J Mater Sci (2008) 43:1501–1504
DOI 10.1007/s10853-007-2382-3

Piezoelectric properties of $[Bi_{0.5}(Na_{0.7}K_{0.25}Li_{0.05})_{0.5}]TiO_3$–$Ba(Ti,Zr)O_3$ binary system ceramics

**Ziying Zhang · Jianfeng Jia · Huizhi Yang ·
Changqing Chen · Hongwei Sun · Xing Hu ·
Delin Yang**

Received: 26 July 2007 / Accepted: 4 December 2007 / Published online: 1 January 2008

Abstract Dense lead-free binary system piezoelectric ceramics $(1-x)[Bi_{0.5}(Na_{0.7}K_{0.25}Li_{0.05})_{0.5}]TiO_3$–$xBa(Ti_{0.95}Zr_{0.05})O_3$ (BNKLT–BZT) were prepared by a two-step sintering process. A phase transition from rhombohedral to tetragonal was observed with increasing BZT fraction in the range $x = 0.06$–0.1 and the morphotropic phase boundary (MPB) between rhombohedral and tetragonal appears in this range. Ceramics containing 10 mol% BZT with tetragonal phase near the MPB region has the maximum piezoelectric constant d_{33}(151pC/N).

Introduction

Presently, lead-based PZT materials dominate the market of piezoelectric components due to their excellent piezoelectric properties. However, PZT are not environmentally friendly because they contain more than 60% lead which is a very toxic material [1, 2]. Therefore, it is necessary to develop environment-friendly lead-free piezoelectric ceramics to replace the PZT-based ceramics.

Sodium bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ (abbreviated as BNT), is a kind of perovskite ferroelectric discovered by Smolenskii et al. in 1960 [3]. BNT has a relatively larger piezoelectricity with a large remnant polarization P_r at room temperature and high Curie temperature. Foremost, it is free of toxicity [3]. However, pure BNT ceramics still cannot replace PZT-based ceramics widely because of the relatively large coercive field (E_c = 73 kV/cm) and high conductivity of BNT. To solve this problem, investigations have been conducted on the new morphotropic phase boundaries (MPB) in the BNT-based binary and ternary systems [4–10]. It was reported that some BNT-based systems, such as BNT-$BaTiO_3$ [4], BNT-$Ba(Hf,Ti)O_3$ [5], BNT-$K_{0.5}Bi_{0.5}TiO_3$ [6] and BNT-$NaNbO_3$ [7], can have excellent piezoelectric properties. Recently, Lin et al. reported that $[Bi_{0.5}(Na_{0.7}K_{0.25}Li_{0.05})_{0.5}]TiO_3$ (BNKLT) ceramics showed fairly satisfactory piezoelectric response with a d_{33} value of 145pC/N at room temperature [11, 12]. Furthermore, early X-ray crystalline structure studies showed that $Ba(Ti_{1-x}Zr_x)O_3$ (BZT) forms a complete solid solution. A phase diagram was subsequently constructed for the solid solution with up to 30 mol% Zr substitution [13]. Yu et al. reported that $Ba(Ti_{0.95}Zr_{0.05})TiO_3$ also showed fairly satisfactory piezoelectric responses with a d_{33} value of 236pC/N at room temperature [14]. However, the remarkable temperature dependence of piezoelectric properties and low Curie temperature of BZT ceramics still limit their practical application as piezoelectric materials.

The aim of the present work is to investigate the BNKLT–BZT binary systems since BZT has a larger piezoelectric response and the accession of a small amount of BZT to BNKLT may improve its piezoelectric properties. $(1-x)[Bi_{0.5}(Na_{0.7}K_{0.25}Li_{0.05})_{0.5}]TiO_3$–$xBa(Ti_{0.95}Zr_{0.05})O_3$ (x from 0 to 0.12) was prepared by using a two-step sintering approach. The piezoelectric properties and dielectric properties of this system were studied with a special emphasis on the MPB of this system between BNKLT (rhombohedral) and BZT (tetragonal).

Experimental

High-purity Bi_2O_3, Na_2CO_3, K_2CO_3, Li_2CO_3, TiO_2, $BaCO_3$ and ZrO_2 powders were used as raw materials. The

---

Z. Zhang · J. Jia · H. Yang · C. Chen · H. Sun · X. Hu ·
D. Yang (✉)
School of Physical Engineering, Key Laboratory of Materials
Physics of Ministry of Education of China, Zhengzhou
University, Zhengzhou 450052, China
e-mail: dlyang@zzu.edu.cn

BNKLT–BZT ceramics were prepared by using a two-step sintering approach, in which BNKLT and BZT source powders were prepared separately and then blended. To prepare the BNKLT source powder, Bi_2O_3, Na_2CO_3, K_2CO_3, Li_2CO_3 and TiO_2 powders were milled in alcohol using carnelian balls for 4 h and dried at 70 °C, followed by calcining at 850 °C for 6 h in air. BZT powder was also prepared with the corresponding primary chemicals under almost the same conditions as for BNKLT except a higher calcination temperature of 1,200 °C. The BNKLT and BZT source powders were then weighted according to the stoichiometrical calculation based on the formula of $(1-x)[Bi_{0.5}(Na_{0.7}K_{0.25}Li_{0.05})_{0.5}]TiO_3$–$xBa(Ti_{0.95}Zr_{0.05})O_3$ and mixed. After ball milling in alcohol for 4 h and drying, the blended dried powder was mixed with PVA and pressed into discs of 10 mm diameter and 1–2 mm thickness. The small disc samples were sintered at 1,100–1,120 °C for 4 h in air.

X-ray diffractometer (XRD, Rigaku, D/Max-3B) was used to evaluate the crystal structure of the sintered ceramics. The density of the sintered samples was measured by Archimedes method. A silver paste was fired on the surfaces of the discs as electrodes. To measure piezoelectric properties, the samples were polarized under 3–4 kV/mm for 20 min in silicon oil at 60 °C. Samples was aged at room temperature for 24 h after poling. The piezoelectric constant d_{33} of the samples were measured on a quasistatic d_{33} meter (China Academy of Acoustics, ZJ-3A). The electrical properties were measured by means of a resonance–antiresonance method using a Low-Frequency Impedance Analyser (HP4192A). The electromechanical coupling factor k_p, room temperature dielectric constant ε_r and dielectric loss $\tan\delta$ were obtained on the basis of the International Standard [15].

Results and discussion

Figure 1 shows the X-ray diffraction patterns of BNKLT–BZT ceramics. Without BZT doping, the pure BNKLT ceramics, labelled BNKLT-BZT0 in this case, shows rhombohedral phase, whose (110) peak is detected at 32.61 (2θ). With the increase of BZT fraction the (110) peaks of the BNKLT–BZT ceramics shift monotonically to lower 2θ angle, which indicates a consecutive increase in lattice constant as a function of the BZT fraction. The X-ray diffraction patterns of these ceramics also indicate a phase transition from rhombohedral to tetragonal with BZT fraction increasing. The difference between these two structures can be seen clearly in the X-ray diffraction patterns from (200) peaks between 40° and 50°. The XRD patterns of the BNKLT–BZT ceramics have a single reflection (200) owing to its rhombohedral symmetry in the range of $x \leq 0.04$. More BZT addition makes the (200) peak become more wide, suggesting the increase of tetragonality of the lattice. These results reveal that a rhombohedral–tetragonal MPB exists in the BNKLT–BZT system.

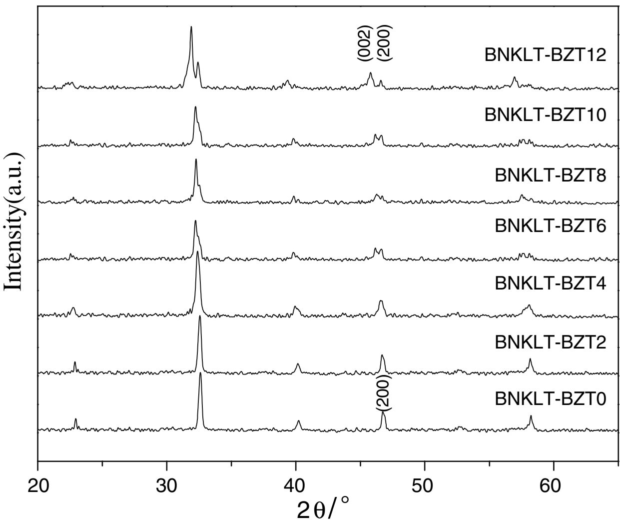

Fig. 1 XRD patterns of BNKLT–BZT ceramics sintered at 1,120 °C for 4 h

Figure 2 displays the SEM micrograph of BNKLT–BZT4 ceramics sintered at 1,120 °C for 4 h. The SEM observation confirms that the BNKLT–BZT ceramics are densely sintered. The relative densities determined by Archimedes method for all the samples are around 97% of theoretical density. Dense BNKLT–BZT ceramics were obtained possibly because the preparation process was modified, in which BNKLT and BZT powders were synthesized separately. We thought that the separate synthesis of BNKLT and BZT powders could avoid the reaction

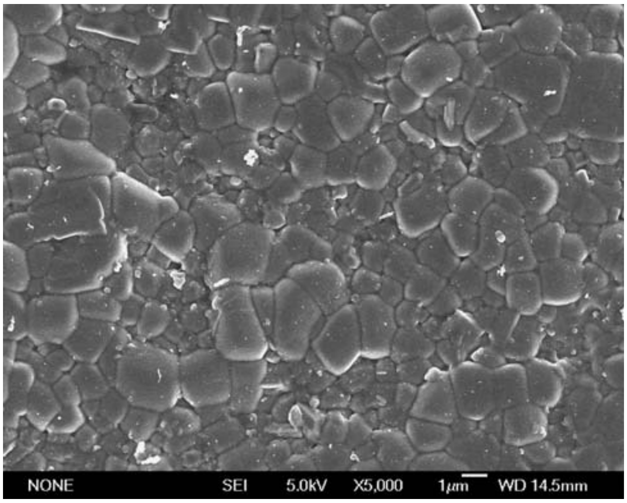

Fig. 2 SEM micrograph of BNKLT–BZT4 ceramics sintered at 1,120 °C for 4 h

between zirconate and sodium carbonate which produces some low-melting compounds [16, 17].

Figure 3 shows the dielectric constant ε_r and the loss tangent tgδ as a function of x for BNKLT–BZT piezoelectric ceramics. The dielectric constant ε_r and the loss tangent tgδ increase with the increase of x and reach a maximum value at $x = 0.08$, then they will decrease when x continues to increase. The maximum values of ε_r and tgδ at $x = 0.08$ are 5.99 and 1,677, respectively.

Figure 4 shows the piezoelectric constant d_{33} and the planar electromechanical coupling factor k_p of the BNKLT–BZT ceramics. The piezoelectric constant d_{33} increases with increasing BZT fraction until $x = 0.1$ up to 151pC/N and then decreases rapidly. The planar electromechanical coupling factor k_p changes as a function of x similar to the piezoelectric constant d_{33}, with a maximum value of 27.8% at $x = 0.08$. Combining with the X-ray diffraction patterns, we can find that the morphotropic phase boundary (MPB) exists in the BNKLT–BZT ceramics with x in the range of 0.06–0.1. Similar to PZT-based ceramics, piezoelectric and dielectric properties of BNKLT–BZT system, such as piezoelectric constant d_{33} and dielectric constant ε_r, vary with the fraction of BZT and reach peak values near the MPB. In the MPB region, the domain can be easily switched under the action of exterior electric field due to the coexistence of rhombohedral and tetragonal. Therefore the dielectric constant and piezoelectric constant enhance.

The Curie temperature T_C was determined by measuring the dependence of dielectric constant and dielectric loss on temperature. With the increase of the ambient temperature the phase transition occurs, which can be recognized by a sharp shape near the Curie point in the ε_r–T curves. Figures 5, 6 show the temperature dependences of dielectric constant and dielectric loss for the samples in the temperature range

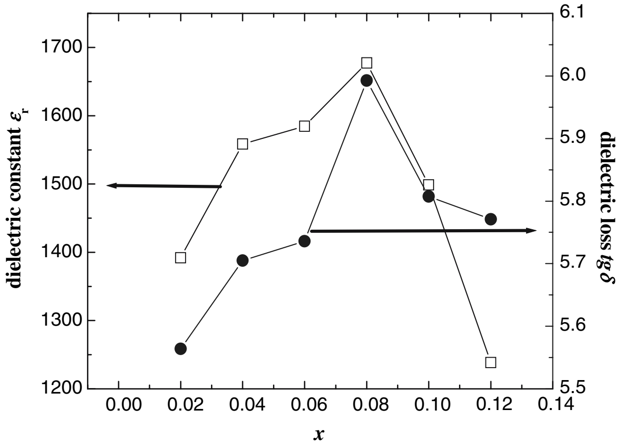

Fig. 3 Dielectric constant ε_r and dielectric loss tgδ as function of x for BNKLT–BZT piezoelectric ceramics

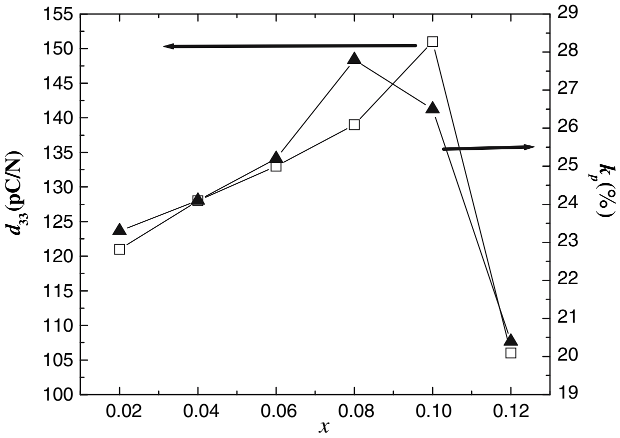

Fig. 4 Piezoelectric constant d_{33} and planar electromechanical coupling factor k_p of BNKLT–BZT ceramics

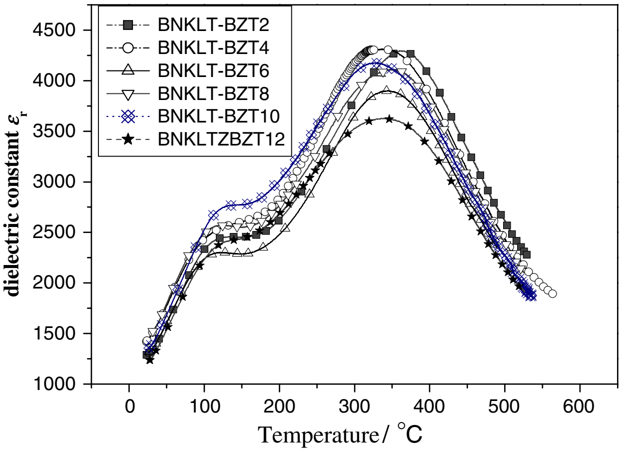

Fig. 5 Temperature dependence of dielectric constant of BNKLT–BZT ceramics

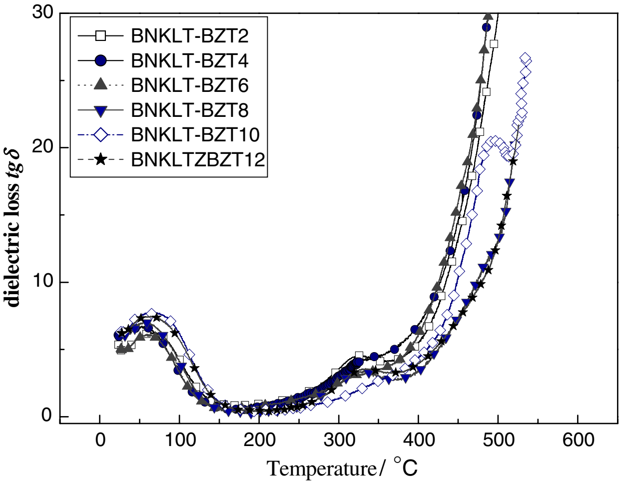

Fig. 6 Temperature dependence of dielectric loss of BNKLT–BZT ceramics

Table 1 Piezoelectric and dielectric properties of BNKLT–BZT ceramics

	ε_r	tgδ	k_p	d_{33}	T_C
BZT2	1392	5.56	23.3	121	359
BZT4	1559	5.70	24.1	128	340
BZT6	1585	5.74	25.2	133	337
BZT8	1677	5.93	27.8	139	350
BZT10	1499	5.81	26.5	151	329
BZT12	1238	5.77	20.4	106	335

from 23 to 600 °C. A small amount of BZT addition decreases the Curie temperature. The reason is that the Curie temperature decreases with the decrease of grains of the BNKLT–BZT ceramics due to the effect of the size of ferroelectric. It is known that with the increase of BZT fraction more metal ions will be pushed to the boundaries, which blocks grain growth. However, when the addition of BZT exceeds 6 mol%, the T_C point increased somewhat irregularly as shown in Table 1 and a wider phase transition temperature range was shown in the samples with BZT dopants. These results are similar with the BNT–BZT and BNT–BT systems as reported by Peng [18] and Chu [19], respectively.

Conclusion

Dense BNKLT–BZT ceramics were prepared successfully by a two-step sintering method. A phase transition from rhombohedral to tetragonal was observed with increasing BZT fraction in the range from 6 to 10 mol%, which indicates the existence of MPB in BNKLT–BZT system. A maximum value of piezoelectric constant d_{33}(151pC/N) can be obtained for the BNKLT–BZT10 ceramics. And a maximum value of planar electromechanical coupling factor k_p can reach 27.8% for BNKLT–BZT8. Dielectric constant under 1 KHz at room temperature is 1,677 for BNKLT–BZT8 ceramics. The Curie temperature T_C decreases slightly with the increase of BZT fraction and then increases irregularly when the amount of BZT exceeds 8 mol%.

References

1. Takenaka T, Nagata H (2005) J Eur Ceram Soc 25:2693
2. Levassort F, Tran-Huu-Hue P, Pingaard E et al (2001) J Eur Ceram Soc 21:1361
3. Smolenskii GA, Isupv VA, Afranovskaya AI et al (1961) Sov Phy Solid State 2:2651
4. Chu BJ, Chen DR, Li GR et al (2002) J Eur Ceram Soc 22:2115
5. Tian HY, Wang DY, Lin DM et al (2007) Solid State Commun 142:10
6. Takenaka T, Maruyama K (1991) Jpn J Appl Phys 30:2236
7. Li YM, Chen W, Zhou J, Xu Q, Sun H, Xu RX (2004) Mater Sci Eng B-Sol State Mater Adv Technol 112:5
8. Guo YP, Kakimoto K, Ohsato H (2005) Mater Lett 59:241
9. Li YM, Chen W, Xu Q, Zhou J, Gu XY (2005) Mater Lett 59:1361
10. Chen W, Li YM, Xu Q, Zhou J (2005) J Electroceramics 15:229
11. Lin DM, Xiao DQ, Zhu JG (2004) Mater Lett 58:615
12. Lin DM, Xiao DQ, Zhu JG, Yu P (2006) Appl Phys Lett 88: 062901-1
13. Neirman SM (1998) J Mater Sci 23:3973. doi: 10.1007/s10832-007-9245-9
14. Yu Z, Ang C, Guo RY, Bhalla AS (2002) J Appl Phys 92:2655
15. IRE standards on Piezoelectric Crystals (1978) Measurement of piezoelectric ceramics 1961, IEEE. Std, 176 pp
16. Iyer VS, Vengopal V, Mohapatra S et al (1988) Thermodynamics 20:781
17. American Ceramic Society (1990) Phase diagrams for ceramists (Final compilation). Columbus, Ohio
18. Peng C, Li JF, Gong W (2005) Mater Lett 59:1576
19. Chu BJ, Chen DR, Li GR, Yin QR (2002) J Eur Ceram Soc 22:2115