Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 2731–2735

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of $SrZrO_3$ on phase structure and electrical properties of $0.974(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$ lead-free ceramics

Tao Huang, Dingquan Xiao*, Chao Liu, Fangxu Li, Bo Wu, Jiagang Wu, Jianguo Zhu

Department of Materials Science, Sichuan University, Chengdu 610064, PR China

Received 12 August 2013; received in revised form 11 October 2013; accepted 12 October 2013
Available online 22 October 2013

Abstract

$(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ lead-free piezoelectric ceramics have been prepared by the conventional solid state sintering method. Systematic investigation on the microstructure, crystalline structures as well as electrical properties of the ceramics was carried out. With the addition of $SrZrO_3$, the rhombohedral–orthorhombic phase transition temperature of the ceramics increases. Both the rhombohedral–orthorhombic and orthorhombic–tetragonal phase transitions of the ceramics were modified to be around room temperature when $x\sim0.05$, and as a result remarkably strong piezoelectricity has been obtained in $0.924(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$0.05SrZrO_3$ ternary system, whose piezoelectric parameters were $d_{33}=324$ pC/N and $k_p=41\%$.

Keywords: C. Piezoelectric properties; Lead-free ceramics; Phase boundary; KNN; $SrZrO_3$

1. Introduction

Lead-based piezoelectric ceramics, such as lead zirconate titanate (PZT), have been widely used in various applications such as sensors, actuators and transducers due to their excellent piezoelectric properties [1,2]. It is well known that the dielectric and piezoelectric properties of ceramics usually maximize around the tetragonal–rhombohedral morphotropic phase boundary (MPB)—a phase boundary that a narrow composition region with orthorhombic or monoclinic phase separating rhombohedral and tetragonal phases in solid solutions—for widely used PZT-based ceramics [3]. However, the lead has been restricted from many commercial applications because of its toxicity. Lead-free piezoelectric ceramics are widely investigated for the environmental protection and human health [4], in which the (K, Na)NbO_3 (KNN) based ceramics have received considerable attention because of their excellent piezoelectric properties and high Curie temperature [5–23]. KNN undergoes several phase transitions with increasing temperature: rhombohedral to orthorhombic (R–O) transition at -123 °C, orthorhombic to tetragonal (O–T) transition at 200 °C, and tetragonal to cubic (T–C) transition at 410 °C, respectively [10,24]. Thus, it is expected that KNN based lead-free ceramics with piezoelectric properties comparable with that of lead-based piezoelectric ceramics could be developed via forming similar MPB in this system.

However, most of the researchers focus on modifying the orthorhombic–tetragonal phase transition temperature (T_{O-T}) down to around room temperature, and the properties obtained are still inferior compared to lead-based piezoelectric ceramics [6–9,11–18]. In order to get similar MPB in KNN based lead-free ceramics, both the rhombohedral–orthorhombic phase transition temperature (T_{R-O}) and the orthorhombic–tetragonal phase transition temperature (T_{O-T}) of the ceramics should be modified to be around room temperature. The usual way to decrease T_{O-T} near room temperature has been conducted by forming solid solutions with compounds such as $Bi_{0.5}Na_{0.5}TiO_3$, $Bi_{0.5}K_{0.5}TiO_3$, $LiSbO_3$, $LiTaO_3$, $BaTiO_3$ etc. [8,14–18]. Among them, $Bi_{0.5}K_{0.5}TiO_3$ falls into the tetragonal ferroelectric and seems to broaden the tetragonal phase zone by shifting T_{O-T} downward, where the optimum content of BKT is in the range of 0.02–0.03 [14]. It was reported that $SrZrO_3$ has an ABO_3 perovskite structure and exhibits an orthorhombic structure at room temperature [25], effectively shifting the T_{R-O} of KNN ceramics to be above room temperature [19].

*Corresponding author. Tel.: +86 28 85412415; fax: +86 28 85416050.
E-mail address: nic0402@scu.edu.cn (D. Xiao).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.10.048

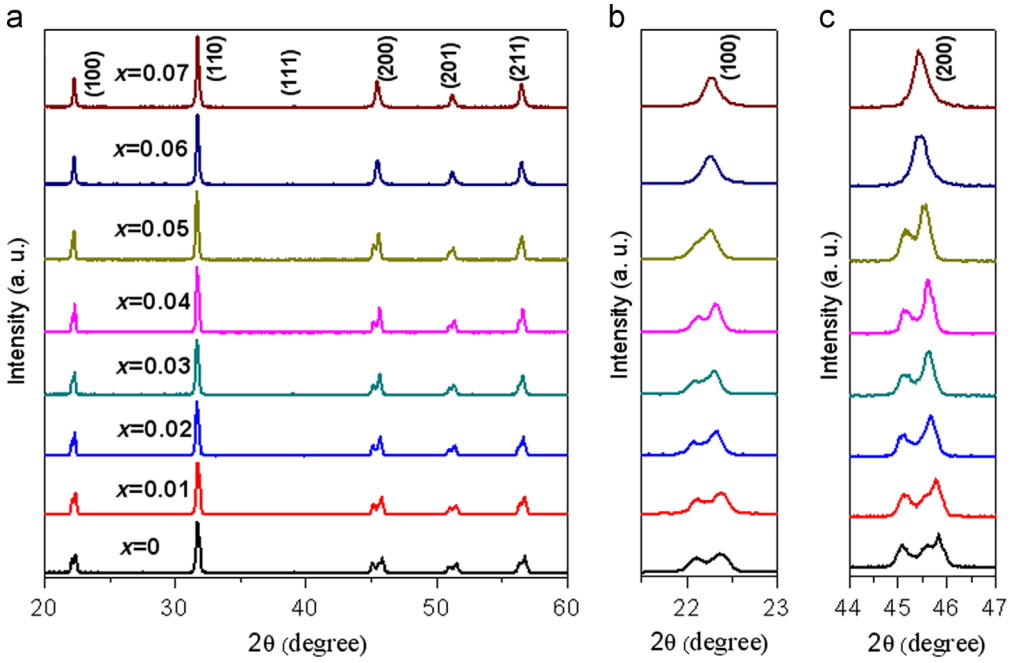

Fig. 1. The XRD patterns of the KNN–BKT–xSZ ceramics in the 2θ range of (a) 20–60°, (b) 21–23°, and (c) 44–47°, respectively.

The purpose of this study is to construct the new phase boundary in $(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ lead-free piezoelectric ceramics and investigate the effect of the phase boundary on their electrical properties. $Bi_{0.5}K_{0.5}TiO_3$ is selected to decrease the T_{O-T} down to be near room temperature, and the $SrZrO_3$ is selected to increase the T_{R-O} to be around room temperature.

2. Experimental procedure

$(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ (abbreviated as KNN–BKT–xSZ, $x=0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07 respectively) ceramics were prepared by the conventional sintering technique. Na_2CO_3 (99.8%), K_2CO_3 (99%), Nb_2O_5 (99.5%), Bi_2O_3 (99%), TiO_2 (98%), $SrCO_3$ (99%), and ZrO_2 (99%) were used as raw powders weighed according to the stoichiometric ratio of the ceramics. The powders were mixed and milled in ethanol for 24 h with zirconia balls, then dried and calcined at 850 °C for 6 h. The calcined powders were milled again for 24 h. Then, the dried mixtures were added with polyvinyl alcohol as a binder for granulation and pressed into disks with the diameter of 10 mm and the thickness of 1 mm under 10 MPa. After removal of the binder, the disk samples were sintered at 1100–1140 °C for 3 h in air. Silver paste electrodes were coated on both sides of these sintered samples and fired at 700 °C for 10 min. These ceramics were poled at room temperature under a DC electric field of 3–4 kV/mm for 20 min in silicon oil, and the electrical properties of the samples were measured after the poling for 24 h.

The crystalline structure of the ceramics was determined by X-ray diffraction (XRD) using Cu K_α radiation in the θ–2θ scan mode (DX 2700, Dandong, China).The grain morphology of the sintered samples was examined by scanning electron microscopy (SEM, S4800, Hitachi Ltd., Japan). The temperature dependence of the dielectric constant of the ceramics was measured using a LCR meter (Agilent 4980A, USA.). The polarization versus electric field (P–E) hysteresis loops of the ceramics were measured using a Radiant Precision Workstation (USA). An impedance analyzer (Solartron Gain Phase Analyzer) was employed to characterize the dielectric properties, and the piezoelectric coefficient (d_{33}) was measured using a piezo-d_{33} meter (ZJ-3A, China).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of KNN–BKT–xSZ ceramics with different SZ content measured at room temperature. All the ceramics measured exhibit a typical perovskite structure, and no secondary phases were detected. Fig. 1(b) and (c) shows the corresponding XRD patterns of KNN–BKT–xSZ ceramics in the range of 2θ equal to 21–23° and 44–47°, respectively. As shown in Fig. 1(b) and (c), the samples with $x=0$ exhibit the orthorhombic and tetragonal phase coexistence at room temperature [14], which also confirmed the results in Fig. 2(b). The dominant tetragonal phase is obtained for the samples with $x=0.01$–0.05. Only one single peak is observed for the samples with $x=0.06$–0.07. The single peak is a character for either rhombohedral or cubic phase [20], thus the temperature-dependent dielectric and ferroelectric behavior is needed to determine the symmetry of the ceramics with $x=0.06$–0.07 beside the XRD patterns.

The temperature dependence of the dielectric constant (ε_r) at 10 kHz for the ceramics is shown in Fig. 2(a). The T_C almost linearly decreases with x as seen from Fig. 2(a), but it is still

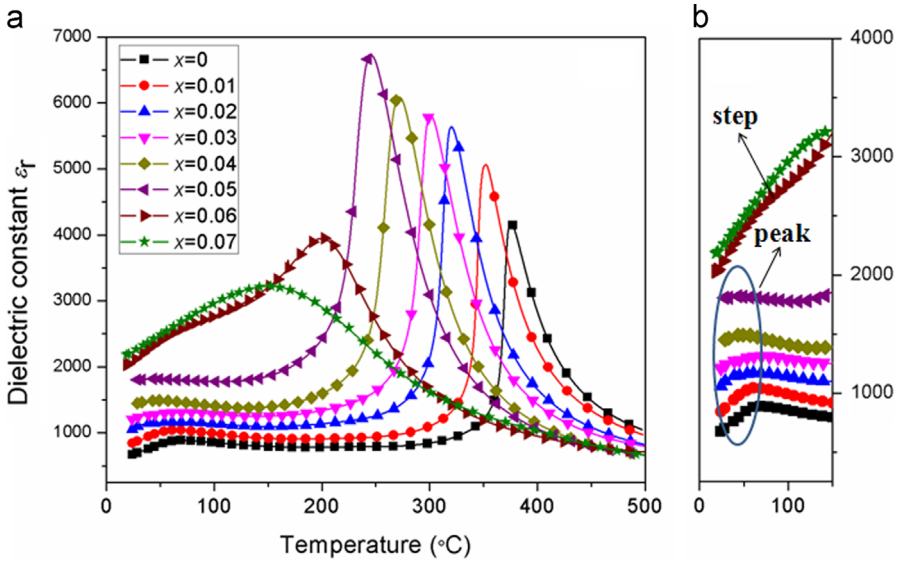

Fig. 2. Temperature dependence of the dielectric constant (ε_r) of the KNN–BKT–xSZ ceramics measured at 10 kHz during the heating process in the temperature range (a) from room temperature to 500 °C and (b) from room temperature to 150 °C.

above room temperature, further indicating that the ceramics with higher x ($x=0.06$ and 0.07) are a rhombohedral phase rather than a cubic phase at room temperature. The maximum ε_r value of the ceramics with $x \leq 0.05$ increases with x and gets the largest value at 0.05, further increase of x leads to the decrease of ε_r, indicating that the concentration of SZ up to 0.06 is too high to enhance the dielectric properties of the ceramics, as shown in Fig. 2(a). It can be seen from Fig. 2(b), that the dielectric anomaly near room temperature exhibits a peak-like dielectric behavior for the samples with $0 \leq x \leq 0.05$, which is generally related to orthorhombic–tetragonal phase transition (T_{O-T}) near room temperature [5–9,11–18]. The T_{O-T} value decreases slightly with increasing SZ content. For the samples with x=0.06, the dielectric anomaly shows a step-like dielectric behavior above room temperature (~75 °C), and ε_r of which increases with the increase of temperature until T_C. The result is attributed to the increase of rhombohedral–orthorhombic phase transition (T_{R-O}) in accordance with other reports about dielectric behavior observed [21,22]. Moreover, its XRD pattern shows rhombohedral phase at room temperature. As a result, it is suggested that the dielectric anomaly for the samples with x=0.06 is related to rhombohedral–tetragonal phase transition. These results indicated that both the T_{O-T} and T_{R-O} of the ceramics are shifted to be near room temperature with the compositions of $0.045 < x < 0.055$.

The SEM micrographs of the ceramics are shown in Fig. 3(a)–(d) with $x=0$, 0.03, 0.05, and 0.07 respectively. It can be seen from Fig. 3(a)–(c) that the ceramics exhibit inhomogeneous grains. Small grains distribute in the large grains. It is noted that the grain size decreases dramatically when x is 0.07, and more uniform grains are observed, as shown in the Fig. 3(d). The result indicates that a low concentration of SZ can well diffuse into the KNN lattices to form a new solid solution, while, if the x is too high, some of SZ may aggregate at the grain boundary thus prohibiting the grain growth and leading to the grain refinement.

The P–E loops of KNN–BKT–xSZ ceramics sintered at optimum temperatures are shown in Fig. 4(a). All the compositions show a typical ferroelectric hysteresis loop. The existence of ferroelectric properties for the compositions with $x=0.06$ and 0.07 are in agreement with the rhombohedral symmetry determined by dielectric and XRD results. The remnant polarization (P_r) and coercive field (E_C) as a function of x are shown in Fig. 4(b). It can be seen that E_C has a decreasing trend with the addition of SZ. This is due to that the tetragonal phase containing 90° domains generally has higher E_C values than rhombohedral phase [23], and SZ leads to the formation of the rhombohedral phase near room temperature. The P_r increases with increasing x and then decreases, giving a maximum value of 23.8 μC/cm^2 at $x=0.04$. A relatively large P_r (19.4 μC/cm^2) was obtained in the samples with $x=0.05$ because the T_{O-T} and T_{R-O} of the ceramics near room temperature causes the instability of the polarization state, such that the polarization direction can be easily rotated by external electric fields.

Fig. 5(a) shows the dielectric properties of KNN–BKT–xSZ ceramics as a function of SZ content measured at 100 kHz and room temperature. The ε_r almost linearly increases with increasing SZ content, and the tan δ firstly decreases, reaching a relatively low value in the range of $0.03 \leq x \leq 0.05$, and then increases dramatically with further rising x. Fig. 5(b) shows the piezoelectric properties of KNN–BKT–xSZ ceramics as a function of SZ content measured at room temperature. It is shown that the ceramic with $x=0.05$ has optimum piezoelectric coefficient ($d_{33}=324$ pC/N) and electromechanical coupling factor ($k_p=41\%$). However, both d_{33} and k_p values decrease sharply when the composition of the samples deviates to $x=0.05$. In this work, the d_{33} value is larger than most of KNN-based systems with T_{O-T} (d_{33}~200–300 pC/N) [6,8,11–16,18], and the enhanced piezoelectric behavior of KNN–BKT–xSZ ceramics could not be simply attributed to the decrease of T_{O-T} or a certain element. The new phase boundary in $(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ ceramics with both T_{O-T} and T_{R-O} around room temperature acts a dominant role. [21–23].

4. Conclusions

Lead-free piezoelectric ceramics $(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ were prepared by the conventional solid state sintering method, and the phase transitions as well as the electrical properties of these ceramics were investigated. According to the measurements of XRD and dielectric constant of the samples, 9nsitions near room

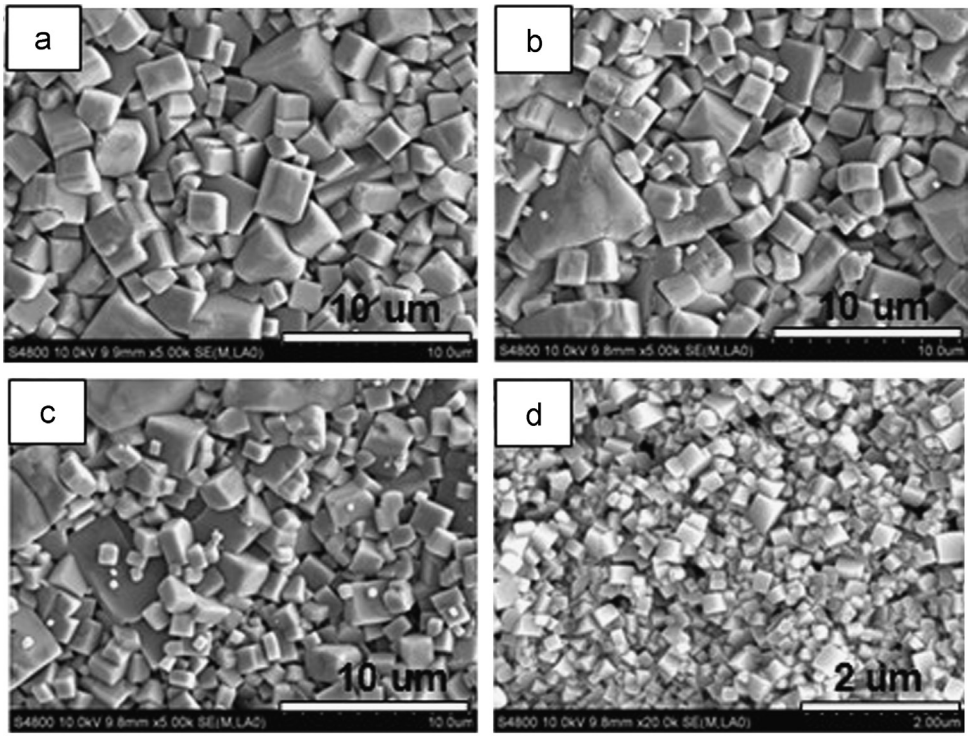

Fig. 3. SEM patterns of KNN–BKT–xSZ ceramics with (a) $x=0$, (b) $x=0.03$, (c) $x=0.05$, and (d) $x=0.07$.

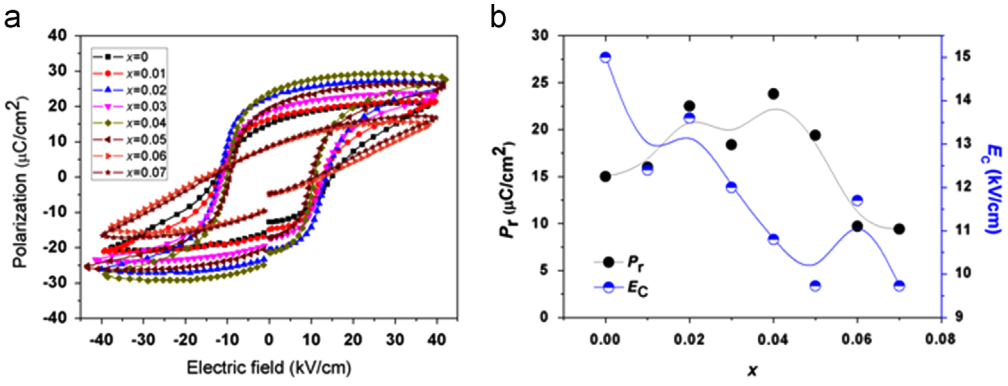

Fig. 4. (a) P–E hysteresis loops for the KNN–BKT–xSZ ceramics and (b) the remnant polarization (P_r) and coercive field (E_C) of the KNN–BKT–xSZ ceramics.

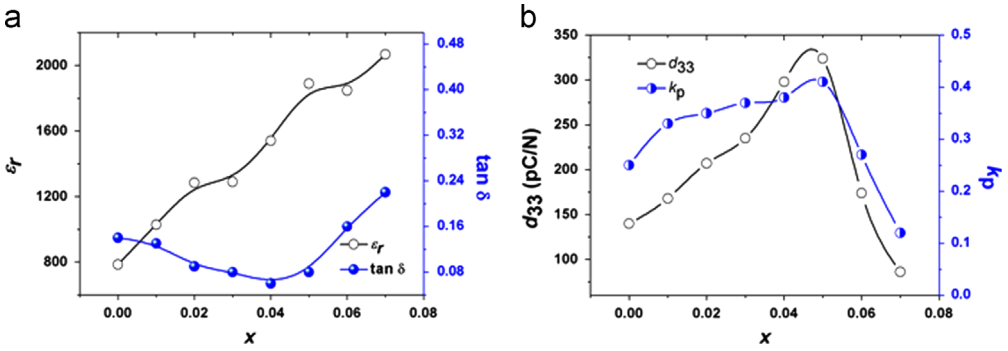

Fig. 5. (a) Dielectric properties and (b) piezoelectric properties of KNN–BKT–xSZ ceramics as a function of SZ content.

temperature was constructed when x is 0.05. Enhanced piezoelectric properties have been observed in the ceramics with $x=0.05$ ($d_{33}=324$ pC/N and $k_p=41\%$), showing that the construction of such a new phase boundary is an effective way to improve the piezoelectric properties of KNN-based ceramics.

Acknowledgments

This work was supported by NSFC (Nos. 50772068, 50972095, and 51272164) and Foundation of Doctor Training Program in University and College in China (Nos. 20030610035 and 20080610020).

References

[1] S.E. Park, T.R. Shrout, Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals, J. Appl. Phys. 82 (1997) 1804–1811.
[2] G.H. Haertling, Ferroelectric Ceramics, J. Am. Ceram. Soc. 82 (1999) 797–818.
[3] D.E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, Y. Yamada, Universal phase diagram for high-piezoelectric perovskite systems, Appl. Phys. Lett. 79 (2001) 400.
[4] J. Rodel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, Perspective on the development of lead-free piezoceramics, J. Am. Ceram. Soc. 92 (2009) 1153–1177.
[5] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84–87.
[6] J.G. Wu, Y.Y. Wang, D.Q. Xiao, J.G. Zhu, Z.H. Pu, Effects of Ag content on the phase structure and piezoelectric properties of $(K_{0.44-x}Na_{0.52}Li_{0.04}Ag_x)(Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ lead-free ceramics, Appl. Phys. Lett. 91 (2007) 132914.
[7] J.G. Wu, D.Q. Xiao, Y.Y. Wang, J.G. Zhu, L. Wu, Y.H. Jiang, Effects of K/Na ratio on the phase structure and electrical properties of $(K_xNa_{0.96-x}Li_{0.04})(Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ lead-free ceramics, Appl. Phys. Lett. 91 (2007) 252907.
[8] R.Z. Zuo, X.S. Fang, C. Ye, Phase structures and electrical properties of new lead free $(Na_{0.5}K_{0.5})NbO_3$–$(Bi_{0.5}Na_{0.5})TiO_3$ ceramics, Appl. Phys. Lett. 90 (2007) 092904.
[9] Y. Guo, K. Kakimoto, H. Ohsato, Phase transition and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiNbO_3$ ceramics, Appl. Phys. Lett. 85 (2004) 4121–4123.
[10] L. Egerton, D.M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium–sodium niobate, J. Am. Ceram. Soc. 42 (1959) 438–442.
[11] R.Z. Zuo, D.Y. Lv, J. Fu, Y. Liu, L.T. Li, Phase transition and electrical properties of lead free $(Na_{0.5}K_{0.5})NbO_3$–$BiAlO_3$ ceramics, J. Alloys Compd. 476 (2009) 836–839.
[12] H.L. Du, W.C. Zhou, F. Luo, D.M. Zhu, S.B. Qu, Z.B. Pei, Perovskite lithium and bismuth modified potassium–sodium niobium lead-free ceramics for high temperature applications, Appl. Phys. Lett. 91 (2007) 182909.
[13] X.P. Jiang, Q. Yang, Z.D. Yu, F. Hu, C. Chen, N. Tu, Y.M. Li, Microstructure and electrical properties of $Li_{0.5}Bi_{0.5}TiO_3$-modified $(Na_{0.5}K_{0.5})NbO_3$ lead-free piezoelectric ceramics, J. Alloys Compd. 493 (2010) 276–280.
[14] R.Z. Zuo, X.S. Fang, C. Ye, L.T. Li, Phase transition behavior and piezoelectric properties of lead-free $(Na_{0.5}K_{0.5})NbO_3$-$(Bi_{0.5}K_{0.5})TiO_3$ ceramics, J. Am. Ceram. Soc. 90 (2007) 2424–2428.
[15] P. Palei, Sonia, P. Kumar, Dielectric, ferroelectric and piezoelectric properties of $(1-x)[K_{0.5}Na_{0.5}NbO_3]$–$x[LiSbO_3]$ ceramics, J. Phys. Chem. Solids 73 (2012) 827–833.
[16] S.J. Zhang, R. Xia, T.R. Shrout, G.Z. Zang, J.F. Wang, Characterization of lead free $(K_{0.5}Na_{0.5})NbO_3$–$LiSbO_3$ piezoceramics, Solid State Commun. 141 (2007) 675–679.
[17] J. Fu, R. Zuo, X. Wang, L. Li, Polymorphic phase transition and enhanced piezoelectric properties of $LiTaO_3$-modified $(Na_{0.52}K_{0.48})(Nb_{0.93}Sb_{0.07})O_3$ lead-free ceramics, J. Phys.s D: Appl. Phys. 42 (2009) 012006.
[18] H.Y. Park, C.W. Ahn, H.C. Song, J.H. Lee, S. Nahm, K. Uchino, H.G. Lee, H.J. Lee, Microstructure and piezoelectric properties of 0.95 $(Na_{0.5}K_{0.5})NbO_3$–$0.05BaTiO_3$ ceramics, Appl. Phys. Lett. 89 (2006) 062906.
[19] R.P. Wang, H. Bando, M. Kidate, Y. Nishihara, M. Itoh, Effects of A-site ions on the phase transition temperatures and dielectric properties of (1-x) $(Na_{0.5}k_{0.5})Nbo_3$-$xAzrO_3$ solid solutions, Jpn. J. Appl. Phys. 50 (2011) 09ND10.
[20] R.P. Wang, H. Bando, T. Katsumata, Y. Inaguma, H. Taniguchi, M. Itoh, Tuning the orthorhombic-rhombohedral phase transition temperature in sodium potassium niobate by incorporating barium zirconate, Phys. Status Solidi RRL 3 (2009) 142–144.
[21] W.F. Liang, W.J. Wu, D.Q. Xiao, J.G. Zhu, J.G. Wu, Construction of new morphotropic phase boundary in $0.94(K_{0.4-x}Na_{0.6}Ba_xNb_{1-x}Zr_x)O_3$–$0.06LiSbO_3$ lead-free piezoelectric ceramics, J. Mater. Sci. 46 (2011) 6871–6876.
[22] W.F. Liang, W.J. Wu, D.Q. Xiao, J.M. Zhu, J.G. Zhu, J.G. Wu, New crystallographic dielectric phase boundary in $K_{0.5}Na_{0.5}NbO_3$-based lead-free ceramics, Phys. Status Solidi RRL 5 (2011) 220–222.
[23] R.Z. Zuo, J. Fu, Rhombohedral–tetragonal phase coexistence and piezoelectric properties of $(NaK)(NbSb)O_3$–$LiTaO_3$–$BaZrO_3$ lead-free ceramics, J. Am. Ceram. Soc. 94 (2011) 1467–1470.
[24] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.
[25] B.J. Kennedy, C.J. Howard, B.C. Chakoumakos, High-temperature phase transitions in $SrZrO_3$, Phys. Rev. B 59 (1999) 4023–4027.