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Phase transitions and electrical properties of $(Na_{0.5}K_{0.5})NbO_3$-$Bi(Sc_{0.5}Fe_{0.5})O_3$ lead-free piezoelectric ceramics

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Lead-free ceramics (1-x)$(Na_{0.5}K_{0.5})NbO_3$-x$Bi(Sc_{0.5}Fe_{0.5})O_3$ (KNN-BSF, x = 0–0.08) were synthesized by conventional solid-state sintering. A morphotropic phase boundary (MPB) is formed in the ceramics near x = 0.01–0.02 at room temperature by X-ray analysis. Dielectric temperature spectra indicate the existence of two dielectric anomalous peaks, which correspond to orthorhombic-tetragonal (T_{OT}) and tetragonal-cubic (T_C) transitions. The ceramic with x = 0.0125 near the MPB exhibits the following optimal electrical properties: $P_r = 33.9$ μC/cm^2, $E_c = 18.1$ kV/cm, $d_{33} = 255$ pC/N, $k_p = 0.44$, and $T_c = 372$ °C.

Key words: Piezoelectric materials, Electrical Properties, Ferroelectrics, Ceramics.

Introduction

Lead-free piezoelectric materials have attracted much attention to replace PZT-based ceramics due to environmental issues [1]. Among various lead-free piezoelectric ceramic candidates, $(Na_{0.5}K_{0.5})NbO_3$ (KNN) has been considered as a good candidate for its strong piezoelectricity and ferroelectricity. However, it is well-known that pure KNN is difficult to fabricate by a conventional solid-state method and can not be used in the electronics industry due to its low piezoelectric properties compared with commercial PZT-based ceramics. In order to improve the electrical properties and enhance the densification, many approaches have been attempted, such as a textured method [2], hot-pressing [3], cold-isostatic pressing [4], spark plasma sintering [5, 6], etc. However, these techniques are unsuitable for use in industrial production. Recently, many attempts have been focused on the different additions to KNN ceramics, such as $LiNbO_3$ [4, 7, 8], $LiTaO_3$ [9], $LiSbO_3$ [10], $(Bi_{0.5}Na_{0.5})TiO_3$ [11], $SrTiO_3$ [12], $BaTiO_3$ [13], $Ba(Zr_{0.05}Ti_{0.95})O_3$ [14], etc. In particular, KNN ceramics doped with $BiMeO_3$ (Me = Sc, Al, Fe, etc.) have attracted more attention for their excellent piezoelectric properties as a candidate to replace the Pb-based system [15, 16].

For piezoelectric ceramics, the morphotropic phase boundary (MPB) plays a key role in the selection of the composition due to the highest piezoelectric response being obtained in this region. It is well-known that the optimal piezoelectric response can be ascribed to the enhanced polarization orientation because of the coexistence of different phases between rhombohedral, tetragonal, and/or orthorhombic ferroelectric phases.

In this case, (1-x)$(Na_{0.5}K_{0.5})NbO_3$-x$Bi(Sc_{0.5}Fe_{0.5})O_3$ (KNN-BSF) was chosen as a new lead-free piezoelectric system. $BiFeO_3$ (BF), has been known as a multiferroic material with a rhombohedral perovskite structure at room temperature [17]. However, $BiScO_3$ (BS) exhibits a monoclinic structure with a high Curie temperature [18]. These two components have been studied for high temperature piezoelectric applications by $PbTiO_3$ doping to form MPB and an excellent piezoelectric response was obtained [19, 20]. In view of the above investigation, current main research activities are also to search for a BSF-doped KNN system with an MPB and to provide a promising candidate for high performance lead-free piezoelectric ceramics.

Experimental Procedure

(1-x)KNN-xBSF ceramics (x = 0, 0.01, 0.0125, 0.015, 0.0175, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08) were synthesized by conventional solid-state sintering. High-purity oxides and carbonates, Nb_2O_5 (99.9%), Bi_2O_3 (99.97%), Fe_2O_3 (99.5%), Sc_2O_3 (99.9%), Na_2CO_3 (99.5%), and K_2CO_3 (99.0%), were used as starting materials. In addition, a special drying process was used with the sodium/potassium carbonates to eliminate moisture before weighing. Then, the mixed powders were milled for 48 h using a planetary milling with a zirconia ball media and ethanol and then calcined at 900-920 °C for 4 h. After the calcinations, the powders were ball-milled again for 24 h. The resulting powders were mixed with a polyvinyl alcohol binder solution and then pressed into disks 12 mm in diameter and 1.5 mm in thickness at 200 MPa. The disk samples were sintered at 1050-1150 °C for 2 h depending on the composition in sealed Al_2O_3 crucibles.

Phase structures were measured by a Siemens x-ray dif-

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fractometer using Cu $K\alpha_1$ radiation. An electrode of fired-on silver paste was used for the measurement of electrical properties, such as dielectric, ferroelectric, and piezoelectric properties. Before the deposition of the silver paste, the ceramic specimens were dried at 120 °C to eliminate water on the surfaces. After the deposition of silver electrodes, the ceramics were poled under a DC field of 50-60 kV/cm in a silicone oil bath for 25 minutes. The poling temperature varied from 50 to 100 °C, considering the composition and the conductivity of each specimen. The dielectric properties were measured using an LCR (Inductance (L), Capacitance (C), and Resistance (R)) meter (Model : HP4284A) from room temperature to 520 °C. The polarization versus electric field hysteresis loops were measured using a radiant precision workstation (RT-66A system).The piezoelectric coefficient d_{33} and the electromechanical coupling factor k_p were measured using a quasi-static piezoelectric d_{33} meter (Model ZJ-3D, Institute of Acoustics Academic, China) and an impedance analyzer (HP4294A) by resonance and anti-resonance techniques, respectively.

Results and Discussion

Fig. 1 shows the x-ray diffraction (XRD) patterns of the KNN-BSF ceramics with increasing BSF content. Seen from these patterns, all these specimens exhibit a single perovskite phase without any secondary phase. This indicates that the two components can form complete solid solutions in the range of compositions studied. The pure KNN displays a typical orthorhombic symmetry at room temperature, as reported in a previous study [21]. With the incorporation of BSF, the crystal structure transforms from orthorhombic to rhombohedral symmetry, with the splitting of (200)/(100) peaks. The (200)/(100) diffraction exhibits double peaks at x0.01 while it shows a single peak at x ≥ 0.02. The compositions above and below this boundary show single rhombohedral and orthorhombic symmetry, respectively. This result indicates a coexistence of rhombohedral and orthorhombic structures can be expected in the compositional range of x = 0.01 – 0.02. This can be ascribed to the formation of a polymorphic phase transition (from the orthorhombic to the tetragonal phase) at room temperature, similar to Du *et al.*s study [15].

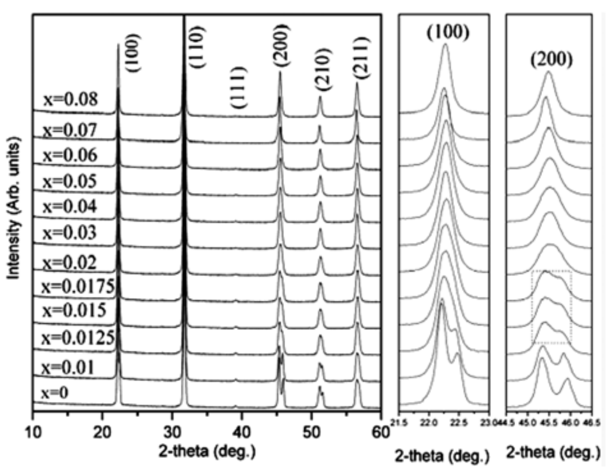

Fig. 1. X-ray diffraction patterns of the KNN-BSF ceramics with increasing BSF content.

It is well-known that a composition near MPB can exhibit an enhancement of piezoelectric properties, such as $Pb(Zr,Ti)O_3$ ceramics (PZTs) [22]. It also can be concluded that the electrical properties near polymorphic phase transition (PPT) can give optimal properties due to enhanced dipolar states, similar to the existence of MPB. Fig. 2 shows the piezoelectric coefficient (d_{33}) and planar coupling factor (k_p) of KNN-BSF ceramics with increasing BSF content. A pure KNN ceramic shows a d_{33} of 97 pC/N and a k_p of 0.36 in this case. The piezoelectric properties of the specimens show a strong dependence on the composition, similar to PZT [22]. It is observed that the optimal piezoelectric properties can be obtained at a composition x = 0.0125 which exhibits a d_{33} of 255 pC/N and a k_p of 0.44, indicating a promising lead-free candidate.

The dependence of polarization on the electric field for KNN-BSF ceramics with increasing BSF content is shown in Fig. 3. All these specimens show saturated *P-E*

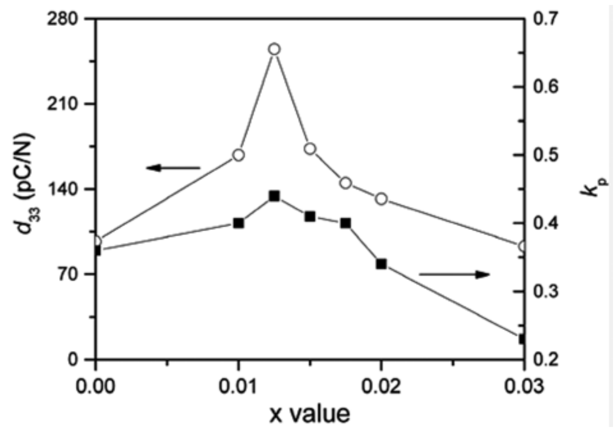

Fig. 2. Piezoelectric coefficient d_{33} and planar coupling factor k_p of KNN-BSF ceramics with increasing BSF content.

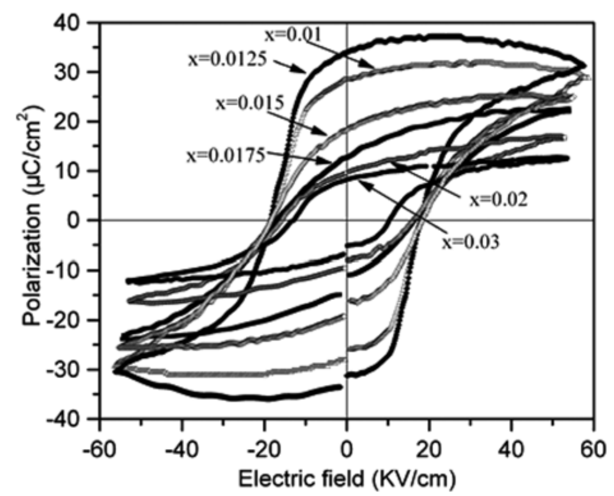

Fig. 3. Dependence of polarization on electric field for KNN-BSF ceramics with increasing BSF content.

curves under a measuring electric field. It can be observed that the ferroelectricity depends sharply on the composition. The composition x = 0.0125 exhibits the best ferroelectric properties with a remnant polarization $P_r = 33.9\ \mu C/cm^2$ and a coercive field $E_c = 18.1$ kV/cm, respectively. The optimum piezoelectric properties observed near PPT should result from a more possible polarization state resulting from the coexistence of the orthorhombic and rhombohedral phases. The coercive field decreases with increasing BSF content, indicating the improvement of the poling process due to the larger domain mobility after BSF substitution [16].

For ferroelectric ceramics, the dielectric temperature spectra can be used to investigate the phase evolution in the temperature range studied. Fig. 4 shows the dielectric temperature spectra of KNN-BSF ceramics with increasing BSF content measured at 10 kHz. From these spectra, it is noticeable that the rhombohedral ferroelectric compositions show much lower peak dielectric constants and broad phase transitions, compared to the orthorhombic ferroelectric compositions. Moreover, there are two anomalous peaks observed in the composition range from x = 0 to x = 0.015. According to a previous study, these two peaks correspond to the phase transitions of orthorhombic-tetragonal (T_{OT}) and tetragonal-cubic (T_C), respectively.

Conclusions

In summary, lead-free piezoelectric ceramics KNN-BSF were fabricated by conventional solid-state sintering. The phase structure and electrical properties of the KNN-BSF system were studied. The main results are as follows:

1) It is confirmed by X-ray diffraction that the coexistence of rhombohedral and orthorhombic phases exist near x = 0.01-0.02; This coexistence can be ascribed to the formation of a polymorphic phase transition (from the orthorhombic to the tetragonal phase) at room temperature.

2) The $0.9875(Na_{0.5}K_{0.5})NbO_3$-$0.0125Bi(Sc_{0.5}Fe_{0.5})O_3$ ceramics near the MPB possess the best properties of $P_r = 33.9\ \mu C/cm^2$, $E_c = 18.1$ kV/cm, $d_{33} = 255$ pC/N and $k_p = 0.44$ with a high Curie temperature $T_c = 372$ °C.

3) The enhanced properties indicate that the ceramics studied can be comparable to hard PZT ceramics, indicating a promising lead-free piezoelectric candidate material.

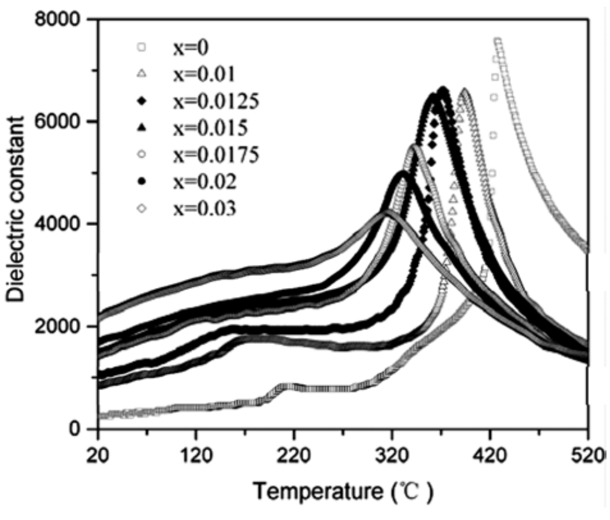

Fig. 4. Dielectric temperature spectra of KNN-BSF ceramics with increasing BSF content measured at 10 kHz.

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References

1. S.J. Zhang, R. Xia and T.R. Shrout, J. Electroceram. 19 (2007) 251-257.
2. Y. Saito, H. Takkao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, Nature 432 (2004) 84-87.
3. R.E. Jaeger and L. Egerton, J Am. Ceram Soc. 45 (1962) 209-213.
4. Y.P. Guo, K. Kakimoto and H. Ohsato, Appl. Phys. Lett. 85 (2004) 4121-3.
5. B.P. Zhang, J.F. Li, K. Wang and H.L. Zhang, J. Am. Ceram. Soc. 89 (2006) 1605-1609.
6. J.F. Li, K. Wang, B.P. Zhang and L.M. Zhang, J. Am. Ceram. Soc. 89 (2006) 706-709.
7. H. Kazuhiko, K. Ken-ichi and O. Hitoshi, J. Eur. Ceram. Soc. 27 (2007) 4107-4110.
8. H.L. Du, F.S. Tang, D.J. Liu, D.M. Zhu, W.C. Zhou and S.B. Qu, Mater. Sci. Eng. B 136 (2007) 165-169.
9. P. Zhao, B.P. Zhang and J.F. Li, Scripta Materialia 58 (2008) 429-432.
10. J.G. Wu, D.Q. Xiao, Y.Y. Wang, J.G. Zhu, P. Yu and Y.H. Jiang, J. Appl. Phys. 102 (2007) 114113-114115.
11. R.Z. Zuo, X.S. Fang and C. Ye., Appl. Phys. Lett. 90 (2007) 092904-3.
12. Y.F. Chang, Z.P. Yang, X.L. Chao, R. Zhang and X.R. Li, Mater. Lett. 61[3] (2007) 785-789.
13. H.Y. Park, C.W. Ahn, H.C. Song, J.H. Lee, S. Nahm, K. Uchino and H. Lee, Appl. Phys. Lett. 89 (2006) 062906-3.
14. D.M. Lin, K.W. Kwok and H.W.L. Chan, Appl. Phys. Lett. 91 (2007) 143513-3.
15. H.L. Du, W.C. Zhou, F. Luo, D.M. Zhu, S.B. Qu, Y. Li and Z.B. Pei, J. Appl. Phys. 104 (2008) 034104-7.
16. R.Z. Zuo, C. Ye and X.S. Fang, J. Phys. Chem. Solids, 69 (2008) 230-235.
17. M.M. Kumar, V.R. Palkara, K. Srinivas and S.V. Suryanarayana, Appl. Phys. Lett. 76 (2000) 2764-6.
18. A.A. Belik, S. Likubo, K. Kodama, N. Igawa, S. Shamoto, M. Maie, T. Nagai, Y. Matsui, S.Y. Stefanovich, B.I. Lazoryak and T.M. Eiji, J. Am. Chem. Soc. 128 (2006) 706-707.
19. D.I. Woodward, I.M. Reaney, R.E. Eitel and C.A. Randall, J. Appl. Phys. 94 (2003) 3313-3318.
20. S.J. Zhang, L. Laurent, R. Sorah, E. Richard, C.A. Randall and T.R. Shrout, J. Cryst. Growth 236 (2002) 210-216.
21. G. Shirane, R. Newnham and R. Pepinsky, Phys. Rev. 96 (1954) 581-588.
22. B. Jaffe, R.S. Roth and S.J. Marzullo, J. Appl. Phys. 25 (1954) 809-810.