Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) S709–S713

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of Al_2O_3 on the ferroelectric properties of sodium potassium lithium niobate lead-free piezoceramics

I.H. Lee[a], H.S. Lee[a], Y.H. Kim[a], S.K. Gil[b], D.H. Kang[a,*]

[a]*Department of Electronic Materials Engineering, RIC, The University of Suwon, Wauan-gil 17, Bongdam-eup, Whaseong 445-743, South Korea*
[b]*Department of Electronic Engineering, RIC, The University of Suwon, Wauan-gil 17, Bongdam-eup, Whaseong 445-743, South Korea*

Available online 23 October 2012

Abstract

Aluminum oxide (Al_2O_3) has been known as a promising additive to modify the piezoelectric properties of lead-based piezoceramics. However there are few reports regarding Al_2O_3 added lead-free piezoceramics. In this study, sodium potassium lithium niobate ($(Na_{0.5}K_{0.5})_{0.925}Li_{0.075}NbO_3$, NKLN) lead-free piezoelectric ceramics have been prepared and their crystal structures, microstructures and dielectric properties have been also investigated with different Al_2O_3 amounts and sintering temperatures. With increasing Al_2O_3 content up to 0.5 wt%, the density and grain size increased, accompanying with the increased dielectric and piezoelectric properties. These results could be explained in terms of sinterability such as density and grain size.
© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Sintering; C. Piezoelectric properties; D. Alkali oxide; D. Al_2O_3

1. Introduction

Lead-based piezoelectric ceramics with high piezoelectric and electromechanical properties such as $Pb(Zr,Ti)O_3$ (PZT), $Pb(Mg,Nb)O_3$ (PMN) have been extensively used for sensor and actuator applications [1]. However, the toxicity of lead and its high vapor pressure during the manufacturing process have led to demand for alternative lead-free piezoelectric materials. The search for alternative piezoelectric materials is now focused on alkali niobate modified bismuth titanates and some oxide compositions which near the morphotropic phase boundary (MPB) [2]. Among them, $(Na_{0.5}K_{0.5})NbO_3$ (NKN) has been considered as a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity, ferroelectricity and high Curie temperature [3–5]. However, NKN ceramics heat-treated in the ordinary sintering process show relatively inferior electrical properties due to difficulty in the processing for densification [4]. Thus various techniques, such as hot pressing [4], cold-isostatic pressing [6] and spark plasma sintering [7], have been utilized to improve the electrical properties of NKN ceramics. At the same time, many studies focusing on the preparation of various NKN based ceramic compositions with different additives by the conventional solid state sintering method. Previous studies have reported that the additive constituents effectively affected the piezoelectric properties of NKN ceramics [5–14]. For Li, Sb, Ag, Ba and Ta oxide additives, the improved piezoelectric properties were mainly attributed to the induced polymorphic phase transition between orthorhombic and tetragonal ferroelectric phases [8–11]. In the case of Cu, Mn, Bi and Fe oxide additives, their piezoelectric properties were obviously improved due to the increased sinterability [12–14]. However, there have been few studies on the piezoelectric properties of NKN ceramics regarding the incorporation of aluminum oxide (Al_2O_3) although Al_2O_3 has been known as a promising additive to modify the piezoelectric properties of lead based piezoceramics [15]. In this study, sodium potassium niobate ceramics containing lithium, $[(Na_{0.5}K_{0.5})_{0.925}Li_{0.075}NbO_3$, NKLN] were prepared as a base composition and their

*Corresponding author. Tel.: +82 31 220 2664; fax: +82 31 220 2665.
E-mail address: dhkang@suwon.ac.kr (D.H. Kang).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.167

crystal structures, microstructures, dielectric and piezoelectric properties were investigated with different Al_2O_3 contents and sintering temperatures.

2. Experimental

An NKN ceramic composition with 7.5 mol% Li ($(Na_{0.5}K_{0.5})_{0.925}Li_{0.075}NbO_3$, NKLN) was used as a base one, which showed the best electrical properties through the pre-experiment [11]. The specimens were prepared by the conventional mixed-oxide technique using commercially available metal oxides or carbonate powders such as Na_2CO_3, K_2CO_3, Li_2CO_3 and Nb_2O_5 with high purity above 99.9%. The powders were weighed and mixed well in ethanol with YSZ balls by the ball-milling for 12 h. The calcination was subsequently conducted at 850 °C for 4 h. After adding Al_2O_3 additive in the range of 0–7.5 wt%, the mixed powders were ball-milled and dried. After mixing with a PVA binder solution and sieving treatment, they were uniaxially pressed into disk specimens with a diameter of 10 mm and a thickness of 2 mm. The pressed pellets were then sintered at the temperature range of 1000–1050 °C for 2 h in air in order to obtain optimum sinterability for each composition. The crystal structures of the specimens were examined using an X-ray diffractometer (290621A, Rigaku). The apparent density of the ceramics was measured by the Archimedes method. The surface morphology was observed by a scanning electron microscopy (JSM 5610, JEOL) equipped an energy dispersive energy spectroscopy. After poling at 3.5 kV for 30 min, dielectric properties of the specimens were examined using an impedance analyzer (4194A, Hewlett Packard) and a precision pro (Radiant Tech.). The piezo-d_{33} meter (APC International) was applied to measure the piezoelectric properties of the specimens.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the sintered NKLN powders as a function of Al_2O_3 content. All the specimens show nearly pure perovskite phases with the orthorhombic symmetry. From the enlarged peaks in the 2 theta range of 44–47° as shown in Fig. 1(b), two splitting peaks of (002) and (200) planes slightly shifted towards lower angle. Considering the ionic radius and valence for all the ions in the composition, it is expected that Al^{+3} (0.51 Å) seems most likely to enter into Nb^{+5} (0.69 Å) site rather than Na^{+1} (0.97 Å) and K^{+1} (1.33 Å) ones. These ionic substitutions may result in cell contraction detected as the peak shift, where lattice constants (a and c) changed from 3.945 Å and 4.047 Å for no Al_2O_3–NKLN specimen to 3.933 Å and 4.021 Å for 0.5 wt% Al_2O_3–NKLN one. It has been reported that some trivalent ions, such as Fe^{+3}, Co^{+3} possibly prefer to enter B site rather than A site in NKN system [14,16,17].

Fig. 2 shows the effect of Al_2O_3 substitution on the apparent density as a function of sintering temperature.

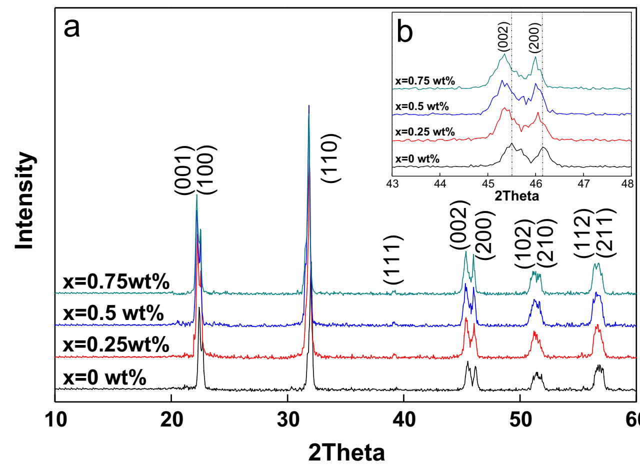

Fig. 1. XRD patterns of NKLN+$x$$Al_2O_3$ ceramics (a) full scale and (b) enlarged peaks in the 2 theta range of 44–47°.

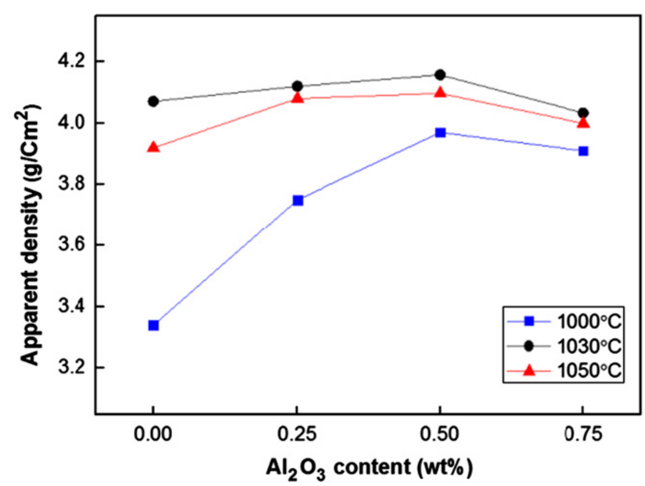

Fig. 2. Apparent density of NKLN+$x$$Al_2O_3$ ceramics sintered at various temperatures as a function of (x)Al_2O_3 content.

The result indicates that all the specimens including no Al_2O_3 added specimen showed relatively higher sinterability at the sintering condition of 1030 °C for 2 h. For all the sintering temperatures, the apparent density tends to increase with increasing Al_2O_3 content, exhibiting the maximum density at 0.75 wt% Al_2O_3 addition.

The SEM photographs of NKLN specimens with different Al_2O_3 contents sintered at 1030 °C for 2 h and different sintering temperatures with the same Al_2O_3 content of $x=0.5$ are shown in Fig. 3. The grain size apparently increased with increase of Al_2O_3 addition and reached to 6–6.5 μm for the 0.5 wt% added specimen as shown in Fig. 3(c). Thus enhanced densification as shown in Fig. 2 can be related to the increase of grain size. As mentioned above, possible substitution of Al^{+3} for Nb^{+5} in the B site, namely acceptor doping, should introduce the system oxygen vacancies, which may facilitate the sintering process as shown in Figs. 2 and 3. The effect of increased grain size and density induced by the acceptor doping has been similarly reported in Fe_2O_3

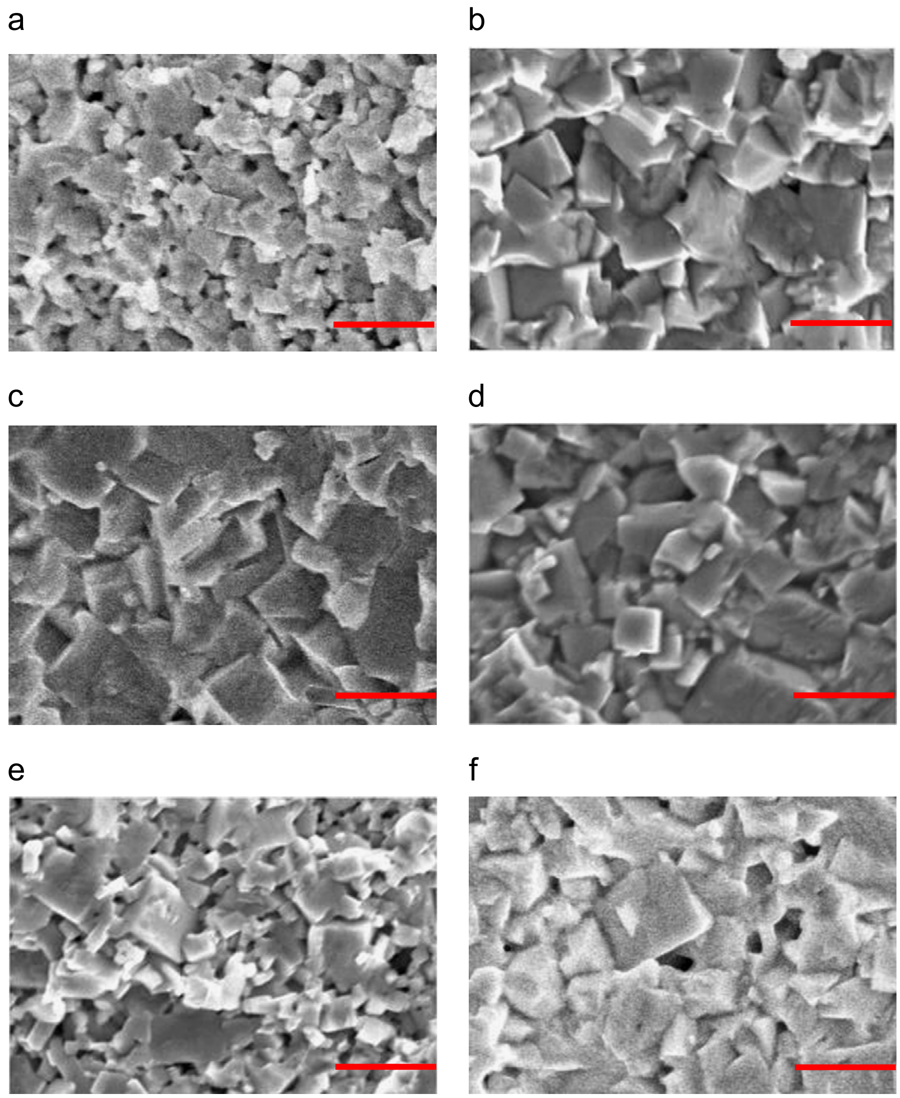

Fig. 3. SEM photographs of NKLN+xAl$_2$O$_3$ ceramics; (a) $x=0$, (b) $x=0.25$, (c) $x=0.5$ (d) $x=0.75$, (e) $x=0.5$, and (f) $x=0.5$. The specimens as shown in (a)–(d) were sintered at 1030 °C and the others appeared in (e) and (f) were sintered at 1000 °C and 1050 °C (bar=10 μm).

and Co_2O_3 doped NKN systems [14,16]. The microstructure for the NKN with $x=0.75$ wt% Al_2O_3 became somewhat nonuniform and porous, resulting in inferior densification. However, it is hard to detect segregation of aluminum by the EDS analysis for this specimen. The variation of sintering temperature as shown in Fig. 3(e) and (f) presents negative effect although the microstructure showing excellent densification with the optimal addition of $x=0.5$ as shown in Fig. 3(c). It is therefore noted that the sintering condition of 1030 °C for 2 h was optimum for the 0.5 wt% Al_2O_3 added NKLN system.

Fig. 4 shows the P-E hysteresis loops of NKLN specimens with various Al_2O_3 contents, which show the typical ferroelectric characteristics. Remanent polarization (P_r), coercive field (E_c) and relative permittivity (ε_r) of the specimens sintered at 1030 °C and 1050 °C are summerized in Table 1, where the relative permittivity and remanaent polarization present similar tendency as mentioned in the

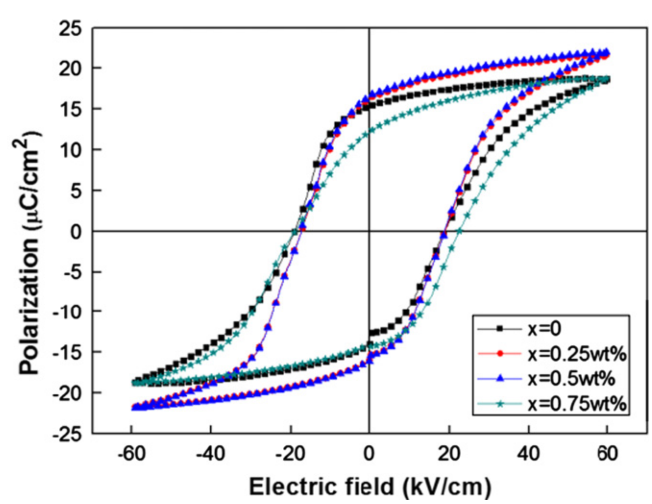

Fig. 4. P-E hysteresis loops of NKLN+xAl$_2$O$_3$ ceramics sintered at 1030 °C for 2 h as a function of x.

Table 1
Dielectric properties of NKLN+xAl_2O_3 ceramics.

x content(wt%)	Ts (°C)[a]	0	0.25	0.5	0.75
ε_r (100KHz)	1030	714	991	1043	902
	1050	608	943	964	813
P_r (uC/cm^2)	1030	15.4	16.3	16.9	12.2
	1050	–	15.4	15.5	12.1
E_c (kV/mm)	1030	18.8	18.9	18.6	22.5
	1050	–	18.8	18.1	18.9

[a]Sintering temperature.

microstructural analysis. It can be obviously seen from the electrical analysis in addition to the structural analysis that the ferroelectric properties of this composition system mainly depend on the density and grain size.

The effects of Al_2O_3 content and sintering temperature on the piezoelectric properties of NKNL+xAl_2O_3 ceramics are shown in Fig. 5. These results clearly reflect the influence of sintering temperature, identical to the variation of piezoelectric properties by means of the density. Higher piezoelectric constant (d_{33}) and coupling factor (k_p) as shown in Fig. 5 can be obtained for the specimen with higher density, i.e. the highest values of d_{33}=204 pC/N and k_p=0.436 for the x=0.5 wt% specimen sintered at 1030 °C. It has been reported by Zuo et al.[14] that the increase of P_r, d_{33} and k_p by increased density and grain size for the Fe_2O_3 doped NKN, similar to our study. The variation of mechanical quality factor Q_m with Al_2O_3 addition is in contrast to those of d_{33} and k_p as shown in Fig. 5. According to the study of Bi_2O_3 added NKN ceramics, such tendency may attribute to the decrease of the inner stress resulting from domain reorientation induced by the increase of grain size [13].

4. Conclusion

Lead-free $(Na_{0.5}K_{0.5})_{0.925}Li_{0.075}NbO_3$+x$Al_2O_3$ specimens have been synthesized by the conventional ceramic processing. All the specimens showed nearly pure perovskite phase within X-ray detection limit. In the sintering temperature range from 1000 °C to 1050 °C, relatively higher density was obtained for all the specimens sintered at 1030 °C for 2 h. The addition of Al_2O_3 promoted densification and grain growth. The relative permittivity, remanent polarization, piezoelectric coupling factor, and piezoelectric constant were improved with the increase of density. The optimal structural and electrical properties were obtained for the 0.5 wt% Al_2O_3 added NKLN ceramics. It was clearly seen that the electrical properties of Al_2O_3 added NKLN mainly depended on the density and grain size. For the 0.5 wt% Al_2O_3 added specimen sintered at 1030 °C for 2 h, ε_r, P_r, k_p, d_{33} and Q_m were 1043, 17 μC/cm^2, 0.436, 204 pC/N and 37, respectively.

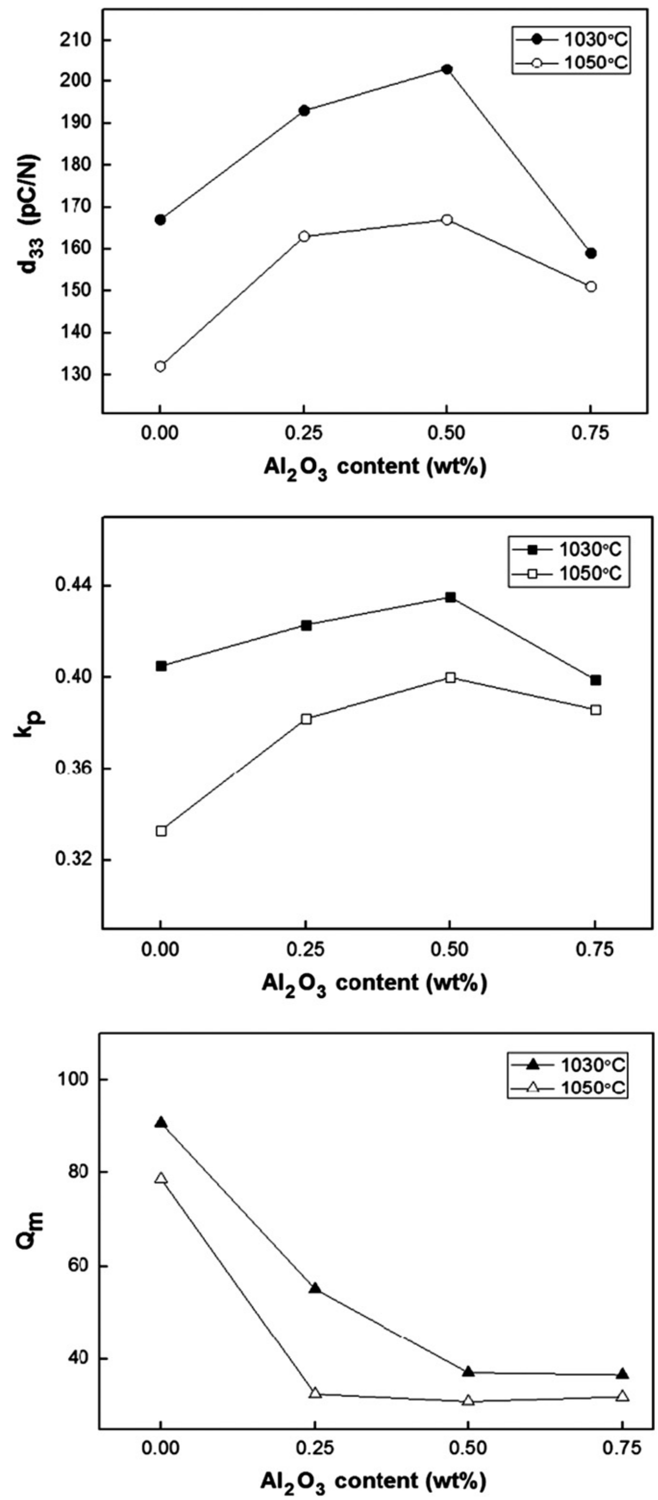

Fig. 5. Piezoelectric properties (d_{33}, k_p and Q_m) of NKLN+$x$$Al_2O_3$ ceramics sintered different temperatures as a function of x.

References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.

[2] H. Hagata, M. Yoshida, Y. Makiuchi, T. Takenaka, Large piezoelectric constant and high Curie temperature of lead free piezoelectric ceramic ternary system based on bismuth sodium titanate-bismuth

potassium titanate-barium titanate near the MPB, Jpn. J. Appl. Phys. 42 (2003) 7401–7403.
[3] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, H. Homma, T. Nagaya, M. Nakamura, Lead free piezoceramics, Nature 432 (2004) 84–87.
[4] L. Egerton, C.A. Bieling, Isostatically hot-pressed sodium-potassium niobate transducer material for ultrasonic devices, Ceram. Bull. 47 (1968) 1151–1156.
[5] Y. Wang, J. Wu, D. Xiao, W. Wu, B. Zhang, J. Zhu, P. Yu, L. Wu, High Curie temperature of (Li, K, Ag)-modified $(K_{0.50}Na_{0.50})NbO_3$, J. Alloys Comp. 472 (2009) L6–L8.
[6] Y. Guo, K. Kakimoto, H. Ohsato, Phase transition behavior and piezoelectric properties of NKN-$LiNbO_3$ ceramics, Appl. Phys. Lett. 85 (2004) 4121–4123.
[7] B.P. Zhang, J.F. Li, Compositional dependence of piezoelectric properties in NKN lead free ceramics prepared by spark plasma sintering, J. Am. Ceram. Soc. 89 (2006) 1605–1609.
[8] H. Du, F. Tang, F. Luo, D. Zhu, S. Qu, Z. Pei, W. Zhou, Influence of sintering temperature on piezoelectric properties of $(K_{0.5}Na_{0.5})$ NbO_3-$LiNbO_3$, Mater. Res. Bull. 42 (2007) 1594–1601.
[9] Y. Guo, K. Kakimoto, H. Ohsato, Phase transition behavior and piezoelectric properties of NKN-$LiNbO_3$ ceramics, Appl. Phys. Lett. 85 (2004) 4121–4123.
[10] Y. Wang, L. Qibin, F. Zhao, Phase transition behavior and electrical properties of $[(K_{0.50}Na_{0.50})_{1-x}Ag_x]$ $(Nb_{1-x}Ta_x)O_3$, J. Alloys Comp. 489 (2010) 175–178.
[11] Y.S. Lee, Y.H. Kim, D.H. Kang, Effect of monovalent ions on the piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$-M(Ta)O_3 ceramics, Ceram Inter. 38S (2012) S305–S309.
[12] C.W. Ahn, S. Nahm, Effect of CuO and MnO_2 on sintering temperature, microstructure, and piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$-$BaTiO_3$, Mater. Lett. 62 (2008) 3594–3596.
[13] H. Du, D. Liu, F. Tang, D. Zhu, W. Zhou, Microstructure, piezoelectric properties of Bi_2O_3-added $(K_{0.5}Na_{0.5})NbO_3$-lead-free ceramics, J. Am. Ceram. Soc. 90 (2007) 2824–2829.
[14] R. Zuo, Z. Xu, L. Li, Dielectric and piezoelectric properties of Fe_2O_3-doped $(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}Nb_{0.86}Ta_{0.1}$ $Sb_{0.04}O_3$ lead-free ceramics, J. Phys. Chem. Sol. 69 (2008) 1728–1732.
[15] Y.M. Kim, J.C. Kim., S.C. Ur, I.H. Kim, Effects of Al_2O_3 on the piezoelectric properties of $Pb(Mn_{1/3}Nb_{2/3})O_3$ - $PbZrO_3$ - $PbTiO_3$ ceramics, J. Electroceram. 16 (2006) 347–350.
[16] G.Z. Zang, X.J. Yi, J. Du, Y.F. Wang, Co_2O_3 doped $(Na_{0.5}K_{0.5})$ NbO_3 piezoceramics, Mater. Lett. 64 (2010) 1394–1397.
[17] R. Zuo, M. Wang, B. Ma, J. Fu, T. Li, Sintering and electrical properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics modified with lamthanum and iron oxides, J. Phys. Chem. Solids. 70 (2009) 750–754.