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Ceramics International 39 (2013) 2135–2139
CERAMICS INTERNATIONAL
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Short communication

Piezoelectric properties and time stability of lead-free $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics

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Received 13 May 2012; received in revised form 18 July 2012; accepted 19 July 2012
Available online 24 July 2012

Abstract

$(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ (NKLNST-x/y) lead-free piezoelectric ceramics were prepared by conventional solid-state reaction method. Their crystal structure was determined by X-ray diffraction, and the temperature dependence of dielectric constants was measured. It is found that Sb^{5+} and Ta^{5+} diffuse into the $(Na_{0.52}K_{0.44}Li_{0.04})NbO_3$ lattice to form a solid solution with a perovskite structure. The co-substitution of Sb^{5+} and Ta^{5+} for B-site Nb^{5+} decreases both the paraelectric cubic-tetragonal phase transition temperature (T_C) and the tetragonal-orthorhombic phase transition temperature ($T_{O\text{-}T}$) of the $(Na_{0.52}K_{0.44}Li_{0.04})NbO_3$ ceramics, and results in significant improvements in piezoelectric properties. Enhanced electrical and electromechanical responses of $d_{33}=335$ pC/N and $k_p=0.46$ are obtained in the ceramics with $x/y=0.08/0.05$. Meanwhile, piezoelectric properties of the NKLNST-0.08/0.05 ceramic show no obvious reduction and dielectric loss increases slightly when exposed in air for 30 day. The results indicate that NKLNST-x/y ceramic is a promising lead-free piezoelectric candidate material.

Keywords: C. Piezoelectric properties; Lead-free; Ceramics; Phase transition

1. Introduction

Lead-based piezoelectric ceramics, represented by lead zirconate titanate (PZT) for example, are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties. However, the use of lead-based piezoelectric materials may pollute the environment and is harmful to human body, which is opposite to the needs of the sustainable development and the environmental protection of the world. Therefore, extensive research has been directed at replacing lead-based ceramics with lead-free piezoelectric materials [1–3].

(K, Na)NbO_3 (KNN)-based piezoelectric ceramics are considered to be excellent candidates for lead-free piezoelectric materials due to their excellent piezoelectric and electromechanical properties at room temperature [4–6]. Nevertheless, pure KNN ceramics are difficult to densify by ordinary sintering method since their phase stability is limited to 1140 °C [7]. KNN modified by other compound has been studied in order to improve its piezoelectric properties [8,9]. It is generally accepted that the addition of Ta can significantly improve the piezoelectric performance of the KNN ceramics and the addition of Sb can enhance stability and compactness of the KNN ceramics [10,11]. Excellent piezoelectric and electromechanical properties have been achieved in Li, Sb and Ta co-modified KNN ceramics since Saito developed KNN-based non-textured ceramics (LF4) with a d_{33} value of 300 pC/N [12], which was comparable to those of unmodified PZT ceramics. Therefore, a number of studies have been focused on Li, Sb and Ta co-modified KNN systems, confirming that they have the potential of practical application as substitutes for lead-based piezoceramics [13,14]. However, there are few reports on the effects of the simultaneous change of Sb and Ta contents on the properties of (K, Na, Li)NbO_3 ceramics. Therefore, in this paper, $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics were chosen as the objects, and further compositional modifications were performed.

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0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.07.063

2. Experimental

$(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ (NKLNST-x/y) ceramics ($x/y=0/0$, 0.04/0.025, 0.08/0.05, 0.12/0.075 and 0.16/0.1) were prepared by the conventional fabrication technique. Powders of K_2CO_3 (99%), Li_2CO_3 (99.99%), Na_2CO_3 (99.8%), Sb_2O_3 (99%), Ta_2O_5 (99.99%) and Nb_2O_5 (99.5%) were used as raw materials. The above chemicals were mixed by ball-milling in ethanol for 12 h and dried. Two calcinations at temperature 890 °C for 4.5 h were performed. The calcined powders were milled for a further 12 h. The dried powders were subsequently pressed into disks of 15 mm in diameter and 1.5 mm in thickness under 200 MPa. Sintering was carried out in ambience at their optimum sintering temperatures between 1090 and 1125 °C for 3 h, which were determined by measuring the maximum mass densities. During sintering, specimens were muffled with the same compositions powders to restrain alkaline elements evaporation. Silver paste was fired on both sides of the samples at 575 °C for 30 min as the electrodes for dielectric and piezoelectric measurements. The sintered samples were poled under a dc field of 4 kV/mm at room temperature in a silicone oil bath for 20 min.

Density of samples was determined by the Archimedes method. The phase structure and microstructure of ceramics were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter. Temperature dependence of dielectric permittivity was measured with an Agilent 4294A precision impedance analyzer. The planar electromechanical coupling factor k_p was calculated by the resonance-antiresonance method using the precision impedance analyzer on the basis of IEEE standards.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics. All the ceramics show perovskite structure and only a trace of the secondary phase can be detected as x/y is 0.16/0.1. The ceramic with $x/y=0/0$ contains the orthorhombic phase only, while the ceramics with $x/y=0.04/0.025$, 0.08/0.05 and 0.12/0.075 display the coexistence of orthorhombic and tetragonal phases. The NKLNST-0.16/0.1 ceramic shows no evidence of peak splitting at about 45° and is labeled as pseudo-cubic.

Fig. 2 shows the temperature dependence of ε_r of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics at 10 kHz. For the sample with $x/y=0/0$, two dielectric peaks are observed at 463 and 157 °C, corresponding to the phase transitions of cubic-tetragonal at T_C and tetragonal-orthorhombic at $T_{T\text{-}O}$. The samples with $x/y=0.04/0.025$, 0.08/0.05, and 0.12/0.075 undergo the same two phase transitions, and their $T_{O\text{-}T}$ is close to room temperature, suggesting that the orthorhombic and tetragonal phases coexist in the ceramics. For the sample with $x/y=0.16/0.1$, only one ε_r peak is observed in the examined temperature range. These results are consistent with the XRD results. As also seen in Fig. 2, T_C decreases gradually with increasing Ta and Sb, accompanied by peak broadening, indicating that the relaxor-like behavior becomes more obvious. The $x/y=0.16/0.1$ sample possesses pseudo-cubic phase and shows a broader dielectric peak, which may be ascribed to the coexistence of ferroelectric domains and nonpiezoactive (paraelectric) regions in the vicinity of T_C [15].

Fig. 3 shows variation of the $1/\varepsilon_r$ as a function of temperature at 10 kHz for the $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{0.935}Sb_{0.04}Ta_{0.025}O_3$ ceramic. The deviation degree from the Curie-Weiss law can be defined by the following ΔT_m:

$$\Delta T_m = T_{dev} - T_m$$

in which T_{dev} is the temperature at which dielectric permittivity starts to deviate from the Curie–Weiss law. It can be seen from Fig. 3 that the dielectric permittivity of the $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{0.935}Sb_{0.04}Ta_{0.025}O_3$ ceramic obeys the Curie–Weiss law at 8 °C higher than the T_m. The calculated ΔT_m increases linearly from 3 to 97 °C with increasing Ta and Sb, indicating an enhanced diffuse phase transition behavior. In order to effectively describe the

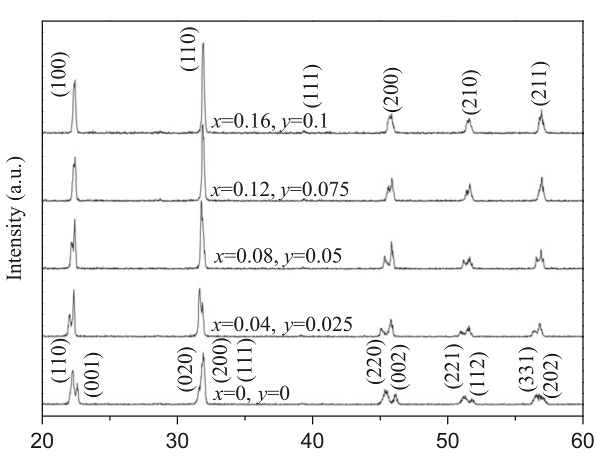

Fig. 1. XRD patterns of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics.

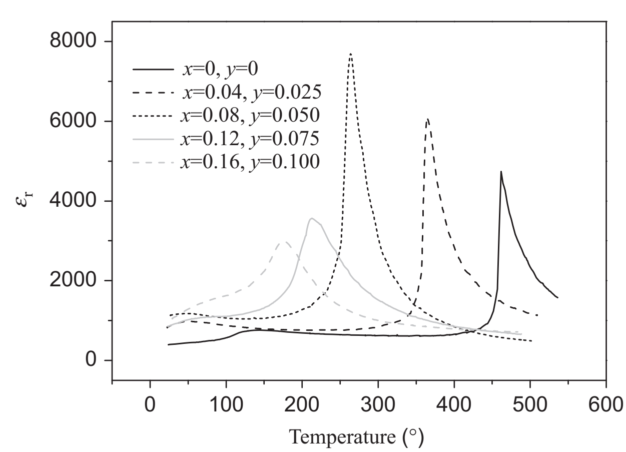

Fig. 2. Temperature dependence of the dielectric constant ε_r of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics at 10 kHz.

diffuseness of a phase transition, a modified Curie–Weiss law has been proposed [16]:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)^{\gamma}}{C}$$

where C is the Curie constant, and γ is the indicator of the diffuseness degree, ranging between 1 corresponding to normal ferroelectric behavior and 2 representing the so-called complete diffuse phase transition. The γ values can be determined from the slopes of $\log(1/\varepsilon-1/\varepsilon_m)$ versus log $(T-T_m)$ lines which are shown in Fig. 4. The γ value varies from 1.105 to 1.723, indicating that the NKLNST-x/y ceramics exhibit obvious diffuse phase transition behavior

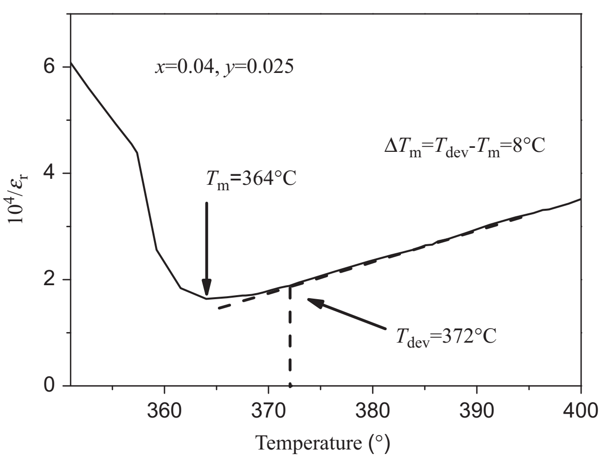

Fig. 3. Variation of the $1/\varepsilon_r$ as a function of temperature at 10 kHz for the $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{0.935}Sb_{0.04}Ta_{0.025}O_3$ ceramic.

at high concentrations of Ta and Sb. The relaxor-like behavior in NKLNST-x/y ceramics should attribute to the cationic disorder and compositional fluctuation induced by *B*-site substitutions.

Fig. 5 presents the surface SEM pictures of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics. As shown in Fig. 5(a)–(c), highly dense microstructures without pores achieve as $x/y=0/0$, 0.04/0.025 and 0.08/0.05. It is observed that the grains are slightly smaller for $x/y=0.08/0.05$ (Fig. 5(c)), suggesting that the growth of the grain could be depressed by the addition of a proper amount of Sb and Ta. With further increasing of the doping contents, the grains grow to oversize themselves by consuming small ones near by and the density begins to decline as shown in the case of samples with $x/y=0.12/0.075$ and 0.16/0.1 (Fig. 5(d) and (e)).

The $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics were sintered at different temperatures depending on their compositions. Table 1 presents the optimum sintering temperature and piezoelectric properties of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics. The optimum sintering temperature determined by the maximum mass density for each composition is found to increase with the Sb and Ta contents. The ceramic with $x/y=0.08/0.05$ shows the optimum piezoelectric properties: $d_{33}=335$ pC/N and $k_p=0.46$. The enhanced piezoelectricity should be ascribed to the orthorhombic-tetragonal polymorphic phase transition near room temperature. Although the ceramics with $x/y=0.04/0.025$ and 0.12/0.075 also contain both the orthorhombic and tetragonal phases, their piezoelectric properties are poorer due to their lower densities. Therefore, the phase coexistence and the high density contribute

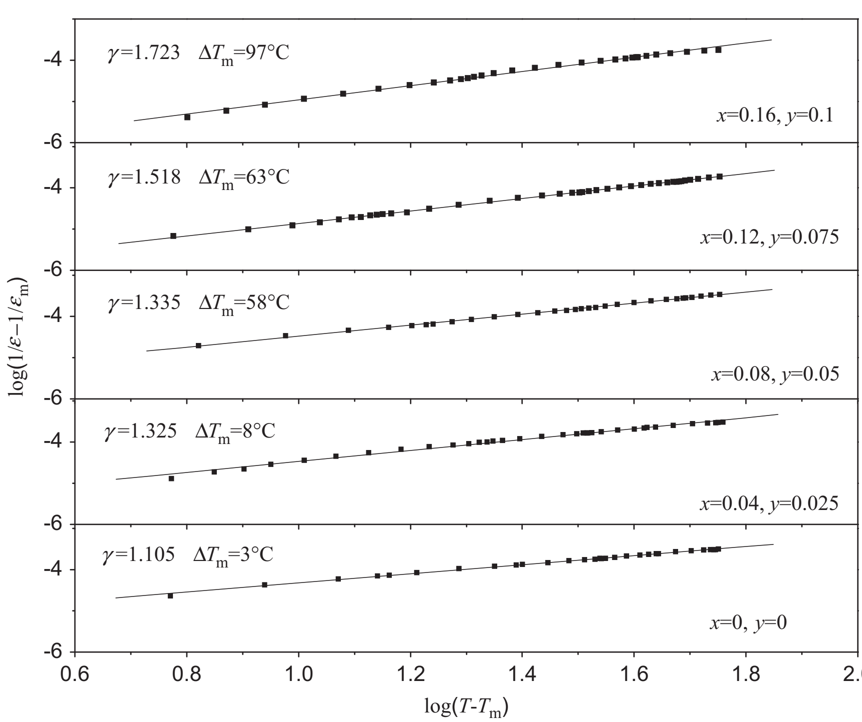

Fig. 4. $\log(1/\varepsilon-1/\varepsilon_m)$ as a function of $\log(T-T_m)$ at 10 kHz for $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics.

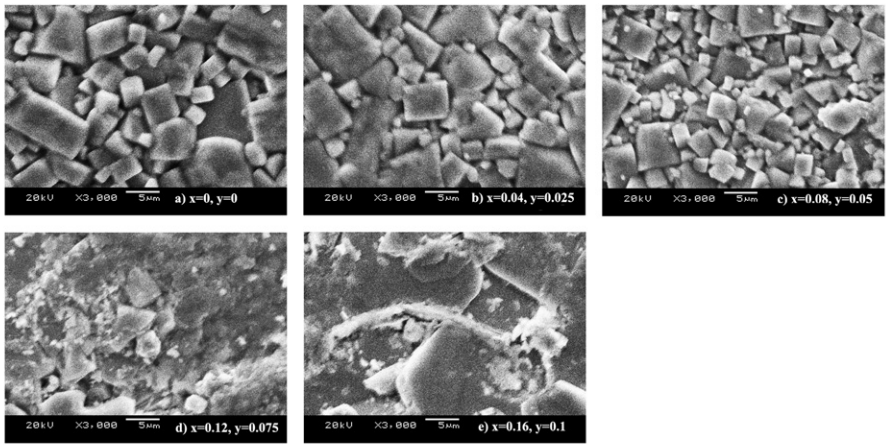

Fig. 5. Surface SEM micrographs of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics: (a) $x/y=0/0$, (b) $x/y=0.04/0.025$, (c) $x/y=0.08/0.05$, (d) $x/y=0.12/0.075$, and (e) $x/y=0.16/0.1$.

Table 1
Optimum sintering temperature and electrical properties of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics.

	$x=0$, $y=0$	$x=0.04$, $y=0.025$	$x=0.08$, $y=0.05$	$x=0.12$, $y=0.075$	$x=0.16$, $y=0.1$
d_{33} (pC/N)	172	267	335	234	190
k_p (%)	34	46	46	30	41
Tanδ (%)	2.4	4.7	4.1	5.4	5.5
ρ (g/cm^3)	4.232	4.260	4.309	3.912	4.095
Sintering temperature (°C)	1090	1100	1108	1117	1125

to the improvement in electrical properties of the NKLNST-0.08/0.05 ceramic.

To characterize the time stability of $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics, all samples were ageing about 30 day at room temperature. The piezoelectric constant d_{33} and dielectric loss tanδ of the one month aged samples are shown in Fig. 6. The initial data determined 24 h after poling are also provided for comparison. It can be observed that the properties of the NKLNST-0.12/0.075 and NKLNST-0.16/0.1 ceramics decrease more significantly than other samples. The grain morphology of the ceramics is believed to associate closely with domain configurations [17]. The increased grain size will lead to a decreased grain boundary area that results in reduced hindrance to domain re-orientation. However, the domain wall relaxation is eased when the poling field is removed for the specimens with large grains. It can be seen from Fig. 5 that the NKLNST-0.12/0.075 and NKLNST-0.16/0.1 ceramics have coarse grain structure. Therefore, their properties decrease obviously after keeping 30 day in air due to the domain wall relaxation. It is also seen that the piezoelectric properties of the NKLNST-0.08/0.05 ceramic show no obvious reduction when exposed in air for 30 day, showing that the ceramic has better time stability.

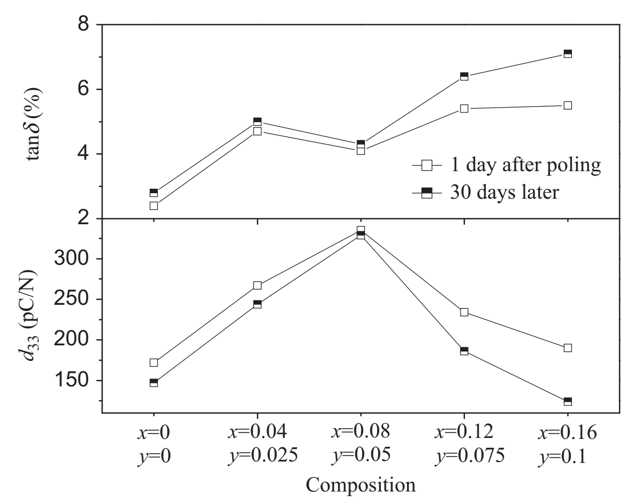

Fig. 6. Values of d_{33} and tanδ of the $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics determined 1 day after poling and 30 day later.

4. Conclusions

In conclusion, pressureless sintering $(Na_{0.52}K_{0.44}Li_{0.04})Nb_{1-x-y}Sb_xTa_yO_3$ ceramics were prepared by the conventional mixed-oxide technique. The effects of varying quantity of Sb and Ta on the electrical properties of $(Na_{0.52}K_{0.44}Li_{0.04})NbO_3$ ceramics are examined. The NKLNST-x/y ceramics have obvious diffuse phase transition characteristics at high concentrations of Ta and Sb. Good piezoelectric properties and enhanced time stability are obtained for the sample of NKLNST-0.08/0.05. The present study shows that dense NKLNST-x/y ceramics with enhanced performances can be achieved by further optimizing Ta and Sb contents.

Acknowledgements

This work was supported by the national natural science foundation of China (No. 50902087), the natural science foundation of Shandong province of China (No. ZR2012EMM004 and No. ZR2009FQ009), and the science and technology development project of Jinan (City) of China (No.201102055).

References

[1] L.J. Liu, Z. Yang, M.X. Wu, L. Fang, C.Z. Hu, Dielectric properties of $(NaBi_{(1-x)}K_x)0.5Ti_{(1-x)}Nb_xO3$ ceramics fabricated by mechanical alloying, Journal of Alloys and Compounds 507 (2010) 196–200.

[2] L.J. Liu, M.X. Wu, Y.M. Huang, L. Fang, H.Q. Fan, H. Dammak, M.P. Thi, Effect of mechanical activation on the structure and ferroelectric property of $Na_{0.5}K_{0.5}NbO_3$, Materials Research Bulletin 46 (2011) 1467–1472.

[3] L.J. Liu, H.Q. Fan, S.M. Ke, X.L. Chen, Effect of sintering temperature on the structure and properties of cerium-doped $0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06BaTiO_3$ piezoelectric ceramics, Journal of Alloys and Compounds 458 (2008) 504–508.

[4] Y.J. Zhao, Y.Z. Zhao, R.X. Huang, R.Z. Liu, He.P. Zhou, Influence of B-site non-stoichiometry on structure and electrical properties of KNLNS lead-free piezoelectric, Materials Letters 75 (2012) 146–148.

[5] W.L. Yang, Z.X. Zhou, B. Yang, Y.Y. Jiang, H. Li, Y.B. Pei, Improvement in temperature stability and modified polymorphic phase transition of La-doped $(Na_{0.52}K_{0.44}Li_{0.04})$ $Nb_{0.8}Ta_{0.2}O_3$ lead-free piezoelectric ceramics, Materials Letters 70 (2012) 146–148.

[6] D.M. Lin, K.W. Kwok, K.H. Lam, H.L.W. Chan, Structure, piezoelectric and ferroelectric properties of Li- and Sb-modified $K_{0.5}Na_{0.5}NbO_3$ lead-free ceramics, Journal of Physics D: Applied Physics 40 (2007) 3500–3505.

[7] H.L. Du, W.C. Zhou, F. Luo, D.M. Zhu, An approach to further improve piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$-based lead-free ceramics, Applied Physics Letters 91 (2007) 202907.

[8] J.H. Cho, Y.J. Choi, Y.J. Lee, Y.H. Jeong, M.P. Chun, J.H. Nam, B.I. Kim, Temperature stability and phase transition of Li0.02 $(K_xNa_{1-x})_{0.98}NbO_3$ ceramics, Ceramics International 38 (2012) 315–318.

[9] J. Liu, J.L. Zhu, M.S. Wang, Y.T. Pu, X.H. Li, P. Sun, L. Feng, X.H. Zhu, J.G. Zhu, D.Q. Xiao, Effects of K/Na ratio on the phase structure and electrical properties of $0.98(K_xNa_{1-x})NbO_3$–$0.02BiScO_3$ lead-free ceramics, Ceramics International 38 (2012) 347–350.

[10] G.Z. Zang, X.J. Yi, J. Du, J.F. Wang, Co_2O_3 doped $(Na_{0.65}K_{0.35})NbO_3$ piezoceramics, Materials Letters 64 (2010) 1394–1397.

[11] B. Shao, J.H. Qiu, K.J. Zhou, X.M. Pang, Q.H. Meng, Tantalum influence on electrical properties of lead-free $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.93-x}Ta_xSb_{0.07})O_3$ piezoelectric ceramics, Journal of Materials Science: Materials in Electronics 23 (2012) 846–850.

[12] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T Nagaya, M. Nakamura, Lead-free piezoceramics, Nature (London) 432 (2004) 84–87.

[13] J. Fu, R.Z. Zuo, D.Y. Lv, Y. Liu, Y. Wu, Structure and piezoelectric properties of lead-free $(Na_{0.52}K_{0.44-x})(Nb_{0.95-x}Sb_{0.05})O_3$–$xLiTaO_3$ ceramics, Journal of Materials Science: Materials in Electronics 21 (2010) 241–244.

[14] R.Z. Zuo, J. Fu, X. Wang, L. Li, Phase transition and domain variation contributions to piezoelectric properties of alkaline niobate based lead-free systems, Journal of Materials Science: Materials in Electronics 21 (2010) 519–522.

[15] V. Shvantsman, W. Kleemann, J. Dec, Z.K. Xu, S.G. Lu, Diffuse phase transition in $BaTi_{1-x}Sn_xO_3$ ceramics: an intermediate state between ferroelectric and relaxor behavior, Journal of Applied Physics 99 (2006) 124111.

[16] K. Uchino, S. Nomura, Critical exponents of the dielectric constants in diffused-phase-transition crystals, Ferroelectrics 44 (1982) 55–61.

[17] C.A. Randall, N. Kim, J.P. Kucera, W. Cao, T.R. Shrout, Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics, Journal of the American Ceramic Society 81 (1998) 677–688.