

Electrical properties of (Na,K)NbO₃-BaTiO₃ ceramics fabricated by a physico-chemical method

Seung-Hwan Lee and Young-Hie Lee*

Dept. of Electronics Materials Engineering, Kwangwoon University, Seoul, Korea

Lead-free piezoelectric (Na_{1/2}K_{1/2})NbO₃ ceramics doped with a BaTiO₃ solution were prepared using a physicochemical method. The results indicate that the addition of the BaTiO₃ solution significantly influences the sintering, microstructure, phase transition and electrical properties of NKN ceramics. The physicochemical method can not only artificially control the grain size but also can regulate the electrical properties. The effects of doping with a BT solution on the bulk density, dielectric, piezoelectric and ferroelectric properties were investigated. The enhanced ferroelectric and piezoelectric properties with a piezoelectric constant d_{33} of 182 pC/N, a planar electromechanical coefficient k_p of 47%, a remanent polarization P_r of 22 $\mu\text{C}/\text{cm}^2$ and a Curie temperature of 415 °C appear in the NKN-0.5BT ceramics of 0.005 mol% of a BT solutions. These results showed that NKN-BT ceramics fabricated by a physicochemical method are promising lead free piezoelectric materials.

Key words: NKN-BT, Piezoelectric properties, Physicochemical method, Lead-free.

Introduction

The development of the electronics industry is highly dependent on devices and an improvement of device properties is a lead in the electronics industry. Recently, piezoelectric materials have been used in various devices such as in ultrasonic cleaning, actuators, energy harvesting, transducers, sensors etc [1-4]. Therefore, research on piezoelectric materials has continued for decades for potential applications. Among piezoelectric materials, lead-based materials are widely used such as Pb(Zr,Ti)O₃ [PZT], Pb(Mg,Nb)O₃ [PMN], Pb(Zn,Nb)O₃ [PZN], because of their excellent electrical and piezoelectric properties. However, lead materials are toxic give environmental contamination and have 90° domains. In response to an environment-friendly policy and the pre-existent lead-based compounds have 90° domains that originate from the paraelectric-ferroelectric phase transition, they have good piezoelectric and ferroelectric properties through a poling process where an applied electric field is used to align the domains. Studies of lead-free piezoelectric materials have been investigated would wide due to these problems. There are many lead-free compounds such as (Bi,Na)TiO₃ [BNT], (Na,K)NbO₃ (hereafter NKN) [NKN], BaTiO₃ (hereafter BT) [BT] etc [5]. The Curie temperature (T_c) of NKN was found to be at 430 °C, with a piezoelectric constant of $d_{33} = 100$ pC/N, and a planar coupling coefficient of 40% [6-8]. However, because of its relatively high volatilization during sintering at high temperature, A-site

vacancies lead to a decrease of its properties. Therefore, a good way to enhance the properties of NKN is to add NKN-xBT. NKN has a $d_{33} = 120$ pC/N, planar coupling coefficient of 45% and its T_c is 430 °C. BT has a low Curie temperature (120 °C) but has a high 130 pC/N for d_{33} and a 45% planar coupling coefficient with the highest dielectric properties among them. NKN-xBT has a higher volatilization temperature than NKN. Moreover, it was expected that NKN-xBT ceramics have a morphotropic phase boundary (MPB) with an orthorhombic (NKN) and tetragonal BT phase coexistence. The properties of NKN-xBT ceramics can be improved in the range of the MPB, which shows that the possibility of using them in devices [9-15].

In this paper, NKN-xBT ceramics were prepared alternately using the NKN powder and a BT solution. The NKN-xBT ceramics have been studied with a high density and a uniform distribution of fine grains. The purpose of the present study is to clarify the phase transition temperatures, and the relationship between T_d and d_{33} and the piezoelectric properties of NKN-xBT fabricated by a physicochemical method.

Experimental

In this study, in order to develop lead-free piezoelectric ceramics with excellent electrical properties, NKN-xBT ceramics were fabricated by a conventional mixed-oxide method and a sol-gel method. Na₂CO₃, K₂CO₃, and Nb₂O₅ as raw materials more than 99.9% pure were weighed as the composition formula and mixed in ethyl alcohol with ZrO₂ ball milling for 24 h. After drying using an oven, the calcination was carried out at 800 °C for 2 h.

A precursor solution of the BiTiO₃ solution was obtained

*Corresponding author:
Tel : +82-2-940-5164
Fax: +82-2-915-8084
E-mail: yhlee@kw.ac.kr

from Ba-acetate [Ba(CH₃COO)₂], Ti iso-propoxide {Ti[(OCH(CH₃)₂)₄] with acetic acid (CH₃CO OH) and 2-methoxyethanol (CH₃OCH₂CH₂OH) as the solvent and the chemical modifier, respectively.

The NKN-xBT ceramics were fabricated with various amounts of BT solution composition ($x = 0, 0.5, 0.1, 0.2, 0.3$ mol%). The mixed powder was pressed into pellet-shape samples with a 1000 kg/cm² pressure. Before sintering, a cold isostatic pressing (CIP) process was performed with 3 MPa to depress volatilization during sintering. The sintering temperature and time were 1100 °C and 2 h, respectively.

Ag paste was put on both sides of the samples as electrodes and heat treated 650 °C for 30 minutes. The samples were poled at 100 °C in stirred silicon oil under a DC field of 4 kVmm⁻¹ for 30 minutes. According to the variations of sintering temperature, their microstructures were investigated on natural surfaces and cross sections of the sintered specimens by means of scanning electron microscopy (SEM). The crystal structures were examined by a X-ray diffractometer (XRD) using CuK α 1 ($\lambda = 1.542$) radiation. The dielectric constant and loss were measured as a function of temperature and frequency using an impedance analyzer (HP4192A) equipped with a programmable temperature box. Then the planer electromechanical coupling factor k_p was measured using the resonant-antiresonant frequency method through an impedance analyzer (HP4192A) and the piezoelectric constant d_{33} measured using a quasi-static Belincourt-meter.

Results and Discussion

Fig. 1 show the X-ray diffraction patterns of the NKN-xBT ceramics as a function of the amount of the BT solution ($x = 0, 0.5, 0.1, 0.2, 0.3$ mol). It can be seen that all the ceramics showed a single perovskite structure. All the NKN-xBT ceramics have a pure perovskite structure, indicating that the BT solution has diffused into the NKN lattice and formed a solid solution. In this case,

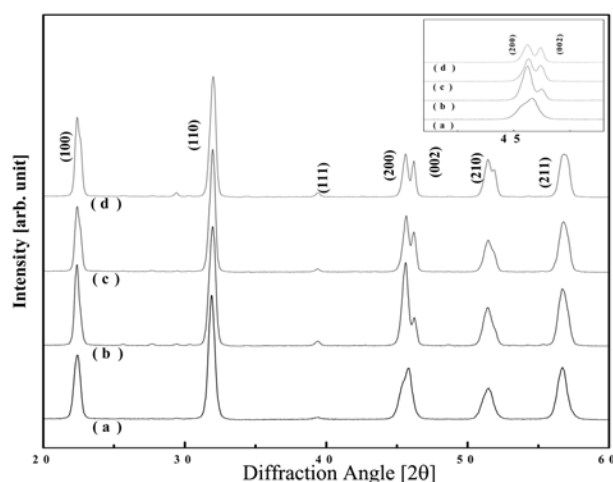


Fig. 1. X-ray diffraction patterns of the NKN-xBT ceramics. (a) 0 mol%, (b) 0.05 mol% (c) 0.01 mol% (d) 0.02 mol%

Ba²⁺ occupy the A sites of the NKN ceramic, while Ti⁴⁺ substitutes the B sites of NKN. It becomes the tetragonal phase when the BT solution is added, the crystal structure exhibited a tetragonal structure with the splitting of the (002) and (200) peaks. The inset of Fig. 1 exhibits the variation of (200) and (002) peaks of NKN-xBT ceramics near $2\theta = 45^\circ$ with the BT solution.

An orthorhombic-tetragonal coexistence is observed in NKN-xBT ceramics. From these results it should be concluded that there was a MPB between the orthorhombic and tetragonal phases with the BT solution in these modified NKN ceramics.

The cross-sectional morphology of modified NKN ceramics sintered at 1100 °C is shown in Fig. 2. The sintering temperature decreases with the addition of the BT solution resulting from the melting point of NKN at 1150 ± 10 °C. It is clear that the grain size becomes smaller gradually. The average grain size drops down with an increase in the content of the BT solution. This is probably related to a restriction of grain growth in the sintering processing. These results prove to us that the physicochemical method can not only artificially control the

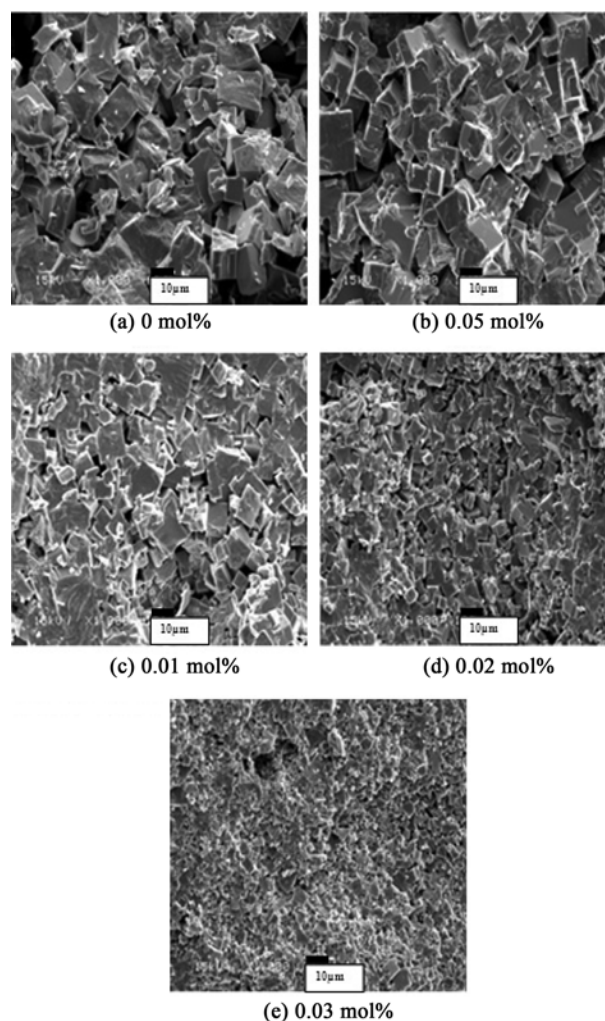


Fig. 2. The SEM images of NKN-xBT ceramics

grain size but also can regulate the electrical properties.

Also, the bulk densities of the doped NKN-3BT ceramics reach up to 4.45 g/cm^3 (theoretical density 4.51 g/cm^3), which may result from the adoption of the CIP processing before sintering. When a small amount of the BT solution (0.3 mol%) was added into NKN, the density could reach up to 98% of the theoretical density.

Fig. 3 shows temperature-dependent dielectric responses of unpoled NKN-xBT ceramics as a function of the amount of BT solution using the different measurement frequencies of 0.1 kHz, 1 kHz, 10 kHz and 100 kHz. The NKN ceramics exhibit the development of maxima in the relative permittivity. The phase transitions of pure NKN ceramics are observed at about 430°C . The T_C of NKN-xBT ceramics decreased gradually from 430°C to 400°C with an increase in the amount of the BT solution. This can be explained by a partial substitution of A-site ions ($\text{Na}_{0.5}\text{K}_{0.5}$)⁺ by Ba^{2+} can decrease T_C .

With an increase in the content of the BT solution, both T_{O-T} (orthorhombic-tetragonal morphotropic phase boundary), and T_C (tetragonal-cubic ferroelectric phase transition) are shifted to lower temperatures. For the NKN-3BT ceramics, T_C was less than room temperature. It is considered that the NKN ceramics changed to a relaxor behavior with an increase in the amount of the BT solution. The $\Delta\epsilon_r(85-25^\circ\text{C})/\epsilon_r(25^\circ\text{C})$ value of NKN-1BT ceramics was $\sim 54\%$ and it satisfied the Y5V specification of EIA (Electronic Industries Alliance). Also, the dielectric loss was lower than 3% from room temperature to the Curie

temperature.

Ferroelectric measurements were carried out at a maximum electric field of 30 kV/cm applied using an amplified bipolar waveform at 20 Hz . Fig. 4 shows typical ferroelectric polarization hysteresis loops. The ferroelectric properties are clearly enhanced after the BT solution is added, P_r changes from $\sim 9 \mu\text{C/cm}^2$ for a pure NKN ceramic to $\sim 21 \mu\text{C/cm}^2$ for a 0.5BT substituted NKN ceramic. For

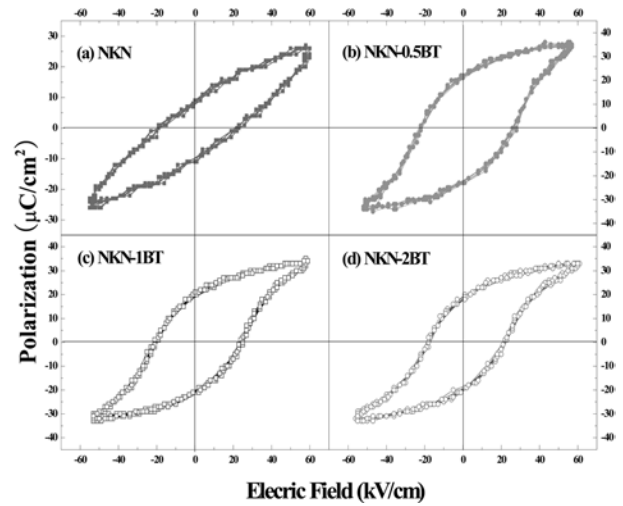


Fig. 4. P-E loops of NKN-BT ceramics measured at room temperature.

(a) 0 mol%, (b) 0.05 mol% (c) 0.01 mol% (d) 0.02 mol%

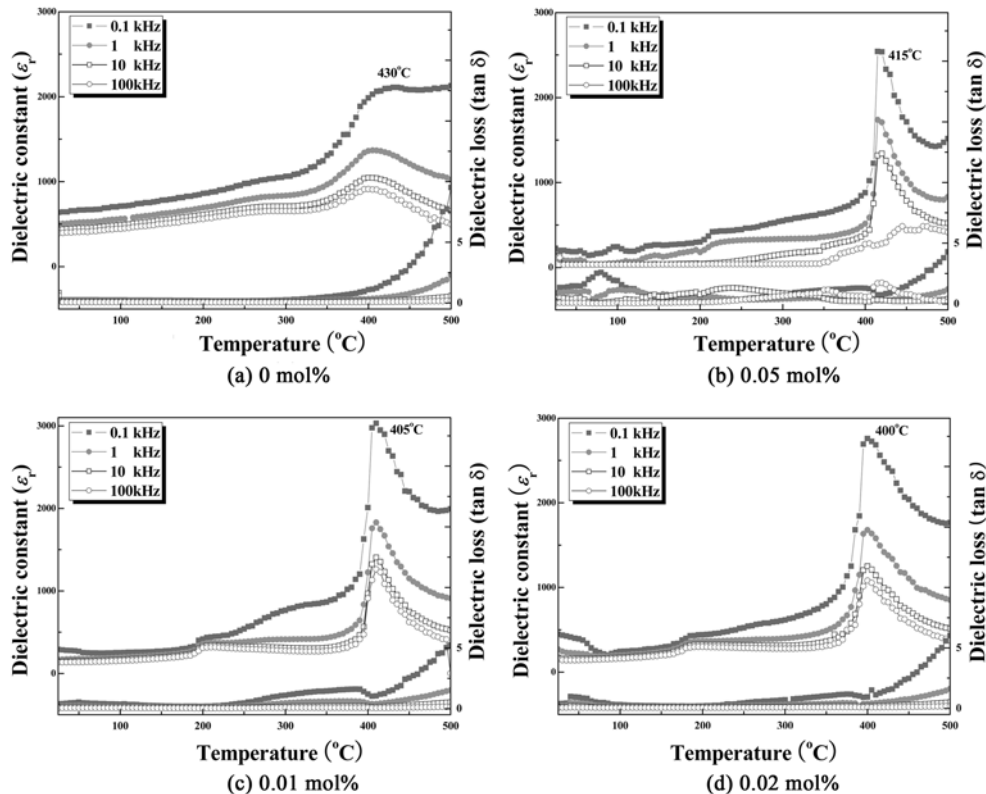


Fig. 3. Temperature dependence of dielectric constant and loss of the NKN-BT ceramics as the function of frequency 1 kHz.

the pure NKN ceramic, the remnant polarization P_r and the coercive electric field E_c are $\sim 9 \mu\text{C}/\text{cm}^2$ and $\sim 2.2 \text{KV}/\text{mm}$, respectively. The value for a 0.5BT solution substituted NKN ceramic change to $\sim 22 \mu\text{C}/\text{cm}^2$ and $\sim 2.8 \text{KV}/\text{mm}$, respectively. These results indicate that the MPB in NKN-xBT ceramics plays an important role in improving the ferroelectric properties.

Also, the piezoelectric constant (d_{33}) and the electromechanical coupling factor (k_p) of the NKN-xBT ceramics were higher than those of pure the NKN ceramic. For a pure NKN ceramic, the piezoelectric and electromechanical properties are $d_{33} = 118 \text{ pC}/\text{N}$ and $k_p = 32\%$, respectively.

The best piezoelectric and electromechanical properties of $d_{33} = 182 \text{ pC}/\text{N}$ and $k_p = 47\%$ appear at the composition of a NKN-0.5BT ceramic. The MPB region between the ferroelectric orthorhombic and rhombohedral phases is formed due to the addition of the BT solution. It is evident that the MPB plays a crucial role in the enhancement of piezoelectric properties. On the other hand, enhanced piezoelectric properties are restricted caused by volatilization of potassium and sodium with relatively high sintering temperatures.

Conclusions

NKN lead-free piezoelectric ceramics doped with different amount of a BT solution were prepared by a physicochemical method. These results indicate that the addition of the BT solution significantly influences the sintering, microstructure, phase transition and electrical properties of NKN ceramics. The relative density of a NKN-0.5BT ceramic is higher than 98%. The physicochemical method can not only artificially control the grain size but also can regulate the electrical properties. For the NKN-0.5BT ceramic, in which the average grain size was

approximately $8 \mu\text{m}$, a high ϵ_r value of 2542, a low $\tan\delta$ of $< 1\%$, excellent piezoelectric and electromechanical properties of $d_{33} = 182 \text{ pC}/\text{N}$ and $k_p = 47\%$ were observed. The physicochemical method confirmed the potential of NKN-xBT ceramics as piezoelectric materials.

References

1. P. Hansen, D. Hennings and H. Schreinemacher, J. Am. Ceram. Soc. 81 (1998) 1369-1373.
2. H. Kishi, N. Kohzu and J. Sugino, J. Eur. Ceram. Soc. 20, (2000) 1997-2007.
3. S.P. Nam, S.G. Lee, S.G. Bae and Y.H. Lee, J. Electrical Engineering & Technology, 2[1] (2007) 98-101.
4. S. Anwar, P.R. Sagdeo and N.P. Lalla, Solid State Commun. 138 (2006) 331-336.
5. I.J. Cho, K.S. Yun and H.J. Nam, J. Electrical Engineering & Technology, 6[1] (2011) 119-122.
6. C.W. Ahn, H.C. Song, S. Nahm, S.H. Park, K. Uchino, S. Priya, H.G. Lee and N.K. Kang, Jpn. J. Appl. Phys. 44 (2005) 1361-1364.
7. B.J. Sung, E.W. Lee and J.G. Lee, J. Electrical Engineering & Technology, 3 293 (2008).
8. E. Hollenstein, M. Davis, D. Damjanovic and N. Setter, Appl. Phys. Lett. 87 (2005) 182905.1-3.
9. S.J. Zhang, R. Xia, T.R. Shrout, G.Z. Zang and J.F. Wang, J. Appl. Phys. 100 (2006) 104108.1-6.
10. S.H. Lee, J. Electrical Engineering & Technology, 2[1] (2007) 102-105.
11. G.L. Yuan and S.W. Or, Appl. Phys. Lett. 88 (2006) 062905.1-3.
12. S.J. Zhang, R. Xia, T.R. Shrout, G.Z. Zang and J.F. Wang, J. Appl. Phys. 100 (2006) 104108.1-6.
13. N.B. Do, H.B. Lee, C.H. Yoon, J.K. Kang, J.S. Lee and I.W. Kim, Trans. Electr. Electron. Mater., 12[2] (2011) 64-67.
14. R.Z. Zuo, Z.K. Xu and L.T. Li, J. Phys. Chem. Solids 69, (2008) 1728-1732.
15. H.J. Bae, J. Koo and J.P. Hong, J. Electrical Engineering & Technology, 1[1] (2006) 120-126.