C , Sample D ($x=1.0\%$) shows a highest p value which is around $76.1 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$, at T_d ($\sim 56.9^\circ\text{C}$). At temperature range from 60°C up to 90°C Sample B illustrates the maximum pyroelectric coefficient value which is around $146.1 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$, at T_d ($\sim 78.8^\circ\text{C}$).

Table 4 and 5 list the pyroelectric coefficient(p) values of all samples at RT and T_d . The p increased from $3.14 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ for Sample A to $5.32 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ for Sample D at RT. Sample B shows the maximum p value of $7.14 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at RT. The huge increase in p at T_d from $23.9 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ for Sample A to $76.1 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ for Sample D was observed. However, Sample B also shows the optimum pyroelectric coefficient value of $146.1 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at T_d .

Tables 4 and 5 clearly reveal that Sample B has the maximum pyroelectric coefficient at RT and at T_d . This may link to two factors: (1) the microstructure change of this sample. The measurement of c/a ratio reveals that Sample B has a bigger ratio (~ 2.4578) than Sample C (~ 2.4536), which means that Sample B is more tetragonal in its structure than Sample C. It has also been supported by tolerance factor measurements (Table 1); (2) the position of the MPB in the composition of this sample. The tolerance factor calculation reveals that its value is 0.0604 which means that the composition of Sample B is in the MPB area. The huge improvements in the p values at T_d may be attributed to the positive correlation between the pyroelectric coefficient (p) and pyroelectric current (I_p), which reaches the maximum at T_d . In pyroelectric materials, the increase of temperature will alter the lattice spacing of the nonsymmetrical ions location, which varies the spontaneous polarization of the pyroelectric material. The variation of the spontaneous polarization generates the I_p [42]. So the optimum current (I_p) and coefficient (p) values appear at T_d because the maximum change of the spacing appears at T_d [42].

Furthermore, the great increase in p at T_d for Sample B may be because the composition of this sample is at MPB, which makes the reorientation of ferroelectric domains easier and results in a sharp change in polarization. This effect appears gradually but with the highest value at T_d . Thus, the pyroelectric coefficient shows a great enhancement at this temperature [6]. It has been reported that the optimum pyroelectric coefficient value of (1-x)NBT-xBT materials can be achieved at phase transition temperature [10, 38, 39, 44]. Hence, the ultimate p values obtained at T_d in this study relates to the phase transition. The T_d coincides with the phase transition temperature as mentioned before. At RT, the p values for doped samples are 7.14, 6.97 and 5.32 ($\times 10^{-4}$ C. m⁻².°C⁻¹) respectively, which are higher than that of PZT (4.14×10^{-4} C. m⁻².°C⁻¹) [4,19,17,22].

The FOM, F_i values of the NBT-0.06BT-xTa samples at RT and T_d or 90 °C are listed in Tables 4 and 5. The F_i values increased from 1.12 to 1.90 ($\times 10^{-10}$ (m/V)) for Samples A to D respectively at RT. While Sample B ($x = 0.2$ %) presents the highest value which is 2.55×10^{-10} (m/V) (Table 4). The comparison between the F_i values at RT and value of PZT (1.415×10^{-10} (m/V)) [37] reveals that the doped Samples have a higher F_i values than PZT at RT. F_i values show further improvement for all samples at T_d or 90°C. It increased from 8.6 to 27.2 ($\times 10^{-10}$ (m/V)). However, Sample B shows the optimum value 52.2×10^{-10} (m/V) at T_d (Table 5). The reason behind the huge F_i value for Sample B at RT and T_d may be due to that it has the greater p values at RT and T_d than all other samples.

The F_v values of the NBT-0.06BT-xTa at RT and T_d or 90°C and at a wide range of frequency are listed in Tables 4, 5, and 6. Table 4 shows the F_v values at RT. F_v increases with Ta⁵⁺ content and reaches a maximum at $x=0.2\%$. Table 5 presents the F_v results at T_d or 90°C. The F_v values increase from 0.19 (m².C⁻¹) for Sample A to 0.34 (m².C⁻¹) for Sample D. The best F_v value is shown for Sample B (0.48 (m².C⁻¹)). Table 6 illustrates the F_v values at both room and T_d or 90°C temperatures at 33Hz up to 10 kHz. F_v values increase with the increase of

frequency at RT and T_d . This increase is due to the inverse relation between the relative permittivity (ϵ_r) and the frequency.

The majority of dielectric and ferroelectric materials are following this relation. This behavior is due to that the dipoles in these materials follow the field at low frequency and contribute to the relative permittivity. While dipole switching starts delaying with the increase of frequency, the dipoles can no longer follow the field at a certain point of frequency [25,43]. It was observed that Sample B seems to have the maximum F_v value in the whole frequency range at RT and this may be due to the lower relative permittivity (ϵ_r) and the higher p at this temperature than all other doped samples. Again, the F_v values for all samples in this study are higher than that of PZT [4, 5].

The enhanced F_v values for Sample B in this study at RT and T_d are due to the following reasons: the higher pyroelectric coefficient and the lower dielectric permittivity (ϵ_r) compared with other doped samples at RT; in addition, the huge pyroelectric coefficient value of Sample B at T_d , compared with the rest of samples.

F_D values of the undoped and doped samples at RT, T_d or at 90°C are listed in Tables 4, 5 and 6. The F_D results show poor values at both RT and T_d . The lower F_D values for doped samples may be related to the higher values of both relative permittivity and the dielectric loss that are higher than the undoped sample, though pyroelectric coefficient values of Samples B, C, and D were quite higher than Sample A value. Table 6 also illustrates the F_D values at a wide range of frequency at both RT and T_d , and the results show poor results in both low and high value of frequencies.

Table 7 illustrates the F_C values of the NBT-0.06BT-xTa at RT and in a wide frequency range (33Hz, 0.1, 1, 10, 100 and 1000 kHz). The F_C values revealed a strong dependence upon Ta⁵⁺ dopant content. The F_C value stabilises at $\sim 3 \pm 1$ C. cm⁻².°C⁻¹ that is suitable for infrared detectors materials [14]. Rodríguez-Ruiz *et al* [14]. investigated the pyroelectric

coefficient of $0.935\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.065\text{BaTiO}_3$ ceramics and calculated its F_C being $1.44 \times 10^{-9} \text{ C} \cdot \text{cm}^{-2} \cdot ^\circ\text{C}^{-1}$, while the results in this study show higher values, particularly for Samples B and C (Table 7). The high F_C values for Samples B and C also link to the high pyroelectric coefficients of these samples as well as to the lower relative permittivity, especially for Sample B at RT.

4. Conclusion

The NBT-0.06BT-xTa ceramics were synthesized by a conventional solid-state route. The pyroelectric properties of these materials were investigated and compared with undoped NBT-0.06BT, other lead-free and PZT ceramics.

The XRD study proves that the compositions of the undoped and doped are both at or near the MPB region. The lattice parameter values and c/a ratio slightly change with increasing the dopant content. The SEM investigation shows the average grain size reduced from 1.82 to 1.62 (μm) with increasing the Ta^{5+} content. Moreover, the doped samples present higher density than the undoped sample. Both relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) increase with Ta content.

The T_d was identified by two different methods and decreased from $\sim 115^\circ\text{C}$ in undoped Sample A to around 70°C (from ϵ_r) or 50°C (from $\tan\delta$) in doped Sample D, according to the dielectric method. However, the T_d values for Samples B, C, and D, are 78.8, 49.1, and 56.9°C respectively according to pyroelectric coefficient method.

Sample B has the optimum p at RT and at T_d . The F_i and F_v increase with the increase of Ta^{5+} content up to $x = 0.2\%$ at both RT and at T_d in a wide range of frequency. The F_C shows higher values in Samples B and C in a wide range of frequency. Results presented in this work demonstrate that NBT-0.06-xTa ceramics at $0.2\% \leq x \leq 0.5\%$ are promising materials for infrared detectors and other pyroelectric applications in a wide temperature.

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Figure and table captions:

Figure 1: (a) X-ray diffraction patterns of NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ %. (b) enlargement of splitting [111] peak into [003] and [021] at 39.6° to 40.6° . (c) enlargement of splitting [200] peak into [200] and [002] at 46.0° to 47.5° .

Figure 2: SEM surface morphology of the NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ % ceramics.

Figure 3: The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with temperature for Samples A to D at three different frequencies (1, 10 and 100) kHz.

--- ϵ_r -1 --- ϵ_r -10 --- ϵ_r -100 --- $\tan\delta$ -1 --- $\tan\delta$ -10 --- $\tan\delta$ -100

Figure 4: The change of the relative permittivity (ϵ_r) (a) and the loss tangent ($\tan\delta$) (b) with temperature for Samples A to D at 1 kHz, and the identification of the depolarization temperature (T_d).

— Sample A — Sample B — Sample C — Sample D

Figure 5: The change of pyroelectric coefficient (p) as a function of Ta^{5+} content and temperature ($^{\circ}\text{C}$) for the NBT-0.06BT- $x\text{Ta}$, $0.0 \leq x \leq 1.0$ %, where

— A, 0.0 %Ta — B, 0.2 %Ta — C, 0.5 %Ta — D, 1.0 %Ta

Table 1: The compositions of the Morphotropic Phase Boundary (MPB), the lattice parameters ($\text{\AA}$), c/a ratio and tolerance factor (t).

Table 2: The average grain size (μm), samples density (gm.cm^{-3}), and comparison with the theoretical density (%) which is ($\rho = 6 \text{ gm.cm}^{-3}$).

Table 3: The dielectric properties at room and at depolarization temperatures and 1 kHz, the depolarization temperature (T_d) obtained by two methods in this work and others.

Table 4: The pyroelectric coefficient and FOMs F_i , F_v , and F_D results at RT in present work and in literature.

Table 5: The pyroelectric coefficient and FOMs F_i , F_v and F_D results of the NBT-0.06BT- $x\text{Ta}$, $0.0 \leq x \leq 1.0$ %, at T_d or 90°C in present work and in literature.

Table 6: FOMs F_v and F_D at RT and T_d or 90°C and at different frequency.

Table 7: The figure of merit, F_C in different frequencies (0.033, 0.1, 1, 10, and 100 kHz) at RT.



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