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Structure–property relation to enhance the piezoelectric and ferroelectric properties in $(Na_{0.5}Bi_{0.5})TiO_3$-based non-MPB lead-free piezoelectric ceramics

D. E. Jain Ruth[1] · L. Venkidu[2] · B. Sundarakannan[2]

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Abstract

Lead-free sodium bismuth titanate-based (NBT) non-MPB solid solutions for different substitutions were synthesized by solid-state reaction method and their structural relation with ferroelectric and piezoelectric properties were analyzed. Extrinsic contribution to piezoelectric coefficient more particularly non-180° domain reorientation was facilitated by enhanced mobility. Minimum strain and low rhombohedral lattice distortion improves mobility and increases the piezoelectric coefficient which in turn enhances remnant polarization and reduces coercive field. Regarding substitution in NBT, as a rule of thumb, substitution of high polarisable ion in the A-site and low polarisable ion in the B-site enhances the piezoelectric coefficient in non-MPB NBT-based systems.

1 Introduction

Bulk piezoelectricity have been reported in many lead-free ceramic structures namely perovskite, tungsten bronze, bismuth layer-structured ferroelectrics and even grain-oriented non-ferroelectric materials. However, in randomly oriented ferroelectric perovskite the higher symmetry prototype cubic perovskite leads to improved poling and subsequently possess enhanced piezoelectric coefficient than other lead-free material structures [1]. The interesting property of ferroelectricity arises from the oxygen octahedron and the corner linking atoms with this oxygen octahedral cage [2].

Sodium bismuth titanate (NBT) is a strong ferroelectric lead-free material and possesses perovskite structure. NBT has been considered as a potential substitute for $Pb(Zr,Ti)O_3$-based compositions which rules the whole commercial and technological world. NBT possess large remnant polarization ($P_r = 38\ \mu C/cm^2$), high Curie temperature above RT ($T_c = 320\ °C$) and medium piezoelectric coefficient ($d_{33} = 73$ pC/N). But, the major drawback of NBT is its high coercive field that inhibits its application in functional devices. Therefore, the vital need to realize NBT in par with $Pb(Zr,Ti)O_3$-based compositions for functionality and commercialization is enhancing the remnant polarization and piezoelectric coefficient and curtail down the coercive field [1–7].

From the application point of view, it is a known fact that memory devices need high remnant polarization and low coercive field and major parameters for actuators are high piezoelectric coefficient and strain [2]. In general, the piezoelectric coefficient $d_{33} = 2\varepsilon_r P_r S$, which is directly proportional to dielectric constant, remnant polarization and strain [8]. Hence increase in piezoelectric coefficient leads to enhancement in other parameters. Moreover, decreasing the coercive field is an important task in NBT-based ceramics.

In the present study, five NBT-based non MPB systems namely A-site rubidium substituted sodium bismuth titanate (NBT:Rb), sodium bismuth titanate–bismuth magnesium titanate [$(1-x)$NBT$-x$BMT], sodium bismuth titanate-bismuth magnesium zirconate [$(1-x)$NBT$-x$BMZ], sodium bismuth titanate–bismuth magnesium zirconate–bismuth magnesium tittante [$(1-x-y)$NBT$-x$BMT$-y$BMZ] and sodium bismuth titanate–bismuth ferrite [$(1-x)$NBT$-x$BFO] solid solutions were analyzed. The crystal structure is an important factor in piezoelectric ceramics, whereas in perovskite structure tolerance factor and ionic polarizability plays a crucial role in stability as well as piezoelectric and ferroelectric behavior of these materials [9].

✉ D. E. Jain Ruth
hccjradp@gmail.com

[1] Department of Physics, School of Physical, Chemical and Applied Sciences, Pondicherry University, Puducherry 605014, India

[2] Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu 627012, India

In this work, the tolerance factor, ionic polarizability and intrinsic structural parameters particularly lattice distortion and homogeneous strain to enhance the piezoelectric coefficient, remnant polarization and dielectric constant and lower the coercive field were evaluated. The evaluated parameters were compared with previously reported NBT-based non-MPB systems and a consolidation was carried out to correlate the structural parameters to improve the piezoelectric coefficient and ferroelectric properties.

2 Experimental

All the samples were synthesized by conventional solid-state reaction method and the preparation process were explained elsewhere [10–14]. Powder X-ray diffraction was recorded using Cu K_α radiation of the diffractometer (PANalytical XPERT-PRO, Netherlands).From the XRD data homogeneous strain (δ) and lattice distortion were calculated. Room temperature frequency dependent dielectric measurement was done using LCR meter (HIOKI 3532-50 LCR Hi tester, Japan). Ferroelectric nature was examined using P–E loop tracer, Precision Multiferroic Tester PMF0713-334 (Radiant Technologies, USA) by applying an ac voltage of 5500 V at 10 Hz. High density pellets were poled under a DC electric field of 4–6 kV/mm for 15 min and piezoelectric coefficient (d_{33}) was measured using d_{33} meter YE2730A (American piezo,USA).

In the present work, five systems were prepared and their structural and electrical properties were studied. Since, main objective of the present work is to enhance the piezoelectric coefficient (d_{33}), remnant polarization (P_r), dielectric constant (ε_r) and reduce the coercive field (E_c) of NBT through substitution; it is pertinent to consolidate the different systems. Each substitutional system has yielded highest d_{33} value for one particular mole fraction. Such a mole fraction from each system is taken for consolidation and considered for further analysis. For consolidation of the present work with the literature reports, ten systems from literature with highest d_{33} values were selected and all the parameters were calculated as done for the present work. Criteria for the selection of NBT based systems from literature were; (i) systems exhibiting phase purity (ii) systems possessing electrical neutrality and (iii) systems maintaining rhombohedral R3c structural symmetry.

3 Results and discussion

Figure 1 shows the piezoelectric coefficient (d_{33}), remnant polarization (P_r), dielectric constant (ε_r) and coercive field (E_c) at the particular mole fraction of the five systems for which the values are highest. From Fig. 1, it is inspected that: (i) the piezoelectric coefficient (d_{33}) is increased for all substitutions than pure NBT. But the highest d_{33} is obtained for BMZ substitution in NBT. (ii) Large remnant polarization (P_r) and increased dielectric constant (ε_r) are observed for Rb substitution in the A-site of NBT. (iii) Even though the coercive field (E_c) is reduced in all systems, drastic decrease in E_c is noticed for NBT-BMT-BMZ ternary system.

Intrinsic structural parameters homogenous strain (Fig. 2) and rhombohedral lattice distortion (Fig. 3) of the five NBT-based systems for different mole fraction of substitution are shown. It is observed that for all substitutions the mole

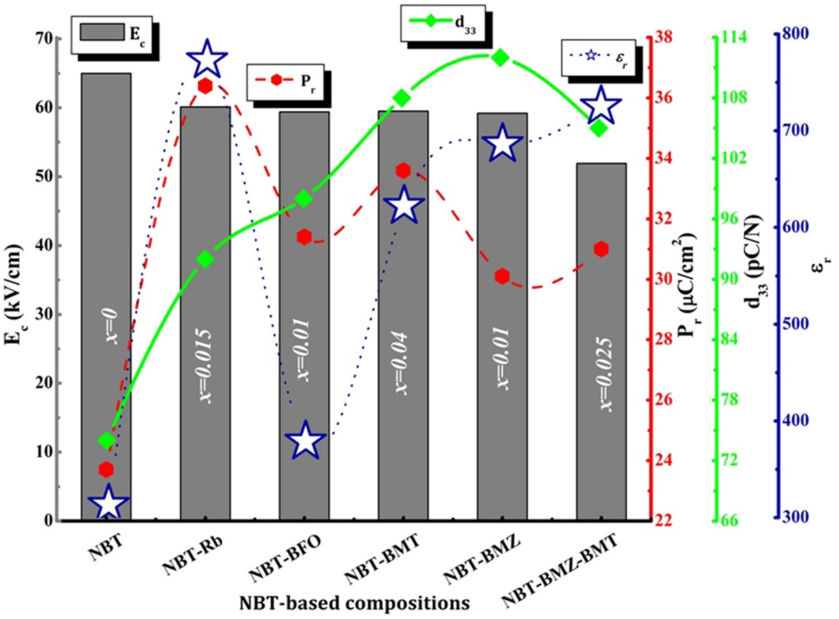

Fig. 1 Piezoelectric coefficient, remnant polarization, coercive field and dielectric constant of NBT-based non-MPB solid solutions for a particular mole fraction of substitution

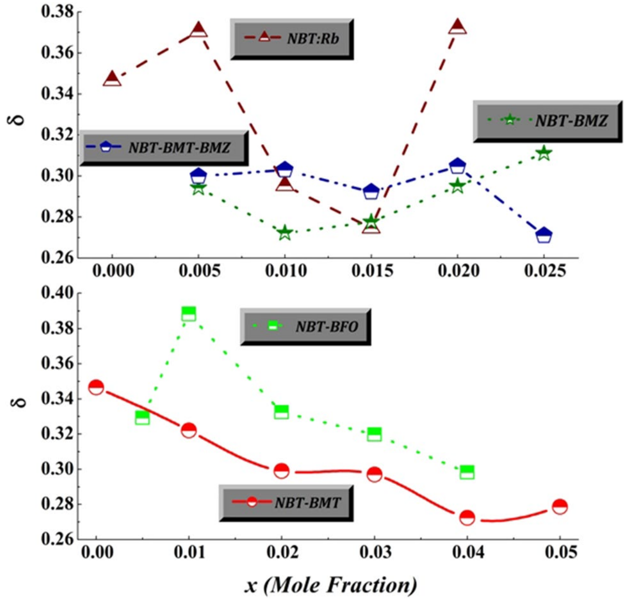

Fig. 2 Homogeneous strain of different NBT-based systems with different compositions

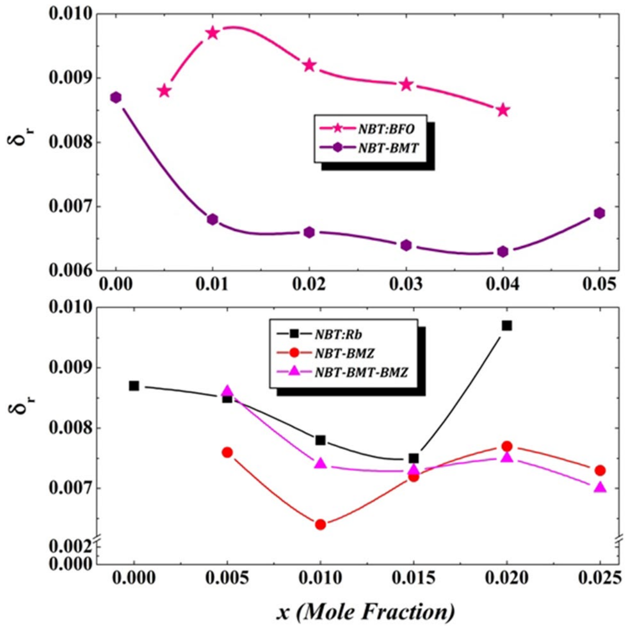

Fig. 3 Rhombohedral lattice distortion of different NBT-based systems with different compositions

fraction with enhanced piezoelectric, ferroelectric and dielectric properties show both the parameters minimum than all other compositions. But a different trend is recognized for BFO substituted system. In BFO substituted sample the highest piezoelectric and ferroelectric values are obtained for $x=0.01$ mole fraction which has maximum strain and lattice distortion.

Room temperature P–E hysteresis loop of the five NBT-based systems at the mole fraction having the highest P_r and lowest E_c is shown in Fig. 4. Distinct saturated ferroelectric loops with enhanced spontaneous polarization (P_s) and remnant polarization (P_r) are observed. Softening of coercive field is noticed in all substitutions. More evidently a significant decrease in E_c is speculated for NBT–BMT–BMZ ternary system. But only a small change is inferred for all other systems. Also highest P_s and P_r are observed for Rb substitution in the A-site of NBT than other substitutions which has large polarisability than all other substituted ions.

Figure 5 shows the room temperature frequency dependent dielectric constant of the five NBT-based systems at the mole fraction having the highest ε_r. For all the systems the dielectric constant is high at RT and it gradually decreases as the frequency increases. At low frequencies all the polarization mechanisms namely space-charge, ionic, dipolar, orientation and electronic are active and contribute to the system. As the frequency increases the polarization with small relaxation time will respond and so, only electronic contribution is present. Therefore the dielectric constant decreases at high frequencies. Above 100 kHz a lower curve is noticed in all samples which are represented as resonance frequency at which the phase reversal occurs. Occurrence of resonance peaks at high frequencies and gradual decrease in dielectric constant with increase of frequency is the peculiar feature of ferroelectrics [15, 16]. A significant enhancement in dielectric constant is observed for all substitutions. Among all substitutions Rb- substituted NBT shows the maximum dielectric constant. BFO substituted system shows medium increase only compared to other samples which may be due to large strain and distortion of the lattice.

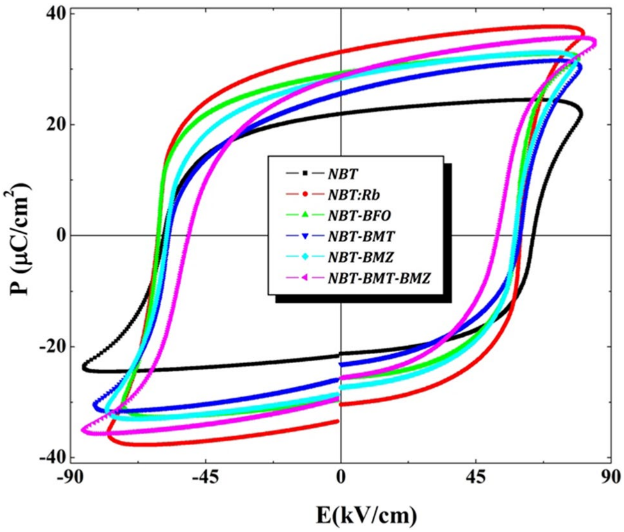

Fig. 4 Room temperature P–E hysteresis loop of different NBT-based systems for a particular mole fraction of substitution

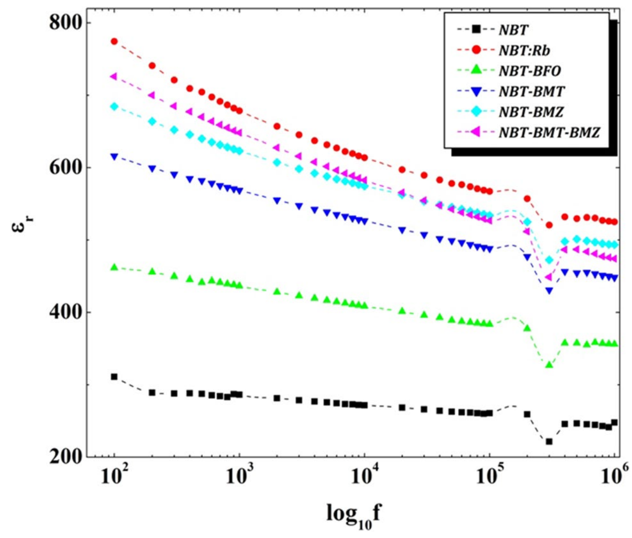

Fig. 5 Room temperature frequency dependent dielectric constant of different NBT-based systems for a particular mole fraction of substitution

An interesting feature of perovskite structure is its ability to substitute wide variety of cations. Stability of the perovskite structure depends on the ionic radii of the ions which can be described by the tolerance factor (t) and is independent of the valency of the substituted ions. Tolerance factor't' is calculated using the relation:

$$t = \frac{R_A + R_o}{\sqrt{2}R_B + R_o}$$

where R_A, R_B, R_O are the ionic radii of A, B, and O ions. A material preserves the perovskite structure type still t lies between 0.78 and 1.05 as evidenced by Goldschmidt. When t = 1 the size of the A- and B-site cations perfectly matches the space provided by the oxygen anions. Lower values of t indicate smaller A-site cations and favors tilting of the BO_6 octahedra [2, 9]. Electrical neutrality condition for rhombohedral structure leads to $\sum_{i=1}^{m} x_{A_i} n_{A_i} + \sum_{k=1}^{n} x_{B_k} n_{B_k} = 6$ with x_{A_i}, x_{B_i} the fractions of the ions and n_{Ai}, n_{Bi} the valencies of the ions, whereas the stoichiometry condition is given as $\sum_{i=1}^{m} x_{A_i} n_{A_i} = 1$ and $\sum_{k=1}^{n} x_{AB_k} n_{B_k} = 1$. Average ionic radius of A- and B-site are calculated using the formula: $\sum_{i=1}^{m} x_{A_i} R_{A_i} = \overline{R_A}$ and $\sum_{k=1}^{n} x_{B_k} R_{B_k} = \overline{R_B}$. Other factors which can be taken into account for substitution besides the ionic radii are polarizability and nature of bonds. Average polarisability of A and B-site are found using the equations: $\sum_{i=1}^{m} x_{A_i} P_{A_i} = \overline{P_A}$ and $\sum_{k=1}^{n} x_{B_k} P_{B_k} = \overline{P_B}$ [9].

Hence, tolerance factor, average ionic radius of A and B-site and average polarisability of A and B-site are calculated and the values are tabulated in order to find a thumb rule for enhancement of d_{33} for the selection of substitutional elements in sodium bismuth titanate-based lead-free piezoelectric ceramics [17].

From Tables 1 and 2 it is found that (i) increasing the average ionic radius of A-site as well as B-site, (ii) simultaneous decrease of average ionic radius of A-site and increase of B-site, and (iii) decrease of both A and B-sites enhances the piezoelectric coefficient. Tolerance factor is not a major factor in improving d_{33}. Increase in average polarisability of A-site and decrease in polarisability of B-site is the key factor in increasing piezoelectric coefficient in present and literature reports. Therefore, a thumb rule for the selection of substitutional element to obtain better piezoelectric coefficient is substitution of high polarisable ions in the A-site and low polarisable ions in the B-site.

The piezoelectric properties of polycrystalline ferroelectric ceramics are generally dependent on both intrinsic and extrinsic mechanisms. Intrinsic contributions are the result of lattice strain due to the displacement of the cations. Changes in polarization of the unit cell are accompanied by a preferential change in the cell axes [9]. At the same time, the mole fraction with highest d_{33} has minimum lattice distortion and homogeneous strain. Intrinsic contributions to the total piezoelectric coefficient of a typical PZT composition are less than 50% at room temperature [16, 27]. The remaining contributions to the piezoelectric effect are extrinsic in nature and arise due to domain wall displacement, defect dipoles, inter phase boundary motion, and inter granular interactions. In the polycrystalline state, a

Table 1 Intrinsic parameters of NBT-based systems in the present work

S. No.	NBT substitutional systems	*x* mole fraction	d_{33} pC/N	Average ionic radius of A-site	Average ionic radius of B-site	Tolerance factor t	Average polarisability of A-site	Average polarisability of B-site
1	NBT-BMZ	0.01	112	1.3446	0.6062	0.9675	3.9816	2.9236
2	NBT-BMT	0.04	108	1.3432	0.6073	0.9665	4.0464	2.8978
3	NBT-BMT-BMZ	0.025	105	1.3437	0.6085	0.9661	4.1472	2.9067
4	NBT-BFO	0.01	98	1.3446	0.6045	0.9683	3.9816	2.9288
5	NBT:Rb	0.015	92	1.34995	0.605	0.9698	4.0124	2.93
6	NBT	0	74	1.345	0.605	0.9681	3.96	2.93

Table 2 Intrinsic parameters of NBT-based systems from the literature reports

S. No	NBT substitutional systems	*x* mole fraction	d_{33} pC/N	Average ionic radius of A-site	Average ionic radius of B-site	Tolerance factor t	Average polarisability of A-site	Average polarisability of B-site	Ref. No.
1	NBT-BT	0.055	280	1.359	0.605	0.9732	4.094	2.93	[18]
2	NBT-BA	0.08	130	1.3414	0.5994	0.9695	4.133	2.759	[19]
3	NBT:Li	0.16	108	1.3226	0.605	0.9602	3.864	2.93	[20]
4	NBT-BMN	0.007	94	1.3447	0.6056	0.9677	3.975	2.925	[21]
5	NBT:La	0.0172	91	1.3337	0.605	0.9641	3.962	2.93	[22]
6	NBT-NN	0.02	88	1.3459	0.6057	0.9681	3.917	2.951	[23]
7	NBT-BCW	0.005	80	1.3463	0.6056	0.9683	3.972	2.906	[24]
8	NBT-CT	0.02	75	1.3449	0.605	0.9680	3.944	2.93	[25]
9	NBT-BS	0.02	74.7	1.3441	0.6078	0.9664	4.003	2.928	[26]
10	NBT	0	74	1.345	0.605	0.9681	3.96	2.93	[3]

ferroelectric ceramic which exhibits only 180° domain walls is $(P_r)_{max} = 0.25\ P_s$. In a rhombohedral ferroelectric with 8 possible domain states, or variants $(P_r)_{max} = 0.87\ P_s$ [16]. In the rhombohedral phase, polarization can orient along 8 possible directions. In materials with non-180° domain walls, the poling process changes the sample dimensions, because reorientation of non-180° domains involves reorientation of the spontaneous strain [9]. Small rhombohedral lattice distortion and low homogeneous strain enhances the mobility of domains and this result in facilitation of non-180° domain reorientation. In ferroelectric ceramics approximately 35% of piezoelectric contribution is from non-180° domain reorientation and domain switching [27]. For lowest rhombohedral distortion, the rhombhohedral domain variants become energetically closer and therefore non-180° domain reorientation is facilitated. Hence, the major result drawn from this study is reduced strain and low lattice distortion increases the mobility of domains and favors the non-180° domain orientation. Therefore the extrinsic contribution is more dominant in Rb, BMT, and BMZ substituted NBT-based systems as well as in ternary system. Hence extrinsic contribution is facilitated for all the substituted samples. For BFO substituted samples a different mechanism is observed. Increase of rhombohedral lattice distortion and strain leads to high piezoelectric coefficient which means the intrinsic contribution is more influenced than extrinsic contribution for enhancement of piezoelectric coefficient.

4 Conclusion

From the five NBT-based non-MPB systems studied in the present work reveals that low strain and minimum distortion are responsible for improved piezoelectric and ferroelectric behavior except BFO substituted system. In BFO substituted system large strain and high distortion showed improved ferroelectric and piezoelectric properties which mean intrinsic contribution is more influential than extrinsic factors. Significant factors for increasing the piezoelectric constant in non-MPB systems maintaining rhombohedral symmetry of NBT ceramics are decreasing the average polarisability of B-site and increasing the polarisability of A-site. Also decreasing the average ionic radius of A-site and increasing the average ionic radius of B-site simultaneously enhances d_{33}. Substitution of highly polarisable ion in the A-site and low polarisable ion in the B-site is the criterion for enhancing the piezoelectric coefficient and ferroelectric properties in non-MPB NBT-based systems since piezoelectric coefficient, remnant polarization and dielectric constant are dependent on each other.

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