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Investigation on the design and synthesis of new systems of BNT-based lead-free piezoelectric ceramics

D. Q. Xiao · D. M. Lin · J. G. Zhu · P. Yu

Abstract Three primary differences between BNT- and PZT-based ceramics were analyzed from the composition and the active component of the materials. Based on the analysis the authors' group developed the new idea of the design of the multiple complex in the A-site ions of BNT compounds. $(Bi_{0.5}Na_{0.5})^{2+}$, Bi^{3+} and Na^{+} in the ABO_3 structure are defined as A-site, A_1-site and A_2-site ions, respectively, and A, A_1 and A_2-site ions can be simultaneously or singly substituted partially by alkaline-earth metal ions, metal ions with +3 valence and metal ions with +1 valence, respectively. Under this consideration, Several new systems of $Bi_{0.5}Na_{0.5}TiO_3$ (abbreviated as BNT)-based lead-free piezoelectric ceramics were proposed. These ceramics can be prepared by conventional ceramic techniques and have excellent piezoelectric performance. Among these materials, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ possesses higher piezoelectric constant ($d_{33} = 230$ pC/N), higher electromechanical couple factor ($k_p = 0.40$), larger remanent polarization ($P_r = 38.9\ \mu C/cm^2$) and a better P-E hysteresis loop until about 200°C.

Keywords $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ · Lead-free piezoelectric ceramics · Piezoelectric constants · Electromechanical couple factor · Remanent polarization

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1 Introduction

Lead-based piezoelectric ceramics, represented by $PbTiO_3$-$PbZrO_3$ (abbreviated as PZT) and PZT-based multi-system, have wide applications in electronic and microelectronic devices due to their excellent piezoelectric properties. However, the toxicity of lead oxide and its high vapor pressure during sintering processing cause a serious ecological problem. Therefore, to reduce and eliminate lead pollution, more and more attentions have been paid to lead-free piezoelectric ceramics. It is necessary to develop lead-free piezoelectric ceramics with excellent piezoelectric properties such as those of lead-based piezoelectric ceramics. And new piezoelectric ceramics should be "lead-free at last" [1].

$Bi_{0.5}Na_{0.5}TiO_3$ (abbreviated as BNT) is considered to be a good candidate of lead-free piezoelectric ceramics with a relatively large remanent polarization ($P_r = 38\ \mu C/cm^2$). However, pure BNT piezoelectric ceramics are difficult to pole because of its relatively large coercive field ($E_c = 73$ kV/cm) and therefore provide too low piezoelectric properties. To improve piezoelectric properties of BNT ceramics, some BNT-based solid solutions have been developed and extensively studied, such as BNT-$BaTiO_3$ [2], BNT-$Bi_{0.5}K_{0.5}TiO_3$ [3], BNT-$BiFeO_3$ [4], BNT-$NaNbO_3$ [5], BNT-$Ba(Cu_{1/2}W_{1/2})O_3$ [6], BNT-$Bi_{0.5}K_{0.5}TiO_3$-$BaTiO_3$ [7], BNT-1/2($Bi_2O_3 \cdot Sc_2O_3$) [8] and so on. However, piezoelectric properties of these solid solutions are not high enough. So, research and development of new BNT-based multi-component systems may be an possible approach to improve efficiently the piezoelectric properties of BNT ceramics.

2 Consideration of the design of BNT-based lead-free piezoelectric ceramics

As well known, compared with PZT ceramics, pure BNT ceramics and BNT-based solid solutions give so much lower piezoelectric properties. There may be three primary differences between BNT- and PZT-based ceramics. Firstly, BNT is a ferroelectric compound with complex ions $(Bi_{0.5}Na_{0.5})^{2+}$ of Bi^{3+} and Na^{+} in its A-site. Completely different from BNT, PZT is a solid solution and is composed of $PbTiO_3$ and $PbZrO_3$ with complex ions of Ti^{4+} and Zr^{4+} in its B-site. Secondly, most BNT-based ceramics are the solid solutions which are made up of ferroelectric BNT and other ferroelectrics or non-ferroelectrics such as $Bi_{0.5}K_{0.5}TiO_3$ [3], $BaTiO_3$ [2], $Ba(Cu_{1/2}W_{1/2})O_3$ [6], $BiFeO_3$ [4] and so on. In contrast, PZT is the solid solution which is composed of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$. That is, there should be a different principle of forming solid solutions between BNT-based and PZT-based ceramics. Finally, $Bi_{0.5}Na_{0.5}TiO_3$ is A-site piezoelectric active, and BNT-based ceramics with relatively good piezoelectric properties can be obtained through partially substitution of A-site $(Bi_{0.5}Na_{0.5})^{2+}$ ions by Ba^{2+}, $(Bi_{0.5}K_{0.5})^{2+}$, Ba^{2+}-$(Bi_{0.5}K_{0.5})^{2+}$ and so on. Modification of BNT in B-site cannot effectively improve the piezoelectric properties. Contrasting with BNT, $PbTiO_3$ is B-site piezoelectric active. It is well known that $PbTiO_3$-based ceramics with excellent piezoelectric properties are the solid solutions that the B-site ions Ti^{4+} of $PbTiO_3$ are partially substituted by Zr^{4+}, $(Mg_{1/3}Nb_{2/3})^{4+}$ and so on. In a word, the modification of BNT and $PbTiO_3$ may obey different rules.

So, in order to improve the electrical properties of BNT-based ceramics for practical applications, the research approaches should be different from those used in the investigation of PZT ceramics. The authors' group did intensive investigation on BNT ferroelectrics in recent years and developed the new idea of the design of the multiple complex in the A-site ions of BNT compounds.

According to this idea, $(Bi_{0.5}Na_{0.5})^{2+}$, Bi^{3+} and Na^{+} in the ABO_3 structure are defined as A-site, A_1-site and A_2-site ions, respectively. And A, A_1 and A_2-site ions can be simultaneously or singly substituted partially by alkaline-earth metal ions (Ba^{2+}, Sr^{+2}, Ca^{+2}), metal ions with +3 valence (La^{3+}, Y^{3+} and so on) and metal ions with +1 valence (K^{+}, Li^{+} and so on), respectively. Under this consideration, some new members of BNT group, such as $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$, $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$, $[Bi_{1-y}(Na_{1-x}Li_x)]_{0.5}Ba_yTiO_3$, $[Bi_{1-y-z}(Na_{1-x-y-z}Li_x)]_{0.5}Ba_ySr_zTiO_3$, $[Bi_{1-y-z}(Na_{1-x-y-z}K_x)]_{0.5}Ba_ySr_zTiO_3$ and so on, were proposed and patented, and the piezoelectric and ferroelectric properties were investigated. The results of the researches are briefly outlined as follows.

3 New systems of BNT-based lead-free piezoelectric ceramics based on the design of the multiple complex in the A-site of ABO_3 compounds

3.1 Experimental

New BNT-based lead-free piezoelectric ceramics were prepared by conventional ceramic fabrication technique. Industrial-grade metal oxides or carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, Li_2CO_3, Ag_2O, $BaCO_3$ and TiO_2 were used as starting raw materials. All the raw materials mixed by ball-milling were calcined at 800–900°C for 2–4 h. After calcination, the ball-milled powders were granulated by adding PVA as a binder and pressed into discs and then sintered at 1100–1200°C for 2–3 h in atmosphere. Silver paste was coated to form electrodes on both sides of sintered ceramic specimens and fired at 810°C. The specimens were poled in silicone oil bath with a dc field of 3–4 kV/mm at 80°C for 20 min.

The crystalline phase of the samples was examined by X-ray diffraction (XRD) technique (DX-1000X, China). The microstructure of the sintered samples was observed using scanning electron microscope (JSM-5900LV). Electromechanical coupling factor k was determined by the resonance-antiresonance method on the basis of IEEE standards by using an impedance analyzer (HP4194A). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-3A). The P-E hysteresis loops were observed using Radiant Precision Workstation.

3.2 Piezoelectric properties of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ lead-free piezoelectric ceramics

The results of the X-ray diffractions of all the samples investigated show that the new ceramics possess a single-phase perovskite structure. It is believed that $K^{+}$and Li^{+} ions substitute partially Na^{+} ion, Ba^{2+} and Sr^{2+} substitute partially $(Bi_{0.5}Na_{0.5})^{2+}$ ions, and La^{3+} and some related ions substitute partially Bi^{3+} ion, and the substitute ions diffuse into the BNT lattices to form solid solutions. All new BNT-based ceramics are well sintered at 1100–1200°C in air. Figure 1 gives a typical XRD pattern of $Bi_{0.5}(Na_{0.70}K_{0.20}Li_{0.10})_{0.5}TiO_3$ ceramics.

Figure 2 shows the microstructures of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ ceramics. Almost no holes are found on the surface of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ ceramics. The bulk densities of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ ceramics are higher than 97% of the theoretical density.

Figure 3 shows the piezoelectric properties as a function of x for $Bi_{0.5}(Na_{0.90-x}K_xLi_{0.10})_{0.5}TiO_3$ ceramics. From Fig. 3, it can be found that new $Bi_{0.5}(Na_{0.90-x}K_xLi_{0.10})_{0.5}TiO_3$ lead-free piezoelectric ceramics based on the design of the multiple complex in the A-site of ABO_3 compounds provide excellent piezoelectric properties. The piezoelectric constant

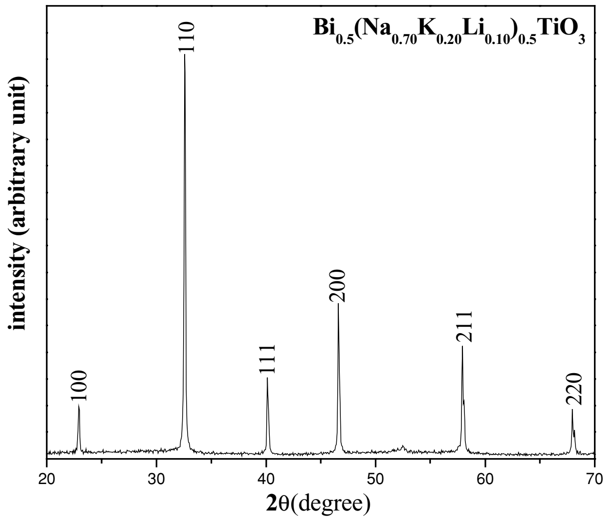

Fig. 1 The XRD pattern of $Bi_{0.5}(Na_{0.70}K_{0.20}Li_{0.10})_{0.5}TiO_3$ ceramics

reaches the maximum of 230 pC/N at $x = 0.20$. And the maximum of the electromechanical factor k_p appears at $x = 0.175$ and reaches 41%. As well known, pure BNT ceramics provide the piezoelectric constant d_{33} of 58 pC/N [9], and some classic BNT-based ceramics, such as BNT-BKT [3], BNT-BT-BKT [7], BNT-$NaNbO_3$ [5], give piezoelectric properties of $d_{33} = 96$, 191, 88 pC/N, and $k_p = 0.314$, 0.33, 0.179, respectively. Obviously, compared with these BNT-based ceramics, the new ceramics developed in present work show much better piezoelectric properties.

Figure 4 shows the P-E hysteresis loops of $Bi_{0.5}(Na_{0.775}K_{0.15}Li_{0.075})_{0.5}TiO_3$ ceramics at different temperature. It can be seen from Fig. 4 that at 20°C the hysteresis loop shows a typical ferroelectric characteristic, and with temperature increasing, the loops begin to become narrower but still keep the very typical ferroelectric feature and large remanent polarization up to 190°C. When the temperature reaches 210°C, the hysteresis loop of the ceramics is deformed and a double-like P-E hysteresis loop appears. It can be concluded from Fig. 4 that the depolarization temperature T_d of the material investigated is about 200°C. T_d is an important factor for BNT-based ceramics from the device applications points of view. Generally, for some classical BNT-based ceramics, the obvious enhancement of piezoelectric properties is accompanied simultaneously by the significant reduction of T_d. However, BNKLT-0.15/0.075 ceramics provide simultaneously good piezoelectric properties ($d_{33} = 146$ pC/N, $k_p = 0.36$), strong ferroelectricity ($P_r = 38.9$ μC/cm^2, $E_c = 3.7$ kV/mm), and higher T_d (about 200°C).

3.3 Piezoelectric properties of $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Ba_yTiO_3$ lead-free piezoelectric ceramics

Figure 5 shows the dependence of piezoelectric properties of $[Bi_{1-y}(Na_{0.925-y}Li_{0.075})]_{0.5}Ba_yTiO_3$ on the amount y of

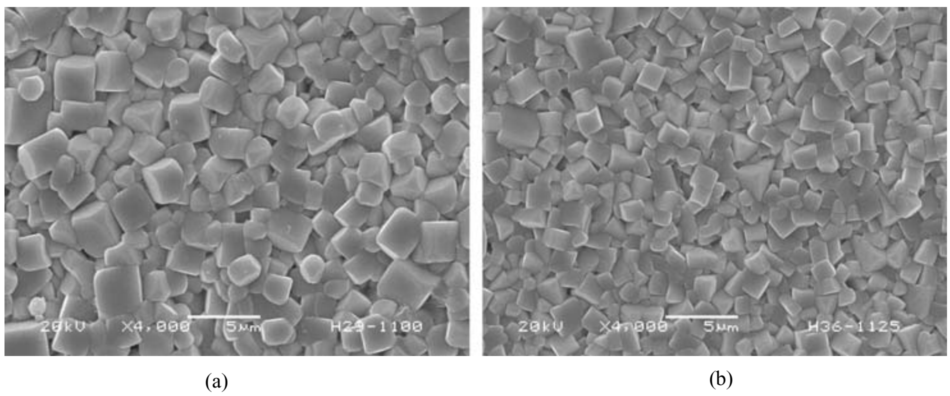

Fig. 2 SEM images of BNKLT-x/y ceramics (a) $Bi_{0.5}(Na_{0.775}K_{0.15}Li_{0.075})_{0.5}TiO_3$ ceramics sintered at 1100°C for 2 h, (b) $Bi_{0.5}(Na_{1-x-y}K_{0.20}Li_{0.10})_{0.5}TiO_3$ sintered at 1125°C for 2 h

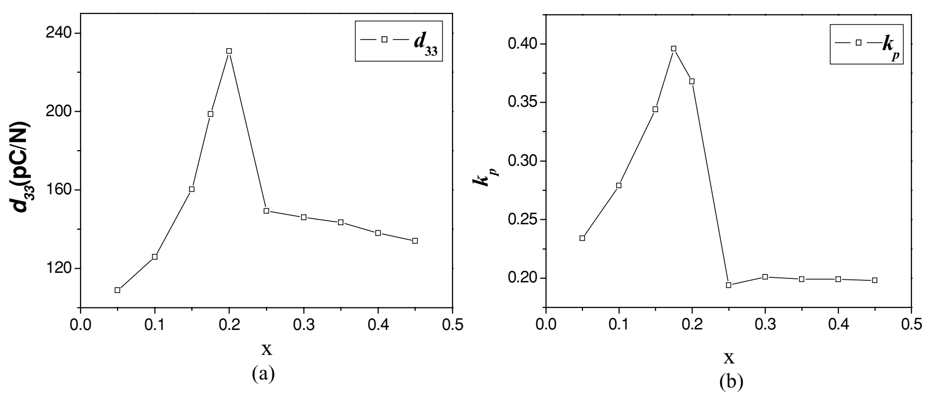

Fig. 3 Piezoelectric constant d_{33} (a) and electromechanical coupling factor (b) as a function of x for $Bi_{0.5}(Na_{0.90-x}K_xLi_{0.10})_{0.5}TiO_3$ ceramics

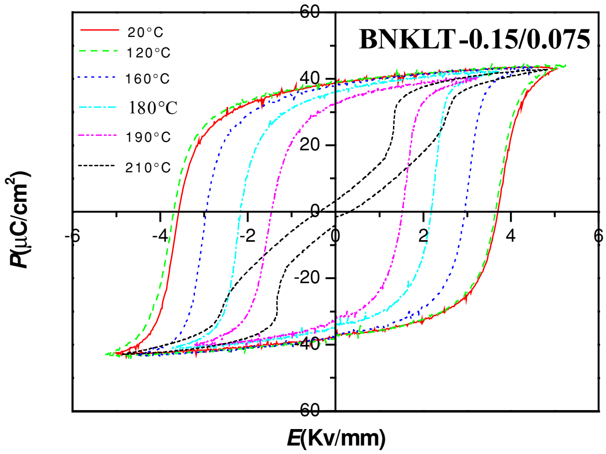

Fig. 4 P-E hysteresis loops of $Bi_{0.5}(Na_{0.775}K_{0.15}Li_{0.075})_{0.5}TiO_3$ ceramics at different temperature

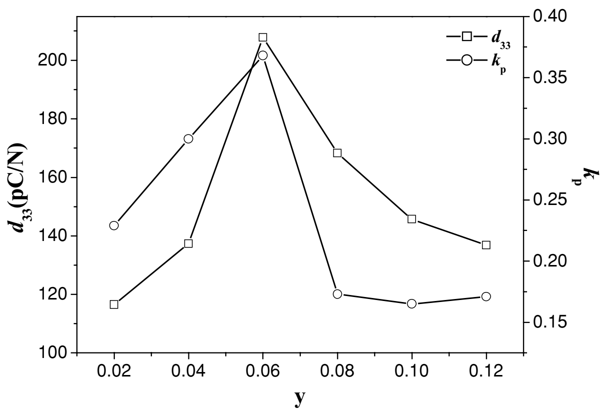

Fig. 5 Piezoelectric properties of $[Bi_{1-y}(Na_{0.925-y}Li_{0.075})]_{0.5}Ba_yTiO_3$ ceramics as a function of the amount of Ba

Ba. From Fig. 5, it can be seen that the piezoelectric constant d_{33} and planar electromechanical coupling factor k_P of the $[Bi_{1-y}(Na_{0.925-y}Li_{0.075})]_{0.5}Ba_yTiO_3$ ceramics sintered at 1100°C for 2 h reach the maximum value of 208 pC/N and 37.0% at $y = 0.06$.

3.4 Piezoelectric properties of $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ lead-free piezoelectric ceramics

Figure 6 shows the piezoelectric properties of $[Bi_{1-z}(Na_{0.75-z}K_{0.15}Li_{0.10})]_{0.5}Ba_zTiO_3$ as a function of z. From Fig. 6, the maximum values of d_{33} (198 pC/N) of the

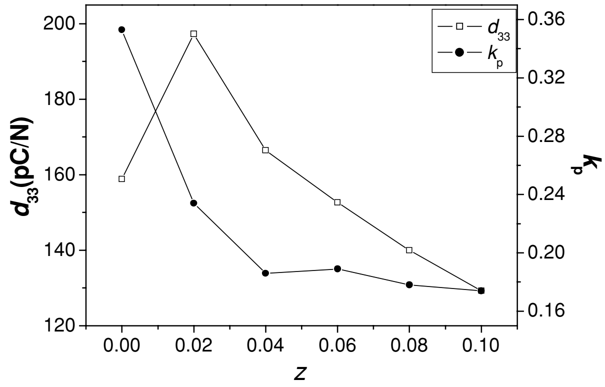

Fig. 6 Piezoelectric constant d_{33} and electromechanical coupling factor k_p of $[Bi_{1-z}(Na_{0.75-z}K_{0.15}Li_{0.10})]_{0.5}Ba_zTiO_3$ as a function of z

$[Bi_{1-z}(Na_{0.75-z}K_{0.15}Li_{0.10})]_{0.5}Ba_zTiO_3$ occur at $z = 0.02$. The planar electromechanical coupling factor k_p decreases sharply with the z increasing.

3.5 Summarization of the lead-free piezoelectric ceramics developed in author's group

Table 1 gives the summarization of the piezoelectric and ferroelectric properties of some new BNT-based ceramics developed in present work. From Table 1, it can be found that these new systems of BNT-based lead-free piezoelectric ceramics based on the design of the multiple complex in the A-site of ABO_3 compounds provide excellent piezoelectric and ferroelectric properties. These new ceramics exhibit good performance and strong ferroelectricity: d_{33} is larger than 200 PC/N, $k_p = 0.34$–0.41, $P_r = 33.8$–$40.4\ \mu C/cm^2$, and $E_c = 2.47$–5.16 kV/mm.

4 Possible applications of new BNT-based lead-free piezoelectric ceramics

The $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ lead free piezoelectric ceramics have been used for making ceramics middle frequency filters. The measurement shows that the performance of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ filer is comparable to that of Pb-based middle frequency filer. In addition, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ and $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$ lead-free piezoelectric ceramic were used

Table 1 The best piezoelectric and ferroelectric properties of the new BNT-based ceramics developed in present work

New BNT-based systems	d_{33}	k_p	P_r	E_c
$Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$	230.8	0.41	40.4	2.5–4.0
$[Bi_{1-z}(Na_{1-y-z}Li_y)]_{0.5}Ba_zTiO_3$	207.8	0.368	38.5	3.29
$[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$	202.7	0.365	38.5	2.8–5.16
$[Bi_{1-z-u}(Na_{1-y-z-u}Li_y)]_{0.5}Ba_zSr_uTiO_3$	202.0	0.338	40.4	2.47–4.98
$Bi_{0.5}(Na_{1-x-y}K_xLi_yAg_z)_{0.5}TiO_3$	215.5	39.3	–	–

d_{33}: pC/N, P_r: $\mu C/cm^2$, E_c: kV/mm.

for making buzzers by ordinary techniques as used for PZT-based piezoelectric buzzers as well. The properties of the buzzers are well comparable with PZT-based piezoelectric buzzers, and the buzzers can be provided commercially. It can be believed that these ceramics can be used in other piezoelectric devices.

5 Conclusion

Three primary differences between BNT- and PZT-based ceramics were analyzed from the composition and the active component. Based on the analysis the authors' group developed the new idea of the design of the multiple complex in the A-site ions of BNT compounds. $(Bi_{0.5}Na_{0.5})^{2+}$, Bi^{3+} and Na^{+} in the ABO_3 structure are defined as A-site, A_1-site and A_2-site ions, respectively, and A, A_1 and A_2-site ions can be simultaneously or singly substituted partially by alkaline-earth metal ions, metal ions with +3 valence and metal ions with +1 valence, respectively. Several new systems of BNT-based lead-free piezoelectric ceramics were proposed based on the design of the multiple complex in the A-site of BNT materials and prepared by the conventional ceramic technique. All new BNT-based ceramics possess a single phase of perovskite structure and are well sintered at 1100–1200°C in air. The ceramics show good piezoelectric performance: $d_{33} = 230$ PC/N, $k_p = 0.40$. Practical devices have been made using BNT-based lead-free piezoelectric ceramics developed in present work.

References

1. E. Cross, *Nature*, **432**, 24 (2004).
2. T. Takennaka, K. Maruyama, and K. Sakata, *Jpn. J. Appl. Phys.*, **30**(9B), 2236 (1991).
3. A. Sasaka, T. Chiba, Y. Mamiya, and E. Otsuki, *Jpn. J. Appl. Phys.*, **38**, 5564 (1999).
4. H. Nagata, N. Koizumi, and T. Takenaka, *Key Eng. Mater.*, **37–40**, 169 (1999).
5. T. Takennaka, T. Takeo, and K. Takegahara, *Ferroelectrics*, **196**, 175 (1997).
6. X.X. Wang, H.L.W. Chan, and C.L. Choy, *J. Am. Ceram. Soc.*, **86**(10), 1809 (2003).
7. H. Nagata, M. Yoshida, Y. Makiuchi, and T. Takenaka, *Jpn. J. Appl. Phys.*, **42**, 7401 (2003).
8. H. Nagata and T. Takenata, *Jpn. J. Appl. Phys.*, **36**(9B), 6055 (1997).
9. Q. Xu, S.T. Chen, W. Chen, S.J. Wu, J. Lee, J. Zhou, H.J. Sun, and Y.M. Li, *Journal of Alloys and Compounds*, **381**, 221 (2004).