

## Giant pyroelectric properties in La and Ta co-doped lead-free 0.94Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-0.06BaTiO<sub>3</sub> ceramics

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### Abstract

La and Ta co-doped Lead-free 0.94NBT-0.06BT ceramics were synthesized by a conventional solid-state route. The compositions remain at a morphotropic phase boundary. The depolarization temperature ( $T_d$ ) decreased with increasing doping contents. The room temperature (RT) pyroelectric coefficient ( $p$ ) was highly enhanced compared with undoped material ( $3.15 \times 10^{-4} \text{ C.m}^{-2} \cdot \text{ }^\circ\text{C}^{-1}$ ) and reached  $12.9 \times 10^{-4} \text{ C.m}^{-2} \cdot \text{ }^\circ\text{C}^{-1}$ , whereas, at  $T_d$ ,  $58.6 \times 10^{-4} \text{ C.m}^{-2} \cdot \text{ }^\circ\text{C}^{-1}$  could be obtained rather than  $23.9 \times 10^{-4} \text{ C.m}^{-2} \cdot \text{ }^\circ\text{C}^{-1}$  for undoped materials. The pyroelectric figure of merits,  $F_i$  and  $F_v$ , also showed a huge improvement from  $1.12 \times 10^{-10} \text{ m.v}^{-1}$  and  $0.021 \text{ m}^2 \cdot \text{C}^{-1}$  of undoped material to  $4.61 \times 10^{-10} \text{ m.v}^{-1}$  and  $0.078 \text{ m}^2 \cdot \text{C}^{-1}$  of doped materials at RT, and to  $20.94 \times 10^{-10} \text{ m.v}^{-1}$  and  $0.28 \times 10^{-10} \text{ m}^2 \cdot \text{C}^{-1}$  at  $T_d$ . RT  $F_C$  values are  $\sim 2.40$ ,  $2.46$ , and  $2.57$  ( $\times 10^{-9} \text{ C.cm}^{-2} \cdot \text{ }^\circ\text{C}^{-1}$ ) at frequency 33, 100 and 1000 (Hz) respectively, at La = Ta = 0.2 %. The pyroelectric coefficient achieved at RT in this study is almost one order of magnitude higher than PZT materials, furthermore, the figure of merits of the new compositions are comparable with or even better in those of PZT materials and other lead-free ceramics. The improvement in the pyroelectric properties makes La and Ta co-doped NBT-0.06BT ceramics possible materials to replace lead-containing PZT ceramics for infrared detector materials at a wide temperature range.

**Keywords:** *Electroceramic; Lead-free ceramics; Lanthanum and Tantalum co-doping NBT-0.06BT; Morphotropic phase boundary (MPB); Depolarization temperature; Pyroelectric properties; Figure of merits.*

## 1. Introduction

Electroceramic materials are becoming increasingly of high demand in a variety of industrial applications such as sensors, infrared detectors, thermal cameras, medical devices, airplanes and etc. [1]. The most widely used ferroelectric materials are lead-based ceramics such as PZT and PZT-based multicomponent ceramics due to their superior ferroelectric properties, but environmental issues relating to the hazardous nature of lead-containing materials and its disposal [2] is driving the need to find lead-free ceramic materials as an alternative to fill the industrial gap.

$(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x\text{BaTiO}_3$  (NBT- $x$ BT) is one of the lead-free ceramics that have attracted the interest of numerous researchers due to its high ferroelectric properties, particularly for compositions near the morphotropic phase boundary (MPB) ( $x = 0.06-0.07$ ) which separates the rhombohedral and tetragonal phases [3–5]. In addition to these improvements, the lower coercive field of NBT-(0.06 or 0.07)BT compared to NBT material makes poling easier [6]. The phase diagram of NBT-0.06BT is complex and presents many phases such as ferroelectric (FE), antiferroelectric (AFE) or relaxor and paraelectric (nonpolar) (PE) and is not fully understood [4,7–11]. These phase transitions occur at different temperatures: firstly, from ferroelectric (FE) to antiferroelectric (AFE) or to relaxor at depolarization temperature ( $T_d$ ) is around 100 to  $\sim 165$  °C [12–14]; secondly, from antiferroelectric (AFE) to nonpolar (PE) phases happens at around 225 to 292 °C, at either the Curie temperature ( $T_c$ ) or the temperature of maximum dielectric permittivity ( $T_m$ ) [7–11,13]. The NBT-0.06BT phase transitions are also accompanying with structural transitions, which is from rhombohedral and tetragonal ( $Rh + Tr$ ) to tetragonal ( $Tr$ ) if the composition is at the

MPB, or from rhombohedral(*Rh*) to tetragonal (*Tr*) if the composition is out of MPB and from tetragonal (*Tr*) to cubic (*C*) [10,12,13]. These structural phase changes are very important to the pyroelectric applications because maximum pyroelectric effects can be induced at these transitions.

For further improvements to NBT-0.06BT ferroelectric, piezoelectric and pyroelectric properties, doping with different elements such as the rare earths can play an important role [15,16].

Although the dielectric, ferroelectric and piezoelectric properties of undoped and doped NBT-xBT have been extensively investigated [17,18], their pyroelectric properties have received less attention [8,17–20]. Depolarization temperature ( $T_d$ ) is one of the most important characters in the pyroelectric studies but its origin and function in pyroelectric materials have not been fully understood, and also it has been reported in the literature less [8–10]. Our previous work investigated the effects of  $Ba^{2+}$  content on the pyroelectric properties of NBT-0.06BT ceramics [21]. We found that  $p$  increases from 2.90 to 3.54 ( $\times 10^{-4}$  C.m<sup>-2</sup>. °C<sup>-1</sup>) at RT when  $x = 1.02$ . In addition, the  $p$  shows huge enhancement from 55.3 to 740.7 ( $\times 10^{-4}$  C.m<sup>-2</sup>. °C<sup>-1</sup>) at  $T_d$  (85 °C) for composition NBT-0.06B<sub>1.02</sub>TiO<sub>3</sub> [21]. We also studied the effects of Ta doped in NBT-0.06BT on the pyroelectric properties and reported that the pyroelectric coefficient highly enhanced from 3.14 to 7.14 ( $\times 10^{-4}$  C.m<sup>-2</sup>. °C<sup>-1</sup>) at RT at Ta=0.2% and the same composition shows the maximum to 146.10  $\times 10^{-4}$  C.m<sup>-2</sup>. °C<sup>-1</sup> at  $T_d$  (78.8 °C) [22]. Furthermore, our recent investigation of NBT-0.06BT doped with La reveals that the pyroelectric properties of NBT-0.06BT were greatly improved by La doping from 3.14 to 7.42 ( $\times 10^{-4}$  C.m<sup>-2</sup>. °C<sup>-1</sup>) at RT at La=0.5% and to 105.40  $\times 10^{-4}$  C.m<sup>-2</sup>. °C<sup>-1</sup> at  $T_d$  (67.9 °C) at La =0.2% [23].

The aim of the present study is to improve the pyroelectric properties of NBT-0.06BT by co-doping the A&B sites with different concentrations of La<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>3</sub> at both RT and  $T_d$ ,

and at the same time to bring the depolarization temperature down these compositions to around RT.

## **2. Experimental**

La<sup>3+</sup> and Ta<sup>5+</sup> doped 0.94NBT-0.06BT (NBT-0.06BT) ceramics were prepared by a solid-state synthesis technique. The raw materials used in this study were lithium oxide (La<sub>2</sub>O<sub>3</sub>), 99.5%, tantalum oxide (Ta<sub>2</sub>O<sub>3</sub>), 99.0%, bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>), 99.999%, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), 99.5%, barium carbonate (BaCO<sub>3</sub>), 99.98%, and Titanium dioxide (TiO<sub>2</sub>), 99.8% (all Sigma- Aldrich).

The amounts of powders were calculated according to the chemical formula xLa<sub>2</sub>O<sub>3</sub>-0.94(NaBi)<sub>0.5</sub>TiO<sub>3</sub>-0.06BaTiO<sub>3</sub>-yTa<sub>2</sub>O<sub>3</sub>, where x = y = 0.0% (Sample A); x = y = 0.2% (Sample B); x= 0.5%, y =0.2% (Sample C); and x = 1.0%, y =0.2% (Sample D). 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, and the dried powder cakes were ground in a mortar for 10 min. and sieved through a 250 μm mesh in order to aid the calcination step. The powders were calcined at 850 °C for 180 min. in a closed alumina crucible with 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 %(wt.) of poly vinyl alcohol (PVA) was added as an organic binder to the dried powders to enhance the mechanical strength of the pellets during pressing. 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 ~78MPs 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<sup>+</sup> and Bi<sup>3+</sup>. The pellets were lapped/polished on both sides using silicon carbide paper and thermally etched for 30 min. at 1000 °C for microstructure studies. 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 mineral 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 mineral oil and then left in air for 3 hrs. to dry. The poled samples were placed at RT for 60 min with their electrodes short-circuited 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 on 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 [24] method on a custom-built computer controlled rig which used thermoelectric heaters to ramp the temperature between 20 and 90 °C, with a constant heating ramp of 1 °C/min of a small copper plate supporting the sample, whilst under vacuum and collecting the pyroelectric current response from a Kiethley electrometer (Model 6217). Temperature was measured using Platinum resistive devices connected to a commercially available interface board (Datashuttle Strawberry Tree™) capable of measuring 0.05°C differences and controlled by a software package (Workbench). The collected data from the Kiethley and the datashuttle could then be used to calculate the pyroelectric coefficient. 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 $T_a$ and $L_a$ on Microstructure**

Fig. 1 (a) depicts XRD patterns of the doped NBT-0.06BT ceramic powders calcined at 850 °C for 3 hrs. All samples (A-D) show a single perovskite phase without any detectable

secondary phase, demonstrating that both dopants ( $\text{La}^{3+}$  and  $\text{Ta}^{5+}$ ) diffused into NBT-0.06BT main lattice and formed new  $x\text{La-NBT-0.06BT-yTa}$ , solid solutions. The different concentrations of the dopant did not cause a significant change to the phase structure of NBT-0.06BT.

Fig.1 (b) shows a split of the peak [111] into [003] and [021] at  $39.0^\circ$  to  $41.0^\circ$  for all the samples indicating the existence of rhombohedral (*Rh*) phase. This split is in agreement with the phase structure of undoped NBT [25,26]. Another split was observed in [200] into [200] and [002] at  $46.0^\circ$ -  $47.5^\circ$ , which indicates the existence of tetragonal (*Tr*) phase in NBT lattice (Fig. 1(c)). The coexistence of both *Rh* and *Tr* phases in  $x\text{La-NBT-0.06BT-yTa}$  ceramics verifies that all the compositions are at morphotropic phase boundary (*MPB*) region. In undoped NBT-xBT the co-existence of *Rh* and *Tr* at  $x = 0.06$ - $0.07$  was reported in literature [8,12,27]. Thus the phase structure of the doped  $x\text{La-NBT-0.06BT-yTa}$  (Samples B, C, and D) are remained in the MPB and consistent with that reported in literature [8,12,27–29].

According to Shannon effective radii [30], for the comparison between the  $\text{La}^{3+}$  and the  $\text{Ta}^{5+}$  ionic radius with the A-site  $\text{Na}^+$ (1.39 Å, CN12) (CN=coordination number),  $\text{Bi}^{3+}$ (1.31 Å, CN12) and  $\text{Ba}^{2+}$ (1.61 Å, CN12) [5,6,11,31] and B-site  $\text{Ti}^{4+}$  (0.605 Å, CN6) ionic radii, it can be assumed that the  $\text{La}^{3+}$ (1.36 Å, CN12) may substitute A-site ions due to the radius similarity; while, the  $\text{Ta}^{5+}$  (0.64 Å, CN6) ions [32,33] can substitute the B-site ions of the NBT-0.06BT.

The calculation of the Goldschmidt tolerance factor (*t*) [15] which helps to determine the stability of the perovskite structure by using Equations 1 [15,28,29,34]:

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

Where  $R_A$  and  $R_B$  are the ionic radius of ions which will occupy A and B sites, and  $R_O$  is oxygen anion radius. The *t* value of stable perovskite structures is in the range of 0.77-0.99

[34]. The calculated t values for all samples compositions in this study is around 0.976, which means that all samples compositions illustrate stable structure.

Table 1 illustrates the lattice parameters ( $\text{\AA}$ ), c/a ratio and average grain size of all samples. The lattice parameters “a=b” and “c” are affected by  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  doped. The c parameter shows a clear increase from Sample A to Sample D (Table 1). The calculations of the c/a ratio reveal that the doped samples (B, C, and D) have higher ratio than undoped sample (A), indicating that Samples B, C, and D have more tetragonality in their structure.

Fig. 2 shows the SEM morphology of the ceramic samples. In general samples A-D show quite dense structures with a few observable pores in Sample A, which appear to diminish with increased doping and further densification. Sample A presents two distinguishable granular and rod shaped grains, in a wide range of sizes. In the co-doped samples only a granular morphology was observed. The average grain size varies with  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  contents and shows increase from Sample A to Sample D (Table 1). The reason behind the growth of grain in size can be linked to dopants effect.  $\text{La}^{3+}$  enhances the growth of the grains in NBT-0.06BT when it substitutes  $\text{Na}^+$  and/or  $\text{Ba}^{2+}$  resulting in A-site vacancies will create in order to keep charge balance [23,25,35]. Generally, creation of the A-site vacancies is quite beneficial for the mass transportation. This mass transport might be responsible for boosting the grain growth in the NBT-0.06BT with increasing  $\text{La}^{3+}$  concentration [10,23].

$\text{Ta}^{5+}$  may affect the composition in a contrary way to  $\text{La}^{3+}$ . The  $\text{Ta}^{5+}$  behaves as an inhibitor to the grains growth in NBT-0.06BT due to the valence difference between  $\text{Ta}^{5+}$  and  $\text{Ti}^{4+}$  [22,32,33]. As a result, A-site vacancies will be created. These A-site vacancies may locate at the grain boundaries due to the thermodynamic stability of the system, which prevents the growth of grains [22,36,37].

The average grains size firstly only shows a slight increase for sample B compared to the undoped sample. This is possibly due to a competing dopant cancelling effect. However, with

increased  $\text{La}^{3+}$  and fixed  $\text{Ta}^{5+}$  concentrations, the effects of  $\text{La}^{3+}$  became more pronounced, and the average grains size is clearly enlarged in Sample D (Fig. 2).

### 3.2 Effects of La and Ta on dielectric properties

Fig.3 (a-d) shows the change of the dielectric properties of poled undoped and doped NBT-0.06BT as a function of temperature in a wide temperature range from 20 up to 150 °C at 1, 10, and 100 kHz.

Sample A shows a relative permittivity ( $\epsilon_r$ ) of  $\sim 396$  at RT and 1 kHz (Fig. 3 (a)). However, Samples B, C, and D (Fig. 3 (b-d)) present much higher  $\epsilon_r$  values as shown in Table 2. Sample C shows the lowest  $\epsilon_r$  value among all other samples. The  $\epsilon_r$  of all the samples increases with temperature, which behaves like a typical ferroelectric material [37]. Samples B, and C show a pronounced inflexion in  $\epsilon_r$  with temperature while it is not recognized in Samples A, and D (Fig. 3(a-d)), although there is evidence that they may appear outside the temperature measurement window.

The dielectric loss ( $\tan\delta$ ) of the undoped sample is around 0.044 at RT and 1 kHz, and although there is a significant increase to  $\sim 0.062$  for Samples B, Samples C and D have similar values as Sample A (Table 2). The  $\tan\delta$  value shows a gradual decrease in the doped samples with increasing  $\text{La}^{3+}$  content from Samples B, C, and D at RT. With increasing the temperature, the  $\tan\delta$  value increases to a maximum value at the temperature that is widely known as the depolarization temperature ( $T_d$ ) [14,38,39]. The  $T_d$  for Sample A is  $\sim 115$  °C while it is around 45, 40 and 45 °C for Samples B, C, and D respectively. The dielectric loss values at  $T_d$  are  $\sim 0.051$ , 0.066, 0.052, and 0.045 for Samples A, B, C, and D respectively (Fig. 4). Also the relative permittivity values at  $T_d$  are around 582, 1209, 721, and 1112 for samples A to D respectively. Obviously, the doped samples show higher  $\epsilon_r$  values than undoped sample at  $T_d$ , (Fig. 4).

### 3-3. Effects of La and Ta on depolarization temperature



Depolarization temperature ( $T_d$ ) represents an important parameter which plays a significant role in the pyroelectric effect as well as in pyroelectric applications. However, in NBT-xBT it still needs better understanding [38,40] and more precise definitions [14,34,39,41]. One such definition is that it is the phase transition temperature from ferroelectric to antiferroelectric or to relaxor [21,42,43].

In this study, the  $T_d$  is successfully identified by two methods: (1) Dielectric method ( $\tan\delta$  vs temperature plots in Fig. 4); (2) Pyroelectric method (temperature vs pyroelectric coefficient ( $p$ ) plots in Fig. 5 (b)).

The dielectric method reveals that  $T_d$  decreased after doping with  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  from 115 °C (Sample A) to around 40 °C for Sample C as mentioned in 3.2. Sample D shows an unexpected depolarization temperature which is more than 5 °C higher than the  $T_d$  for Sample C whereas it should shift to lower temperature with increasing the A and B sites dopant content (Fig. 4).

The second method to obtain the  $T_d$  is from the maximum pyroelectric coefficient ( $p$ ) value. It is widely known that at phase transitions, maximum  $p$  values can be observed [21–23,25,44–46]. In this study, the lower phase transition (*FR to relaxor AFE*) temperature of the NBT-0.06BT [38,41,46,47] was utilised to identify the  $T_d$  with observed values of 61, 55, and 33 °C for Samples B, C, and D, respectively. Unfortunately, the exact  $T_d$  could not be identified for Sample A by this method due to the upper temperature limit of equipment being at 90 °C (Fig. 5 (b)).

The reason behind the observed decrease in the  $T_d$  might be attributed to two factors. Firstly: the generation of A-site vacancies due to  $\text{La}^{3+}$  replacement of  $\text{Na}^+$  and/or  $\text{Ba}^{2+}$  [25,35]. The ferroelectric domain stability is affected by the coupling between A-site cations and ferroelectric ( $\text{TiO}_6$ ). This stability decreases with the increase of A-site dopant content [23].

Doping with B-site donor can also create A-site vacancies, which will maintain the charge neutrality in the structure [22,48,49]. Secondly: the reduction of the degree of freedom for B-site ion movement in the TiO<sub>6</sub> octahedra due to doping with B-site ions which have a bigger ionic radius, such as the Ta<sup>5+</sup> (0.64 Å) for Ti<sup>4+</sup> (0.605 Å) [16,32,33]. The Ta<sup>5+</sup> will occupy a larger space in oxygen octahedral than the Ti<sup>4+</sup> due to the difference in the ionic radii. As a consequence of this, the ferroelectric properties become weakened [16,22,50]. As a result of both effects, these induce the phase transition from ferroelectric (*FE*) to relaxor anti-ferroelectric (*relaxor AFE*) to be at lower depolarization temperature [3,12,22,23,46,51].

### 3-4. Effects of La and Ta on pyroelectric properties

The figure of merits (*FOMs*) represent a standard and an efficient way to evaluate pyroelectric material performance [9,26], and have been characterized as key parameters in the pyroelectric applications [38].

The calculation of the *FOMs* is based on the values of pyroelectric coefficient, relative dielectric permittivity, the dielectric loss tangent and the specific heat [52]. There are several types of *FOMs* which are more appropriate to certain pyroelectric materials applications and are derived from these application requirements [9,19,38].

In this study, the pyroelectric coefficient (*p*) of xLa-NBT-0.06BT-yTa was measured from 20 to 90 °C for all samples.

The measurements of the *p* and *FOMs* were carried out using the Equations 2 - 6 [10,13,19,21].

$$I_p = pA \frac{dT}{dt} \quad (2)$$

$$F_1 = \frac{p}{Cv} \quad (3)$$

$$F_v = \frac{p}{Cv\epsilon_0\epsilon_r} \quad (4)$$

$$F_D = \frac{p}{Cv\sqrt{\epsilon_0\epsilon_r} \tan\delta} \quad (5)$$

$$F_c = \frac{p}{\sqrt{\epsilon_r}} \quad (6)$$

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 ( $2.8 \text{ JK}^{-1}\text{cm}^{-3}$ , quoted from [19]),  $\epsilon_r$  the relative dielectric permittivity and  $\epsilon_0$  the permittivity of free space.

Fig. 5(b) shows the variation in pyroelectric coefficient ( $p$ ) as a function of temperature for xLa-NBT-0.06BT-yTa from 20 to 90°C. Samples B and C show very similar profiles differentiated only by their own relative  $T_d$  values which coincide with the maximum observed  $p$  values for the Samples. The  $T_d$  value for Sample A clearly lies outside the measurement window as previously mentioned so it is difficult to comment on its likely profile. Although all sample compositions are believed to be at the MPB according to the XRD results, Sample D shows significantly different responses to B and C. There is a clear evidence of a broad  $p$  maximum for Sample D, which indicates a relaxor phase transition, and the peak value of  $5.4 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$  at  $T_d$ , although it is small compared to Samples B and C, it still represents a better value than PZT. **The higher concentration of  $\text{La}^{3+}$  dopant can give lower pyroelectric coefficient for NBT-0.06BT at  $T_d$  because it shifts the composition outside MPB [23] and also the A-site vacancies created by doping  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  may locate outside the grain boundary, which suppresses the movement of grain boundaries, and**

therefore reduces the polarisation. As a result, it significantly decreases the pyroelectric coefficient for Sample D.

The pyroelectric results seem strongly affected by the  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  concentrations as well as the depolarization temperature.

The shape of the profiles for samples B and C may be indicative of two phase changes, ((1 and 2) in Fig.5 (b)) taking place within the temperature window. According to the (1-x)NBT-xBT phase diagram ( Fig 5 (a))[4], by  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  co-doping, the triple point was lowered, which means the phase transition from FE to AFE occurs at lower temperature and at the same time, MPB was shifted either to BT-poor end (in case La replaces Na and/or Bi and Ta replaces Ti) or BT-rich end (in case La replaces Ba and Ta replaces Ti). Thus the two phase changes are from ferroelectric MPB ( $Rh + Tr$ ) to ferroelectric ( $Tr$ ), (Fig. 5 (b), phase change 1) and then from ferroelectric ( $Tr$ ) to antiferroelectric (Fig.5 (b), phase-change 2).

At RT, the  $p$  values show an increase for Samples A to C. This trend can possibly be linked to the microstructure change of these samples. The trend in the values of c/a ratio in Table 1 matches the trend in  $p$  values. Sample C has the largest value which means that it has a more tetragonal unit cell which contributes to a greater pyroelectric response.

The huge increase in the pyroelectric value at  $T_d$  is clearly linked to the effect of the phase transition as confirmed in literature [1,25,41,44,46,52–54]. At RT, the pyroelectric coefficient values for Samples B and C are higher than those of PZT and other lead-free ceramic compositions (Tables 3 and 4) [9,41,42,52].

At RT, the  $F_i$  and  $F_v$  values show an increase from Samples A to C then decrease and at  $T_d$ , they show an even larger increase. Samples B and C show the optimum values at RT and  $T_d$  respectively, which is due to the large  $p$  values and lower  $\epsilon_r$  of these two samples achieved at

RT and  $T_d$ . These values are higher than those of PZT and other lead-free ceramic compositions at RT (Tables 3 and 4).

$F_D$  values of all samples at RT and 90°C or  $T_d$  show lower values; however,  $F_D$  values for doped samples are much less than for undoped sample. These values for Sample B, C, and D may be linked to the higher values of the relative permittivity and the dielectric loss than the undoped sample though the pyroelectric coefficient values of Samples B and C are quite higher than its value in Sample A.

The  $F_C$  values of xLa-NBT-0.06BT-yTa at RT and at three of frequencies from 33 to 1000 (Hz) were calculated and listed in Table 5. In general, the materials suitable for infrared detectors should have the  $F_C$  threshold value at  $\sim 3 \pm 1 \times 10^{-9} \text{ C.cm}^{-2} \cdot \text{°C}^{-1}$  [8]. The composition of 0.002La-NBT-0.06BT-0.002Ta (Sample B) presents  $F_C$  values which are suitable for infrared detectors at RT and this frequency range (Table 4). However, Samples A, C, and D show  $F_C$  values which are either less than the threshold value (Samples A and D) or higher than its value (Samples C) (Table 5). Rodríguez-Ruiz *et al.*, [8] calculated the  $F_C$  of 0.935Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-0.065BaTiO<sub>3</sub> ceramics which equals to  $1.44 \times 10^{-9} \text{ C.cm}^{-2} \cdot \text{°C}^{-1}$ , this value lower than the threshold value. The high  $F_C$  values for Sample B are due to the high  $p$  and the low relative permittivity.

The stability of pyroelectric materials with frequency and temperature represents one of the important parameters in pyroelectric applications [55]. Figures 6 (a, b, and c) and 7 (a and b) present the FOMs ( $F_V$ ,  $F_D$ , and  $F_C$ ) dependence of xLa-NBT-0.06BT-yTa ceramics on frequency and temperature. The  $F_V$ ,  $F_D$ , and  $F_C$  show an excellent frequency stability at the whole measurement window. However, Sample C (Figure 6 (b)) presents a fluctuation in  $F_D$  at frequency ranging from 33 to 200 Hz, which shows the highest value  $\sim 20.33 \text{ (}\mu\text{Pa}^{-1/2}\text{)}$  at 33 Hz and then decreases to  $14.85 \text{ (}\mu\text{Pa}^{-1/2}\text{)}$  at 80 Hz. After that,  $F_D$  increases again to  $16.04 \text{ (}\mu\text{Pa}^{-1/2}\text{)}$  at 200 Hz (Figure 6 (b)).

$F_v$  and  $F_D$  show two different temperature dependences in the measurement window. In Figure 7, Samples A and D show reasonably stable profiles, while Samples B and C show an increasing dependence at the same measurement window. The unstable profile of  $F_v$  and  $F_D$  for Samples B and C follows the similar trend in pyroelectric coefficient that highly increases with rising temperature (Figure 5).

### **Conclusion**

$\text{La}^{3+}$  and  $\text{Ta}^{5+}$  co-doping in NBT-0.06BT ceramics does not significantly change the crystal lattices and the doped samples remain in MPB region. Depolarization temperature ( $T_d$ ) was significantly reduced and pyroelectric coefficient of NBT-0.06BT ceramics greatly increases both at room temperature and  $T_d$  upon doping  $\text{La}^{3+}$  (0.2 - 0.5%) and  $\text{Ta}^{5+}$  (0.2%). FOMs,  $F_i$ ,  $F_v$  and  $F_C$ , are increased with the dopants with  $F_C$  value suitable for infrared detector application at RT. The pyroelectric coefficient of  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  co-doped NBT-0.06BT shows one order of magnitude higher than those observed in PZT materials and other lead-free compositions, and also the FOMs are comparable with or even better than those shown in PZT and other lead-free ceramics, demonstrating that  $x\text{La-NBT-0.06-yTa}$  ceramics, particularly at  $0.2 \leq x \leq 0.5$  (%) and  $y = 0.2\%$ , are promising materials for infrared detectors and other pyroelectric applications in a wide temperature range.

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**Figures and tables caption:**

Figure 1: (a) XRD patterns of NBT-0.06BT and xLa-NBT-0.06BT-yTa; (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 46.0° to 47.5°.

Figure 2: SEM morphology of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.

Figure 3: Relative permittivity ( $\epsilon_r$ ) and loss tangent ( $\tan\delta$ ) vs temperature for (a) NBT-0.06BT, (b) 0.002La-NBT-0.06BT-0.002Ta, (c) 0.005La-NBT-0.06BT-0.002Ta and (d) 0.01La-NBT-0.06BT-0.002Ta at three different frequencies 1, 10 and 100 (kHz), where

-----  $\epsilon_r$ -1    -----  $\epsilon_r$ -10    - - - -  $\epsilon_r$ -100    ———  $\tan\delta$ -1    ———  $\tan\delta$ -10    ———  $\tan\delta$ -100

Figure 4: The identification of the  $T_d$  values of all samples by dielectric method (loss tangent ( $\tan\delta$ ) against temperature (°C)) for all samples at 1 kHz, where

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

Figure 5: (a) Part of the (1-x)NBT-xBT phase diagram; (b) pyroelectric coefficient ( $p$ ) vs temperature for all samples and the identification of the depolarization temperature ( $T_d$ ), where

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

The two phase changes in Samples B and C that correspond to the change of FE( $Rh + Tr$ ) to FE( $Tr$ ) (phase change 1) and the change of FE( $Tr$ ) to AFE (phase change 2) were pointed out in the (1-x)NBT-xBT phase diagram (Fig5 (a)).

Figure 6: FOMs ( $F_v$ ,  $F_D$ , and  $F_C$ ) vs. frequency ranging from 33 to 2000 Hz. (a)  $F_v$  vs.  $f$ ; (b)  $F_D$  vs.  $f$  and (c)  $F_C$  vs  $f$  where, ----- $F_v$ ,  $F_D$ , and  $F_C$ -Sample A; -----  $F_v$ ,  $F_D$ , and  $F_C$ -Sample B; -----  $F_v$ ,  $F_D$ , and  $F_C$ -Sample C; and -----  $F_v$ ,  $F_D$ , and  $F_C$ -Sample D.

Figure 7: FOMs ( $F_v$  and  $F_D$ ) vs. temperature ranging from 25 to 55 °C. (a)  $F_v$  vs. T and (b)  $F_D$  vs. T, where, ----- $F_v$  and  $F_D$  -Sample A; -----  $F_v$  and  $F_D$  -Sample B; -----  $F_v$  and  $F_D$ -Sample C; and -----  $F_v$  and  $F_D$ -Sample D.

Table 1: Lattice parameters ( $\text{\AA}$ ),  $c/a$  ratio and average grain size values of all NBT-0.06BT and  $x\text{La-NBT-0.06BT-yTa}$  ceramic compositions.

Table 2: The relative permittivity ( $\epsilon_r$ ) and loss tangent ( $\tan\delta$ ) values at room and depolarization temperatures.

Table 3: Pyroelectric coefficient ( $p$ ) and FOMs ( $F_i$ ,  $F_v$ , and  $F_D$ ) results at RT of NBT-0.06BT and  $x\text{La-NBT-0.06BT-yTa}$  in the present study and literature.

Table 4: Pyroelectric coefficient ( $p$ ) and FOMs ( $F_i$ ,  $F_v$ , and  $F_D$ ) results at  $T_d$  of NBT-0.06BT and  $x\text{La-NBT-0.06BT-yTa}$  ceramics in the present study and literature.

Table 5: The figure of merit  $F_C$ , results at room temperature and wide frequency range from 33 to 1000 (Hz) of NBT-0.06BT and  $x\text{La-NBT-0.06BT-yTa}$  ceramics in the present study and literature.