

# LEAD-FREE BNKT PIEZOELECTRIC ACTUATOR

A. Moosavi, M. A. Bahrevar and A. R. Aghaei

\* a-moosavi@srbiau.ac.ir

Received: May 2015

Accepted: January 2016

Materials and Energy Research Centre, Karaj, Iran.

**Abstract:** An actuator is a device that converts input energy into mechanical energy. According to various types of input energy, various actuators have been advanced. Displacement in the electromagnetic, hydraulic and pneumatic actuators achieve by moving a piston via electromagnetic force or pressure, however the piezoelectric actuator (piezoceramic plates) displace directly. Therefore, accuracy and speed in the piezoelectric device are higher than other types of actuators. In the present work, the high-field electromechanical response of high-quality  $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$  samples abbreviated to BNKT $x$  with  $x = 0.18, 0.20, 0.22$  and  $0.24$  ceramic materials across its MPB was investigated. The piezoelectrics and actuation characteristics were characterized. Our results indicate that  $x = 0.20$ , indeed, constitutes the best choice for the MPB composition in the system. Maximum of remanent polarization ( $37.5 \mu\text{C cm}^{-2}$ ) was obtained for  $x=0.20$ . High-field electromechanical responses were also obtained for BNKT $0.20$  samples. This material exhibited giant field induced strains of  $0.13\%$  under  $1 \text{ kV mm}^{-1}$  at room temperature.

**Keywords:** Piezoelectrics, Lead-free, BNKT, Actuator.

## 1. INTRODUCTION

Ferroelectric (FE) perovskite materials have found widespread applications in electrical devices such as piezoelectric motors and generators, transducers, sensors and actuators. Despite superior electromechanical properties of lead-based ferroelectrics like  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , they need to be replaced by lead-free compounds due to environmental concerns related to the toxicity of lead.  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT) based materials and, especially its solid solution with  $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$  (BKT), be obvious for their enhanced properties at the morphotropic phase boundary (MPB) [1]. With regard to the room temperature (RT) FE phase, BNT exhibits a remanent polarization of  $P_r=38 \mu\text{C cm}^{-2}$  and a coercive field of  $E_c=73 \text{ kV cm}^{-1}$  [2]. The high value of coercive field and the relatively high electrical conductivity of this material are considered to be its major disadvantages [1, 3]. The high value of coercive field makes domain switching and thus poling difficult and high electrical conductivity results in high dielectric loss ( $\tan \delta$ ). In order to overcome these problems, appropriate modifier compounds are preferred, which can form a MPB with BNT. This would not only decrease the

coercive field, but also enhance the electromechanical response significantly. Bismuth potassium titanate (BKT) possesses perovskite structure and form solid solutions with BNT [4, 5]. The resultant compound BNKT $x$  is a complex FE oxide with the perovskite structure, the three cations:  $\text{Bi}^{+3}$ ,  $\text{Na}^+$  and  $\text{K}^+$  all occupying the A-site of  $\text{ABO}_3$  structure with the atomic ratio of the  $\text{Bi}^{+3}$  to the combined ( $\text{Na}^+$ ,  $\text{K}^+$ ) ions being always unity. In analogy with PZT, the MPB compositions of BNKT exhibit superior piezoelectric properties [6].

In the present work, we report the high-field electromechanical response of high-quality BNKT $x$  ceramic materials across its MPB. Piezoelectric charge ( $d_{33}$ ) coefficients significantly larger than those previously reported were obtained after poling. Additionally, mechanisms responsible for the very high strain are discussed.

## 2. EXPERIMENTAL

$(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$  samples abbreviated to BNKT $x$  with  $x = 0.18, 0.20, 0.22$  and  $0.24$  were prepared using a conventional ceramic route. Raw materials,  $\text{Bi}_2\text{O}_3$  (99.9%, Aldrich),  $\text{Na}_2\text{CO}_3$  (99.95%,

Aldrich),  $K_2CO_3$  (>99.0%, Aldrich) and nano-sized  $TiO_2$  (Degussa—75% anatase, 25% rutile), were used. The powders were weighed according to the molar ratios in the chemical formula and milled in a planetary mill at 180 rpm for 2 h in ethanol. The milled powder was dried and calcined at 850 °C for 2 h. The calcined powder was reground for 3 h, and then, uniaxially pressed at 250 MPa into pellets of 13 mm diameter and 1 mm thickness. The compacts were sintered at 1150 °C for 2 h in closed alumina crucibles using heating/cooling rates of 5 °C min<sup>-1</sup>. After removal of the surface layer of the sintered pellets, density measurements were carried out by the Archimedes method.

X-ray diffraction (XRD) of the sintered ceramics was carried out using a Siemens D500 powder diffractometer with Cu K $\alpha$  radiation. A  $2\theta$  range from 20° to 50° was scanned in steps of 0.05° with a counting time of 3 s/step. Silver paste electrodes were sintered on the surfaces of the ceramic discs at 600 °C for 1 h for the electrical and electromechanical characterizations. The polarization versus electric field (P–E) hysteresis loops were recorded at RT. Voltage sine waves of 0.1 Hz was applied using a combination of synthesizer/function generator (HP 3325B) and a

high voltage amplifier (TREK model 10/40) and the charge was measured by a home built charge-to-voltage converter. For piezoelectric characterization, the ceramic specimens were poled under 4 kV mm<sup>-1</sup> at 150 °C for 15 min. The piezoelectric coefficient ( $d_{33}$ ) was measured after 24 h with a Berlincourt type meter. The actuation characteristics were characterized by measuring the direct longitudinal deformation of the discs under positive (parallel to the polarization) fields. Driving voltages of biased sine waves at a frequency of 0.1 Hz were applied by a combination of a digital signal generator (NI-SCXI 1302) and a bipolar operational power supply/amplifier (KEPCOBOP 1000 M), while deformation was measured with a linear variable differential transducer.

### 3. RESULTS AND DISCUSSION

#### 3.1. XRD Patterns

The XRD patterns of the BNKT<sub>x</sub> samples with different values of  $x$  are shown in Fig. 1, indicating only perovskite phases for all samples (Miller indices in the figure correspond to the pseudocubic symmetry). The splitting of the

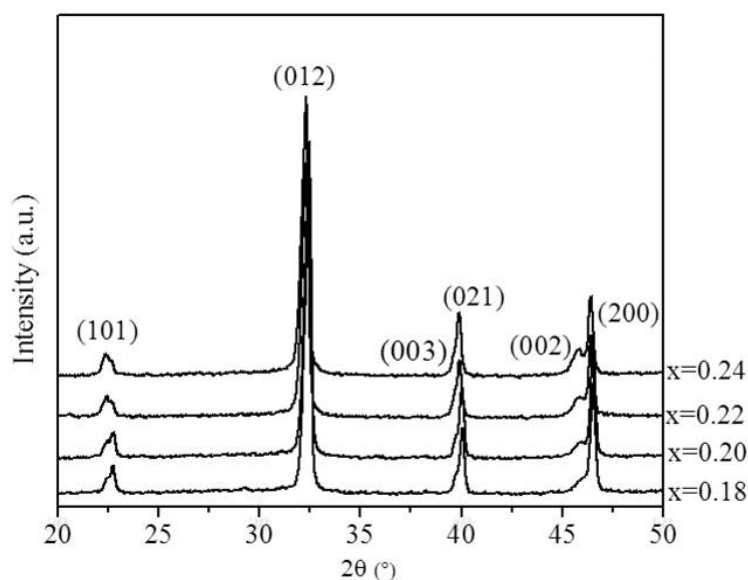


Fig. 1. XRD patterns of the BNKT<sub>x</sub> ceramics ( $x = 0.18$ – $0.24$ )

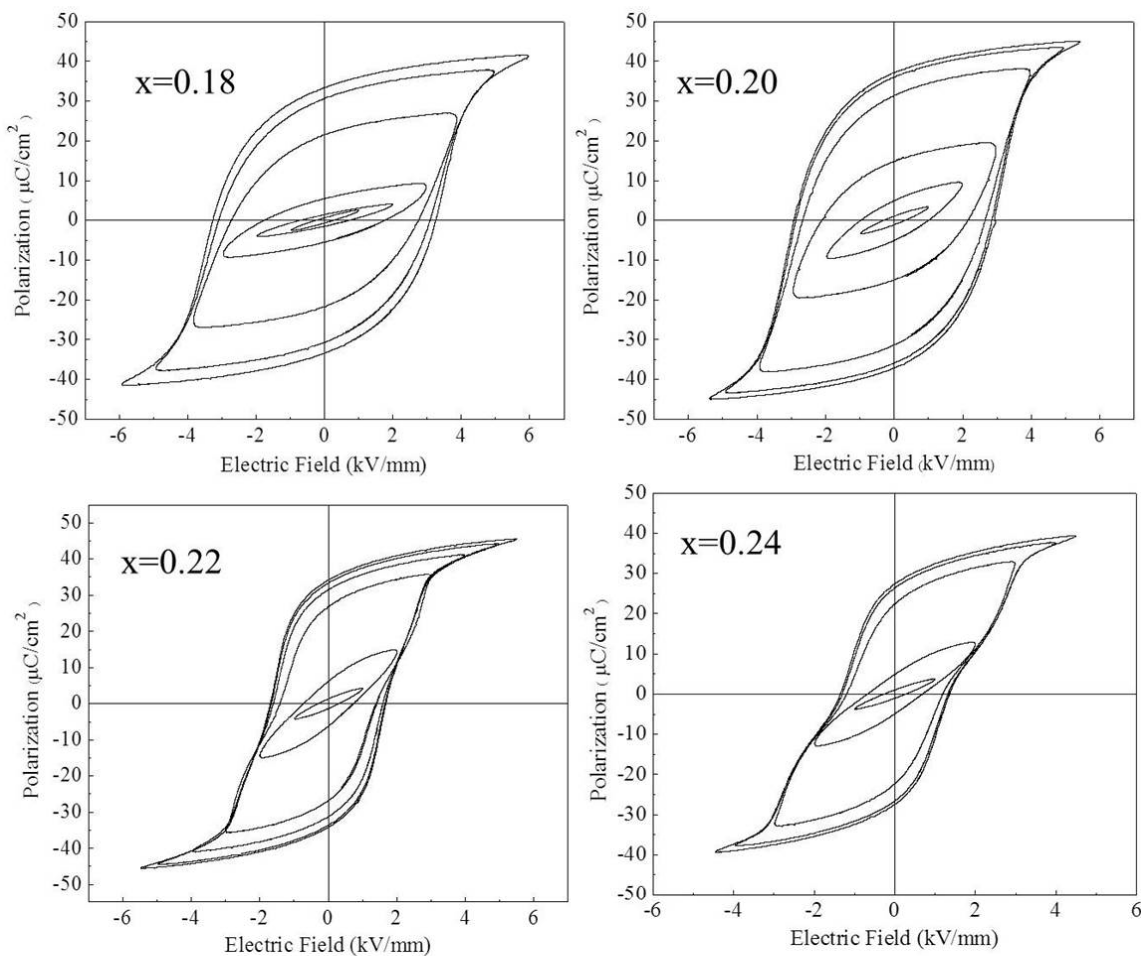
(003) and (021) reflections in the  $39^{\circ}$ – $41^{\circ}$   $2\theta$  range is due to rhombohedral symmetry like that of BNT, whereas the peak splitting of (002)/(200) in the  $45^{\circ}$ – $48^{\circ}$   $2\theta$  range is due to tetragonal symmetry like that of BKT. The splitting of both peaks indicates the coexistence of perovskite rhombohedral and tetragonal polymorphs at these MPB compositions in the BNKT $x$  solid solutions as anticipated [1].

### 3. 2. Hysteresis Loops

The P–E hysteresis loops of BNKT $x$  samples for different values of  $x$  are plotted in Fig. 2. The measurements were carried out on the unpoled samples. Conventional loops close to saturation

were obtained for all samples except for BNKT0.24, for which a pinched loop was plotted. The coercive field ( $E_c$ ) is observed to systematically decrease with  $x$ , from  $3.2 \text{ kV mm}^{-1}$  for  $x = 0.18$  down to  $1.3 \text{ kV mm}^{-1}$  for  $x = 0.24$ , with an abrupt reduction for  $x = 0.22$ , from which pinched loops start to develop.

Remanent polarizations between 28 and  $37.5 \mu\text{C cm}^{-2}$  are obtained, with a maximum for  $x = 0.20$ . It is observed that increasing the potassium-to-sodium ratio, in general, results in thinner hysteresis loops. In several reports, the presence of AFE order in BNT-based ceramics has been supposed to be the cause of the pinched loops [7, 8]. Nevertheless, similar loops have also been reported in relaxor systems such as PLZT and



**Fig. 2.** Polarization hysteresis loops (P–E) of the BNKT $x$  ceramics for different values of  $x$  ( $x = 0.18$ – $0.24$ )

PMN-0.1PT, at the onset of FE long-range. In these perovskite ferroelectrics, the pinched loops are not attributed to the presence of AFE phases but rather to the presence of a ‘non-polar’ or ‘weakly polar’ phase converting to a polar phase upon the application of the electric field [9]. With regard to the significant values of  $P_r$ , even for the BNKT0.24, the constriction may be due to the presence of a non-polar or weakly polar phase in

the BNKT system.

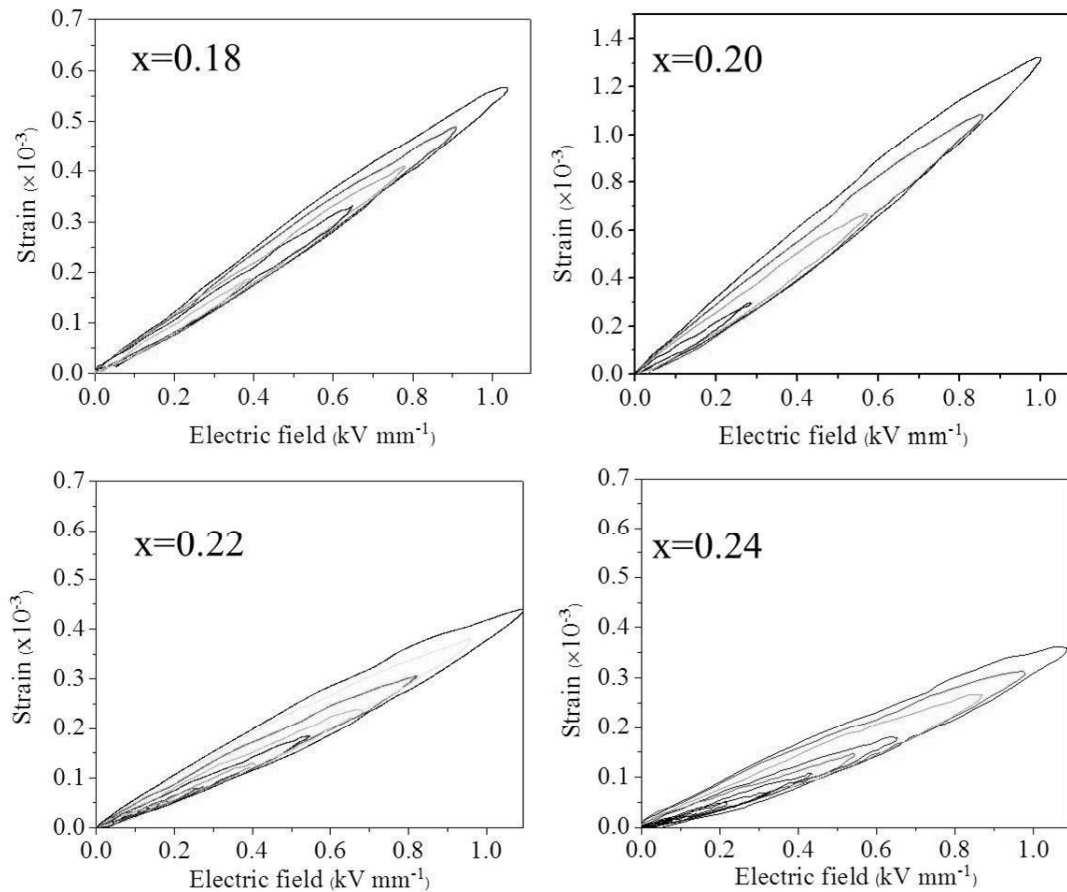
### 3. 3. Electromechanical Properties

The longitudinal  $d_{33}(pC N^{-1})$  and effective piezoelectric coefficients  $d_{33}^*(pmV^{-1})$  of all compositions were reported in table 1.

To estimate the suitability of BNKT<sub>x</sub> for actuator applications the strain responses of the

**Table 1.** The longitudinal and effective piezoelectric coefficients of all compositions

| Sample                | $x=0.18$ | $x=0.20$ | $x=0.22$ | $x=0.24$ |
|-----------------------|----------|----------|----------|----------|
| Relative density (%)  | 98.2     | 98.5     | 98.7     | 95.5     |
| $d_{33} (pC N^{-1})$  | 150      | 195      | 71       | 65       |
| $d_{33}^* (pmV^{-1})$ | 560      | 1320     | 440      | 360      |



**Fig. 3.** The unipolar strain (S-E) loops of the BNKT<sub>x</sub> ceramics for different values of x (x = 0.18–0.24)

samples under unipolar electric field were measured. Figure 3 shows the unipolar electric field-induced strain curves of ceramics for different values of  $x$  up to 1 kV mm<sup>-1</sup>. Induced-field strain shows a maximum for  $x = 0.20$ , like the  $d_{33}$  piezoelectric coefficient, confirming this composition to be the MPB one. A strain as high as  $S = 0.13\%$ , was obtained for  $x = 0.20$  under this field. This giant strains in BNT-based systems are thought to occur for compositions with an electric field induced phase change between the short-range polar state and long-range FE order [10].

#### 4. CONCLUSION

Lead-free BNKT $x$  piezoceramics with  $x$  ranging between 0.18 and 0.24 have been synthesized using a conventional solid state reaction ceramic method. It has been established that all compositions exhibit pure perovskite ferroelectric phase. It was found that BNKT0.20 showed optimum properties. A very large phase-change electromechanical response with a strain as high as  $S = 0.13\%$  was obtained at 1 kV mm<sup>-1</sup> for BNKT0.20. These driving fields are significantly lower than those previously reported for BNT-based systems with similar giant electric field induced strain, and are a clear advantage for actuation.

#### REFERENCES

1. Sasaki, A., Chiba, T., Mamiya, Y. and Otsuki, E., "Dielectric and piezoelectric properties of (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-(Bi<sub>0.5</sub>K<sub>0.5</sub>)TiO<sub>3</sub> systems". Japan. J. Appl. Phys., 1999, 38, 5564.
2. Smolenskii, G. A., Isupov, V. A., Agranovskaya, A. I. and Krainik, N. N., "New ferroelectrics of complex composition". Sov. Phys.—Solid State, 1961, 2, 2651.
3. Takenaka, T. and Sakata, K., "Piezoelectric and Pyroelectric properties of (Bi Na)<sub>1/2</sub>TiO<sub>3</sub>-based ceramics". Ferroelectrics, 1989, 95, 153.
4. Chu, B. J., Chen, D. R., Li, G. R. and Yin, Q. R., "Electrical properties of Na<sub>1/2</sub>Bi<sub>1/2</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub> ceramics". J. Eur. Ceram. Soc., 2002, 22, 2115.
5. Hiruma, Y., Nagata, H. and Takenaka, T., "Phase diagrams and electrical properties of (Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub>-based solid solutions". J. Appl. Phys., 2008, 104, 124106.
6. Otonari, M., Skapin, S. D., Spreitzer, M. and Suvorov, D., "Compositional range and electrical properties of the morphotropic phase boundary in the Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-K<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> system". J. Eur. Ceram. Soc., 2010, 30, 971.
7. Zhang, S. T., Kounga, A. B., Aulbach, E., Jo, W. and Granzow, T., "Lead-free piezoceramics with giant strain in the system Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub>-K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>." II. Temperature dependent properties. J. Appl. Phys., 2008, 103, 034107.
8. Singh, A. and Chatterjee, R., "Structural, electrical and strain properties of stoichiometric 1-x-y(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-x(Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub>)-y(Na<sub>0.5</sub>K<sub>0.5</sub>)NbO<sub>3</sub> solid solutions". J. Appl. Phys., 2011, 109, 024105.
9. Jo, W., Schaab, S., Sapper, E., Schmitt, L. A., Kleebe, H. J., Bell, A. J. and Rodel, J., "On the phase identity and its thermal evolution of lead free (Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub>-6 mol% BaTiO<sub>3</sub>". J. Appl. Phys., 2011, 110, 074106.
10. Jo, W., Granzow, T., Aulbach, E., Rodel, J. and Damjanovic, D., "Origin of the large strain response in (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>-modified (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-BaTiO<sub>3</sub> lead-free piezoceramics". J. Appl. Phys., 2009, 105, 094102.