J Electroceram (2012) 29:144–148
DOI 10.1007/s10832-012-9744-1

Dielectric and piezoelectric properties of $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3$ ceramics doped with Bi_2O_3

Jungrae Noh · Juhyun Yoo

Received: 29 February 2012 / Accepted: 17 May 2012

Abstract In this study, to develop the optimal composition of ceramics for low loss piezoelectric actuator and ultrasonic motor applications, $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3+0.009\ K_{5.4}Cu_{1.3}Ta_{10}O_{29}+0.1wt\%Li_2CO_3+xwt\%Bi_2O_3(x=0\sim0.9)$ lead-free piezoelectric ceramics with a fixed quantity of 0.009 $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ (abbreviated as KCT) were manufactured using the conventional solid-state solution processes. The effects of Bi_2O_3 addition on the dielectric and piezoelectric properties were then investigated. From the X-ray diffraction analysis result the specimens demonstrated orthorhombic symmetry when Bi_2O_3 was less 0.6 wt%, a pseudo-cubic phase appeared when Bi_2O_3 was 0.9 wt%. SEM images indicate that a small amount of Bi_2O_3 addition affect the microstructure. The piezoelectric properties of $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3$ ceramics were greatly improved by a certain amount of Bi_2O_3 addition. Excellent properties of density=4.54 g/cm^3, relative densities=98.5 %, $k_p=0.468$, $Q_m=1{,}715$ and $d_{33}=183$ pC/N were obtained with a composition of 0.3 wt% Bi_2O_3

Keywords Piezoelectric · Bi_2O_3 · KNN · Electromechanical coupling coefficient (k_p) · Mechanical quality factor (Q_m).

1 Introduction

Lead-based piezoelectric ceramics such as $Pb(Zr,Ti)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$and $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ systems have attracted the attention of many researchers due to their excellent piezoelectric properties. However, these lead-based ceramics can cause critical environmental pollution and damage to the human body. Therefore, in recent years, lead-free piezoelectric ceramics have increasingly been studied. Among these, lead-free piezoelectric compositions such as $K_{0.5}Na_{0.5}$ NbO_3(KNN) are considered promising candidates due to their strong piezoelectricity and ferroelectricity [1]. In typically sintered KNN ceramics, a piezoelectric constant (d_{33})=80pC/N, electromechanical coupling factor (k_p)=36–40 %, and mechanical quality factor (Q_m)=130 are obtained [2].

The major disadvantage of pure KNN, however, is difficulties in obtaining sufficiently dense ceramics by conventional sintering in air. In order to improve the densification and piezoelectric properties of KNN-based ceramics, additives have been incorporated in KNN-based ceramic systems, with notable examples being KNN-$LiSbO_3$ and KNN-$LiNbO_3$-$(Ag_{0.5}Li_{0.5})TaO_3$ [3–8].

In addition, specialized sintering processes (spark plasma sintering (SPS), hot pressing, hot forging, RTGG(reactive template grain growth), etc.) have been introduced for preventing the evaporation of Na_2O and K_2CO_3 and to lower the sintering temperature to overcome the drawback of insufficient density [9–12]. Many researchers have found that improved piezoelectric properties can be obtained at the polymorphism phase transition (PPT) temperature, which is different from the morphotropic phase boundary (MPB) in a PZT system. At various compositions, the piezoelectric properties were improved at PPT that occurs at room temperature, but the piezoelectric properties at the PPT temperature are very sensitive to temperature. Therefore, many studies have been performed with the aim of shifting the PPT to higher temperature than room temperature [13].

Piezoelectric actuators and ultrasonic motors require a high electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) in order to induce large strain that is proportional

---

J. Noh · J. Yoo (✉)
Department of Electrical Engineering,
Semyung University Jechon,
Chungbuk, South Korea
e-mail: juhyun57@semyung.ac.kr

to the applied electric field. Furthermore, in order to prevent heat generation of the actuator, when it is driven with high voltage for a long time, a high mechanical quality factor (Q_m) and temperature stability are required as temperature instability can limit the applicability of the piezoelectric device [14–16].

We previously reported that the sintering aid $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ (KCT) could remarkably improve the density and piezoelectric properties of KNN ceramics prepared by an ordinary sintering process [17].

In this study, the effect of Bi_2O_3 addition on the structure, phase transition behavior, and piezoelectric properties of $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3+0.009\ K_{5.4}Cu_{1.3}Ta_{10}O_{29}+$ 0.1 wt% Li_2CO_3 ceramics with a fixed 0.009 $K_{5.4}Cu_{1.3}T_{10}O_{29}$ composition were investigated for application to a low loss piezoelectric actuator and ultrasonic motor .

2 Experimental

The specimens were manufactured using a conventional mixed oxide process. The compositions used in this study were as follows;

$$(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3 + 0.009\,K_{5.4}Cu_{1.3}Ta_{10}O_{29} + 0.1\text{wt\%}Li_2CO_3 + x\text{wt\%}Bi_2O_3 (x = 0,\ 0.3,\ 0.6,\ 0.9)$$

The raw materials, Na_2CO_3 (99.5 %), K_2CO_3 (99.5 %), Sb_2O_5 (99.9 %), Nb_2O_5 (99.9 %), CuO (99.9 %), Li_2CO_3 (99 %) and Bi_2O_3 for the given composition were weighted by mole ratio and the powders were ball-milled for 24 h. After drying, they were calcined at 880 °C and 950 °C for 6 h and 5 h, respectively. Thereafter, Bi_2O_3 and KCT were added as sintering aids and then the specimens were ball-milled and dried again. Polyvinyl alcohol (PVA: 5 wt% aqueous solution) was subsequently added to the dried powders. The powders were molded under pressure of 2,000 kg/cm^2 in a mold, burned out at 600 °C for 3 h, and then sintered at 1080~1120°Cfor 5 h. The dimensions of the specimens were 17.2Φ(diameter)×1 mm(thickness). Poling was carried out at 100 °C in a silicon oil bath by applying a field of 3 kV/mm for 30 min. In order to investigate the dielectric properties, capacitance was measured at 1 kHz using an LCR meter (ANDO AG-4034) and the dielectric constant (ε_r) was calculated. Piezoelectric constants were obtained using a d_{33} meter (APC 8000 piezo d_{33} tester). For investigating the piezoelectric properties, the resonant and anti-resonant frequencies were measured by an Impedance Analyzer (Agilent 4294A) according to the IEEE standard and then k_p and Q_m were calculated [18].

An X-ray diffractometer (XRD) (Rigaku, D/MAX 2500 V) with CuKα1 radiation (λ=1.5406 Å) was utilized to identify the crystal structure.

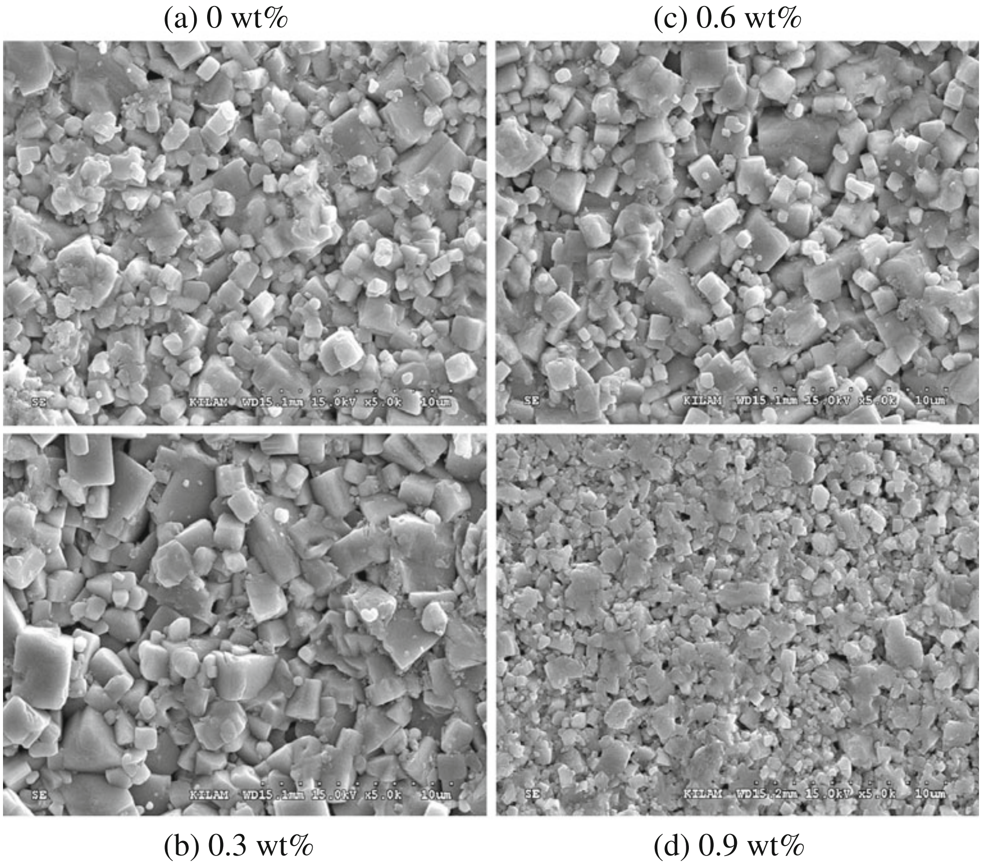
(a) 0 wt%
(c) 0.6 wt%
(b) 0.3 wt%
(d) 0.9 wt%

Fig. 1 Microstructure as a function of Bi_2O_3 addition. (**a**) 0 wt%, (**b**) 0.3 wt%, (**c**) 0.6 wt% and (**d**) 0.9 wt%

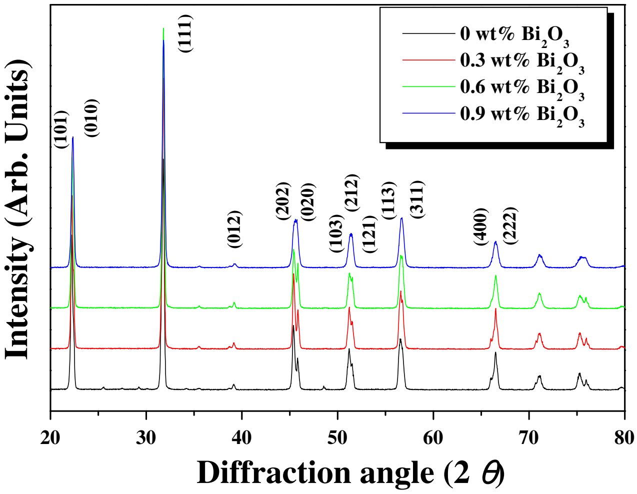

Fig. 2 X-ray diffraction pattern as a function of Bi_2O_3 addition

3 Results and discussion

Figure 1 shows the microstructures of specimens as a function of Bi_2O_3 addition. It can be observed that all samples have dense microstructures. The grain size showed an increasing trend up to 0.3 wt% Bi_2O_3 addition and then decreased gradually. Li_2CO_3 and Bi_2O_3 can form a liquid phase in the KNN-based ceramics at 690 °C. The formation of a liquid phase has a significant impact on improving the density and the grain growth process of ceramics. On the other hand, the grain size showed a slight decreasing trend at more than 0.6 wt% Bi_2O_3 as shown in Fig. 1. This may be due to the existence of Bi_2O_3 which is speculated to segregate at grain boundaries.

Figure 2 shows the X-ray diffraction pattern as a function of Bi_2O_3 addition. The XRD pattern of the ceramics in range of 2θ from 45° to 50° indicated that the specimens have orthorhombic symmetry when $Bi_2O_3 \leq 0.6$ wt%. Furthermore, the two diffraction peaks, (202) and (020), merged into a single peak when $Bi_2O_3 \geq 0.9$ wt%. The phase structure was changed from an orthorhombic phase to pseudo-cubic phase due to excess addition of Bi_2O_3. At room temperature, the crystal structures of all samples were the pure perovskite without any secondary phases.

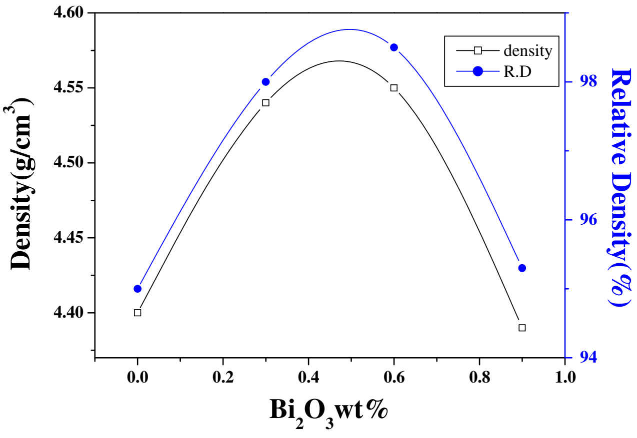

Fig. 3 Density and relative density as a function of Bi_2O_3 addition

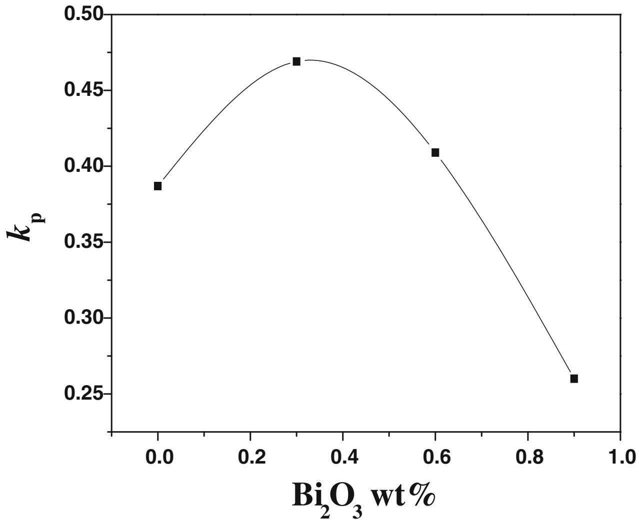

Fig. 4 Electromechanical coupling factor (k_p) as a function of Bi_2O_3 addition

Figure 3 shows the bulk density and relative density of the specimens as a function of Bi_2O_3 addition. As shown in Fig. 3, the (bulk) density gradually increased from 4.4 g/cm^3 to 4.55 g/cm^3 and then decreased. The relative densities as a function of Bi_2O_3 addition were 95, 98, 98.5 and 95.3 %, respectively. This is attributed to Bi_2O_3 addition yielding improved density though the formation of a liquid phase due to the low-melting point of Bi_2O_3 and Li_2CO_3. The decrease of density at 0.9 wt% Bi_2O_3 is attributed to segregation of Bi^{3+} at the grain boundary by excess addition. It is found that the (bulk) density and relative density reach maximum values of 4.55 g/cm^3 and 98.5 %, respectively, at 0.6 wt% Bi_2O_3 addition.

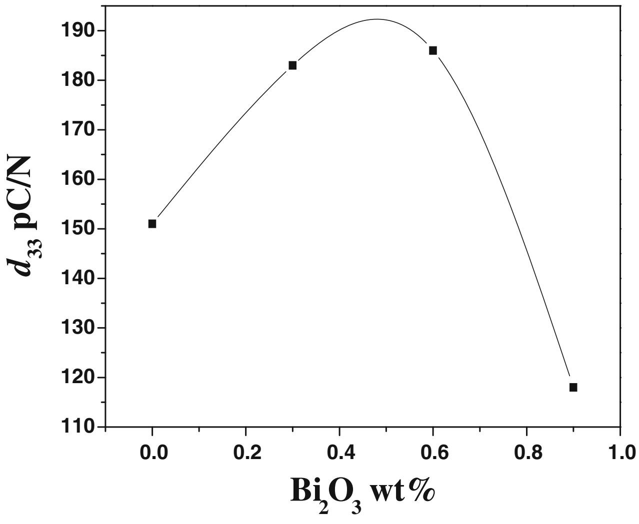

Fig. 5 Piezoelectric constant(d_{33}) as a function of Bi_2O_3 addition

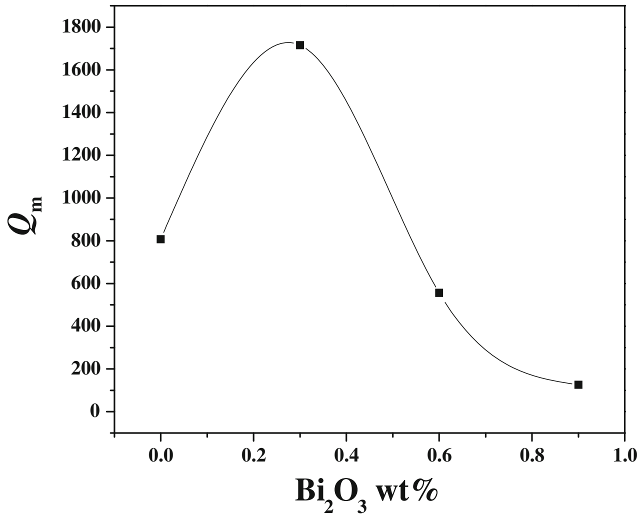

Fig. 6 Mechanical quality factor (Q_m) as a function of Bi_2O_3 addition

Figures 4 and 5 show the electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) as a function of Bi_2O_3 addition. k_p and d_{33} gradually increased and then decreased. It is found that k_p and d_{33} reach maximum values of 0.468 and 183 pC/N respectively, at 0.3 wt%. Therefore, it can be concluded that Bi_2O_3–doped ceramics can offer improved the k_p and d_{33}. In addition, the formation of a liquid phase has a significant impact on improving the k_p and d_{33}.

Figure 6 shows the mechanical quality factor (Q_m) according to the amount of Bi_2O_3 addition. Q_m rapidly increased and then decreased. A similar tendency was observed for k_p. In general, it is well known that soft-doping deteriorates Q_m, however, in this system, Q_m increased due to the improved sinterability. Therefore, in this system, 0.3 wt% Bi_2O_3 addition is regarded as the optimum composition. It is found that Q_m reaches a maximum value of 1,715 at 0.3 wt% Bi_2O_3.

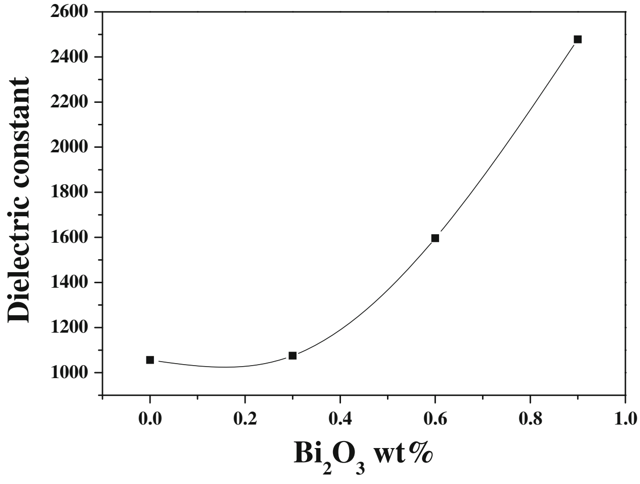

Fig. 7 Dielectric constant (ε_r) as a function of Bi_2O_3 addition

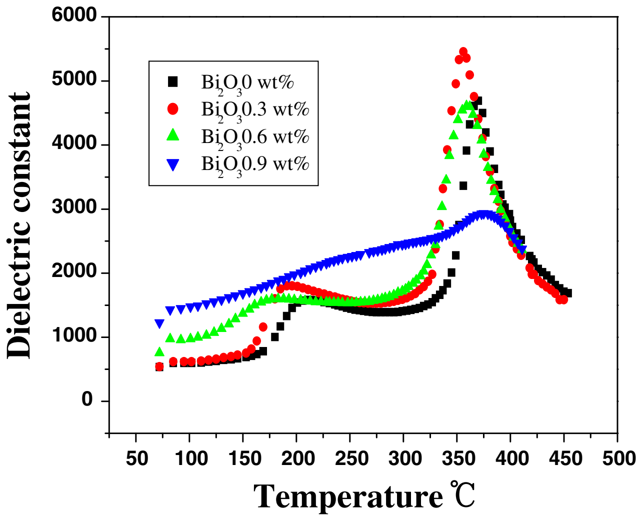

Fig. 8 Temperature dependence of dielectric constant as a function of Bi_2O_3 addition

Figure 7 shows the dielectric constant (ε_r) as a function of Bi_2O_3 addition. The dielectric constant (ε_r) gradually increased from 1056 to 1075 as x increased from 0 wt% to 0.3 wt% and then rapidly increased from 1075 to 2478 as x increased from 0.3 wt% to 0.9 wt%. It is found that the dielectric constant (ε_r) reaches a maximum value of 2478 at 0.9 wt% Bi_2O_3 addition. This phenomenon can be illustrated by the finding that with the substitution of the Bi $^{3+}$ ion for the A site of an ABO_3 perovskite structure, may act as a donor dopant and then increase dielectric constant (ε_r) of the specimen. Figure 8 shows the temperature dependence of the dielectric constant at 10 kHz. The 0.9 wt% Bi_2O_3 added specimen shows weak ferroelectric properties. This result corresponds with the XRD-pattern. With increasing Bi_2O_3 addition, the Curie temperature T_c and orthorhombic-tetragonal phase transition temperature $T_{o\text{-}t}$ shifted toward

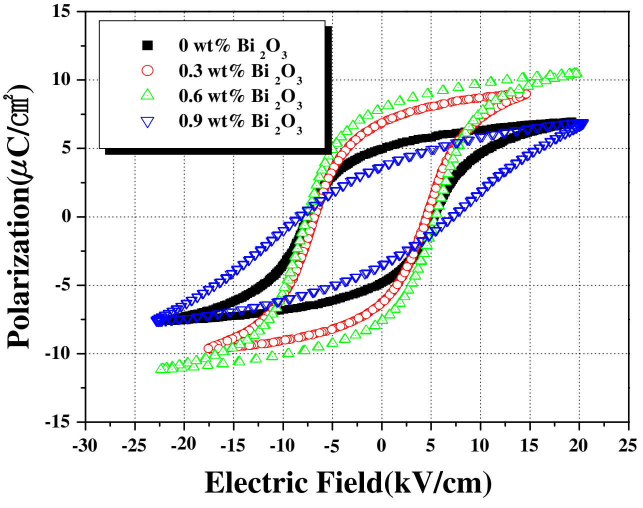

Fig. 9 Effect of Bi_2O_3 addition -level on P-E hysteresis loop

Table 1 Physical characteristics of the specimens as a function of Bi_2O_3 addition

Sintering temp. [°C]	Bi_2O_3 (wt%)	Density (g/cm^3)	Relative density (%)	k_p	Q_m	d_{33} (pC/N)	Dielectric constant
1080 °C	0	4.40	95	0.387	807	134	1056
1080 °C	0.3	4.54	98	0.468	1715	183	1075
1080 °C	0.6	4.55	98.5	0.409	556	149	1596
1120 °C	0.9	4.39	95.3	0.26	126	121	2478

the lower temperature region. For KNNS-0.009 KCT-0.1 wt%Li_2CO_3-x wt% Bi_2O_3 ceramics, two sharp phase transitions known as $T_{o\text{-}t}$ and T_c varied from 211 °C to 183 °C and from 370 °C to 359 °C, respectively.

Figure 9 shows the *P-E* hysteresis loop of KNNS-0.009 KCT-0.1 wt%Li_2CO_3-x wt% Bi_2O_3 ceramics with $x=0$, 0.3, 0.6 and 0.9 wt% sintered at 1080–1120 °C. All the specimens showed a typical hysteresis loop. The remnant polarization (P_r) gradually increased from 4.98 $\mu C/cm^2$ to 7.97 $\mu C/cm^2$ as x was increased from 0 wt% to 0.6 wt%, while the coercive field (E_c) gradually decreased from 5.26 kV/cm to 4.54 kV/cm as x was increased from 0 wt% to 0.3 wt%. Table 1 shows the physical characteristics of the specimens as a function of Bi_2O_3 addition.

4 Conclusion

Lead-free $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3+0.009\ K_{5.4}Cu_{1.3}Ta_{10}O_{29}+0.1$ wt%Li_2CO_3+ x wt%Bi_2O_3 piezoelectric ceramics were prepared by the conventional solid state reaction and normal sintering processes. Their piezoelectric and dielectric properties were investigated as a function of Bi_2O_3 addition. The results obtained from the experiment are as follows:

1. Bi_2O_3 doped $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3+0.009\ K_{5.4}Cu_{1.3}Ta_{10}O_{29}+0.1$wt%$Li_2CO_3$ ceramics showed enhanced piezoelectric and dielectric properties due to improved sinterability.
2. The crystal structure of the specimens demonstrated orthorhombic symmetry when Bi_2O_3 was less than 0.6 wt% and the two diffraction peaks, (202) and (020), merged into a single peak when $Bi_2O_3 \geq$ 0.9 wt%. The crystal structure changed from orthorhombic phase to pseudo-cubic phase at composition exceeding 0.9 wt% Bi_2O_3.
3. At the composition with 0.3 wt% Bi_2O_3 sintered at 1080 °C, excellent physical properties (density=4.54 [g/cm^3], $k_p=0.468$, $Q_m=1{,}715$ and $d_{33}=183$ pC/N) were obtained, suitable for low loss piezoelectric actuator and ultrasonic motor applications.

References

1. Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nagamura, Lead-free piezoceramics. Nature **432**, 84 (2004)
2. L. Egerton, D.M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium—sodium niobate. J. Am. Ceram. Soc. **42**, 438 (1959)
3. Y. Guo, K. Kakimoto, H. Ohsato, Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiNbO_3$ ceramics. Appl. Phys. Lett. **85**, 4121 (2004)
4. M. Matsubara, K. Kikuta, S. Hirano, J. Appl. Phys. **97**, 114105 (2005)
5. Y. Guo, K. Kakimoto, H. Ohsato, Mater. Lett. **59**, 241 (2005)
6. M. Matsubara, T. Yamaguchi, W. Sakamoto, K. Kikuta, T. Yogo, S.J. Hirano, J. Am. Ceram. Soc. **88**, 1190 (2005)
7. S.J. Zhang, R. Xia, T.R. Shrout, G.Z. Zang, J.F. Wang, J. Appl. Phys. **100**, 104108 (2006)
8. E. Hollenstein, M. Davis, D. Damjanovic, N. Setter, Appl. Phys. Lett. **87**, 182905 (2005)
9. Y. Lee, B. Seo, Y. Oh, J. Yoo, J. Kor. Phys. Soc. **57**, 959 (2010)
10. B. Seo, J. Yoo, J. Kor. Phys. Soc. **23**, 617 (2010)
11. Y. Lee, J. Yoo, K. Lee, I. Kim, J. Song, Y. Park, J. Alloys Compd. **506**, 872 (2010)
12. D. Kim, J. Yoo, I. Kim, J. Song, J. Appl. Phys. **105**, 061642 (2009)
13. Y. Oh, J. Yoo, Mater. Lett. **79**, 180 (2012)
14. Y. Jeong, J. Yoo, S. Lee, J. Hong, Sens. Actuators A **135**, 215 (2007)
15. K. Chung, J. Yoo, C. Lee, D. Lee, Y. Jeong, H. Lee, Sens. Actuators A **125**, 340 (2006)
16. L. Wu, D. Xiao, J. Wu, Y. Sun, D. Lin, J. Zhu et al., J. Eur. Ceram. Soc. **28**, 2963 (2008)
17. S. Lee, K. Lee, J. Yoo, Y. Jeong, H. Yoon, Trans. Electr. Electron. Mater. **12**(2), 72 (2011)
18. IEEE Standard on Piezoelectricity, IEEE Std. 176, Institute of Electrical and Electronics Engineers, Inc. (1978)