Microstructure and Piezoelectricity of (Na,K,Li)(Nb,Sb)O₃–(Bi,Na)(Sr)ZrO₃–BaZrO₃ Ceramics

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Abstract: In this paper, (Na,K)ₓLi₁₋ₓ(Nb,Sb)O₃–(Bi,Na)(Sr)ZrO₃–BaZrO₃ ceramics were fabricated with x (= Li) substitution by two-step sintering method, and their physical characteristics were investigated. When Li substitution was added to the ceramics, piezoelectric constant (d₃₃) and electromechanical coupling factor (k_p) were rapidly reduced. However, mechanical quality factor (Q_m) was enhanced. For the KNN-BNZ((K,Na)(Nb)O₃–(Bi,Na)(Sr)ZrO₃) ceramics with Li(x) = 0 substitution, the best physical properties of d₃₃ = 300 [pC/N], k_p = 0.40, Q_m = 33 and dielectric constant (ε_r) = 2430 were shown, respectively. Additionally, the KNN-BNZ ceramics with Li(x) = 0.02, the d₃₃ of 246[pC/N], the k_p of 0.37, the Q_m of 42 and the ε_r of 2090 appeared, which were suitable for the low-loss piezoelectric actuator.

Keywords: two-step sintering method; (Na,K)NbO₃; piezoelectric actuator; piezoelectric constant (d₃₃)

1. Introduction

Nowadays, lead zirconate titanate ceramics are widely used in ultrasonic surgery instruments, piezoelectric transformers, piezoelectric speakers and ultrasonic sensors [1,2]. Because the composition ceramics involve more than 60 wt % PbO, when they are sintered at temperatures above 1200 °C, the PbO component becomes very harmful to the human body because it volatilizes rapidly from 1000 °C [3–11].

Sato et al. have presented (Na,K)NbO₃-system ceramics with excellent piezoelectric properties as Pb-free materials capable of being substituted for PZT ceramics. Nevertheless, it is not very easy to manufacture KNN(K,Na)(Nb)O₃ ceramics with the excellent piezoelectric properties owing to the volatilization of alkali elements such as Na and K. Recently, Juhyun Yoo et al. [12] have reported composition ceramics with an excellent piezoelectric constant (d₃₃) of ~269 [pC/N] and a high Curie temperature (Tc) of ~275 (°C) in the (Bi,Na)ZrO₃-substituted NKN ceramics with rhombohedral-tetragonal (R-T) phase boundary regions. In general, PZT system ceramics show excellent piezoelectric properties in R-T phase regions [13,14]. Accordingly, we added (Bi₀.₅Na₀.₅)ZrO₃ and BaZrO₃ to NKN system ceramics in order to form these R-T phase regions. (Bi₀.₅Na₀.₅)ZrO₃ and BaZrO₃ can increase rhombohedral-orthorhombic transition temperature (T_R-O) and decrease orthorhombic–tetragonal transition temperature (T_O-T) of (Na,K)NbO₃ ceramics near room temperature. As a result, by forming the R-T phase regions, superior d₃₃ can be induced. It is necessary that the low-loss piezoelectric actuators have low dielectric constant, high d₃₃, and temperature stability of piezoelectric properties.

In this experiment, for the application to the low-loss piezoelectric actuator, the (Na,K)NbO₃ systems substituted with (Bi, Na)(Sr) ZrO₃ and BaZrO₃ were manufactured with lithium substitution by the two-step sintering method and their physical properties were analyzed.
2. Experiments

The ceramic samples were fabricated using following composition formula:

\[0.955(Na_{0.5}K_{0.5})_{1-x}Li_{x}(Nb_{0.96}Sb_{0.04})O_3-0.035(Bi_{0.5}Na_{0.5})_{0.9}(Sr)_{0.1}ZrO_3-0.01BaZrO_3\]

The high-purity powders above 99% of K₂CO₃, Na₂CO₃, Li₂CO₃, Sb₂O₅, SrCO₃, Bi₂O₃ and ZrO₂ were weighed from \(x = 0\) to \(x = 0.05\), and the weighed powders were ball-milled as 270 r.p.m. for 24 h. After finishing ball-milling, the powders were calcined at 900 °C for 6 h. Then, a 5 wt% polyvinyl alcohol was mixed with the powders. The powders were uni-axially pressured by 17 MPa in a mold with 17 mm diameter. The formed sample was sintered by two-step sintering technique. In sintering process, temperature was increased suddenly at 15 °C/min to 1180 °C, maintained for 5 min, then cooled down for 5 min to 1070 °C and kept for 20 h to cool down further. The ceramic specimens were polished to thickness 1.0 mm and then electro-deposited with Ag paste at 600 °C for 30 min. Capacitance (C) at 1 kHz was measured using an LCR meter (ANDO AG-43040, Rancho Cordova, CA, USA), and the dielectric constant (\(\varepsilon_r\)) was analyzed. For investigation of the electromechanical coupling factor and mechanical quality factor, the fr (resonant frequency) and fa (anti-resonant frequency) were measured by an Agilent 4294 A Impedance Analyzer (1150 Raymond Avenue SW Renton, WA, USA) and then were calculated. The \(d_{33}\) was measured using the \(d_{33}\) meter (APC-90-2030, 46 Heckman Gap Road, Mill Hall, PA 17751, USA). In order to determine the crystal structure of the specimen, the used X-ray diffraction meter was irradiated at a diffraction angle 2θ between 20° and 80° by a powder method using a CuKα line having a wavelength of \(\lambda = 1.5406\) Å. Additionally, the microstructure of the specimen was observed as 3000 magnification using scanning electron microscopy.

3. Results and Discussions

Figure 1 presents the X-ray diffraction (XRD) pattern according to \(x (= Li)\). All the specimens exhibit pure perovskite phase, and no second phases are observed. As can be seen in Figure 1b, all the ceramic specimens from \(x = 0\) to \(x = 0.05\) according to the increase in lithium substitution include R-T phase regions, which are characterized by the tetragonal (002) and (200) peaks along with the rhombohedral (200) peak between 42° and 50°. R-T coexistence has a large number of polarization directions that can be formed into eight directions (rhombohedral phases) and six directions (tetragonal phases) in the equivalent orientation of spontaneous polarization. Accordingly, the polarization of specimens can be done easily, and strong piezoelectricity can be induced.
Figure 1. X-ray diffraction patterns of specimens with x. (a) $2\theta = 20^\circ$–$80^\circ$; (b) $2\theta = 40^\circ$–$50^\circ$.

Figure 2 presents the microstructure of specimens of from x = 0 to x = 0.05 according to the increase in lithium substitution. An average grain size of the specimen slowly reduced with the increase of the lithium substitution, and also presented a slow decrease in porosity. This phenomenon can be explained by the results that the Li$^{1+}$ ion may refine the grain size according to the increase of lithium substitution. That is, the grain size was decreased to values of $\sim 6.98$, $\sim 4.51$, $\sim 3.41$, $\sim 2.99$ and $\sim 3.15$ (μm) for x = 0, 0.02, 0.03, 0.04 and 0.05, respectively.
Figure 2. Cont.
Figure 2. Scanning electron microscopy (SEM) of specimens with \(x\) ((a) \(x = 0\); (b) \(x = 0.02\); (c) \(x = 0.03\); (d) \(x = 0.04\); (e) \(x = 0.05\)).

The density of the specimen with \(x\) is shown in Figure 3. The density was enhanced owing to the lithium substitution. In this experiment, because the eutectic point of \(\text{Li}_2\text{CO}_3\) and \(\text{Na}_2\text{CO}_3\) is 514 °C, the liquid phase can be performed during the sintering process. In this experiment, the two-step sintering method was used for the purpose of increasing the piezoelectricity of the KNN-BNZ ceramics. For the sintering process, the temperature was increased suddenly to 1180 °C, maintained for 5 min, then cooled down for 5 min to 1070 °C and kept for 20 h to cool down further. Through these methods, the densification of the ceramics can be performed [15].
Figure 3. Density of specimens with x.

Figure 4 presents the kp of the specimen with x. Electro mechanical coupling factor kp ensures the efficient conversion of electrical energy into mechanical energy. Here, a maximum value of 0.400 was obtained when the lithium substitution was 0. Thereafter, the kp was continuously decreased. Here, in spite of the increase of density, the reason why electro mechanical coupling factor kp is continuously decreased can be analyzed by the fact that the average grain size of the specimens is reduced according to the increase of lithium substitution, and lithium substitution also acts as acceptor dopant.

Figure 4. Electromechanical coupling factor (kp) of specimens with x.

The mechanical quality factor (Qm) with x is presented in Figure 5. When x was 0.05, the maximum value of 54 appeared. This is because kp and dielectric constant were decreased at the same time. Here, the oxygen vacancies were performed, causing in the enhancement of Qm through prohibiting the domain wall motion. The $\varepsilon_r$ according to lithium substitution is shown in Figure 6. The maximum value of $\varepsilon_r$ was 2014 at the lithium = 0. After x of lithium substitution increased to more than 0.1, $\varepsilon_r$ was abruptly decreased because lithium substitution also acts as acceptor dopant.
The dependence of the $d_{33}$ piezoelectric constant with $x$ is presented in Figure 7. The maximum value of $d_{33}$ was 300 [pC/N] when $x = 0$. In this composition, rhombohedral and tetragonal (R-T) coexistence phases appeared to be weak. Additionally, the decrease of $d_{33}$ according to lithium substitution is considered because lithium ion largely acted as the cause of decreasing grain size. In general, in the case of grain size decrement, $Q_m$ was increased, and $k_p$ and $d_{33}$ were decreased from 5.47 μC/cm² to 4.98 μC/cm², and coercive field (Ec) gradually showed the trend of decrease. The dependence of $d_{33}$ was abruptly decreased because lithium substitution also acts as acceptor dopant.

Additionally, the decreases of average grain size reduced the dielectric constant of the specimens because of the increase of grain boundary layer containing lower dielectric constant. The remnant polarization ($P_r$) decreased from 5.47 μC/cm² to 4.98 μC/cm², and coercive field (Ec) gradually showed the trend of increment from 6.27 kV/Cm to 7.3, 7.32, 7.02 and 7.17 kV/Cm, respectively, as a function of $x$. These results can be also analyzed in light of the fact that the lithium substitution acts as acceptor dopant.
The variation of the dielectric constant with temperature is shown in Figure 9. The $T_c$ was constantly maintained from 230 °C ($x = 0$) to 240 °C ($x = 0.05$) according to the increase in lithium substitution. The peak value of dielectric constant at $T_c$ was also largely decreased according to the increase in lithium substitution, because of the decrease of grain size. The KNN-BNZ ceramics with $Li(x) = 0$, and the best physical properties of $d_{33} = 300 \text{ pC/N}$, $k_p = 0.40$, $Q_m = 33$ and $\varepsilon_r = 2430$ were shown, respectively. In case of using low-loss piezoelectric actuator, because of low dielectric constant $\varepsilon_r$ of 2090 at the KNN-BNZ ceramics with $Li(x) = 0.02$, low power consumption is anticipated.
Figure 9. Temperature dependence of dielectric constant with x.

Table 1 presents physical properties of samples with x.

| Sinter. Temp. (°C) | X (= Li) | Density [g/cm³] | k_p | Dielectric Constant | d33 (pC/N) | Q_m | ε_r  |
|-------------------|---------|-----------------|-----|---------------------|------------|-----|------|
| 1070              | 0       | 4.321           | 0.400 | 2430                | 300        | 33  |      |
|                   | 0.02    | 4.372           | 0.370 | 2090                | 246        | 42  |      |
|                   | 0.03    | 4.379           | 0.351 | 2072                | 240        | 47  |      |
|                   | 0.04    | 4.444           | 0.327 | 1957                | 203        | 52  |      |
|                   | 0.05    | 4.502           | 0.287 | 1827                | 161        | 54  |      |

4. Conclusions

In this paper, (Na,K)1−xLi.x(Nb,Sb)O3–(Bi,Na)(Sr)ZrO3–BaZrO3 ceramics were fabricated with x (= Li) substitution by two-step sintering method, and their physical characteristics were investigated.

1. All the specimens exhibited pure perovskite phase, and no second phases were observed;
2. An average grain size of the specimen slowly reduced with the increase of the lithium substitution;
3. When Li substitution was added to the ceramics, d33 and k_p were slowly reduced;
4. With increasing Li substitution, the remnant polarization (P_r) decreased from 5.47 µC/cm² to 4.98 µC/cm², and coercive field (E_c) gradually showed the trend of increment;
5. The KNN-BNZ ceramics with Li(x) = 0.02, the d33 of 246 [pC/N], k_p of 0.37, Q_m of 42 and ε_r of 2090 appeared to be suitable for low-loss piezoelectric actuator application;
6. The KNN-BNZ ceramics with Li(x) = 0, and the best physical properties of d33 = 300 [pC/N], k_p = 0.40, Q_m = 33 and ε_r = 2430 were shown, respectively.

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References

1. Minho, P.; Juhyun, Y. Piezoelectric and Dielectric Properties of Nonstoichiometric (Na_{0.5}K_{0.5})_{0.97}(Nb_{0.90}Ta_{0.1})O_3 Ceramics Doped with MnO_2. *J. Electron. Mater.* 2012, 41, 3095–3099.
2. Kim, S.G. Recent Trend of Electronic Speaker. *Electric. Electron. Mater.* 2006, 19, 33.
3. Juhyun, Y. High Dielectric and Piezoelectric Properties of Low-Temperature Sintering PNNPMN-PZT Ceramics for Low-Loss Piezoelectric Actuator Application. *Trans. Electr. Electron. Mater.* 2018, 19, 249–253.

4. Bomlai, P.; Muensit, N.; Milne, S.J. Structural and electrical properties of (1−x)(Na0.465K0.465Li0.07)CaTiO3−x lead-free piezoelectric ceramics with high Curie temperature. *Proc. Eng.* 2012, 32, 814–820. [CrossRef]

5. Gou, Q.; Zhu, J.; Wu, J.; Li, F.; Jiang, L.; Xiao, D. Microstructure and electrical properties of (1−x)K0.5Na0.5NbO3−xBi0.5Na0.5Zr0.85Sn0.15O3 lead-free ceramics. *J. Alloys Compd.* 2018, 730, 311–317. [CrossRef]

6. Zheng, T.; Zu, Y.; Wu, J. Composition dependence of phase structure and electrical properties in lead-free (1−x)(K0.42Na0.585)(Nb1−ySby)O3−xBi0.5K0.5ZrO3 piezoceramics. *J. Alloys Compd.* 2015, 647, 927–934. [CrossRef]

7. Sunmin, B.; Juhyun, Y. Dielectric and Piezoelectric Properties of (1−x)K0.5Na0.5NbO3−xBi0.5Na0.5Zr0.85Sn0.15O3−0.03(Bi0.5Na0.5)TiO3–SrTiO3 Ceramics as a Function of (Bi,Na)TiO3 Substitution. *Ferroelectrics* 2012, 437, 55.

8. Yiping, G.; Ken-ichi, K.; Hitoshi, O. Dielectric and piezoelectric properties of (Na0.5K0.5)NbO3–SrTiO3 ceramics. *Solid State Commun.* 2004, 129, 279–284.

9. Juhyun, Y. Effect of sintering temperature on the dielectric and piezoelectric properties of (Na0.525K0.44)Li0.037(Nb0.885Sb0.08Ta0.037)O3 Pb-free ceramics for actuator. *Ferroelectrics* 2017, 507, 12–18.

10. Jungrae, N.; Juhyun, Y. Dielectric and piezoelectric properties of KCT added Li0.02(Na0.56K0.44)Li0.98(Nb0.81Ta0.15Sb0.04)O3 ceramics. *J. Electroceramics* 2014, 30, 139–144.

11. Sang-Hoon, S.; Juhyun, Y.; Sang-Don, L. Dielectric and piezoelectric properties of (Ba0.85Ca0.15)(Ti1−xZrx)O3 + 0.004 CuO ceramics for piezoelectric actuator. *Ferroelectr. Lett.* 2014, 41, 56.

12. Sungjin, C.; Juhyun, Y. Dielectric and Piezoelectric Properties of (Na0.5K0.5)Li0.037(Nb0.96−xSbx)Ta0.037O3−0.03(Bi0.5Na0.5)TiO3–Sr0.1ZrO3 Ceramics for Pizoelectric Actuator. *Trans. Electr. Electron. Mater.* 2019, 20, 328–333.

13. Zhang, B.; Zhu, J. Lead-free Piezoelectrics Based on Potassium–Sodium Niobate with Giant d33. *ACS Appl. Mater. Interfaces* 2013, 5, 7718–7725. [CrossRef] [PubMed]

14. Shi, H.; Chen, J.; Wang, R.; Dong, S. Full set of material constants of (Na0.5K0.5)NbO3–BaZrO3–(Bi0.5La0.5)TiO3 lead-free piezoelectric ceramics at the morphotropic phase boundary. *J. Alloys Compd.* 2016, 655, 290–295. [CrossRef]

15. Zhou, C.; Zhang, J.; Yao, W. Remarkably strong piezoelectricity, rhombohedral-orthorhombic-tetragonal phase coexistence and domain structure of (K,Na)(Nb,Sb)O3–(Bi,Na)ZrO3–BaZrO3 ceramics. *J. Alloys Compd.* 2020, 820, 153411. [CrossRef]

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