MICROSTRUCTURE, ELECTRICAL PROPERTIES AND PROCESSING DEPENDENCE OF CuO MODIFIED $(Na_{0.52}K_{0.48})NbO_3$ CERAMICS

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The CuO modified $(Na_{0.52}K_{0.48})NbO_3$ (NKN) piezoelectric ceramics were prepared by a solid-state reaction method. On the one hand, CuO doping can improve the densification behavior and simultaneously promote the grain growth, however, has little effect on the Curie temperature. On the other hand, the mechanical quality factor Q_m obviously increases, the dielectric loss $tan\delta$ decreases, and the piezoelectric constant d_{33} and the planar electromechanical coupling coefficient k_p tend to drop. Moreover, an obvious effect comes from the sintering conditions. The 1mol% CuO doped NKN ceramics sintered at 1090 °C for 3 h own the electrical properties: $Q_m = 1727$, $tan\delta = 0.29$ %, $d_{33} = 74$ pC/N, $k_p = 0.22$ and a dielectric constant $\varepsilon_r = 410$. All these effects of CuO doping are considered to result from the liquid phase and oxygen vacancies formed during sintering.

INTRODUCTION

Traditional lead containing piezoelectric ceramics, such as lead zirconate titanate, were recognized to have threats to the environment owing to the toxicity of lead oxide, although they have been widely used for many years as sensor, transducer and actuator materials. It is thus urgent to search for lead-free alternatives to those lead based piezoelectric materials.

Sodium potassium niobate was known to be a typical candidate of lead-free piezoelectric compositions with a perovskite structure. It was reported that it has good piezoelectric and electromechanical properties and relatively high Curie temperature (~420 °C) [1-6]. It has a morphotropic phase boundary (MPB) composition of $(Na_{0.5}K_{0.5})NbO_3$ in equal mole of $NaNbO_3$ and $KNbO_3$ which shows the best piezoelectric properties among compositions with different ratios [7]. However, it has been recognized that there exist a few problems with this material system. These problems can be categorized into two aspects: on the one hand, the difficulty in processing due to the volatilization of K and Na at high temperature and the deliquescence features in air, leading to poor density and low electrical properties [2-4]. Although hot press, hot isostatic pressing or spark plasma sintering was used to make highly dense bodies [8-11], yet it costs much and restricts the sample sizes, thus being unsuitable for mass production. Therefore, it is definitely necessary to develop a low-temperature sintering processing; on the other hand, the properties of $(Na_{0.5}K_{0.5})NbO_3$ ceramics are soft [12-20], meaning that the mechanical quality factor Q_m is low, the coercive field is not high, the dielectric loss $tan\delta$ is high and the remanent polarization P_r is relatively high, making them inappropriate for high power application. Thus, it is desirable to harden the properties through a suitable processing procedure, which may obviously broad the scope of applications.

CuO added into alkaline niobates was expected to form a liquid phase, $K_4CuNb_8O_{23}$ (its melting point 1050°C) and therefore was used to aid sintering of many compositions based on niobates [21-28]. Additionally, Cu^{2+} tends to occupy B-site in a perovskite cell considering its ionic size, thus producing oxygen vacancies in the case of alkaline niobates. Sintering additives such as $K_4CuNb_8O_{23}$, $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ and CuO were mostly doped in $Na_{0.5}K_{0.5}NbO_3$ ceramics with 1:1 Na/K ratio. However, Dai et al recently reported that the highest piezoelectric properties of $Na_{1-x}K_xNbO_3$ were obtained at the optimum Na/K ratio of 0.52/0.48 [29]. Therefore, $(Na_{0.52}K_{0.48})NbO_3$ (NKN) was investigated as the objective in this study. The NKN ceramics were prepared by pressureless sintering using CuO as a sintering aid.

A special focus was made on the relationship between the content of CuO, sintering temperature, microstructure and electrical properties.

EXPERIMENTAL

Ceramics with compositions of (1-x)NKN-xCuO were prepared by using a traditional mixed oxide route. The raw chemicals used in this study are K$_2$CO$_3$ (≥ 99.0%), Na$_2$CO$_3$ (≥ 99.8%), Nb$_2$O$_5$ (≥ 99.5%) and CuO (≥ 99.0%). The powder of NKN was firstly prepared by mixing the raw materials in a nylon jar for 8 h and then calcined at 870°C for 4 h after removing the ethanol. The as-prepared NKN powder was divided into six batches in each of which a prescribed amount of CuO was added according to the above chemical formula (x = 0, 0.125, 0.25, 0.5 , 1 and 2 mol.%). The powder mixtures together with 0.5 wt.% PVB binder were then milled again in ethanol for 24 h. The dried powder was compacted into disk specimens by uniaxial pressing in a stainless steel die. Finally, the green specimens were fired in the temperature range of 1060-1120°C for 3 h.

The density of the sintered samples was measured by the Archimedes method. The grain morphology was observed by using a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). For the piezoelectric and electromechanical measurements, the silver electrodes were made on two major surfaces of each sample by pasting the silver paste and firing it at 550°C for 30 min. The poling treatment was carried out by applying a dc field of 2-3 kv/mm at 110°C for 20 min in stirred silicone oil. The piezoelectric constant d$_{33}$ was measured directly on a quasi-static d$_{33}$ meter (YE2730A, Yangzhou, China). Both Q$_m$ and the planar elecromechanical coupling coefficient k$_p$ were measured through a resonance-antiresonance method by means of a high precision impedance analyzer (PV70A, Beijing Band ERA Co., Ltd. China) according to the following formulas:

$$k_p^2 = 0.395 \frac{f_R}{f_A - f_R} + 0.574 \qquad (1)$$

$$Q_m = \frac{1}{2\pi \cdot f_R \cdot R_1 \cdot C_f \{1 - (f_R/f_A)^2\}} \qquad (2)$$

where f$_R$ is the resonance frequency, f$_A$ the antiresonance frequency, R$_1$ the resonance impedance, and C$_f$ the capacitance at 1 kHz. The dielectric constant ε$_r$ versus temperature curves were measured by a LCR meter (Agilent E4980A, USA) equipped with a programmable temperature box.

RESULTS AND DISCUSSION

The XRD patterns of (1-x) NKN + x mol.% CuO are shown in Figure 1. A pure orthorhombic NKN phase was well developed without detectable amount of secondary phases within the doping range of x ≤ 2 mol.%. The

results also indicated that the synthesized powder before CuO doping consists of single orthorhombic phases. Furthermore, the diffraction peaks of CuO doped NKN slightly shift to the lower angle, compared to those of pure NKN, implying that the lattice parameter becomes larger. This would be attributed to that Cu^{2+} ions replace B-site Nb^{5+} ions, considering that Cu^{2+} has a relatively large ionic radius compared with Nb^{5+} (ionic radii: 0.73 and 0.64 Å for Cu^{2+} and Nb^{5+}, respectively, CN = 6).

Figure 2 shows the microstructure of CuO modified NKN ceramics sintered at 1090°C. The average grain size for undoped NKN ceramics is relatively small, however inhomogeneous. There exists a bimodal grain size distribution. By comparison, the inhomogeneity of grain size is gradually improved with increasing the doping content of CuO, although the grains tend to grow rapidly. The 1mol% CuO doped NKN ceramics have an average size of ~10 μm. Moreover, the addition of CuO shows a clear effect on the densification of NKN ceramics as well. Pure NKN ceramics are known to have difficulty in sintering [3]. It has been alleviated by doping a small amount of CuO and the best densification appears when 1 mol.% CuO is doped. With further increasing the content of CuO, the density of NKN ceramics decreases and the samples look porous together with significantly grown grains as shown in Figure 2d. The change in the microstructure can be interpreted in terms of the low melting point of a liquid phase, K$_4$CuNb$_8$O$_{23}$, which could be formed during the sintering process [22, 23, 27]. It is possible that the liquid phase of the K$_4$CuNb$_8$O$_{23}$ with a low melting point induces a transient liquid phase sintering, meaning that the liquid phase will be absorbed into grains at the final stage of sintering. This would be the reason why the secondary phase of K$_4$CuNb$_8$O$_{23}$ was not detected in Figure 1. The liquid phase affects the densification in the way that grains become easily rearranged, and that the grain boundary mobility is
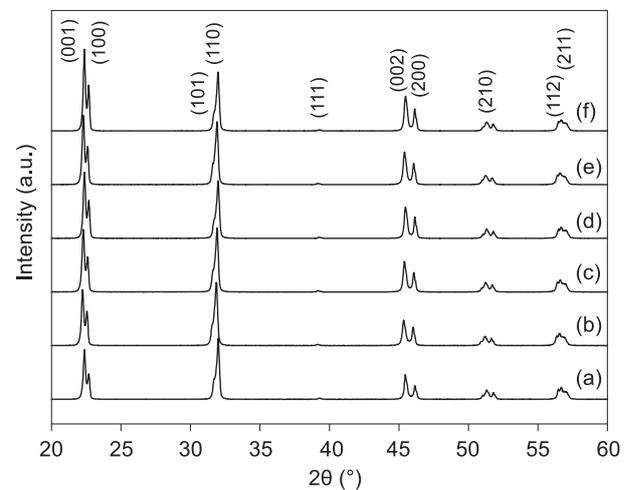
Figure 1. X-ray diffraction patterns of CuO doped NKN: a) x = 0 mol.%, b) x = 0.125 mol.%, c) x = 0.25 mol.%, d) x = 0.5 mol.%, e) x = 1 mol.%, and f) x = 2 mol.%.

raised through mass transfer in a liquid. On the other hand, the liquid phase simultaneously causes grains to grow rapidly in the early period of sintering, resulting in a fast decrease of sintering driving force. Therefore, when more than 1 mol.% CuO is added, the densification is deteriorated. The same results can be confirmed by the Archimedes method. The maximum density (~ 97 % of the theoretical density) can be achieved in the 1 mol.% CuO NKN samples sintered at 1090°C, as shown in Figure 3.

The dielectric constants ε_r at 100 kHz of CuO doped NKN samples as a function of temperature are shown in Figure 4. It can be seen that all samples show two phase transitions: orthorhombic to tetragonal transitions at ~ 180°C (T_{o-t}) and tetragonal to cubic transitions at 410°C (T_c). With increasing the content of CuO, $\underline{T}_c$ is hardly changed but T_{o-t} is slightly lowered. On the one hand, T_{o-t} is altered after doping CuO, meaning that Cu^{2+} has dissolved into the lattice. On the other hand, T_c is not changed by doping CuO, implying that Cu^{2+} may occupy B-site in NKN lattices as an acceptor. Compared with donor dopants, acceptors usually have little effect on the Curie temperature [30]. The fact that Cu^{2+} is prone to diffuse into the lattice and to occupy B-site of a perovskite structure was previously confirmed by X-ray diffraction measurements [24].

Figure 5 provides various electrical properties for NKN ceramics doped with different contents of CuO. It can be seen that both d_{33} and k_p decrease with increasing the amount of CuO; On the contrary, Q_m first increases with doping CuO and then drops when the doping content is over 1 mol.%. The value of tanδ just shows an opposite tendency with Q_m. The change in the properties means that the materials become hard due to the addition of CuO. The hardening effect can be believed to result from oxygen vacancies probably produced by the substitution of Cu^{2+} for Nb^{5+}. The emergence of oxygen vacancies makes three-dimensional oxygen octahedron in a perovskite structure shrink and distort, pinning the domain wall motion. On the one hand, the formed oxygen vacancies prevent domains from reversing during polarization. On the other hand, tanδ is mainly from the internal friction due to the domain wall movement, and that Q_m responds to the energy consumption. The materials become hard, meaning that domains turn over difficultly. When the content of CuO surpasses 1 mol.%, tanδ starts to increase due to the increased leakage current. The 1mol% CuO doped NKN ceramics own the electrical properties: Q_m = 1727, d_{33} = 74 pC/N, k_p = 0.22, ε_r = 410, tanδ = 0.29%.

Figure 6 shows the effect of sintering temperature on the 1 mol.% CuO doped NKN ceramics. The d_{33} is slightly reduced along with the sintering temperature;
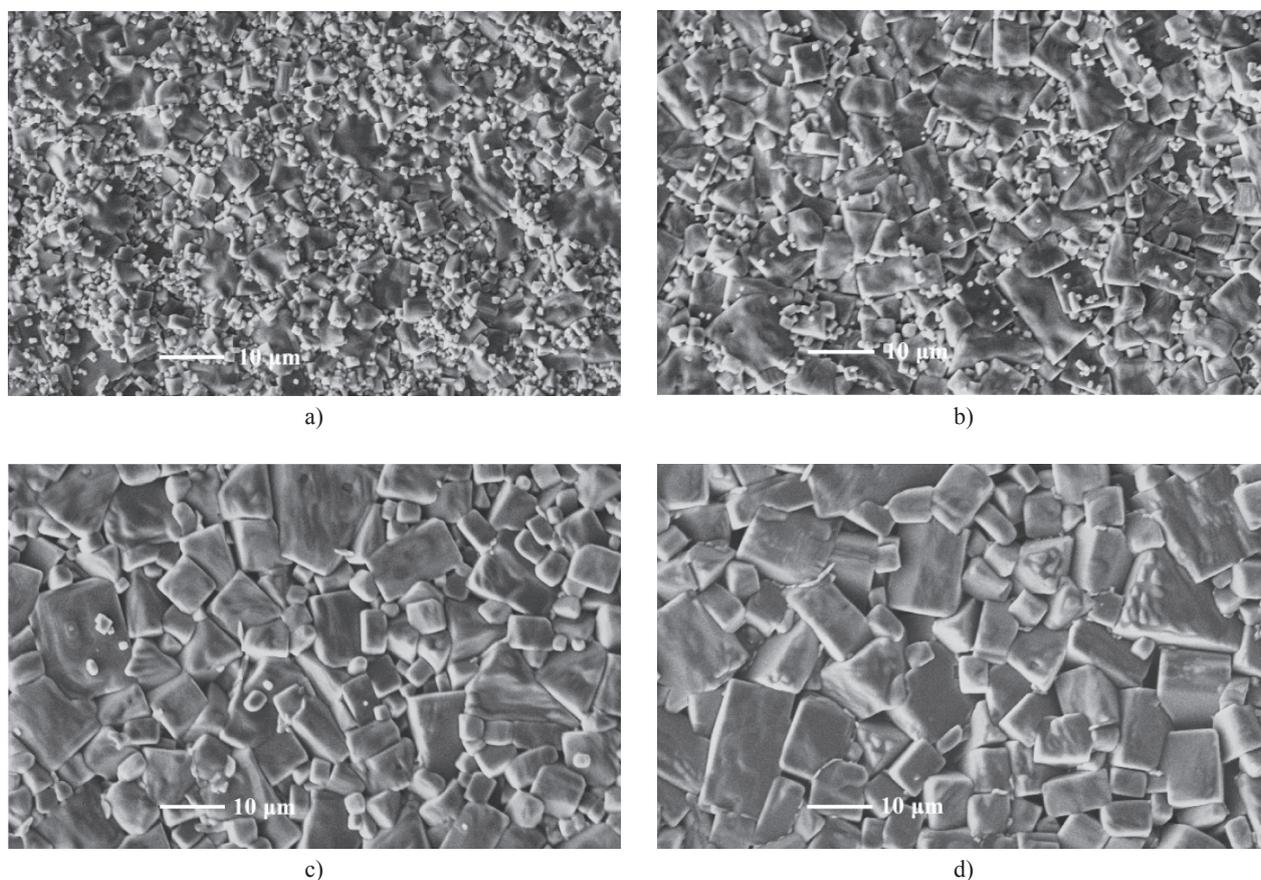
Figure 2. SEM photographs of CuO doped NKN ceramics sintered at 1090°C: a) x = 0 mol.%, b) x = 0.5 mol.%, c) x = 1 mol.% and d) x = 2 mol.%.
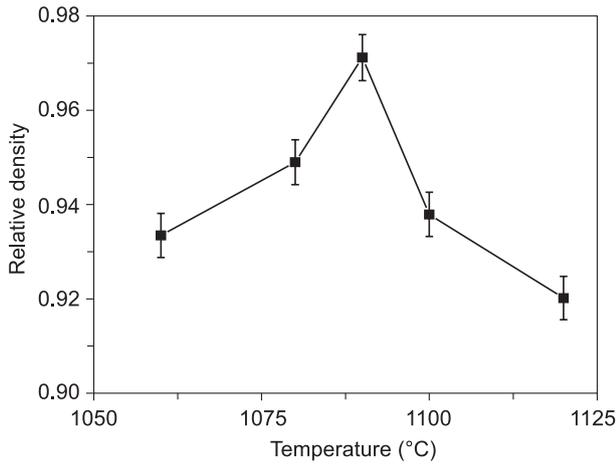
Figure 3. Densities of the 1 mol.% CuO doped NKN samples as a function of sintering temperature.
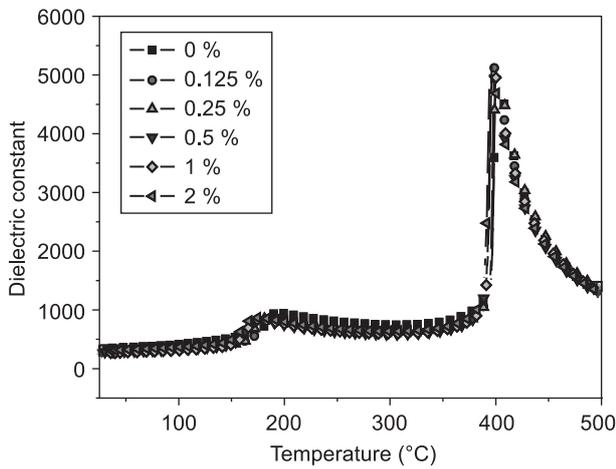
Figure 4. Temperature dependence of the dielectric constants for NKN samples doped with different contents of CuO as indicated.
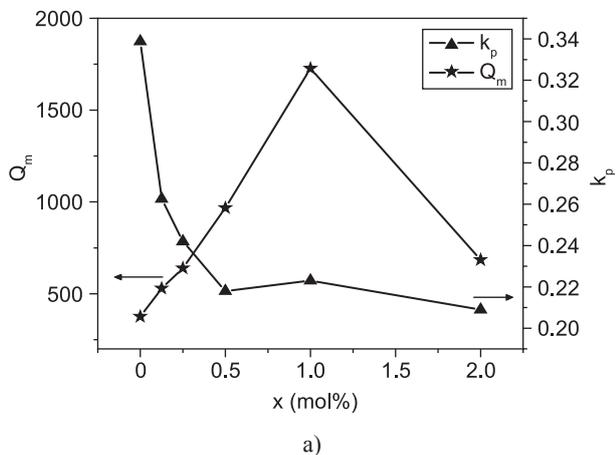
however, both Q_m and tanδ reach the best values at the sintering temperature of 1090°C. These changes are probably due to both a hardening effect from the substitution of Cu^{2+} for Nb^{5+}, and a changing densification with increasing the sintering temperature. As known, the hardened piezoelectric ceramics tend to have smaller d$_{33}$ values and increased Q_m, as discussed above. Therefore, the CuO modified NKN ceramics show a processing dependence of electrical properties.

CONCLUSIONS

The CuO modified NKN lead-free piezoelectric ceramics were successfully prepared by ordinary sintering. The effect of the addition of CuO on the sintering behavior, microstructure and various electrical properties was investigated. The results indicate that the densification behavior is sensitive to both the content of CuO and the sintering temperature. Moreover, the
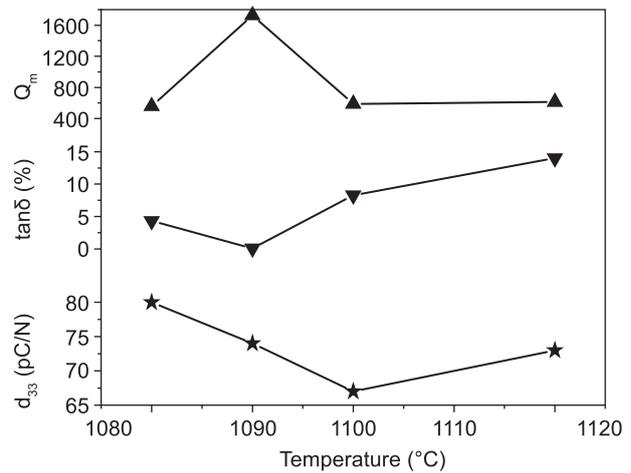
Figure 6. Various electrical properties of the 1 mol.% CuO modified NKN samples sintered at different temperatures.

a)

b)
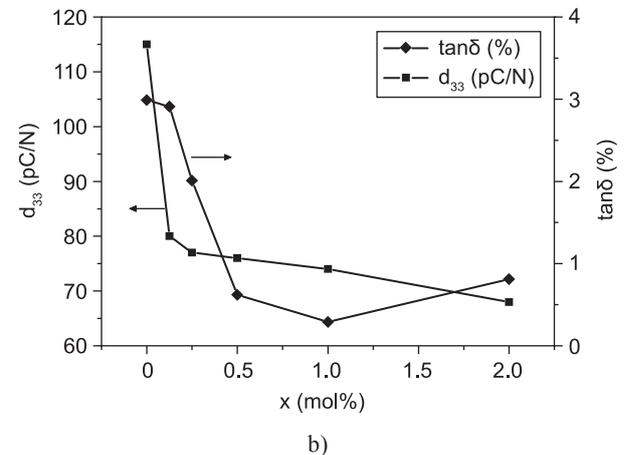
Figure 5. Various electrical properties of NKN ceramics with changing the doping content of CuO: a) Q_m and k_p, b) d_{33} and tanδ.

B-site substitution of Cu ions acts as an acceptor and significantly makes the property of NKN ceramics hard. The 1mol% CuO doped NKN ceramics sintered at 1090°C for 3 h own the electrical properties: Q_m=1727, tanδ = 0.29 %, d_{33} = 74 pC/N, k_p= 0.22, ε_r = 410.

Acknowledgements

References

1. Ahn Z., Schulze W.A.: J. Am. Ceram. Soc. *70*, 18 (1987).
2. Ichiki M., Zhang L., Tanaka M., Maeda R.: J. Am. Ceram. Soc. *24*, 1693 (2004).
3. Zuo R.Z., Roedel J., Chen R.Z., Li L.T.: J. Am. Ceram. Soc. *89*, 2010 (2006).
4. Birol H., Damjanovic D., Setter N.: J. Eur. Ceram. Soc. *26*, 861 (2006).
5. Du H.L., Li Z.M., Tang F.S., Qu S.B., Pei Z.B., Zhou W.C.: Mater. Sci. Engi. B *131*, 83 (2006).
6. Malic B., Jenko D., Holc J., Hrovat M., Kosec M.: J. Am. Ceram .Soc. *91*, 1916 (2008).
7. Egerton L., Dillon D.M.: J. Am. Ceram. Soc. *42*, 438 (1959).
8. Jaeger R.E., Egerton L.: J. Am. Ceram. Soc. *45*, 209 (1962).
9. Egerton L., Bieling C.A.: Ceram. Bull. *47*, 1151 (1968).
10. Wang R.P., Xie R.J., Sekiya T., Shimojo Y.: Mater. Res. Bull. *39*, 1709 (2004).
11. Li J.F., Wang K., Zhang B.P., Zhang L.M.: J. Am. Ceram. Soc. *89*, 706 (2006).
12. Murty S.N., Umakantham K., Bhanumathi A.: Ferroelectrics *82*, 141 (1988).
13. Park S.H., Ahn C.W., Nahm S., Song J.S.: Jpn. J. Appl. Phys. *43*, L1072 (2004).
14. Matsubara M., Kikuta K., Hirano S.: J. Appl. Phys. *97*, 114105 (2005).
15. Du H.L., Luo F., Qu S.B., Pei Z., Zhu D.M., Zhou W.: J. Appl. Phys. *102*, 054102 (2007).
16. Lin D.M., Kwok K.W., Chan H.L.W.: Appl. Phys. Lett. *90*, 232903 (2007).
17. Li E.Z., Kakemoto H., Wada S., Tsurumi T.: J. Am. Ceram. Soc. *90*, 1787 (2007).
18. Chen Q., Chen L., Li Q.S., Yue X., Xiao D.Q., Zhu J.G.: J. Appl. Phys. *102*, 104109 (2007).
19. Li E.Z., Kakemoto H., Wada S., Tsurumi T.: IEEE T. Ultrason. Ferr. *55*, 980 (2008).
20. Lv Y.G., Wang C.L., Zhang J.L., Zhao M.L., Li M.K., Wang H.C.: Mater. Lett. *62*, 3425 (2008).
21. Matsubara M., Yamaguchi T., Sakamoto W., Kikuta K., Yogo T., Hirano S.I.: J. Am. Ceram. Soc. *88*, 1190 (2005).
22. Matsubara M., Yamaguchi T., Kikuta K., Hirano S.I.: Jpn. J. Appl. Phys. *44*, 25 (2005).
23. Park H.Y., Ahn C.W., Cho K.H., Nahm S., Lee H.G., Kang H.W., Kim D.H., Park K.S.: J. Am. Ceram. Soc. *90*, 4066 (2007).
24. Lin D.M., Kwok K.W., Chan H.L.W.: Appl. Phys. A *88*, 359 (2007).
25. Zuo R.Z., Ye C., Fang X.S., Yue Z. X., Li L. T.: J. Am. Ceram. Soc. *91*, 914 (2008).
26. Park H.Y., Choi J.Y., Choi M.K., Cho K.H., Nah S., Lee H.G., Kang H.W.: J. Am. Ceram. Soc. *91*, 2374 (2008).
27. Ahn C.W., Karmarkar M., Viehland D., Kang D.H., Bae K.S., Priya .S.: Ferroelectric Letters *35*, 66 (2008).
28. Lin D.M., Kwok K.W., Chan H.L.W.: J. Phys. D: Appl. Phys. *41*,045401 (2008).
29. Dai Y.J., Zhang X.W., Chen K.P.: Appl. Phys. Lett. *94*, 042905 (2009).
30. Chen Y.H., Uchino K., Viehland D.: J. Appl. Phys. *89*, 3928 (2001).