Journal of Ceramic Processing Research. Vol. 12, No. 2, pp. 195~198 (2011)

J O U R N A L O F
Ceramic Processing Research

Piezoelectric and dielectric properties of lead-free $(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ ceramics with a CuO content

Seung-Hwan Lee[a], Sung-Pill Nam[b], Sang-Chul Lee[a], Sung-Gap Lee[c] and Young-Hie Lee[a,*]
[a]*Dept. of Electronics Materials Engineering, Kwangwoon University, 447-1 Wolgyedong, Nowongu, Seoul 139-701, Korea*
[b]*Dept. of Smart Grid Research, Korea Electrotechnology Research Institute, Korea*
[c]*Dept. of Ceramic Engineering, Eng. Res. Insti., Gyeongsang National University, Korea*

Lead-free NKN-LST ceramics with a content of CuO were fabricated by a conventional mixed oxide method. The results indicate that the content of CuO significantly influences the sintering, microstructure, phase transition and electrical properties of NKN-LST ceramics. For the NKN-LST-xCuO ceramics sintered at 1050 °C, the bulk density increased with the content of CuO and showed a maximum value at a content of 2.0 mol% CuO. The Curie temperature of the NKN-LST-xCuO ceramics slightly decreased towards a lower temperature with increasing CuO content. The dielectric constant, piezoelectric constant and electromechanical coupling factor increased with a small amount of CuO content, which might be due to the increase in density. A high d_{33} = 153 pC/N, k_p = 35% and ε = 925 were obtained for the NKN-LST-0.5CuO ceramics sintered at 1050 °C for 2 h.

Key words: Lead-free, NKN-LST, CuO, Piezoelectric constant, Dielectric constant.

Introduction

Lead zirconate titanate (PZT) based ceramics are the most widely used materials for actuators, transducers, and sensor materials because of their superior electrical and piezoelectric properties. It is believed that in these systems, excellent properties are associated with a morphotropic phase boundary (MPB) between the rhombohedral, tetragonal, or monoclinic phases. However, they contain 60 wt% of PbO, which pollutes the environment strongly and threatens the health of humans [1-4]. Therefore, extensive research on lead-free piezoelectric materials with piezoelectric properties comparable to those of PZT ceramics has been conducted. Generally two lead-free ceramic materials have been extensively investigated: $(Bi_{0.5}Na_{0.5})TiO3$ (BNT) based and $(Na_{0.5}K_{0.5})NbO_3$ (NKN) based materials. BNT-based ceramics have a perovskite structure with a rhombohedral symmetry at room temperature [5]. It is considered as one of the promising candidate materials because BNT shows fairly satisfactory remanent polarization (P_r = 38.0 μC/cm²). However, a high coercive field (E_c = 7.30 kV/mm) for pure BNT makes the poling of the ceramic difficult and thus BNT usually has relatively poor piezoelectric properties (d_{33} = 58ρC/N). By comparison, NKN-based ceramics have superior piezoelectric properties (d_{33} = 80-110ρC/N, k_p = 36-40%) and a high Curie temperature (T_c) of 420 °C. However, difficulties in the sintering process of pure NKN ceramics have lead to a deviation from these excellent properties, for example, relatively low electrical properties (d_{33} = 70ρC/N, k_p = 25%) [6-9]. To improve the densification and piezoelectric properties, a number of additions have been made to NKN ceramics to form new NKN-based ceramics, such as NKN-$BaTiO_3$, NKN-$LiNbO_3$, NKN-$Bi_{0.5}Na_{0.5}TiO_3$, NKN-Bi_2O_3 etc [10-12]. These NKN-based ceramics exhibit enhanced piezoelectric properties owing to the formation of a MPB. It is well known piezoelectric and dielectric properties show a maximum around the MPB. Alternatively, to obtain piezoelectric ceramics with a high density hot pressing, cold-isostatic pressing and spark plasma sintering have been used. However, these techniques are not easily used in many fields due to their high cost. Therefore, finding advanced ceramics with different compositions are demanded [13-16]. This paper reports our experimental results for a NKN-based ceramic of $(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ (hereafter NKN-LST) ceramics, which not only deviates largely from the well-believed essential compositional condition of a nearly equal moral ratio of K/Na but also is K-rich instead of the previously investigated Na-rich compositions that show high piezoelectric properties. CuO has been used to lower the sintering temperature of NKN-LST ceramics [17, 18]. 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-LST with a CuO content.

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

Experiments

NKN-LST ceramics with x-mol% CuO content (0.5 ≤ x ≤ 2.0) were fabricated by a conventional mixed oxide method from Na_2CO_3, Nb_2O_5, Li_2CO_3, Sb_2O_3, Ta_2O_5

as the staring materials. These powders were separately dried in an oven at 100 °C for 4 h. They were ball-milled for 24 h using zirconia balls in alcohol. After being dried at 110 °C for 24 h, The powders were calcined at 820 °C for 5 h. After re-milling with a content of CuO, the powders were dried and pressed into disk samples of 12 mm diameter. The samples were sintered at 1050 °C for 2 h. After the samples were polished to 0.8 mm thickness, silver paste was screen-printed on the surfaces as electrodes and then fired at 400 °C for 10 minutes. We used X-ray diffraction (XRD) and scanning electron microscopy (SEM) to analyze the crystallinity and microstructures. The dielectric properties were measured using an LCR meter (PM6306, Pluke). Hysteresis loops of the samples were measured by a Sawyer-Tower circuit. The samples were poled under a DC field of 3 kV/mm for 20 minutes. The piezoelectric strain constant d_{33} was measured by a d_{33} meter (Channel Product DT-3300). The electromechanical coupling factor k_p was calculated by measuring the anti-resonance and resonance frequencies.

Results and Discussion

Fig. 1 shows the X-ray patterns of pure NKN-LST ceramics sintered at 1050 °C for 2 h and NKN-LST-xCuO ceramics sintered at 1050 °C for 2 h. The $(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ ceramics were sintered at 1150. The NKN-LST ceramics with a CuO content has been used to lower the sintering temperature. As a result of CuO content, the NKN-LST-xCuO ceramics were sintered at 1050 °C. All the peaks were indexed as perovskite and no evidence of a secondary phase was found. Compared to the pure composition, CuO modification results in enhancement of the orthorhombic to tetragonal phase. It becomes the tetragonal phase when a CuO content 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-LST ceramics near 2θ = 46° with a CuO content. It is considered that the Cu ions were incorporated into the matrix of the NKN-LST phases which slightly changed even with a small CuO content. The coexistence of orthorhombic-tetragonal phase is observed in NKN-LST-CuO ceramics. From this result it should be concluded that there was a MPB between the orthorhombic and tetragonal phases with a CuO content in these modified NKN-LST ceramics. This indicates that the Cu^{2+} (0.73 Å) ions have entered the B site (Nb or Ti ion site) of the perovskite unit cell of the NKN-LST lattice. The inset of Fig. 1 exhibits the variation of (200) and (002) peaks of NKN-LST ceramics near 2θ = 45° with a CuO content. It can be inferred that the NKN-LST-xCuO ceramics with x ≤ 1.0 a exhibit an orthorhombic structure. However, with an increase in the CuO content from 1.0 to 2.0, NKN-LST-xCuO ceramics present a tetragonal structure.

The cross-sectional morphology of NKN-LST-xCuO (x = 0, 1.0, 2.0) ceramics sintered at 1050 °C for 2 h are shown in Fig. 2 NKN-LST ceramics have an average grain

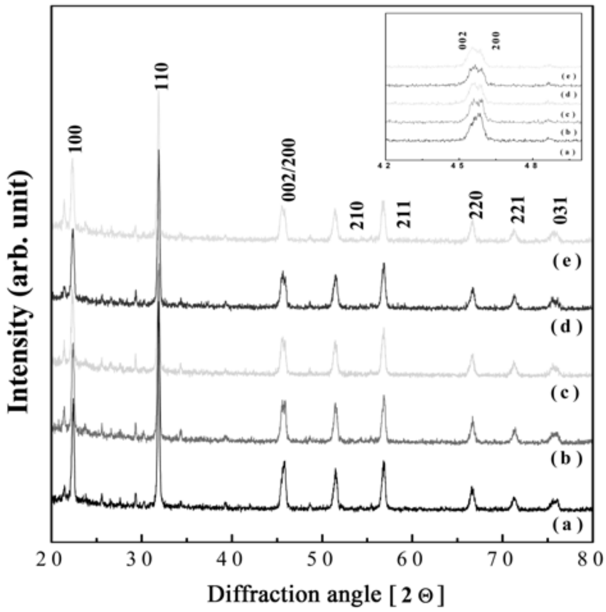

Fig. 1. XRD patterns of the NKN-LST +CuO (x mol%) ceramics (a) 0.0 mol%, (b) 0.5 mol% (c) 1.0 mol% (d) 1.5 mol% (e) 2.0 mol%.

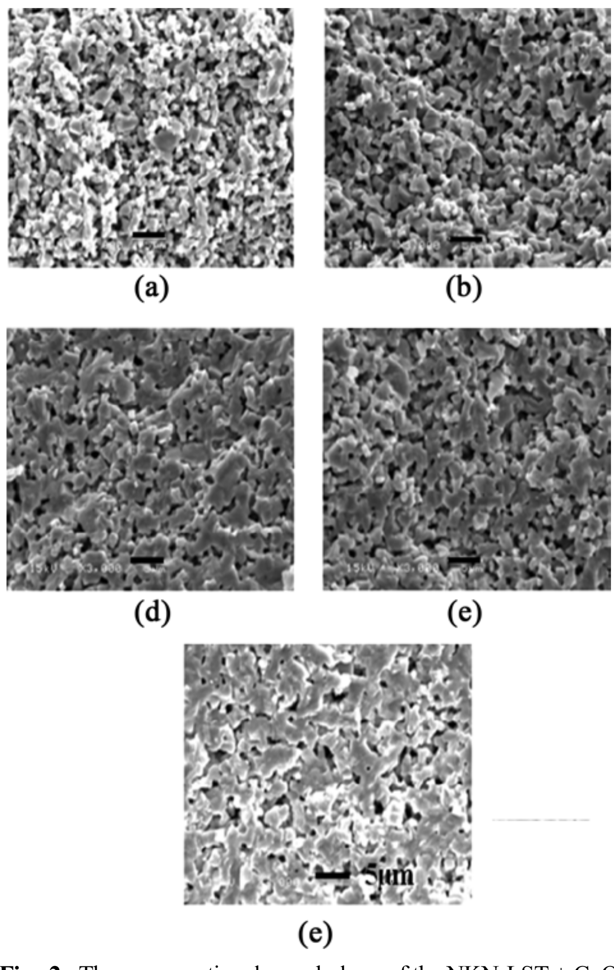

Fig. 2. The cross-sectional morphology of the NKN-LST + CuO (x mol%) ceramics (a) 0.0 mol%, (b) 0.5 mol% (c) 1.0 mol% (d) 1.5 mol% (e) 2.0 mol%.

size of 2 μm and show a porous microstructure. However, it can be seen that the grain size of NKN-LST-xCuO ceramics increases with an increase in the CuO content. Because the CuO content can be considerably decreased the sintering temperature for achieving grain growth. In the case of 1 mol% CuO content, the pore size is reduced and grains have grown to 2.5 μm. Moreover, a dense microstructure with an average grain size of 5 μm was developed at x = 2 mol%. As, grain growth usually occurred in the presence of a liquid phase which was considered to exist x > 1.0 mol% of CuO, NKN-LST ceramics containing a small amount of CuO were well sintered at 1050 °C.

Fig. 3 shows the temperature-dependent dielectric properties of NKN-LST-xCuO ceramics at 1 kHz. The NKN-LST-xCuO ceramics show similar dielectric behavior to NKN-LST. The NKN-LST-xCuO ceramics show a dielectric peak, which corresponds to the phase transition from orthorhombic-tetragonal. It should be noted that the content of CuO causes the transition to shift to a lower temperature. With an increase in the CuO content from 0 to 2 mol%, the Curie temperature (T_c) of NKN-LST-xCuO ceramics is decreased slightly from 313.7 °C to 291.4 °C. The change in the T_c further implies that elements from CuO entered the lattice of the NKN-LST ceramics. Interestingly, with an increase in the CuO content, the NKN-LST-xCuO ceramics show a broad phase transition behavior. This result can be attributed to the decreasing tetragonality and the finer grain morphology.

Fig. 4 shows the polarization-electric field curves of NKN-LST-xCuO sintered at 1050 °C for 2 h. With an increase in the CuO content, the P-E hysteresis loops grow larger and wider. The remnant polarization of the NKN-LST is about 15 μC/cm^2, which increased with the content

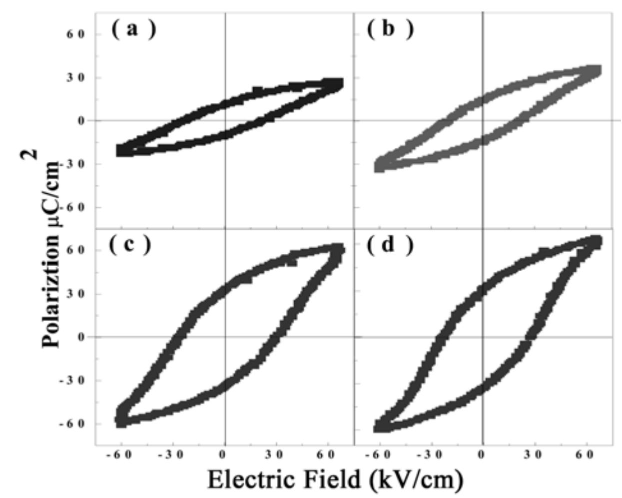

Fig. 4. Hysteresis loops of the NKN-LST+CuO (x mol%) ceramics (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, (d) 2.0 mol%.

of CuO, exhibiting a maximum value of 32 μC/cm^2 when the CuO content was 2.0 mol%. The increase in P_r could be related to the increase in bulk density. In addition, when the CuO content exceeded 1.0 mol%, the coercive field also increased. Therefore, it is considered that CuO, which entered the matrix of the NKN-LST ceramics, might behave as a hardener.

Fig. 5 shows the variations in d_{33} and kp values of the NKN-LST-xCuO ceramics sintered at 1050 °C for 2 h. The d_{33} and kp values showed a similar variation with the CuO content. The NKN-LST ceramics with a CuO content exhibit a compositional dependence of the piezoelectric properties near the MPB. When the CuO content was 0.5 mol%, NKN-LST ceramics showed the highest piezoe-

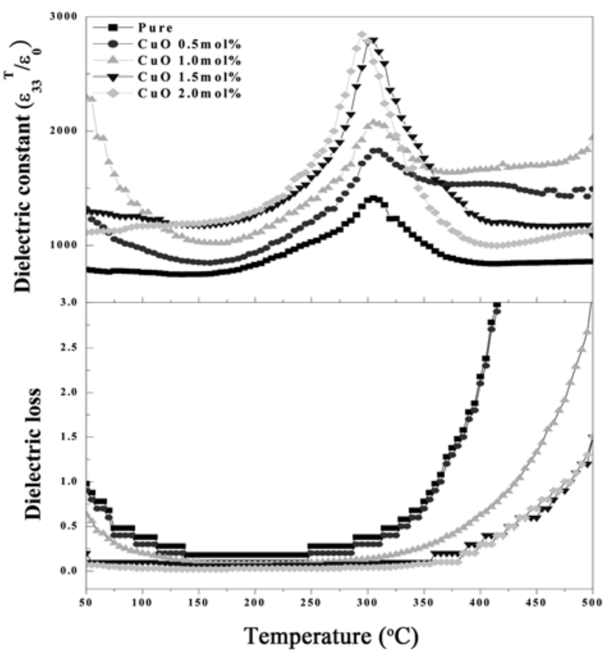

Fig. 3. The dielectric constant and loss of the NKN-LST+CuO (x mol%) ceramics at frequency of 1 kHz.

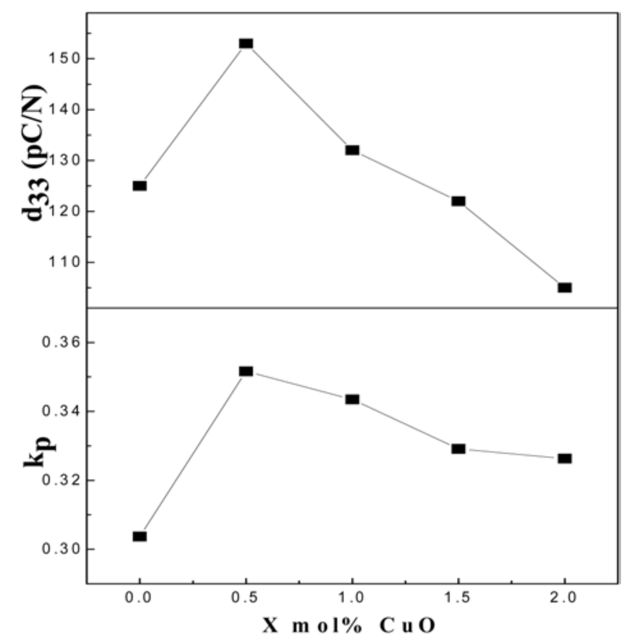

Fig. 5. Piezoelectric properties of the NKN-LST+CuO (x mol ceramics

lectric properties. The increase in d_{33} and *kp* could be explained by the increase in bulk density. Over this boundary, the piezoelectric properties decline rapidly with increasing CuO content. Although the enhancement of piezoelectric properties might be partially due to the change in microstructure, it should be significantly noted that the MPB plays the most important factor in improving the piezoelectric properties of NKN-LST ceramics with a CuO content.

Conclusions

In summary, lead-free $(Na_{0.44}K_{0.52})Nb_{0.84}O_3$-$Li_{0.04}(Sb_{0.06}Ta_{0.1})O_3$ ceramics with a CuO content were fabricated by a conventional mixed oxide method at a relatively low sintering temperature. The phase structure of NKN-LST ceramics demonstrated the coexistence of orthorhombic and tetragonal phases due to the decrease in the polymorphic phase transition (from the tetragonal to orthorhombic phase) with 0.5 mol% CuO content. Improved piezoelectric properties (d_{33} = 153ρCN, *kp* = 35%, P_r = 16ρC/cm^2) were obtained in the ceramics with 0.5 mol% CuO content. The results in this study indicate that improved NKN-LST ceramics are promising lead-free piezoelectric candidate materials for actuator and transducer applications.

References

1. J.H. Heo, Trans. Electr. Electron. Mater., 11[6] (2010) 275-278.
2. S. Anwar, P.R. Sagdeo and N.P. Lalla, Solid State Commun. 138 (2006) 331.
3. S.Y. Kim and I.S. Kim, Trans. Electr. Electron. Mater., 12[1] (2011) 16-19.
4. S.J. Park, H.Y. Park, K.H. Cho, S. Nahm and H.G. Lee, Materials Research Bulletin 42 (2008) 3580-3586.
5. Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, Nature, 432 (2004) 84-87.
6. Z.X. Chen, Y. Chen and Y.S. Jiang, J. Phys. Chem. B, 106 (2002) 9986-9992.
7. 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.
8. R. Zuo and C. Ye, Appl. Phys. Lett. 91 (2007) 062916.
9. M. Jiang, X. Li, J. Liu, J. Zhu, X. Zhu, L. Li, Q. Chen, J. Zhu and D. Xiao, J. Alloys Compounds 479 (2009) L18-L21.
10. J.L. Zhang, X.J. Zong, L. Wu, Y. Gao, P. Zheng and S.F. Shao, Appl. Phys. Lett. 95 (2009) 022909.
11. P. Hansen, D. Hennings and H. Schreinemacher, J. Am. Ceram. Soc. 81 (1998) 1369.
12. M.S. Kim, Y.M. Jeon, Y.M. IM, Y.H. Lee and T.H. Nam, Trans. Electr. Electron. Mater., 12[1] (2011) 20-23.
13. Z. Feng and S.W. Or, J. Alloys Compd. 480 (2009) L5.
14. X.K. Niu, J.L. Zhang, L. Wu, P. Zheng and T.R. Shrout, Appl. Phys. Lett. 91 (2007) 132913.
15. S. Anwar, P.R. Sagdeo and N.P. Lalla, Solid State Commun. 138 (2006) 331.
16. R. Zuo, J.R.R. Cen and L. Li, J. Am. Ceram. Soc., 89[6] (2006) 2010-2015.
17. J.R. Yoon, C.B. Lee and K.M. Lee, Trans. Electr. Electron. Mater., 11[3] (2010) 126-129.
18. E. Hollenstein, M. Davis, D. Damjanovic and N. Setter, Appl. Phys. Lett. 87 (2005) 182905.