

Effect of Bi_2O_3 addition on the microstructure and electrical properties of lead-free $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ - $\text{Bi}(\text{Na}_{0.80}\text{K}_{0.20})\text{TiO}_3$ ceramics

Chun-Huy Wang

Department of Electronic Engineering, Nan-Jeon University of Technology, Tainan City, 73746, Taiwan

Although PbZrO_3 - PbTiO_3 (PZT)-based ceramics are playing a dominant role in piezoelectric materials, their evaporation of harmful lead oxide during the sintering process causes a crucial environment problem. It is necessary to search for lead-free piezoelectric materials that have such excellent properties as those found in the PZT-based ceramics. Therefore $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ -based solid solutions were studied to improve piezoelectric properties. In the present study, various quantities of Bi_2O_3 were added into $0.98(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ - $0.02\text{Bi}(\text{Na}_{0.80}\text{K}_{0.20})\text{TiO}_3$ (0.98NKN-0.02BNKT) ceramics. It was found that 0.98NKN-0.02BNKT with the addition of 0 ~ 0.5 wt.% Bi_2O_3 exhibit relatively good piezoelectric properties. For 0.98NKN-0.02BNKT ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.35 and 0.41, respectively, at the sintering of 1100 °C for 3 hrs. For 0.98NKN-0.02BNKT ceramics with the addition of 0.3 wt.% Bi_2O_3 , the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.42 and 0.46, respectively, at the sintering of 1100 °C for 3 hrs. It is obvious that 0.98NKN-0.02BNKT solid solution ceramic by adding low quantities of Bi_2O_3 is one of the promising lead-free ceramics for electromechanical transducer applications.

Key words: lead-free piezoceramics, piezoelectric property, crystal structure, dielectric property, poling.

Introduction

At present, the most widely-used piezoelectric materials are $\text{Pb}(\text{Zr,Ti})\text{O}_3$ [abbreviated as PZT]-based ceramics because of their superior piezoelectric properties. However, high volatilization and its toxicity of PbO during firing process can contaminate the environment and damage human health. In recent years, lead-free piezoelectric ceramics have attracted considerable attentions as one of important piezoelectric materials because of its outstanding advantages in free control atmosphere and no lead pollution. Lead-free piezoelectric materials such as sodium potassium niobate-based oxides, bismuth layer structure oxides and tungsten bronze-type oxides have been studied in order to replace the PZT-based ceramics. $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN) ceramics have been considered a good candidate for lead-free piezoelectric ceramics because of its high piezoelectricity and ferroelectricity. The hot pressed NKN ceramics (~99% of theoretical density) have been reported to possess large piezoelectric longitudinal response (d_{33} ~ 160 pC/N), high planar coupling coefficient (k_p ~ 45%) and high phase transition temperature (T_c = 420 °C). [1] The NKN ceramics sintered by ordinary sintering show relatively lower values (k_p = 29.5%) due to difficulty in the processing of dense ceramics by ordinary sintering. [2] It has received a lot of attention and been

thoroughly investigated. [3] Recently, an efficient solution to improve these problems has been realized by using some additives in NKN ceramics, such as ZnO [4], BaTiO_3 [2], LiNbO_3 [5], LiTaO_3 [6], SrTiO_3 [7] CaTiO_3 [8], $\text{Ba}(\text{Sn,Ti})\text{O}_3$ [9], and $\text{Ba}(\text{Zr,Ti})\text{O}_3$ [10], etc. A comparison of the properties of NKN ceramics based on the previous reports of various groups is shown in table 1. Thus, the addition of some perovskite compounds to form solid solutions with NKN or synthesizing by Spark Plasma Sintering (SPS) has been made to obtain lead-free materials suitable for industrial applications.

Perovskite structure $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ [abbreviated as BNT] ceramics are considered as one of the candidates for lead-free piezoelectric ceramics because of its high ferroelectric properties and high Curie temperature (T_c = 320 °C). Some modifications of BNT ceramics have proved to be helpful by forming solid solution with other perovskite oxides. [11, 12] $\text{Bi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ is well-known lead-free piezoelectric materials, which has a tetragonal symmetry at room temperature and show better piezoelectric response. [13] However, there have been few studies on the properties of NKN ceramics modified with $\text{Bi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ [abbreviated as BNKT]. Therefore, it is desirable to expect that the solid mixtures of NKN and BNKT have better piezoelectric properties. For the most important perovskite BNT family, Bi_2O_3 has been common used as an additive to improve their physical and electric properties. [14] Despite of these investigations, the role of Bi on the structure and electrical properties of NKN-based ceramics remains somewhat ambiguous. Therefore, further

*Corresponding author:
Tel : +886-6-6523111 ext 8221
Fax: +886-6-6533935
E-mail: wangch@mail.njtc.edu.tw

Table 1. Comparison of properties of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ ceramics based on previous reports of various groups.

COMPOSITION	K_o	k_p	k_t	Ref.
NKN	-----	0.295	0.41	4
NKN-ZnO	500	-----	0.4	3
0.98NKN-0.02BaTiO ₃	-----	0.29	0.38	4
0.94NKN-0.06LiNbO ₃	-----	0.42	0.48	5
0.94NKN-0.06LiTaO ₃	570	0.36	-----	6
0.995NKN-0.005SrTiO ₃	412	0.325	0.438	7
0.995NKN-0.005CaTiO ₃	553	0.42	0.38	8
0.98NKN-0.02 Ba(Sn _{0.02} Ti _{0.98})O ₃	365	0.31	0.39	9
0.98NKN-0.02Ba(Zr _{0.04} Ti _{0.96})	875	0.30	0.55	10
0.98NKN-0.02Bi _{0.5} (Na _{0.80} K _{0.20}) _{0.5} TiO ₃	1280	0.35	0.41	This study

investigation on this subject is necessary.

The aim of this study is to investigate the physical and electrical properties of $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-xBi}_{0.5}\text{Bi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ system. The effects of the dielectric and piezoelectric properties of 0.98NKN-0.02BNKT ceramics added with various amounts of Bi₂O₃ were discussed in this work, and the influence of the Bi₂O₃ addition on the microstructure and electrical properties was examined.

Experimental procedure

The $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-xBi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ [abbreviated as $(1-x)\text{NKN-xBNKT}$] ceramics were prepared by solid-state reaction method. Additive amounts of Bi₂O₃ were added to the 0.98(Na_{0.5}K_{0.5})NbO₃-0.02Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO₃ ceramics powders in concentration varying from 0 to 0.5 wt.%.

Starting materials were K₂CO₃, Na₂CO₃, Bi₂O₃, Nb₂O₅, TiO₂ with purities of at least 99.5% and weighted according to the stoichiometric composition ($x = 0, 0.01, 0.02, 0.03, 0.04$ and 0.05). Additive amounts of Bi₂O₃ were added after the calcination at 900 °C for 10 hrs. The calcined powders were pressed (CIP) at 180 MPa into pellets with 15 mm in diameter. The disc samples were sintered in alumina crucible at 1100 °C for 3 hrs in air atmosphere. To measure relevant piezoelectric properties, the prepared ceramic samples were polarized in silicone oil at 120 ~ 200 °C under the electric field of 3 ~ 4 kV/mm for 30 min. An X-ray diffractometer (Seimens D5000) using Cu K α radiation was used to evaluate the crystal structure of the sintered ceramics. The room temperature dielectric constant was measured by LCR meter (Angilent 4284A) at 1 kHz. The temperature dependence of the electrical permittivity of an unpoled specimen was automatically measured at 1 kHz using an HP4192A LF impedance analyzer under computer control from 30 °C to 510 °C. The Curie temperature T_c and the

maximum dielectric constant at T_c were determined from this measurement. The piezoelectric properties were measured by a resonance-antiresonance method based on IEEE standards [15] using an impedance/gain-phase analyzer (Angilent 4194).

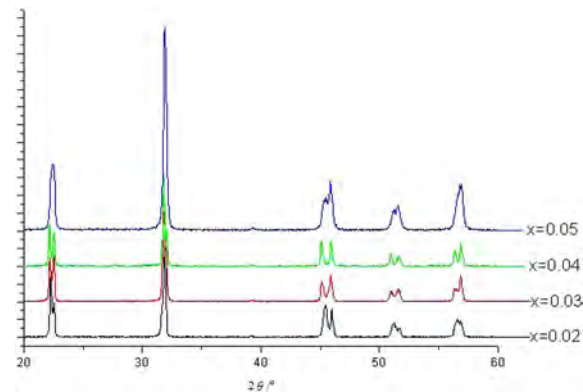
The samples for observation of the microstructure were polished and thermally etched. The microstructures were observed using a scanning electron microscope (SEM). The mean grain size was calculated by the line intercept method. [16] The density was measured by Archimedes method.

Results and discussion

In this system, none of the samples showed deliquescence when exposed under water for a long period, indicating no existence of the unstable second phase. Figure 1 shows the X-ray diffraction (XRD) patterns of $(1-x)\text{NKN-xBNKT}$ ceramics for $x = 0.01, 0.02, 0.03, 0.04$ and 0.05 . The orthorhombic symmetry of $(1-x)\text{NKN-xBNKT}$ ceramics at room temperature is characterized in the XRD patterns in the 2θ range of 44 ~ 48 °. The XRD analysis of sintered samples shows that $(1-x)\text{NKN-xBNKT}$ has a single phase with a perovskite structure and forms a solid solution. The BNKT appears to have diffused into the NKN lattice to form a solid solution, in which Bi occupies (Na,K) lattice and Ti enters Nb sites of NKN. It can be concluded that the $(1-x)\text{NKN-xBNKT}$ ceramics have orthorhombic structures in this case.

Table II shows the physical and electrical properties of $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-xBi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ ceramics under different x compositions. For 0.98(Na_{0.5}K_{0.5})NbO₃-0.02Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO₃ [abbreviated as 0.98NKN-0.02BNKT] ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.35 and 0.41, respectively. The dielectric constant ($K_o = 1280$) is found for 0.98NKN-0.02BNKT ceramics.

Figure 2 shows the microstructure of $(1-x)\text{NKN-xBNKT}$ ceramics under different compositions. It can be seen that $(1-x)\text{NKN-xBNKT}$ ceramics with $x = 0.02$

**Fig. 1.** X-ray diffraction (XRD) patterns of $(1-x)\text{NKN-xBNKT}$ ceramics system for different x compositions.

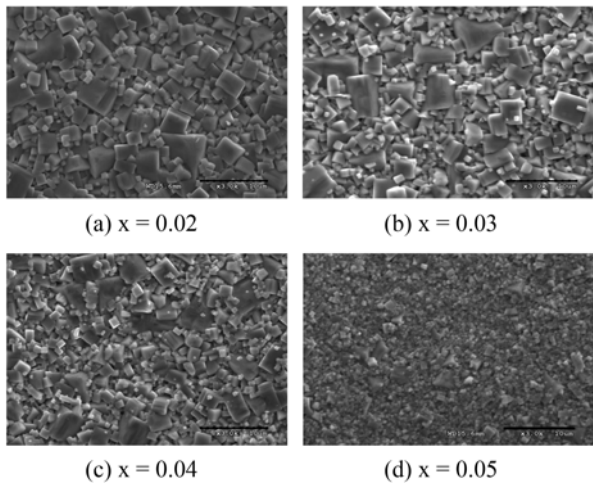


Fig. 2. The microstructure of $(1-x)\text{NKN}-x\text{BNKT}$ ceramics under different compositions: (a) $x = 0.02$ (b) $x = 0.03$ (c) $x = 0.04$ and (d) $x = 0.05$. Bar = 10 μm .

Table 2. Physical and electrical properties of $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-x\text{Bi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ ceramics under different compositions.

x	K_o	k_p	k_t
0.02	1280	0.35	0.41
0.03	1250	0.32	0.38
0.04	1100	0.26	0.32
0.05	1020	0.18	0.25

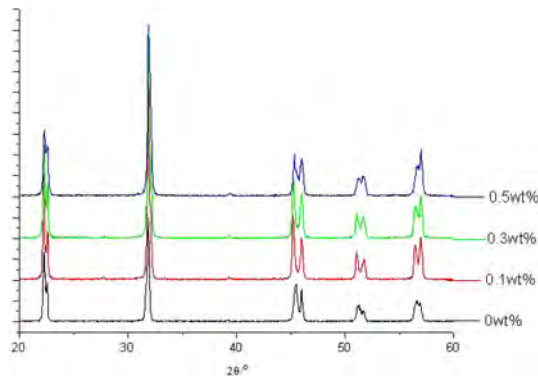


Fig. 3. XRD patterns of 0.98NKN-0.02BNKT ceramics with addition of different Bi_2O_3 doping.

consist of larger grains and denser structure in Fig. 2(a). The grain size of $(1-x)\text{NKN}-x\text{BNKT}$ decreases with increasing the BNKT content. With increasing porosity and decreasing the grain size of $(1-x)\text{NKN}-x\text{BNKT}$ ceramics, the piezoelectric and dielectric properties decrease gradually as shown in Table 2.

Figure 3 shows the XRD patterns of 0.98NKN-0.02BNKT ceramics with different Bi_2O_3 addition. All the compositions were sintered in air at 1100 $^{\circ}\text{C}$ for 3 hrs. The orthorhombic symmetry of 0.98NKN-0.02BNKT ceramics at room temperature is characterized in the XRD patterns in the 2θ range of $44 \sim 48^{\circ}$. Only an

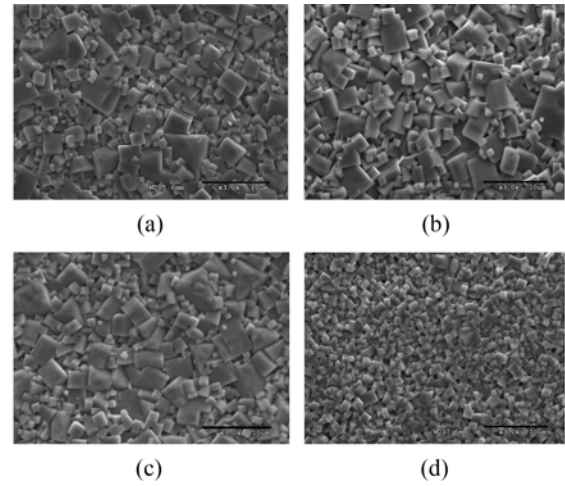


Fig. 4. SEM images of 0.98NKN-0.02BNKT ceramics with addition of different Bi_2O_3 doping: (a) 0 wt.% (b) 0.1 wt.% (c) 0.3 wt.% (d) 0.5 wt.%. Bar = 10 μm .

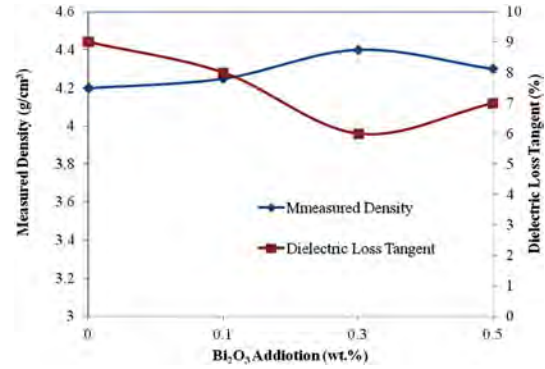


Fig. 5. Measured density and dielectric loss tangent of 0.98NKN-0.02BNKT ceramics with addition of different Bi_2O_3 doping.

orthorhombic phase with a perovskite structure was observed. It indicates that the addition of small amounts of Bi_2O_3 did not give rise to an obvious change in crystal structure.

The microstructure of 0.98NKN-0.02BNKT ceramics with different Bi_2O_3 addition is shown in Fig. 4. It can be seen that the 0.98NKN-0.02BNKT ceramics consist of small grains, with a loose structure, and a high porosity. The SEM images of 0.98NKN-0.02BNKT with 0.3 wt% Bi_2O_3 addition are denser, with low porosity, and exhibit a larger grain size of $\sim 3 \mu\text{m}$ in Fig. 4(c). It seems that Bi_2O_3 addition at amount less than 0.3 wt% enhances the grain growth. However, at the addition more than 0.3 wt%, the grain size is decreased.

Figure 5 shows the measured density and dielectric loss tangent of 0.98NKN-0.02BNKT ceramics with various Bi_2O_3 contents. The measured density of the sintered samples is 93-98% of the theoretical density. The measured density increases with an increase of Bi_2O_3 contents until they reach a maximum value at 0.3 wt.%, then decrease for higher Bi_2O_3 contents. The variation trend of dielectric loss tangent with Bi_2O_3 contents is inverse to that of the measured density.

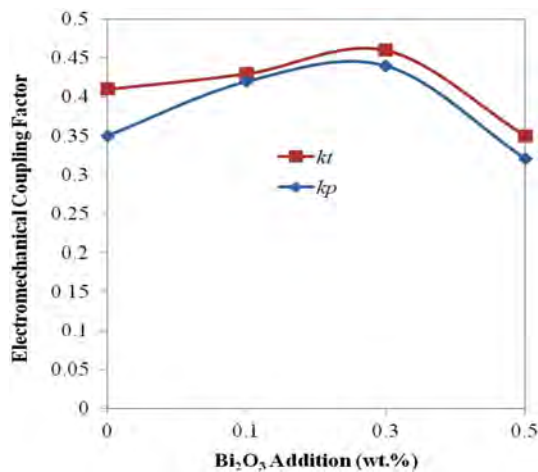


Fig. 6. Electromechanical coupling factor of 0.98NKN-0.02BNKT ceramics with addition of different Bi₂O₃ doping.

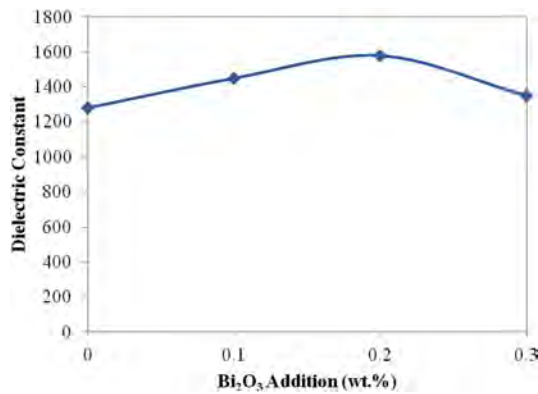


Fig. 7. Dielectric constant of 0.98NKN-0.02BNKT ceramics with addition of different Bi₂O₃ doping.

The planar coupling factor (k_p) and thickness coupling factor (k_t) of 0.98NKN-0.02BNKT ceramics with various Bi₂O₃ contents in Fig. 6. The electromechanical coupling factor has been used extensively as a measure of the piezoelectric response of PZT type ceramics. It was found that the electromechanical coupling factor depended on the material parameters [17] such as grain size, porosity, and chemical composition. Usually, the piezoelectric activity increases with the value of the electromechanical coupling factor in radial mode k_p and in thickness mode k_t . [18] For 0.98NKN-0.02BNKT ceramics, the k_p and the k_t reach 0.35 and 0.41, respectively, at the sintering of 1100 °C for 3 hrs. The k_p and k_t increases with an increase of Bi₂O₃ contents until it reaches a maximum value at 0.3 wt.%, then decreases for higher Bi₂O₃ contents.

Figure 7 shows the dielectric constant of 0.98NKN-0.02BNKT ceramics with various Bi₂O₃ contents. The addition of small amounts of Bi₂O₃ (≤ 0.3 wt.%) did not give rise to an obvious change in the variation trend of the dielectric constant. But, there is a deep fall of dielectric constant in the high Bi₂CO₃ content region (> 0.3 wt.%).

The 0.98NKN-0.02BNKT ceramics with 0.3 wt.% Bi₂O₃ addition have better properties than without the addition of excess Bi₂O₃. The relative density was raised to 98% and the grain size was increased to 3 μm for the 0.98NKN-0.02BNKT ceramic with 0.3 wt.% Bi₂O₃ addition as shown in Fig. 4(c). In this research, Bi was introduced into 0.98NKN-0.02BNKT composition in the form of Na⁺ or K⁺. Bi³⁺ has cationic radii of 1.4 Å close to that of Na⁺ (1.39 Å) and K⁺ (1.64 Å). Thus, Bi³⁺ can enter into the octahedral site of the perovskite structure to substitute for Na⁺ and K⁺ because of radius matching. Similar to the case of PZT-based piezoelectric ceramics, the incorporation of Bi into the perovskite structure as a donor can generate a soft effect on the electrical properties. The variation of the electrical properties with the addition of Bi₂O₃ can be tentatively interpreted with respect to the doping effect and microstructural evolution. When the addition amount of Bi₂O₃ is relatively low (≤ 0.3 wt.%), the soft doping effect on the electrical properties appears to be predominant. In the low Bi₂O₃ content region (≤ 0.3 wt.%), the slight increase of the electromechanical coupling factor together correspond well to the feature of a soft doping effect on the electrical properties. In the case of low Bi₂O₃ content (> 0.3 wt.%), the grain growth became remarkable. The increase of grain size favors improving the electromechanical coupling factor and the dielectric constant, which is known as grain size effect. [17] The degradation of the dielectric constant and the electromechanical coupling factor in the high Bi₂O₃ content region (> 0.3 wt.%) may be attributed to the decrease of the grain size in the microstructure. Therefore, it is likely that the doping and microstructural effects contribute to the electrical properties of the ceramics in a cooperative way.

Conclusions

The specimens of 0.98NKN-0.02BNKT ceramics added with Bi₂O₃ maintain an orthorhombic phase. It indicates that the addition of small amounts of Bi₂O₃ did not give rise to an obvious change in crystal structure. The electromechanical coupling coefficients of the planar mode k_p and k_t of 0.98NKN-0.02BNKT ceramics reach 0.35 and 0.41, respectively. For 0.98NKN-0.02NBT ceramics by doping 0.3 wt.% Bi₂O₃ the electromechanical coupling coefficients of the planar mode k_p and the dielectric constant reach 0.42 and 0.46, respectively. The addition of excess Bi₂O₃ is a helpful method on ceramic processing to improve densification and properties.

References

1. G. Shirane, R. Newnham, and R. Pepinsky, Phys. Rev. 96 (1954) 581-588.
2. H. Birol, D. Damjanovic, and N. Setter, J. Eur. Ceram. Soc. 26 (2006) 861-866.

3. S.H. Park, C.W. Ahn, S. Nahm, and J.S. Song, Jpn. J. Appl. Phys. 43 (2004) L1072-1074.
4. Y. Guo, K. Kakimoto, and H. Ohsato, Jpn. J. Appl. Phys. 43 (2004) 6662-6666.
5. Y. Guo, K. Kakimoto, and H. Ohsato, Appl. Phys. Lett. 85 (2004) 4121-4123.
6. Y. Guo, K. Kakimoto, H. Ohsato, Mater. Lett. 59 (2005) 241-244.
7. Y. Guo, K. Kakimoto, and H. Ohsato, Solid State Comm. 129 (2004) 279-284.
8. R.C. Chang, S.Y. Chu, Y.F. Lin, C.S. Hong, and Y.P. Wong, J. Eur. Ceram. Soc. 27 (2007) 4453-4460.
9. C.H. Wang, Jpn. J. Appl. Phys. 48 (2009) 041-403.
10. C.H. Wang, J. Ceram. Soc. Jpn, 117[5] (2009) 680-684.
11. C.H. Wang, J. Ceram. Soc. Jpn. 116 (2008) 632-636.
12. Z. Chen, J. Hu, and X. He, J. Ceram. Soc. Jpn. 116 (2008) 661-663.
13. C.H. Wang, J. Ceram. Soc. Jpn. 239-242 (2011) 3240-3243.
14. C. H. Wang, J. Ceram. Soc. Jpn. 117 [5] (2009) 693-697.
15. Anon., Proc. IRE. 49 (1961) 1161-1168.
16. T. Senda, and R.C. Bradt, J. Am. Ceram. Soc. 73 [1] (1990) 106.
17. K. Okazaki and K. Nagata, J. Am. Ceram. Soc. 56 [2] (1973) 82-86.
18. K. H. Hartal, Ferroelectrics 12 (1976) 9-19.