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# Chemical composition and tolerance factor at the morphotropic phase boundary in $(Bi_{0.5}Na_{0.5})TiO_3$-based piezoelectric ceramics

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## Abstract

A quantitative relation between the morphotropic phase boundary (MPB) composition and the tolerance factor ($t$) in $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT)-based piezoelectric ceramics was established. The $t$ value of the MPB compositions in BNT-based ceramics is around 0.990–0.993 and is independent of the types of added compounds. In order to experimentally demonstrate it, two piezoelectric ceramic systems $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{1-a}Sr_a)TiO_3$, $a = 0.05$ and 0.3 (BNBST5-$x$ and BNBST30-$x$, $x < 12\%$), were used. X-ray diffraction patterns and the lattice parameter investigations revealed that these two systems formed solid solutions within the studied stoichiometry and showed a rhombohedral–tetragonal phase transformation. Furthermore, both the structure analysis and electric properties measurements indicated that the MPB compositions were BNBST5-6 and BNBST30-8 and their corresponding $t$ value were 0.9900 and 0.9903, respectively. The results confirm the relation between the MPB composition and $t$ value and provide a method for designing new piezoelectric materials.

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*Keywords:* Perovskites; Piezoelectric properties; X-ray method; Tolerance factor; (Bi, Na)$TiO_3$

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## 1. Introduction

The most used piezoelectric materials are $PbTiO_3$–$PbZrO_3$ (PZT)-based ceramics because of their excellent piezoelectric properties. However, PZT-based ceramics are environmentally burdened materials. Therefore, it is necessary to investigate and develop environment-friendly materials to replace PZT-based ceramics.

Lead-free piezoelectric materials, such as langasite single crystal, ferroelectric ceramics with the perovskite structure, and Bi-layered structure oxides have been reported.[1] Among these materials, bismuth sodium titanate $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), firstly reported by Smolenskii et al.,[2] is considered to be a candidate to replace the widely used lead-contented perovskite materials due to its high remanent polarization ($P_r = 38\ \mu C/cm^2$). Nevertheless, the applications of BNT are limited by its high coercive field ($E_c = 7.3$ kV/mm) and its high conductivity. To solve these problems and improve the electric properties, various types of compounds were added into BNT to form solid solutions, such as $CaTiO_3$, $NaNbO_3$, $BaTiO_3$, etc.[3–17] It is found that the piezoelectric properties of these "modified" BNT-based materials were effectively enhanced when a MPB composition was attained. Usually the determination of MPB composition requires a series of time-consuming experiments and a method that allows a prediction of the MPB composition in BNT-based ceramics has not yet been reported. The present work demonstrates a relation between the MPB composition and tolerance factor and suggests a simple method to evaluate the feasibility of new BNT-based lead-free piezoelectric ceramics.

## 2. MPB–tolerance factor relation in BNT-based ceramics

The tolerance factor ($t$) is a concept for the arrangement of interpenetrating dodecahedra and octahedra in a $ABO_3$ perovskite structure introduced by Goldschmidt,[18] which is given by,

$$t = \frac{R_a + R_o}{\sqrt{2}(R_b + R_o)}$$

where $R_a$, $R_b$, and $R_o$ are the ionic radii of cation A, B and oxygen, respectively. For complex perovskite system,

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Table 1
The optimal piezoelectric constant ($d_{33}$) and electromechanical coupling factor ($k_p$) of the composition in various BNT-based piezoelectric ceramics

| BNT-based solid solution | MPB | $d_{33}$ (μC/N) | $k_p$ (%) | $t$ | Ref. |
|---|---|---|---|---|---|
| BNT | – | 58 | 12 | 0.9857 | [3] |
| $0.99BNT–0.01CaTiO_3$ | – | 50 | 13.8 | 0.9855 | [4] |
| $0.87BNT–0.13(Sr_{0.5}Ca_{0.5})TiO_3$ | – | – | 12 | 0.9855 | [5] |
| $(Bi_{0.5}Na_{0.5})_{0.9742}La_{0.0172}TiO_3$ | – | 91 | 13 | 0.9812 | [3] |
| $0.98BNT–0.02BiScO_3$ | – | 74.7 | 14.4 | 0.9844 | [6] |
| $0.995BNT–0.005Ba(Cu_{0.5}W_{0.5})O_3$ | – | 80 | 18.1 | 0.9862 | [7] |
| $0.985BNT–0.01EuTiO_3$ | – | 46 | – | 0.9828 | [8] |
| $0.98BNT–0.02NaNbO_3$ | – | 88 | 17.9 | 0.9853 | [9] |
| $0.993BNT–0.007Bi(Mg_{2/3}Nb_{1/3})O_3$ | – | 94 | – | 0.9854 | [10] |
| $0.994BNT–0.006BaNb_2O_6$ | – | 94 | – | 0.9844 | [11] |
| $0.94BNT–0.06BaTiO_3$ | O | 125 | 20 | 0.9902 | [12] |
| $0.88BNT–0.12PbTiO_3$ | O | 106.6 | 33.2 | 0.9907 | [13] |
| $0.84BNT–0.16(Bi_{0.5}K_{0.5})TiO_3$ | O | – | 31.4 | 0.9926 | [14] |
| $0.9BNT–0.05(Bi_{0.5}K_{0.5})TiO_3–0.05BaTiO_3$ | O | 163 | 28 | 0.9922 | [15] |
| $0.91BNT–0.09Ba(Ti_{0.942}Zr_{0.058})O_3$ | O | 147 | – | 0.9922 | [16] |
| $Bi_{0.49}Na_{0.3775}K_{0.075}Li_{0.02}Ba_{0.02}TiO_3$ | O | 205 | 29.0 | 0.9915 | [17] |
| $Bi_{0.495}Na_{0.3825}K_{0.075}Li_{0.02}Ba_{0.01}TiO_3$ | O | 178 | 37.0 | 0.9907 | [17] |

$R_a$ and $R_b$ are the ionic radii of composed ions normalized by the atomic ratio. For the example of $(Ba_{0.7}Sr_{0.3})TiO_3$, $R_a = 0.7 \times 1.61\,Å + 0.3 \times 1.44\,Å = 1.559\,Å$ ($R_{Ba^{2+}}/R_{Sr^{2+}} = 1.61/1.44\,Å$), $R_b = 0.605\,Å$ ($R_{Ti^{4+}} = 0.605\,Å$), $R_o = 1.40\,Å$ ($R_{O^{2-}} = 1.40\,Å$), so that $t = 1.0435$ is deduced. The ionic radii refer to those reported by Shannon.[19] In general, the perovskite structure is stable in the region $0.880 < t < 1.090$,[18] and the symmetry is higher as the $t$ value is close to 1. For example, the $t$ value of a cubic $SrTiO_3$ ($t = 1.001$) is closer to 1 than an orthorhombic $CaTiO_3$ ($t = 0.966$). The $t$ value also provides an indication about how far the atoms can move from the ideal packing positions and be still "tolerated" in the perovskite structure. It reflects the structural modification such as distortion, rotation, tilt of the octahedra.[20] These structure factors consequently affect the electric property. Recently, some investigations are trying to find out the relation between the $t$ and some material properties. For example, Reaney et al. have described that the temperature coefficient of dielectric constant ($\tau_\varepsilon$) is controlled by the $t$, and Suchomel et al. have suggested a MPB-$t$ relation in lead-based piezoelectric ceramics.[21–23] It is believed that a MPB-$t$ relation may also exists in BNT-based lead-free piezoelectric ceramics.

Plenty of research results for the BNT-based lead-free piezoelectric ceramics have been published in the past years,[3–17] and the compositions with optimal piezoelectric properties of each system are summarized in Table 1. It is shown that Table 1 can be separated into two parts according to the existence of the MPB composition and their corresponding $t$ value related to pure BNT ($t = 0.9857$). For the upper part, the chosen non-BNT end compounds cause a decrease of $t$ value in comparison with pure BNT. These systems are either difficult to form a solid solution with BNT or no phase transformation is found. For the lower part, the non-BNT end compounds make the $t$ value increase and results in a phase transformation at their MPB composition where superior piezoelectric properties are observed. The piezoelectric constant ($d_{33}$) and electromechanical coupling factor ($k_p$) of the compositions listed in Table 1 is plotted as function of $t$ in Fig. 1. It is obviously found that the $t$ values of the MPB compositions for all the types of compounds are in the range of 0.990–0.993. It implies a fact that the MPB composition for the BNT-based solid solution systems is related to the $t$ value and can be determined by adjusting the $t$ value into this region.

This observation can be explained by the $t$ value because it provides a general information for the crystal structure. For $(Bi_{0.5}Na_{0.5})TiO_3$, whose stable phase is rhombohedral ($R3c$) corresponding to a $t$ value of 0.986. If a non-BNT end compound with a higher $t$ value is added and forms a solid solution with BNT, a phase transformation may take place at certain composition when the added compound is not tolerated anymore in the rhombohedral structure. Moreover, no matter what the non-BNT end compounds are, the "tolerated" limit of the rhombohedral-BNT is approximate. Due to these reasons, the $t$ values of the MPB compositions in BNT-based ceramics should be a definite

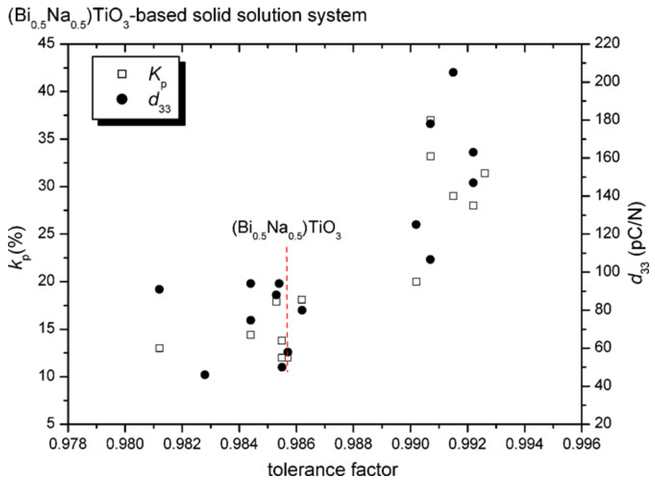

Fig. 1. Piezoelectric constant ($d_{33}$) and electromechanical coupling factor ($k_p$) against the tolerance factor ($t$) in $(Bi_{0.5}Na_{0.5})TiO_3$-based piezoelectric ceramics.

range. Referring to Table 1 and Fig. 1, this range is located at 0.990–0.993. It is worthy mentioned that the $t$ value related to MPB composition was found at an approximate range but not a definite point because the present evaluation for $t$ value simply takes ionic radii into account but ignores the other structure factors such as ionic valence and electronegativity. As a consequence, the MPB composition can be predicted by $t$ value in BNT-based solid solution systems and thus applies for the material design.

Based on the discussion presented above, the non-BNT end compound with a larger $t$ value in comparison with pure BNT is an important characteristic to induce a phase transformation and a MPB composition. Besides, the MPB composition is found at a small amount of non-BNT end compound when its $t$ value is great. Experimentally, $(Ba_{1-a}Sr_a)TiO_3$ (BST) was chosen as non-BNT end compound in this work. This design makes the $t$ value easily control by adjusting the $Sr^{2+}$ ratio in BST. Two non-BNT end members were used, either $(Ba_{0.95}Sr_{0.05})TiO_3$ (BST5) or $(Ba_{0.7}Sr_{0.3})TiO_3$ (BST30) and their $t$ value are 1.0585 and 1.0435, respectively. According to the calculation of $t$ value mentioned above, the MPB composition should locate around 0.94BNT–0.06BST5 ($t = 0.9900$) and 0.92BNT–0.08BST30 ($t = 0.9903$).

## 3. Experimental procedure

The starting materials were $Bi_2O_3$ (Alfa Aesar, 99.97%), $Na_2CO_3$ (Showa Chemical, 99.5%), $BaCO_3$ (Alfa Aesar, 99.8%), $SrCO_3$ (Alfa Aesar, 99.7%), and $TiO_2$ (anatase, Alfa Aesar, 99.9%). All compositions were prepared by a conventional solid state reaction. The powders with various stoichiometries were mixed in ethanol and ball-milled for 24 h by taking yttrium-stabilized zirconia-ball as milling medium. The mixing powders were calcined at 900 °C for 1 h to form the compositions $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{0.95}Sr_{0.05})TiO_3$ (labeled as BNBST5-$x$), and $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{0.7}Sr_{0.3})TiO_3$ (labeled as BNBST30-$x$), where $x = 0$, 2, 4, 6, 8, 10, and 12%, respectively. The calcined powders were ground and ball-milled again for 12 h to deagglomerate. The dried powders were mixed with a binder (polyvinyl alcohol) and crushed to pass through a 50-mesh sieve for granulation. The granulated powders were filled into a die of 13 mm and pressed under uniaxial pressure of 350 MPa to form a green bulk with a thickness of 1.5 mm. These bulks were sintered in a platinum crucible at various temperatures (1125–1150 °C) for 2–4 h to get dense ceramics with 97% (relative density) at least. The as sintered ceramics were polished parallel with a final 6 μm SiC abrasive grit, and silver paste was fired on the surfaces of the ceramics as electrodes. The ceramics for measuring the piezoelectric properties were poled in silicon oil at 80 °C at 6 kV/mm for 20 min. The ceramics for microstructure observation were polishing using a final grit of 0.3 μm $Al_2O_3$ abrasive and thermal etched at the temperatures below its sintering temperature to 125 °C for 5 min.

The crystal structure was investigated by X-ray diffractometer (Seimens D5000) with Cu Kα radiation and step size of 0.02° at room temperature. The X-ray diffraction pattern was refined by the Rietveld method with program GSAS,[24] the peak shape was modeled as a pseudo-Voigt function, taking into account both Gaussian and Lorentzian broadening. The microstructure was observed under a scanning electron microscope (Hitachi S4100). The dielectric constant ($\varepsilon_r$) was measured by LCR meter (Agilent 4284A) at 1 kHz. The piezoelectric coefficient ($d_{33}$) was recorded by a quasistatic $d_{33}$ meter (APC model 8000). The electromechanical coupling factor ($k_p$) was measured by means of the resonance–antiresonance method by an impedance/gain-phase analyzer (HP 4194).

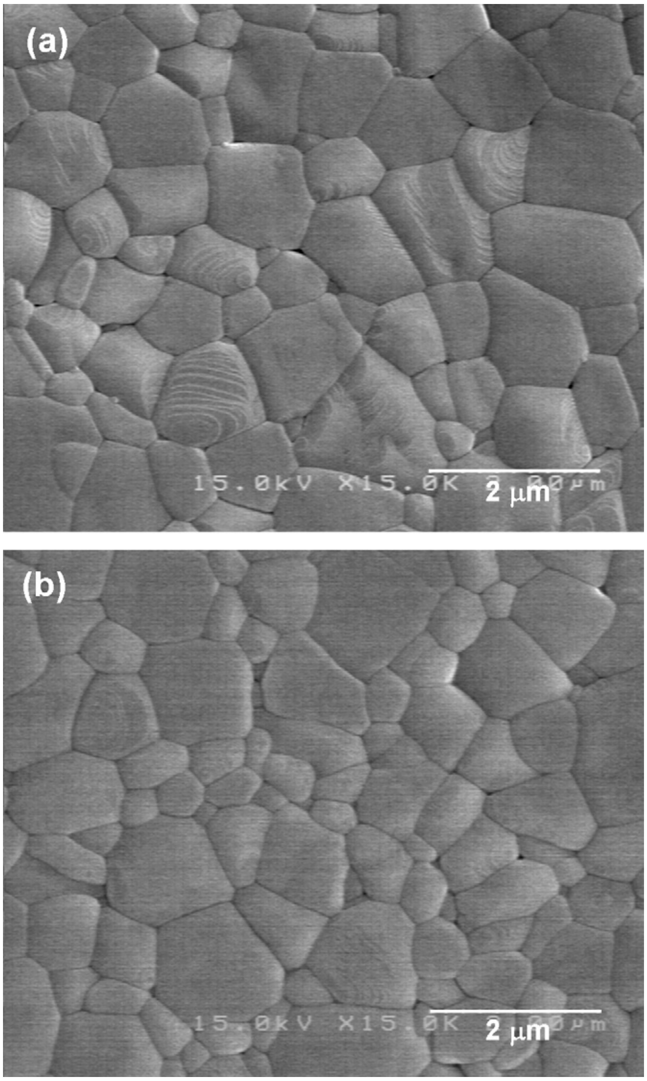

Fig. 2. SEM micrographs of (a) $0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06(Ba_{0.95}Sr_{0.05})TiO_3$ and (b) $0.92(Bi_{0.5}Na_{0.5})TiO_3$–$0.08(Ba_{0.7}Sr_{0.3})TiO_3$ ceramic sintered at 1125 °C for 4 h.

## 4. Results and discussion

The typical microstructures of BNBST5 and BNBST30 ceramics are shown in Fig. 2. The SEM observations confirm that the ceramics are densely sintered and exhibit relative densities higher than 97%. The observations also reveal that the microstructure of the different compositions do not show a significant variation.

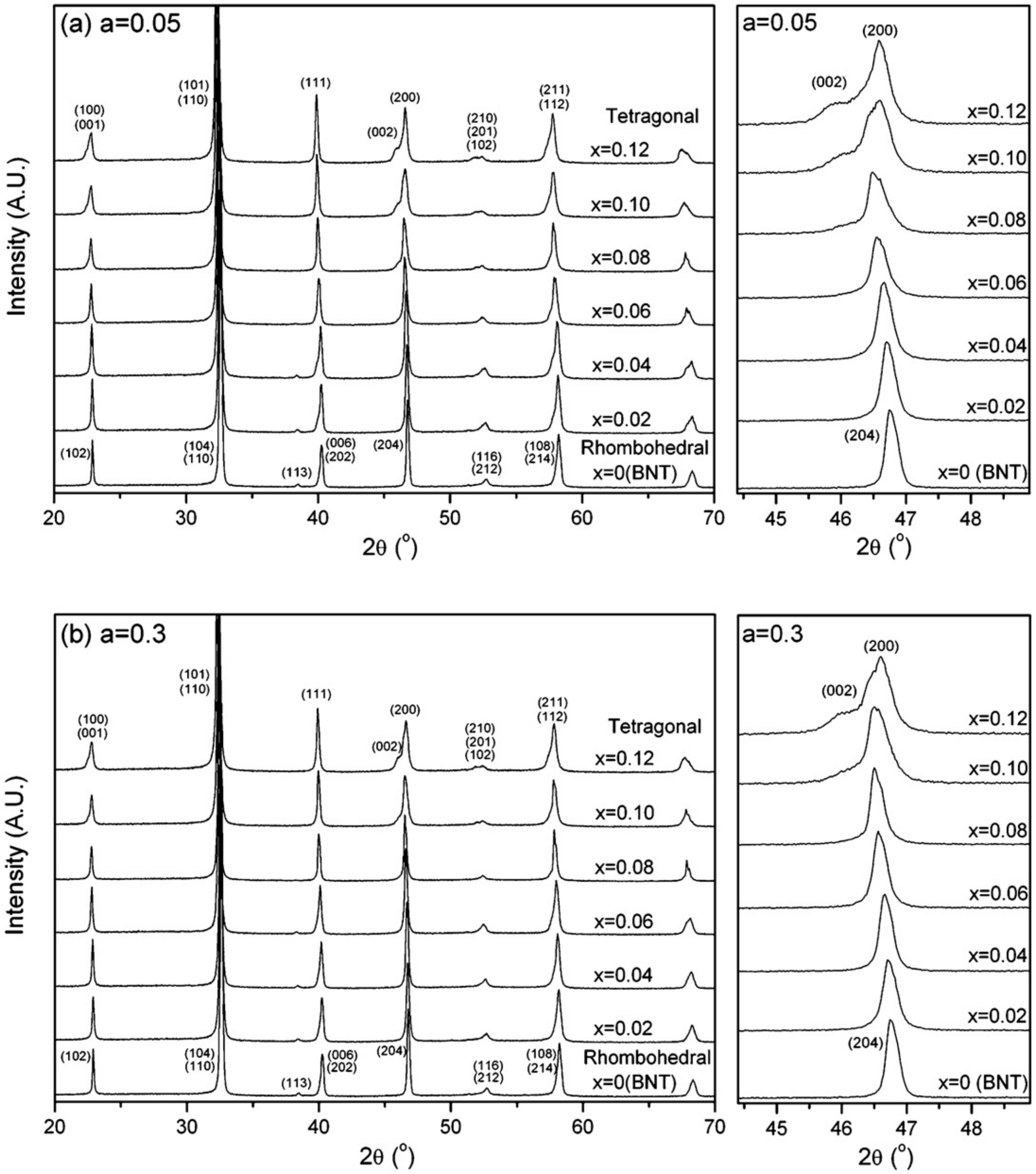

Fig. 3. X-ray diffraction patterns of (a) $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{0.95}Sr_{0.05})TiO_3$ system, and (b) $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{0.7}Sr_{0.3})TiO_3$ system.

The variation in crystal phase of BNBST5 and BNBST30 systems was investigated by XRD and their patterns are shown in Fig. 3. Generally, a single perovskite phase without extra-peaks is observed for both systems and show that a solid solution is formed. All the peaks are found to shift slightly to lower angle in comparison with pure BNT pattern, and the shift is proportional to the amount of BST in the compositions. Moreover, the (1 1 3) peak, which is assigned to rhombohedral phase is also found to decrease with increasing the amount of BST indicating an occurrence of phase transformation. Further XRD analysis is preformed over the (2 0 4) peak of BNT at 46°. As the amount of BST increases, the (2 0 4) peak undergoes an asymmetric broadening and gradually splits into two peaks that are clearly observed at BNBST5-6 and BNBST30-8, respectively. According to the pattern index, the two splitting peaks (2 0 0) and (0 0 2), are indicative of the tetragonal phase (*P*4*mm*). It is shown that the addition of BST effectively generates a phase transformation from rhombohedral (*R*3*c*) to tetragonal (*P*4*mm*) phase.

The evolution of lattice parameters of BNBST5 and BNBST30 systems calculated by the Rietveld method with XRD patterns is shown in Fig. 4. The Rietveld method allows a precise calculation for lattice parameters. It is observed that the lattice parameters increase with increasing the amount of BST in the compositions. It implies that the $Ba^{2+}$and $Sr^{2+}$ ions ($R_{Ba^{2+}}/R_{Sr^{2+}} = 1.61/1.44$ Å) with larger ionic radii have diffused into the BNT lattice ($R_{Bi^{3+}}/R_{Na^{+}} = 1.40/1.39$ Å) and result in the enlargement of lattice. A phase transformation occurs around BNBST5-6 and BNBST30-8, respectively. The phase transformation in BNBST system is due to the ion shift from its standard position of rhombohedral perovskite structure (*R*3*c*) as BST is incorporated in the composition. The increase of ion shift results in an increasing of lattice energy and finally induces a phase transformation to tetragonal phase in order to stabilize the structure.

The dielectric and piezoelectric properties ($\varepsilon_r$, $d_{33}$ and $k_p$) in BNBST systems were measured and are shown in Fig. 5. It reveals that the evolutions of these three properties as function of BST amount in BNBST5 and BNBST30 systems are similar. Those properties enhance with increasing the BST ratio and attain to their maximum at BNBST5-6 and BNBST30-8 for the two systems, respectively. The $\varepsilon_r$, $d_{33}$ and $k_p$ of BNBST5-6 are 1344, 145 pC/N, and 30.1%; for BNBST30-8 are 1480, 160 pC/N, and 30.8%, respectively. Both the X-ray diffraction patterns and electric properties indicate that the MPB compositions are BNBST5-6 and BNBST30-8 in these two systems, and their corresponding $t$ values are 0.9900 and 0.9903, respectively. The result is in agreement with the previous prediction that the $t$ value of the MPB compositions in BNT-based ceramics are at the region of 0.990–0.993. In this work, the $t$ value of BST30 is lower than that of BST5, so that a greater amount of the former has to be added to attain the MPB composition. The present work confirms the MPB-$t$ relation in BNT-based piezoelectric ceramics. Suitable composition can be determined by the evaluation of $t$ value before experimental examination. The method of MPB determination presented in this work should be suitable for other material systems. Based on the MPB-$t$ relation, a further study will be carried out to investigate the new lead-free piezoelectric ceramics.

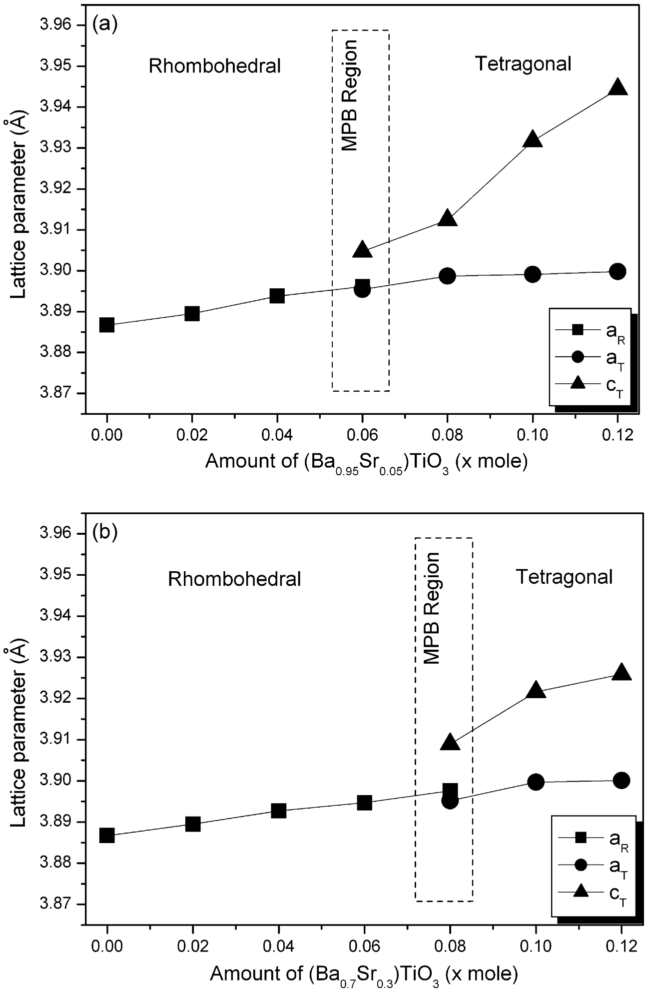

Fig. 4. Lattice parameters of (a) $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{0.95}Sr_{0.05})TiO_3$ system, and (b) $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{0.7}Sr_{0.3})TiO_3$ system.

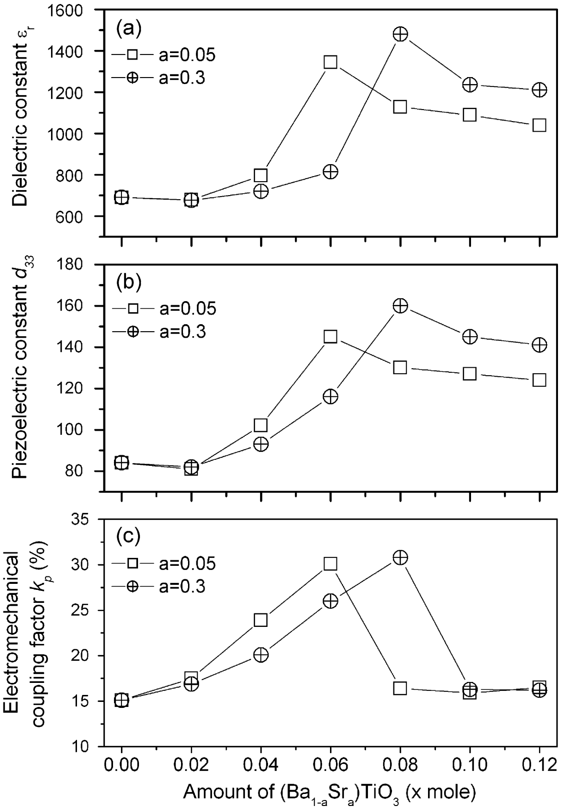

Fig. 5. (a) Dielectric constant, $\varepsilon_r$, at 1 kHz, (b) piezoelectric constant, $d_{33}$, and (c) electromechanical coupling factor, $k_p$, of $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x(Ba_{1-a}Sr_a)TiO_3$ ($a = 0.05, 0.3$) systems.

## 5. Conclusions

A quantitative relation between the MPB composition and tolerance factor ($t$) is established according to the reported literatures for various BNT-based piezoelectric ceramics. The $t$ value corresponding to the MPB composition is found to be around 0.990–0.993 and is independent of the types of added non-BNT end compounds. Experiments were carried out BNBST5 and BNBST30 systems and confirmed that a phase transformation is found when the $t$ value of a composition is within the investigated range. The BST content of the MPB composition shifts from 6% to 8% where the $Sr^{2+}$ content in $(Ba_{1-a}Sr_a)TiO_3$ increases from 5% to 30%. This work suggests an efficient method to determine the MPB composition by adjusting the $t$ value that allows a prediction of an optimal composition with excellent piezoelectric properties.

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