Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 40 (2014) 4341–4344
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Enhanced piezoelectric properties of $(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$ lead-free ceramics by optimizing the sintering temperature

Tao Chen[a,*], Hongli Wang[b], Ting Zhang[a], Guangchang Wang[a], Jifang Zhou[a], Jianwei Zhang[a], Yuhong Liu[a]

[a]Teaching and Research Section of Physics, Chengdu Medical College, Chengdu 610083, PR China
[b]Teaching and Research Section of Chemistry, Chengdu Medical College, Chengdu 610083, PR China

Received 19 August 2013; received in revised form 23 August 2013; accepted 23 August 2013
Available online 30 August 2013

Abstract

Effects of sintering temperature on the microstructure and electrical properties of $(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$ (KNLNS) lead-free ceramics are investigated. The grain size gradually becomes larger with increasing sintering temperature from 1055 °C to 1105 °C, and the piezoelectric property could be enhanced by optimizing their sintering temperature. The ceramic sintered at 1075 °C has optimum electrical properties, i.e., $d_{33} \sim 272$ pC/N, $k_p \sim 43.5\%$, $\varepsilon_r \sim 1152$, tan $\delta \sim 0.026$, and $T_C \sim 346$ °C. These results show that the sintering temperature can optimize electrical properties of KNLNS ceramics.

Keywords: C. Electrical properties; C. Piezoelectric properties; $(KNa)NbO_3$; Lead-free ceramics; Sintering temperature

1. Introduction

Lead-based piezoceramics have been widely used for piezoelectric actuators, sensors, and transducers because of their excellent electrical properties [1]. However, the lead of lead-based ceramics has resulted in the environmental pollution during their preparation and process [1]. Therefore, lead-free piezoceramics have been extensively investigated for protecting the living environment, the material system including barium titanate, bismuth titanate, and alkali niobate [2–23]. Among those, considerable attention has been given to (K,Na) NbO_3 (KNN) lead-free piezoceramics because of their good piezoelectric properties and high Curie temperature [6–23].

Some efforts have been made to improve the d_{33} of KNN-based ceramics [6–23], such as ion substitution, sintering aids, and different preparation methods. It is well known that the ion substitution can improve the piezoelectric properties of KNN [6–18]. Enhanced piezoelectric properties of 212–280 pC/N have been observed in Li^+ and Sb^{5+}-modified KNN ceramics due to the involvement of the orthorhombic–tetragonal phase boundary [9–18]. For example, Wu et al. reported an enhanced d_{33} of 262–280 pC/N in Li^+ and Sb^{5+}-doped KNN ceramics [9,12,13]. Palei et al. reported that $LiSbO_3$-modified KNN ceramics have a d_{33} of ~215 pC/N [14]. These results shows that piezoelectric properties of Li^+ and Sb^{5+}-doped KNN ceramics are sensitive to the preparation condition [9–18]. In addition, the sintering temperature is a key factor to determine the electrical properties of KNN-based ceramics [24,25]. Zhao et al. reported that the piezoelectric coefficient of ~268 pC/N can be achieved by optimizing the sintering temperature of $LiTaO_3$-doped KNN ceramics [25]. However, there are few reports on the effect of the sintering temperature on the microstructure and piezoelectric properties of $(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$ lead-free ceramics.

In this work, we studied the effect of the sintering temperature on the microstructure and electrical properties of $(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$ (KNLNS) lead-free ceramics prepared by the conventional solid-state method. Enhanced

*Corresponding author.
E-mail addresses: chentaocmc@163.com, myfriendsroom@163.com (T. Chen).

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.2013.08.102

piezoelectric properties of $d_{33} \sim 272$ pC/N and $k_p \sim 43.5\%$ are achieved by optimizing the sintering temperature. Underlying physical mechanisms for enhanced piezoelectric properties were also discussed.

2. Experimental procedure

$(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$ lead-free piezoceramics were prepared by the conventional solid-state method. Raw materials of Li_2CO_3 (99%), Nb_2O_5 (99.5%), Sb_2O_3 (98%), K_2CO_3 (99%), and Na_2CO_3 (99%) were weighed according to the stoichiometric formula of $(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$, and were then mixed for 24 h by the ZrO_2 balls using the ethanol as the medium. These powders were dried and calcined at 800 °C for 4 h, and then these sintered powders were pressed into disks of 1.0 cm in diameter and 1.0–1.2 mm in thickness under 15 MPa. These green pellets were sintered at the temperature range of 1055–1105 °C for 3 h. These sintered pellets were polished and then coated with the silver paste on both surfaces as the electrode for the electrical measurement, and were polarized in the silicone oil of 50 °C under an electric field of 4.0 kV/mm for 20 min.

The crystal structure of these sintered ceramics was measured using the X-ray diffraction (XRD) with Cu-K_a radiation, and their surface morphologies were detected using the scanning electron microscope. The density of the sintered samples was measured by the Archimedes method. Their dielectric behavior as a function of the measurement temperature was obtained using an *LCR* meter (HP 4980, Agilent, USA). Their piezoelectric constant (d_{33}) was characterized using the quasi-static piezoelectric d_{33} meter (ZJ-3A, China), and the planar coupling factor (k_p) was calculated using the resonance and anti-resonance method.

3. Results and discussion

Fig. 1 shows the XRD patterns of KNLNS ceramics sintered at different temperatures of 1055–1105 °C, and all the data was collected at room temperature. All ceramics have a pure perovskite structure, and secondary phases cannot be detected in the measurement range of the XRD machine. As a result, the sintering temperature of 1055–1105 °C does not change the phase structure of KNLNS ceramics.

Fig. 2(a–c) shows the SEM patterns of KNLNS ceramics sintered at different temperatures. The grain size becomes larger as the sintering temperature increases. It was found that some large grains with >10 μm exist in the ceramics sintered at a higher temperature of ≥ 1075 °C, as shown in Fig. 2(b) and (c). In addition, some small grains locate at the gaps among the larger ones, giving rise to a dense microstructure [Fig. 2(b)]. In order to confirm the effect of the sintering temperature on their density, the relative density is given in Fig. 3. It was observed that the optimal sintering temperature results in the denser microstructure, that is, the ceramics sintered at 1065–1085 °C have a higher density. It was reported that the low sintering temperature results in the formation of some pores, thus a lower density is formed in the KNN-based ceramics [24]. However, a high processing temperature easily causes the loss of Na and K [25,26], showing a poor density. As a result, the optimal sintering temperature causes the denser microstructure of KNLNS ceramics [24–26].

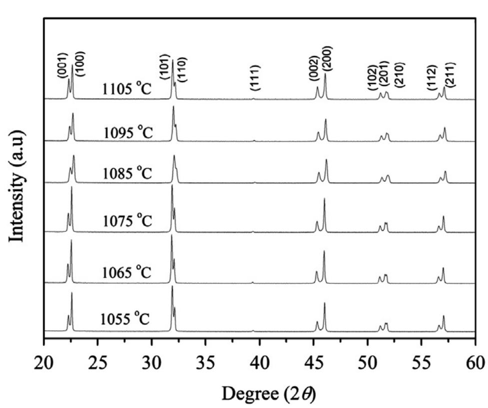

Fig. 1. XRD patterns of KNLNS ceramics sintered at different temperatures.

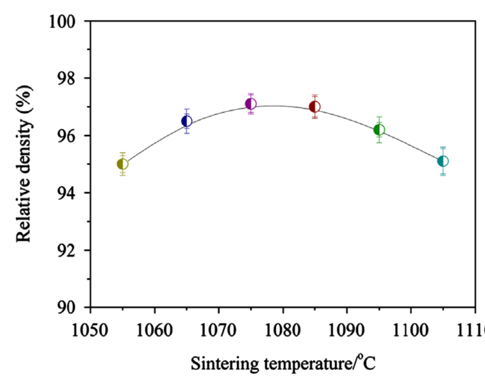

Fig. 3. Relative density of KNLNS ceramics as a function of the sintering temperature.

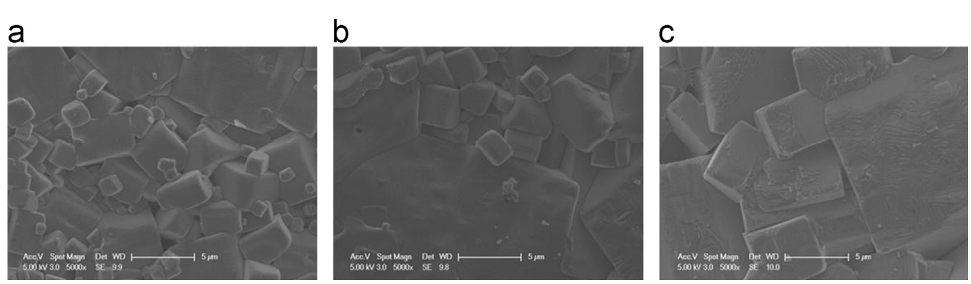

Fig. 2. Surface morphologies of KNLNS ceramics sintered at (a) 1055 °C, (b) 1075 °C, and (c) 1105 °C.

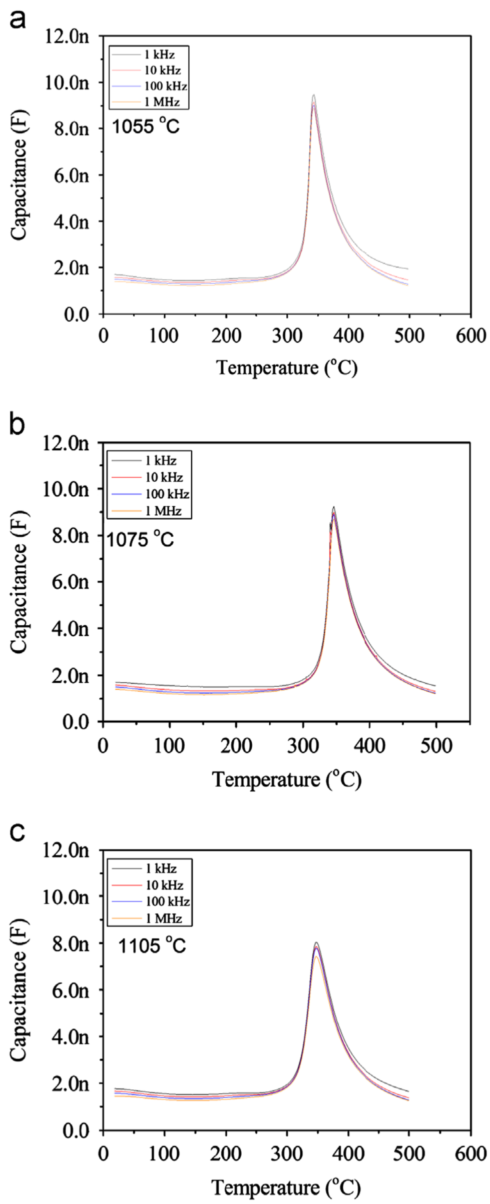

Fig. 4. Temperature-dependent dielectric constant of KNLNS ceramics sintered at (a) 1055 °C, (b) 1075 °C, and (c) 1105 °C.

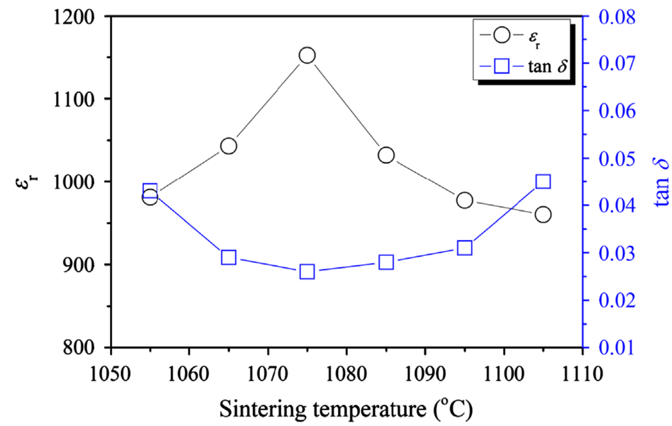

Fig. 5. Dielectric properties of KNLNS ceramics as a function of the sintering temperature.

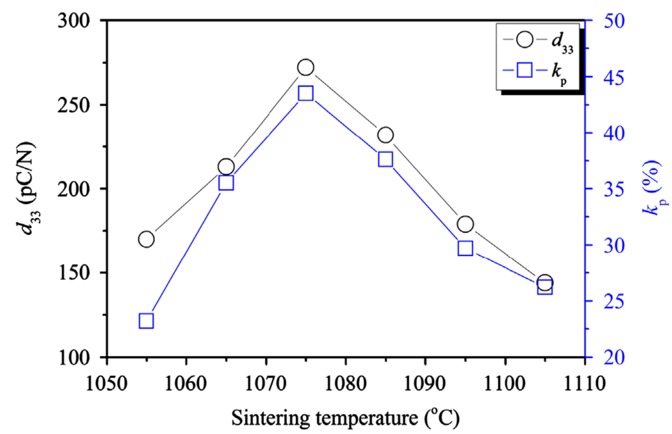

Fig. 6. Piezoelectric properties of KNLNS ceramics as a function of the sintering temperature.

Fig. 4(a–c) shows the temperature dependence of the dielectric constant of KNLNS ceramics sintered at different temperatures, measured at room temperature ∼500 °C and 1 kHz–1 MHz. Only one peak has been observed, which is defined as the phase transition from a tetragonal phase to a cubic phase (T_C) [6,9], showing that all ceramics have a tetragonal phase. Moreover, the T_C of KNLNS ceramics changes with the variation of the sintering temperature. T_C gradually increases as the sintering temperature increases from 1055 to 1075 °C, and then drops as the sintering temperature increases from 1075 to 1105 °C, which can be put down to the loss of excessive Na [27,28]. Similar results were observed in KNN-based ceramics reported by other researchers [27,28]. It was also observed that the T_C of all ceramics almost keeps unchanged as a function of measurement frequencies.

Fig. 5 shows the dielectric properties of KNLNS ceramics as a function of the sintering temperature (T_s), measured at 100 kHz and room temperature. Their dielectric constant (ε_r) gradually increases and then drops as the T_s increases, reaching a maximum of ∼1152 when T_s=1075 °C. Their dielectric loss (tan δ) decreases from 0.043 to 0.026 with increasing T_s, getting a minimum value of ∼0.026 at T_s=1075 °C, and again rises with further increasing T_s. As a result, the ceramic sintered at 1075 °C has an enhanced dielectric behavior of ε_r∼1152 and tan δ∼0.026.

Fig. 6 shows piezoelectric properties of KNLNS ceramics as a function of T_s, measured at room temperature. Their piezoelectric constant (d_{33}) gradually rises and then drops as the T_s increases, getting a maximum d_{33} of ∼272 pC/N for the ceramic sintered at 1075 °C. Similarly, the electromechanical coupling factor (k_p) also reaches a maximum value of ∼43.5% when T_s=1075 °C. In the present work, the d_{33} is comparable to those reported results of Li and Sb-doped KNN ceramics [9,12,13]. As a result, the ceramic sintered at 1075 °C gets an enhanced piezoelectric behavior of d_{33}∼272 pC/N and k_p∼43.5% because of the increase of their bulk density [27,29].

4. Conclusions

$(K_{0.40}Na_{0.60})_{0.94}Li_{0.06}Nb_{0.94}SbO_3$ (KNLNS) lead-free piezoceramics were prepared by the conventional solid-state method. Their grain size gradually increases as the sintering temperature increases. Their electrical properties were very sensitive to the sintering temperature. Enhanced electrical properties (e.g., $d_{33}\sim272$ pC/N, $k_p\sim43.5\%$, $\varepsilon_r\sim1152$, tan $\delta\sim0.026$, and $T_C\sim346$ °C) were obtained in the KNLNS ceramic sintered at 1075 °C, these results showing that piezoelectric properties of KNLNS ceramics could be modified by changing the sintering temperature.

Acknowledgments

Authors gratefully acknowledge the support of the Chengdu Medical College and the Scientific Research Foundation of the Education Department of Sichuan Province, China (09ZC085).

References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic, New York115.
[2] W.F. Liu, X.B. Ren, Large piezoelectric effect in Pb-free ceramics, Physical Review Letters 103 (2009) 257602.
[3] J. Wu, D. Xiao, W. Wu, Q. Chen, J. Zhu, Z. Yang, J. Wang, Role of room-temperature phase transition in the electrical properties of (Ba, Ca)(Ti, Zr)O_3 ceramics, Scripta Materialia 65 (2011) 771–774.
[4] A. Sasaky, T. Chiba, Y. Mamiya, E. Otsuki, Dielectric and piezoelectric properties of $(Bi_{0.5}Na_{0.5})TiO_3$–$(Bi_{0.5}K_{0.5})TiO_3$ systems, Japanese Journal of Applied Physics 38 (1999) 5564–5567.
[5] S. Qiao, J. Wu, B. Wu, B. Zhang, D. Xiao, J. Zhu, Effect of $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ content on the microstructure and electrical properties of $Bi_{0.51}(Na_{0.82}K_{0.18})_{0.50}TiO_3$ ceramics, Ceramics International 38 (2012) 4845–4851.
[6] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84–87.
[7] S.J. Zhang, R. Xia, T.R. Shrout, G. Zang, J. Wang, Piezoelectric properties in perovskite $0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3$ lead-free ceramics, Journal of Applied Physics 100 (2006) 104108.
[8] X. Cheng, J. Wu, X. Wang, B. Zhang, J. Zhu, D. Xiao, X. Wang, X. Lou, Giant d_{33} in (K,Na)(Nb,Sb)O_3–(Bi,Na,K, Li)ZrO_3 based lead-free piezoelectrics with high T_c, Applied Physics Letters 103 (2013) 052906.
[9] J. Wu, Y. Wang, D. Xiao, J. Zhu, P. Yu, L. Wu, W. Wu, Piezoelectric properties of $LiSbO_3$-Modified $(K_{0.48}Na_{0.52})NbO_3$ lead-free ceramics, Japanese Journal of Applied Physics 46 (2007) 7375–7377.
[10] D.M. Lin, K.W. Kwok, K.H. Lam, H.L.W. Chan, Structure and electrical properties of$K_{0.5}Na_{0.5}NbO_3$–$LiSbO_3$lead-free piezoelectric ceramics, Journal of Applied Physics 101 (2007) 074111.
[11] Y.M. Li, Z.Y. Shen, L. Jiang, F. Wu, Z.M. Wang, Y. Hong, R.H. Liao, Microstructure, phase transition and electrical properties of $LiSbO_3$-doped $(K_{0.49}Na_{0.51})NbO_3$ lead-free piezoelectric ceramics, Journal of Materials Science 22 (9) (2011) 1409–1414.
[12] J.G. Wu, D. Xiao, Y. Wang, J. Zhu, P. Yu, Effects of K content on the dielectric, piezoelectric, and ferroelectric properties of $0.95(K_xNa_{1-x})NbO_3$–$0.05LiSbO_3$ lead-free ceramics, Journal of Applied Physics 103 (2008) 024102.
[13] J. Wu, D. Xiao, Y. Wang, J. Zhu, P. Yu, Y. Jiang, Compositional dependence of phase structure and electrical properties in $(K_{0.42}Na_{0.58})NbO_3$-$LiSbO_3$ lead-free ceramics, Journal of Applied Physics 102 (2007) 114113.
[14] G.Z. Zang, J.F. Wang, H.C. Chen, W.B. Su, C.M. Wang, P. Qi, B.Q. Ming, J. Du, L.M. Zheng, S. Zhang, T.R. Shrout, Perovskite $(Na_{0.5}K_{0.5})_{1-x}(LiSb)_xNb_{1-x}O_3$ lead-free piezoceramics, Applied Physics Letters 88 (2006) 212908.
[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, Journal of Physics and Chemistry of Solids 73 (7) (2012) 827–833.
[16] Y. Zhao, R. Huang, R. Liu, X. Wang, H. Zhou, Enhanced dielectric and piezoelectric properties in Li/Sb-modified (Na, K)NbO3 ceramics by optimizing sintering temperature, Ceramic International 39 (2013) 425–429.
[17] H. Li, W.Y. Shih, W.H. Shih, Effect of antimony concentration on the crystalline structure, dielectric, and piezoelectric properties of $(Na_{0.5}K_{0.5})_{0.945}$-$Li_{0.055}Nb_{1-x}Sb_xO_3$ solid solutions, Journal of the American Ceramic Society 90 (2007) 3070–3072.
[18] Z.P. Yang, Effects of composition on phase structure, microstructure and electrical properties of $(K_{0.5}Na_{0.5})NbO_3$–$LiSbO_3$ ceramics, Materials Science & Engineering: A 432 (2006) 292–298.
[19] C. Wattanawikkam, N. Vittayakorn, T. Bongkarn, Low temperature fabrication of lead-free KNN-LS-BS ceramics via the combustion method, Ceramics International 39 (2013) S399–S403.
[20] Y. Li, C. Hui, M. Wu, Y. Li, Y. Wang, Textured $(K_{0.5}Na_{0.5})NbO_3$ ceramics prepared by screen-printing multilayer grain growth technique, Ceramics International 38 (2012) S283–S286.
[21] F. Rubio-Marcos, J.J. Reinos, X. Vendrell, J.J. Romero, L. Mestres, P. Leret, J.F. Fernández, P. Marchet, Structure, microstructure and electrical properties of Cu^{2+} doped (K,Na,Li)(Nb,Ta,Sb)O_3 piezoelectric ceramics, Ceramics International 39 (2013) 4139–4149.
[22] T. Chen, H. Wang, T. Zhang, G. Wang, J. Zhou, J. Zhang, Y. Liu, Piezoelectric behavior of $(1-x)K_{0.50}Na_{0.50}NbO_3$–$xBa_{0.80}Ca_{0.20}ZrO_3$ lead-free ceramics, Ceramics International 39 (2013) 6619–6622.
[23] B. Zhang, X. Wang, X. Cheng, J. Zhu, D. Xiao, J. Wu, Enhanced d_{33} value in $(1-x)[(K_{0.50}Na_{0.50})_{0.97}Li_{0.03}Nb_{0.97}Sb_{0.03}O_3]$–$xBaZrO_3$ lead-free ceramics with an orthorhombic–rhombohedral phase boundar, Journal of Alloys Compounds 581 (2013) 446–451.
[24] R. Huang, Y. Zhao, Y. Zhao, R. Liu, H. Zhou, Effects of sintering temperature and alkaline elements excess on the structure and electrical properties of $(K_{0.462}Na_{0.48}Li_{0.058})_{1-x}NbO_3$ lead-free piezoelectric ceramics, Current Applied Physics 11 (2011) 1205–1209.
[25] P. Zhao, B. Zhang, J. Li, Enhanced dielectric and piezoelectric properties in $LiTaO_3$-doped lead-free (K,Na)NbO_3 ceramics by optimizing sintering temperature, Scripta Materialia 58 (2008) 429–432.
[26] Z. Shen, Y. Zhen, K. Wang, J. Li, Influence of sintering temperature on grain growth and phase structure of Compositionally optimized high-performance Li/Ta-modified(Na,K)NbO_3 ceramics, Journal of the American Ceramic Society 92 (2009) 1748–1752.
[27] P. Kumar, P.P. Kumar, Role of sintering temperature on the phase stability and electrical properties of $0.94(K_{0.5}Na_{0.5}NbO_3)$–$0.06(LiSbO_3)$ ceramics, Japanese Journal of Applied Physics 51 (2012) 011503.
[28] P. Zhao, B.P. Zhang, J.F. Li, High piezoelectric d_{33} coefficient in Li-modified lead-free (Na,K)NbO_3 ceramics sintered at optimal temperature, Applied Physics Letters 90 (2007) 242909.
[29] Y. Guo, K. Kakimoto, H. Ohsato, Structure and electrical properties of lead-free $(Na_{0.5}K_{0.5})NbO_3$–$BaTiO_3$ ceramics, Japanese Journal of Applied Physics 43 (2004) 6662.