



# Giant strain, thermally-stable high energy storage properties and structural evolution of Bi-based lead-free piezoceramics



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## ABSTRACT

In this study, the mechanism of electric-field-induced phase transition in  $0.96[\text{Bi}_{0.5}(\text{Na}_{0.84}\text{K}_{0.16})_{0.5}\text{Ti}_{1-x}\text{Ta}_x\text{O}_3]-0.04\text{SrTiO}_3$ , (where  $0.00 \leq x \leq 0.030$ , abbreviated as BNKTT–ST) ceramics was discussed based on crystal structure and electromechanical properties. X-ray powder diffraction (XRD) showed a phase transition from mixed rhombohedral-tetragonal to single pseudocubic when  $x \geq 0.020$ . Large electro-mechanical strain of  $\sim 0.42\%$  with a dynamic piezoelectric constant ( $S_{\text{max}}/E_{\text{max}}$ ) of  $\sim 700$  pm/V at 6 kV/mm was recorded for 2 mol. % Ta content. Interestingly, at lower field of 4 kV/mm, the  $S_{\text{max}}/E_{\text{max}}$  attained the highest value of  $\sim 830$  pm/V. Poled, unpoled XRD analysis and electrical properties suggest that the relatively high  $S_{\text{max}}/E_{\text{max}}$  at  $x = 0.020$  may be attributed to the combined effect of composition and ferroelectric (FE) to ergodic relaxor (ER) phase transition. Furthermore, the energy storage density was studied as a function of both composition and temperature to demonstrate the suitability for capacitor applications. This system also revealed improved energy storage properties. Particularly, for  $x = 0.020$ , a nearly temperature-invariant large recoverable energy density ( $W = 0.65$  J/cm<sup>3</sup>) was achieved over a wide temperature range (75–150 °C). These properties demonstrate that the fabricated system might be a promising lead-free candidate for actuators and high temperature energy storage capacitor applications.

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## 1. Introduction

In the past few decades, there has been heightened interest to investigate efficient lead-free piezoelectric materials to replace toxic  $\text{Pb}(\text{ZrTi})\text{O}_3$  (PZT) based ones for electromechanical applications such as sensors, actuators, and energy harvesting devices [1]. Considerable attention has been given to  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT) based systems on account of their environmental friendliness, excellent ferroelectric (FE), and piezoelectric properties [1,2]. However, poling of pure BNT is difficult due to its high conductivity and coercive field ( $E_c$ ), resulting in comparatively low piezoelectric properties, which are insufficient for practical applications. Impedance and secondary ion mass spectrometry measurements revealed that the high conductivity and coercive fields are associated with the pinning of domain walls, caused by oxygen vacancies

due to Bi vaporization at high sintering temperatures [3–5]. In addition, thermogravimetric analysis revealed that the weight loss of BNT ceramics starts at about  $\sim 1130$  °C [6].

A variety of modifications have been introduced into pure BNT in order to form new BNT-based materials [7–14]. Analogous to PZT, improved piezoelectric properties were observed in these materials at morphotropic phase boundary (MPB) compositions. However, the MPB composition for the BNT–BKT binary system has received considerable attention due to their superior response at  $0.16 \leq x \leq 0.20$  compositions [7,8], a relatively high electric field-induced strain (EFIS) of 0.19% with a corresponding strain ( $d_{33}^* = S_{\text{max}}/E_{\text{max}}$ ) of  $\sim 240$  pm/V was observed, which is one of the most important parameters for electromechanical actuators. A large electromechanical strain, comparable to some PZT ceramics, was recently observed for lead-free BNT-based ceramics. The origin of this large strain was associated with the formation of an ergodic relaxor (ER) phase, which transformed into a long-range FE state under the influence of an external electric field (E-field) [15–20].

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BNT ceramics are also promising candidates for energy storage applications due to their large saturation polarization and relatively low remnant polarization. Dielectric materials having high energy storage properties at high operating temperatures are needed in high temperature dielectric applications, such as capacitors used in the automotive and aerospace industries [21–24]. Until now, limited attention has been given to lead-free BNT-based materials for energy storage applications.

Strontium titanate (SrTiO<sub>3</sub>) is a well-known centrosymmetric paraelectric perovskite material and has been reported to improve the field-induced strain response [25–28]. Yo et al. [29] modified Bi<sub>0.5</sub>(Na<sub>0.84</sub>K<sub>0.16</sub>)TiO<sub>3</sub> (BNKT) with SrTiO<sub>3</sub> in the  $x = 0$ –0.10 compositional range and reported an improvement in dielectric and piezoelectric properties at the MPB composition (4 mol.% SrTiO<sub>3</sub>). Moreover, our group recently reported high strain at a relatively low field in Nb-doped BNKT–ST ternary systems [25]. Liu et al. used this system to investigate the electric field dependent *in situ* transmission electron microscopy (TEM), and reported that the large strain response originated from phase transitions between the ER (in the form of mixed rhombohedral R3c and tetragonal P4bm nanometer-sized domains) and the FE R3c phases in the form of lamellar domains [30]. Modification of the BNKT–ST ternary system with Ta<sup>5+</sup> as B-site donor seems interesting in order to further investigate their structural and electromechanical properties. However, although Ta<sup>5+</sup> has been used to modify the electrical properties of other binary systems [31,32], its potential as a dopant in ternary BNKT–ST systems has not yet been explored, and to the best of our knowledge, no similar studies have been published in the literature.

The objective of this work is to develop a new lead-free system with both high field-induced strain and large electrical energy storage density for electromechanical applications. A new lead-free Ta-doped BNKT–ST ceramics were prepared by a conventional solid-state method, and the correlation between structure and properties was studied in detail. The underlying mechanism of compositional, temperature and field-induced polymorphic and structural phase transition were investigated and discussed.

## 2. Experimental procedure

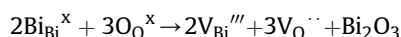
Ceramics with composition BNKTT–ST ( $x = 0$ –0.030) were synthesized by solid-state reaction (CSSR) technique. Commercially available reagent grade oxide and carbonate powders of Bi<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, SrCO<sub>3</sub>, and Ta<sub>2</sub>O<sub>5</sub> (99.9% Sigma Aldrich Co. St. Louis, MO) were used as starting materials. These materials were weighed according to the stoichiometric formula and powder mixtures were ball milled for 24 h in ethanol with zirconia balls as milling media. The slurries were subsequently dried and calcined at 850 °C for 2 h. Disk-shaped ceramic specimens with a diameter of 10 mm were then prepared by compacting the granulated powders at 98 MPa. The pressed disks were sintered at 1160 °C for 2 h in covered alumina crucibles. To minimize the evaporation of the volatile Bi and Na elements, the disks were embedded in a powder of the same composition. Electrical characterizations were performed according to our previously published methods [20,25,28].

## 3. Results and discussions

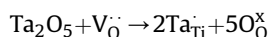
Fig. 1 shows the room temperature (RT) X-ray diffraction (XRD) patterns of unpoled BNKTT–ST,  $x = 0$ –0.030, ceramics measured in  $2\theta = 20$ –80° range. All the ceramics had a pure perovskite phase within the detection limit of XRD, showing a stable solid solution [33]. Fig. 1 (b), shows a mixed phase region of rhombohedral and tetragonal co-existed phases for compositions  $x = 0.00$ , 0.005, and 0.010, evident from (111)/(1 $\bar{1}$ 1) and (002)/(200) peaks splitting at

40° and 46° respectively. A single pseudocubic phase was identified for  $x \geq 0.020$ , where the highlighted (111)/(1 $\bar{1}$ 1) peaks of the rhombohedral phase merged into a single (111) peak and the tetragonal (002)/(200) peaks merged into a single (200) peak.

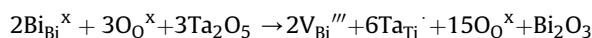
The secondary electron microscopic images of sintered BNKTT–ST ceramics with  $x = 0$ –0.030 are shown in Fig. 2. Noticeably dense microstructures were observed for all specimen. The partial substitution of Ta for Ti seemed little influence on the morphology of BNKT–ST ceramics; however, the average grain size decreased slightly with increasing Ta content. A decrease in grain size was previously observed for Ta/Nb doped BNT [32], and Bi-excess/Na-deficient BNT ceramics [34,35]. The slight decrease in grain size was attributed to an excess of A-site cation vacancies and suppression of oxygen vacancies (produced by volatilization of Bi<sub>2</sub>O<sub>3</sub> during ceramic processing) with B-site donor doping. The defect chemistry of BNT clarified that Bi-deficiency or Na-excess could induce oxygen vacancies and high oxide ion conductivity, whereas Bi-excess or Na-deficiency could suppress the presence of oxygen vacancies and oxide ion conductivity in BNT ceramics [36,37]. It was commonly observed that the presence of oxygen vacancies in metal oxides can enhance mass transport and increase ceramic grain size [38]. Hence, in this study, it is also possible that bismuth and oxygen vacancies were generated through the loss of a small amount of Bi<sub>2</sub>O<sub>3</sub> during ceramic processing [3–6] as given by the Kroger-Vink equation.



However, donor doping (such as Ta at Ti-site) can fill the oxygen vacancies and reduce oxide ion conductivity according to the equation [36].



The overall reaction is given as



Thus, the oxygen vacancies were suppressed and the cation vacancies existed along the grain boundaries rather than inside the grains, which was thermodynamically more stable. Grain boundaries would be pinned by these defects, inhibiting grain growth and resulting in relatively small grains in the case of donor doping [39].

Plots of temperature-dependent relative permittivity ( $\epsilon_r$ ) and loss factor ( $\tan \delta$ ) at different frequencies of poled samples are presented in Fig. 3, for  $x = 0.00$ , 0.010, 0.020, and 0.030 compositions. Two dielectric anomalies were observed for  $\epsilon_r$  at all measured frequencies, corresponding to the maximum dielectric constant temperature ( $T_m$ ) and FE-relaxor transition temperature ( $T_{F-R}$ ) which might be related to the thermal evolution of tetragonal (P4bm) polar nanoregions (PNRs) emerged from rhombohedral (R3c) PNRs [40–42]. All samples showed broad peaks with frequency dispersion for  $\epsilon_r$  and dielectric tangent loss near  $T \sim T_m$ , consistent with relaxor dielectric behavior of BNT-based ceramics [15–20]. The decreases in  $\epsilon_r$  with temperature for  $T > T_m$  might be related to dynamically uncorrelated PNRs due to high thermal energy in paraelectric state; on the other hand the decline in  $\epsilon_r$  with decreasing temperature for  $T < T_m$  can be related to the glassy-like ER state, where the dynamics of PNRs slow down and grow in size with decreasing temperature. Thus, the sluggish movement of correlated PNRs in the low temperature regime does not follow properly the external A.C field and causes the dispersive degradation of  $\epsilon_r$  [18,19]. The  $T_m$  value decreased slightly from ~300 °C for undoped ( $x = 0.00$ ) to ~286 °C for  $x = 0.030$ . However, above  $T_m$ , higher losses (in particular for  $x = 0.00$ ) may be related to the conduction due to evaporation of bismuth oxide during high

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