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Studies on new systems of BNT-based lead-free piezoelectric ceramics

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Abstract Several new systems of $Bi_{0.5}Na_{0.5}TiO_3$-based lead-free piezoelectric ceramics were proposed based on the design of the multiple complex in the A-site of ABO_3 compounds. These ceramics were prepared by conventional ceramic techniques. The comparison of the piezo- and ferroelectric properties of these ceramics with those of the best properties of the $Bi_{0.5}Na_{0.5}TiO_3$-based lead-free piezoelectric ceramics published recently shows that these ceramics of the new systems have better ferroelectric and piezoelectric performance, and better temperature characteristic of the properties. Among these materials, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ possesses higher piezoelectric constant (d_{33}=230.8 pC/N), higher electromechanical couple factor (k_p=0.41), larger remanent polarization (P_r=40 μC/cm^2) and a better *P–E* hysteresis loop below 200 °C. Practical devices such as ceramic middle frequency filters and buzzers have been made by using these lead-free piezoelectric ceramics.

Keywords $Bi_{0.5}Na_{0.5}TiO_3$ · Lead-free piezoelectric ceramics · Piezoelectric constant · Electromechanical couple factor · *P–E* hysteresis loop

1 Introduction

Lead oxide-based piezoelectric ceramics, such as Pb(Ti, Zr)O_3 (PZT), are now widely used in various applications such as transducers, filters, oscillators and actuators because of their superior piezoelectric properties. However, from the sustainable development point of view, the toxicity of lead oxide and its high vapor pressure during material processing may bring serious problems, resulting in an increasing demand for environmentally benign alternative materials. Therefore, lead-free ferro- and piezoelectric materials have received much attention in recent years.

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) is considered to be an excellent candidate for lead-free piezoelectric ceramics because of its relatively high remnant polarization (38 μC/cm^2) [1]. However, the BNT ceramics without substitutive ions and/or additives are very difficult to pole because of their relatively large coercive field (E_c=73 kV/cm) and high electrical conductivity. To improve the piezoelectric properties, BNT-based solid solutions with another perovskite components and the doping with other elements were widely investigated, such as BNT–$BaTiO_3$ [1], BNT–$Bi_{0.5}K_{0.5}TiO_3$[2], BNT–$BiFeO_3$[3], BNT–$NaNbO_3$[4], BNT–$Bi_{0.5}K_{0.5}TiO_3$–$BaTiO_3$[5], BNT–$Ba(Cu_{1/2}W_{1/2})O_3$[6], CeO_2-doping BNT–$BaTiO_3$[7], TiO_2-nonstoichiometric BNT–$BaTiO_3$[8] and so on. However, the piezoelectric properties of these ceramics are not high enough for most practical uses.

In order to further enhance the properties of BNT ceramics and meet the requirements for practical uses, it is necessary to develop new BNT-based multi-component systems. Recent years, the authors' group did further investigation on BNT-based lead-free piezoelectric ceramics. Several new systems of BNT-based lead-free piezoelectric ceramics were proposed based on the design of the multiple complex in the A-site of ABO_3 compounds.

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2 Design of new BNT-based lead-free piezoelectric ceramics

Compared with PZT ceramics, pure BNT ceramics and BNT-based solid solutions give much lower piezoelectric properties. There may be three primary differences between BNT- and PZT-based ceramics. Firstly, BNT is a ferroelectric compound with complex ions $(Bi_{0.5}Na_{0.5})^{2+}$ of Bi^{3+} and Na^{+} in its A-site. Completely different from BNT, PZT is a solid solution and is composed of $PbTiO_3$ and $PbZrO_3$ with complex ions of Ti^{4+} and Zr^{4+} in its B-site. Secondly, most BNT-based ceramics are the solid solutions which are made up of ferroelectric BNT and other ferroelectrics or non-freeoelectrics such as $Bi_{0.5}K_{0.5}TiO_3$ [2], $BaTiO_3$ [1], $Ba(Cu_{1/2}W_{1/2})O_3$ [6], $BiFeO_3$ [3] and so on. In contrast, PZT is the solid solution which is composed of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$. That is, there may be different situation of forming solid solutions between BNT-based and PZT-based ceramics. Finally, $Bi_{0.5}Na_{0.5}TiO_3$-based ceramics are piezoelectric materials with the complex in their A-site, and the ceramics with relatively good piezoelectric properties can be obtained through partially substitution of A-site $(Bi_{0.5}Na_{0.5})^{2+}$ ions by Ba^{2+}, $(Bi_{0.5}K_{0.5})^{2+}$, Ba^{2+}–$(Bi_{0.5}K_{0.5})^{2+}$ and so on. Modification of BNT in B-site cannot effectively improve the piezoelectric properties[15–20]. Contrasting with BNT, $PbTiO_3$ is B-site piezoelectric active. It is well known that $PbTiO_3$-based ceramics with excellent piezoelectric properties are the solid solutions that the B-site ions Ti^{4+} of $PbTiO_3$ are partially substituted by Zr^{4+}, $(Mg_{1/3}Nb_{2/3})^{4+}$ and so on. In a word, the modification of BNT and $PbTiO_3$ may be different.

According to the discussion mentioned above, $(Bi_{0.5}Na_{0.5})^{2+}$, Bi^{3+} and Na^{+} in the ABO_3 structure are defined as A-site, A_1-site and A_2-site ions, respectively. And A, A_1 and A_2-site ions can be simultaneously or singly substituted partially by alkaline-earth metal ions (Ba^{2+}, Sr^{+2}, Ca^{+2}), metal ions with +3 valence (La^{3+}, Y^{3+} and so on) and metal ions with +1 valence (K^{+}, Li^{+} and so on), respectively. Under this consideration, some new members of BNT group, such as $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$, $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$, $[Bi_{1-y}(Na_{1-x}Li_x)]_{0.5}Ba_yTiO_3$, $[Bi_{1-y-z}(Na_{1-x-y-z}Li_x)]_{0.5}Ba_ySr_zTiO_3$, $[Bi_{1-y-z}(Na_{1-x-y-z}K_x)]_{0.5}Ba_ySr_zTiO_3$ $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Sr_yTiO_3$ $(Bi_{0.5}Na_{0.5})_{1-x-y-z}Ba_xSr_yCa_zTiO_3$, $[(Bi_{1-x-y}L_x)Na_{1-y}]_{0.5}Ba_y TiO_3$ and so on, were proposed and patented, and the piezoelectric and ferroelectric properties were investigated. The results of the researches are briefly outlined as follows.

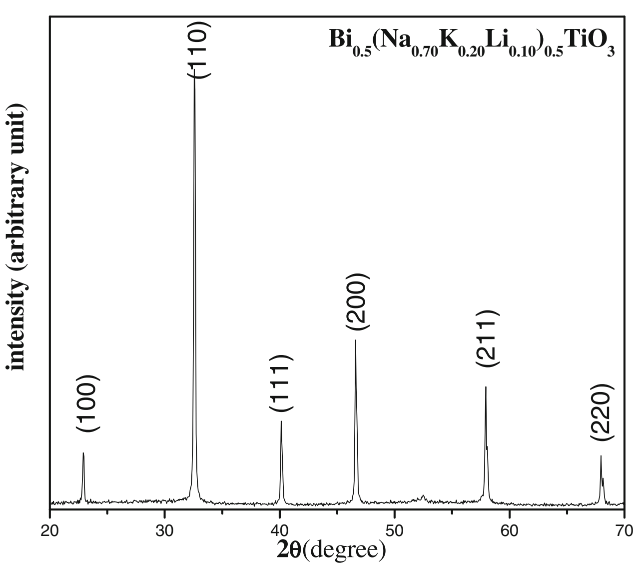

Fig. 1 XRD pattern of $Bi_{0.5}(Na_{0.70}K_{0.20}Li_{0.10})_{0.5}TiO_3$ ceramics

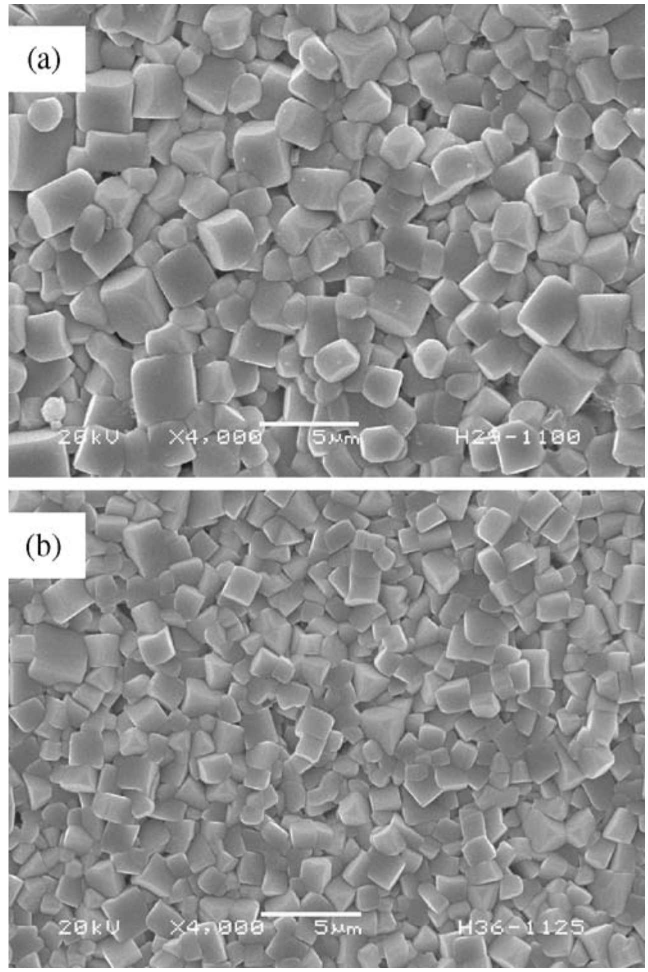

Fig. 2 SEM images of BNKLT−*x*/*y* ceramics (**a**) BNKLT−0.15/0.075 ceramics sintered at 1100 °C for 2 h; and (**b**) BNKLT−0.20/0.10 sintered at 1125°C for 2 h

3 Experimental

New BNT-based lead-free piezoelectric ceramics were prepared by conventional ceramic fabrication technique. Industrial-grade metal oxides or carbonate powders of

Table 1 The piezoelectric and ferroelectric properties of the new BNT-based ceramics developed in present work.

New BNT-based systems	d_{33} (pC/N)	k_p	P_r (μC/cm^2)	E_c (kV/mm)
$Bi_{0.5}(Na_{1-x-y}K_x Li_y)_{0.5}TiO_3$	230.8	0.41	40.4	2.5–4.0
$[Bi_{1-z}(Na_{1-y-z}Li_y)]_{0.5}Ba_zTiO_3$	207.8	0.368	38.5	3.29
$[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$	202.7	0.365	38.5	2.8–5.16
$[Bi_{1-z-u}(Na_{1-y-z-u}Li_y)]_{0.5}Ba_zSr_uTiO_3$	202.0	0.338	40.4	2.47–4.98
$[Bi_{1-z-u}(Na_{1-x-z-u}K_x)]_{0.5}Ba_zSr_uTiO_3$	191.4	0.364	34.4	2.58
$Bi_{0.5}(Na_{1-x-y}K_xLi_yAg_z)_{0.5}TiO_3$	215.5	39.3	–	–
$[(Bi_{1-x-y}La_x)Na_{1-y}]_{0.5}Ba_yTiO_3$	183.0	0.355	–	–
$(Bi_{0.5}Na_{0.5})_{1-x-y-z}Ba_xSr_yCa_zTiO_3$	161.8	0.327	–	–

Bi_2O_3, Na_2CO_3, K_2CO_3, Li_2CO_3, Ag_2O, $BaCO_3$, $SrCO_3$, La_2O_3, Y_2O_3 and TiO_2 were used as raw materials. All the raw materials mixed by ball-milling were calcined at 800–900 °C for 2–4 h. After calcination, the ball-milled powders were granulated by adding PVA as a binder and pressed into discs and then sintered at 1,100–1,200 °C for 2–3 h in air. Silver paste was coated to form electrodes on both sides of sintered ceramic specimens and fired at 810 °C. The specimens were poled in silicone oil bath with a dc field of 3–4 kV/mm at 80 °C for 20 min.

The crystalline phase of the samples was examined by X-ray diffraction (XRD) technique (DX-1000X, China). The microstructure of the sintered samples was observed using scanning electron microscope (JSM-5900LV). Electromechanical coupling factor k was determined by the resonance–antiresonance method on the basis of IEEE standards by using an impedance analyzer (HP4194A). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-3A). The P–E hysteresis loops were observed using Radiant Precision Workstation.

4 Results and discussion

The results of the X-ray diffractions of all the samples investigated show that the new ceramics possess a single-phase perovskite structure. It is believed that K^+ and Li^+ ions substitute partially Na^+ ion, Ba^{2+} and Sr^{2+} substitute partially $(Bi_{0.5}Na_{0.5})^{2+}$ ions, and La^{3+} and some related ions substitute partially Bi^{3+} ion, and the substitute ions diffuse into the BNT lattices to form solid solutions. All new BNT-based ceramics are well sintered at 1,100–1,200 °C in air. Figure 1 gives a typical XRD pattern of $Bi_{0.5}(Na_{0.70}K_{0.20}Li_{0.10})_{0.5}TiO_3$ ceramics.

Figure 2 shows the microstructures of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ (BNKLT−x/y) ceramics. Almost no pores are found on the surface of BNKLT−x/y ceramics. The bulk densities of BNKLT−x/y ceramics are higher than 97% of the theoretical density.

Table 1 exhibits the piezoelectric and ferroelectric properties of new BNT-based ceramics developed in present work. From Table 1, it can be found that these new systems

Table 2 Piezoelectric and ferroelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$-based lead-free piezoelectric ceramics published in papers and patents.

BNT-based ceramics	d_{33} (pC/N)	k_p	P_r (μC/cm^2)	E_c (kV/mm)
Pure BNT [1, 9]	58	0.12	38	7.3
CeO_2-added and TiO_2-nonstoichiometric NT–$BaTiO_3$ [7, 8]	152	0.34	37.7	3.71
BNT–BKT [2, 10]	96	0.314	19.9	3.0
BNT–$NaNbO_3$ [4, 11]	88	0.179	32.6	4.64
BNT–$NaSbO_3$ [12]	–	0.368	–	–
BNT–BKT–BT [13]	191	0.34	35.9	–
BNT–BT–$NaNbO_3$ [14, 25]	110	–	–	–
BNT–BKT–$NaNbO_3$ [15]	–	0.289	–	–
BNT–BKT–BT–$NaNbO_3$ [15]	–	0.421	–	–
Modified BNT–BKT and BNT–BT by partially substitution in B-site [15–20]	–	0.32	–	
BNT–$BiCrO_3$ [21]	–	0.312	–	–
$(Bi_{0.5}Na_{0.5})_{(1-1.5x)}L_xTiO_3$ (L=La, Bi) [22, 23]				
BNT–$Ba(Cu_{1/2}W_{1/2})O_3$ [6]	95	0.21	–	–
$Bi_{0.5}(Na_{0.84}K_{0.16})_{0.5}TiO_3$–$SrTiO_3$ [24]	185	0.34		

BNT $(Bi_{0.5}Na_{0.5})TiO_3$, *BKT* $(Bi_{0.5}K_{0.5})TiO_3$, *BT* $BaTiO_3$

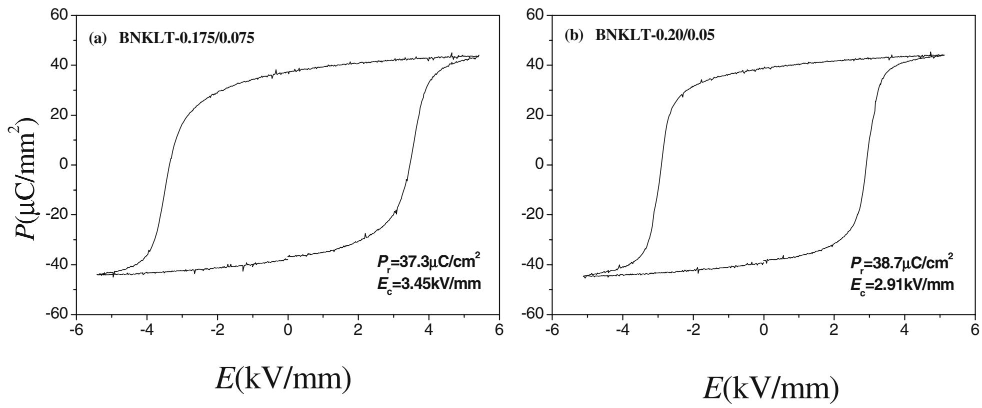

Fig. 3 *P–E* hysteresis loops of BNKLT−*x*/*y* ceramics at room temperature (**a**) BNKLT−0.175/0.075; and (**b**) BNKLT−0.20/0.05

of BNT-based lead-free piezoelectric ceramics based on the design of the multiple complex in the A-site of ABO_3 compounds provide excellent piezoelectric and ferroelectric properties. These new ceramics exhibit good performance and strong ferroelectricity: d_{33}=161.8–230 pC/N, k_p=0.327–0.40, P_r=34.4–40.4 μC/cm^2, and E_c=2.47–5.16 kV/mm.

Table 2 shows the piezoelectric and ferroelectric properties of BNT-based ceramics published recently in papers and patents prepared by conventional ceramic technique. It can be seen that pure BNT ceramics provide the piezoelectric constant d_{33} of 58 pC/N [9], and some classic BNT-based ceramics, such as BNT–BT [5], BNT–BKT [2], BNT–BT–BKT [5], BNT–$NaNbO_3$ [4], give piezoelectric properties of d_{33}=152, 96, 191, 88 pC/N, and k_p=0.24, 0.314, 0.33, 0.179, respectively. Obviously, compared with these BNT-based ceramics, some ceramics in the new systems developed in present work show much better piezoelectric properties. At the same time, it should be pointed out that the ceramics developed in present work provide the very large remanent polarization P_r and low coercive field E_c, which facilitates the poling process of BNT-based ceramics and results in the great improvement of electrical properties. From Tables 1 and 2, it is concluded that the design of the multiple complex in the A-site of BNT ferroelectrics is effective to develop BNT-based lead-free piezoelectric ceramics.

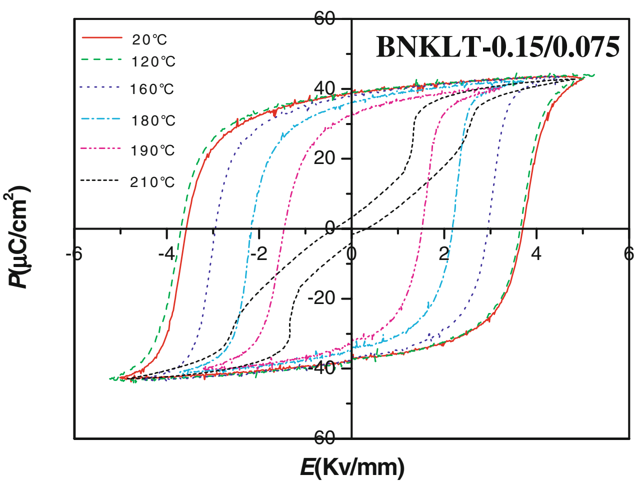

Fig. 4 *P–E* hysteresis loops of BNKLT−0.15/0.075 ceramics at different temperatures

Among the new BNT-based ceramics, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ ceramics possess excellent electrical properties. Figure 3 shows the *P–E* hysteresis loops of BNKLT−*x*/*y* ceramics at room temperature. As well known, pure BNT ceramics have a remanent polarization P_r of 38 μC/cm^2 and relatively high coercive field E_c of 7.3 kV/cm. Compared with pure BNT ceramics, BNKLT−*x*/*y* ceramics possess simultaneously a very large P_r and a relatively low E_c, which leads to an significant enhancement of piezoelectric properties.

Figure 4 shows the *P–E* hysteresis loops of BNKLT−0.15/0.075 ceramics at different temperature. It can be seen that the hysteresis loop shows a typical ferroelectric characteristic at the temperature of 20 °C, and with the temperature increasing, the loops begin to become narrower but still keep the very typical ferroelectric feature and large remanent polarization up to 190 °C. When the temperature reaches 210 °C, the hysteresis loop of the ceramics is deformed and a double-like *P–E* hysteresis loop appears. It can be concluded from Fig. 4 that the depolarization temperature T_d of the material investigated is about 200 °C. T_d is an important factor for BNT-based ceramics from the device applications points of view. Generally, for some classical BNT-based ceramics, the obvious enhancement of piezoelectric properties is accompanied simultaneously by the significant reduction of T_d. However, BNKLT−0.15/0.075 ceramics provide simultaneously good piezoelectric properties (d_{33}=146 pC/N, k_p=0.36), strong ferroelectricity (Pr=38.9 μC/cm^2, E_c=3.7 kV/mm), and higher T_d (about 200 °C).

The BNKLT−*x*/*y* lead-free piezoelectric ceramics have been used for making ceramic middle frequency filter. The frequency characteristic of the middle frequency filter is shown in Fig. 5. The filter was made by ordinary techniques as used for PZT-based piezoelectric middle frequency filter. The measurement shows that the performance of BNKLT−*x*/*y* filter is comparable to that of Pb-based middle frequency filter. In addition, BNKLT−*x*/*y*

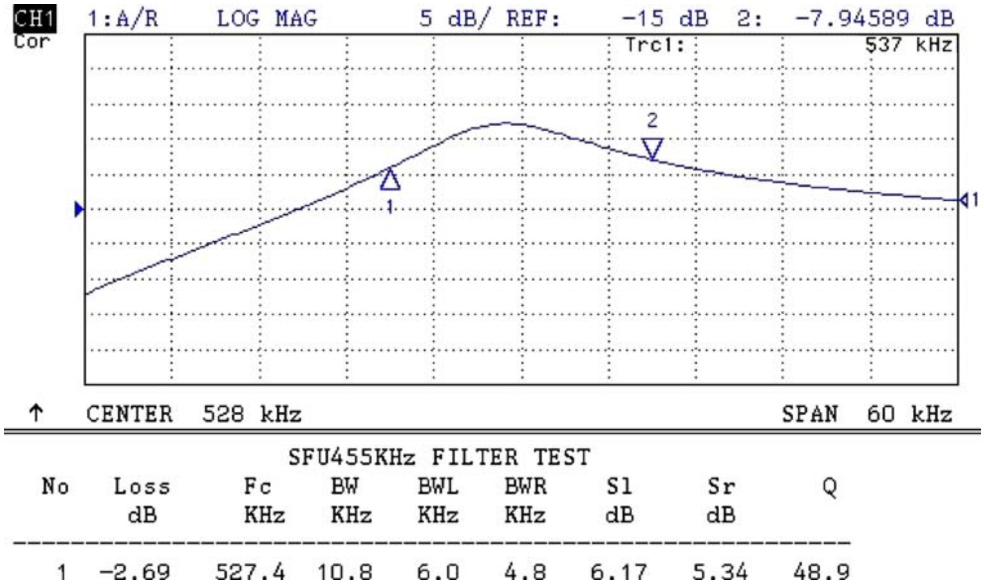

Fig. 5 Frequency characteristic of the middle frequency filter made by using BNKLT−*x*/*y* lead-free ceramics

lead-free piezoelectric ceramic were used for making buzzers by ordinary techniques as used for PZT-based piezoelectric buzzers as well. The properties of the filter and the buzzers will be discussed in detail in another paper.

5 Conclusion

Several new systems of BNT-based lead-free piezoelectric ceramics were proposed based on the design of the multiple complex in the A-site of BNT materials with emphasis on system of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ (BNKLT−*x*/*y*). All the ceramics were prepared by the conventional ceramic technique and sintered at 1,100–1,200 °C in air. The ceramics of the new systems have better ferroelectric and piezoelectric performance, and better temperature characterization of the properties. Among these materials, BNKLT−*x*/*y* possesses higher piezoelectric constant (d_{33}=230.8 pC/N), higher electromechanical couple factor (k_p=0.41), larger remanent polarization (P_r=40 μC/cm^2) and a better *P*–*E* hysteresis loop below 200 °C. Practical devices such as middle frequency ceramic filters and ceramic buzzers have been made by using BNKLT−*x*/*y* piezoelectric ceramics.

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References

1. T. Takennaka, K. Maruyama, K. Sakata, Jpn. J. Appl. Phys. **30** (9B), 2236 (1991)
2. A. Sasaka, T. Chiba, Y. Mamiya, E. Otsuki, Jpn. J. Appl. Phys. **38** (Part 1), 5564 (1999)
3. H. Nagata, N. Koizumi, T. Takenaka, Key Eng. Mater. **37–40**, 169 (1999)
4. T. Takennaka, T. Takeo, K. Takegahara, Ferroelectrics **196**, 175 (1997)
5. H. Nagata, M. Yoshida, Y. Makiuchi, T. Takenaka, Jpn. J. Appl. Phys. **42**(Part 1), 7401 (2003)
6. X.X. Wang, H. L.W. Chan, C.L. Choy, J. Am. Ceram. Soc. **86** (10), 1809 (2003)
7. X.X. Wang, H. L.W. Chan, C.L. Choy, Solid State Commun. **125**, 395 (2003)
8. X.X. Wang, S.W. Or, X.G. Tang, H.L.W. Chan, P.K. Choy, P.C.K. Liu, Solid State Commun. **134**, 659 (2005)
9. Q. Xu, S.T. Chen, W. Chen, S.J. Wu, J. Lee, J. Zhou, H.J. Sun, Y. M. Li, Journal of Alloys and Compounds **381**, 221 (2004)
10. O. Elkechai, M. Manier, J.P. Mercurio, Phys. Status. Solidi, A Appl. Res. **157**, 499 (1996)
11. Y.M. Li, W. Chen, J. Zhou, Q. Xu, H. J. Sun, R.X. Xu, Mater. Sci. Eng. B **112**, 5 (2004)
12. S. Atsushi, Japanese Patent, Pub. No. 2000-335968 (2000).
13. X.X. Wang, X.G. Tang, H.L.W. Chan, Appl. Phys. Lett. **85**(1), 91 (2004)
14. Y.G. Wu, H.L. Zhang, Y. Zhang, J.Y. Ma, D.H. Xie, J. Mater. Sci. **38**, 987 (2003)
15. F. Masahito, H. Kenji, I. Yoshiko, Japanese Patent, Pub. No. 2002-220280 (2002)
16. T. Yasuki, Japanese Patent, Pub. No. 2004-43210 (2004)
17. T. Yasuki, Japanese Patent, Pub. No. 2003-238245 (2003)
18. Y. Hiroyuki, Japanese Patent, Pub. No.2004-35350 (2004)
19. T. Yasuki, Y. Hiroyuki and M. Yoichi, Japanese Patent, Pub. No.2003-201171 (2003)
20. T. Yutaka and K. Tomoyoshi, Japanese Patent, Pub. No. 2004-75449 (2004)
21. S.i Atsushi, Japanese Patent, Pub. No. 2000-335967 (2000).
22. A. Herabut, A. Safari, J. Am. Ceram. Soc. **80**(11), 1464 (1997)
23. X.X. Wang, K.W. Kwok, X.G. Tang, H.L.W. Chan, C.L. Choy, Solid State Commun. **129**, 319 (2004)
24. J. Yoo, D. Oh, Y. Jeong, J. Hong, M. Jung, Mater. Lett. **58**, 3831 (2004)
25. H. Nagata, M. Yoshida, Y. Makiuchi, T. Takenaka, Jpn. J. Appl. Phys. **42**, 7401 (2003)