Journal of Alloys and Compounds 525 (2012) 133–136

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Fabrication and electrical properties of $0.94Na_{0.5}Bi_{0.5}TiO_3$–$0.06BaTiO_3$ textured ceramics by RTGG method using micrometer sized $BaTiO_3$ plate-like templates

Shi Su, Ruzhong Zuo*

Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, PR China

ARTICLE INFO

Article history:
Received 13 December 2011
Received in revised form 9 February 2012
Accepted 13 February 2012
Available online xxx

Keywords:
$BaTiO_3$
Texture
Molten salt method
Piezoelectric

ABSTRACT

Two-step molten salt driven micrometer-scaled tabular (1 0 0) $BaTiO_3$ (BT) template seeds were used for the first time to make ⟨1 0 0⟩ textured $0.94Na_{0.5}Bi_{0.5}TiO_3$–$0.06BaTiO_3$ (NBT–BT) piezoelectric ceramics. The use of platelet $Bi_4Ti_3O_{12}$ powders instead of Bi_2O_3 and TiO_2 as raw chemicals would not only benefit to the alignment of BT templates during tape casting, but also avoid the dissolution of BT seeds in liquid Bi_2O_3 during sintering. The results also proved that a pre-reaction procedure at a low temperature is unnecessary during reactive templated grain growth owing to the structure similarity between BT seeds and target compound. Well-textured NBT–BT lead-free piezoelectric ceramics ($f \sim 91\%$) show excellent dielectric and piezoelectric properties of dielectric constant $\varepsilon_r \sim 1300$ and piezoelectric charge constant $d_{33} = 260$ pC/N.

1. Introduction

Textured NBT–BT ceramics have been often reported using different templates. So far, plate-like $Bi_4Ti_3O_{12}$ (BIT) [1–3], $SrTiO_3$ [1], $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ [4] and $Na_{0.5}Bi_{0.5}TiO_3$ [5] crystals have been synthesized and successfully used as templates in texturing of NBT–BT ceramics. Moreover, BT crystal ($a_o = 3.992$ Å, $c_o = 4.036$ Å at room temperature) [6] was often chosen as templates for some perovskite systems such as $Pb(Mg_{1/3}Nb_{2/3})$–$PbTiO_3$ textured ceramics [7,8] owing to both similar structures, and chemical stability at high temperature and under PbO liquid environment [8]. Unfortunately, it was never successfully applied in texturing NBT–BT ceramics although it seems to be an ideal candidate template as far as its composition and structure are concerned. Messing et al. have reported that BT seeds were unstable in a matrix of NBT [1], but no explanation was given.

Nanometer-sized spherical, cuboidal or dendritic BT particles were usually synthesized by hydrothermal method [9–11] and micrometer-sized (0 0 1)-oriented BT fibers were prepared through an ion-exchange reaction by molten salt and hydrothermal methods [12,13]. Millimeter-scaled (0 0 1) oriented BT crystal platelets ($\sim 1.0\,mm^2 \times 0.4\,mm$) were synthesized utilizing a molten salt method by Remeika [14,15]. However, the employment of such big template particles resulted in coarsened microstructure and compromised the mechanical strength of the textured ceramics [7,16]. Liu et al. [17] synthesized micrometer-scaled BT platelets by means of a three-step molten salt process, but the residual Bi still existed. Therefore, how to synthesize pure and fine BT crystals with desired crystallographic orientation is still a challenging task.

In this study, phase-pure and micrometer-scaled tabular (0 0 1) faceted BT particles (6 mol%) with a high aspect ratio (10–40) were firstly synthesized using a modified two-step molten method, and then used as template seeds to texture 0.94NBT–0.06BT ceramics by means of an RTGG method. Considering the fact that the instability of crystal seeds in matrix compositions at elevated temperatures is usually the result of corrosive oxide liquids such as PbO [18,19] and Bi_2O_3. Plate-like BIT powders were conventionally synthesized and used as raw chemicals instead of Bi_2O_3 and TiO_2. Moreover, the similar particle morphology of BIT powders and BT seeds would be beneficial to the alignment of particles along the tape casting direction. The influence of pre-reaction at low temperature on the densification and the texture formation was investigated together with a study on anisotropic electrical properties in the parallel and perpendicular cuts of textured 0.94NBT–0.06BT ceramics.

2. Experimental procedures

The (1 0 0) faceted BT seeds were synthesized by a modified two-step molten salt method. The first step was to synthesize plate-like BIT particles using Bi_2O_3 (≥99.0%) and TiO_2 (≥99.0%) as raw materials. The second step was to prepare plate-like BT template particles by mixing as-prepared BIT precursor, excessive $BaCO_3$ (≥99.0%) (BIT:$BaCO_3$ is 1:10 in mol) and NaCl salt (NaCl:(BIT + $BaCO_3$) = 1:1 in weight), and then heating at 1020 °C for 3 h in a sealed alumina crucible. The detailed procedures could be referred to elsewhere [20]. To avoid the existence of single Bi_2O_3, Bi_2O_3 (≥99.0%) and TiO_2 (≥99.0%) were reacted into BIT compound by a conventional mixed oxide method. The purpose to do so was to avoid staying of BT template seeds in Bi_2O_3 liquid at high temperature. The as-prepared BIT powders were milled again to reduce the particle size for better densification. Finally, BIT powders, Na_2CO_3

---

* Corresponding author. Tel.: +86 551 2905285; fax: +86 551 2905285.
E-mail address: piezolab@hfut.edu.cn (R. Zuo).

0925-8388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2012.02.090

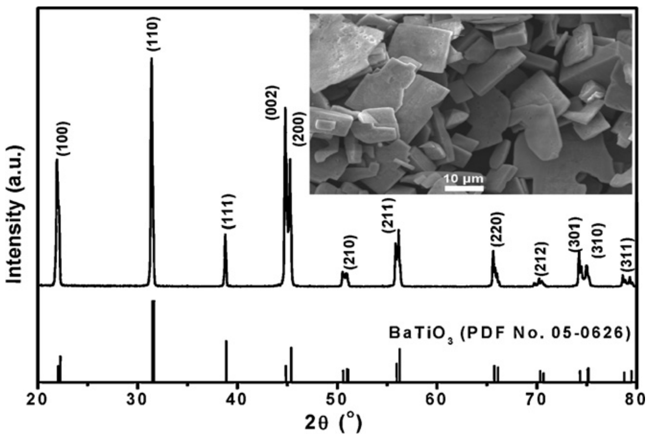


Fig. 1. XRD pattern of the BT seeds synthesized at 1020 °C for 3 h (inset is the corresponding SEM image).

(≥99.8%) and TiO_2 were homogeneously mixed with 6 mol% BT templates according to the following equation:

$$0.94(Bi_4Ti_3O_{12} + 2Na_2CO_3 + 5TiO_2) + 8(0.06BaTiO_{3(T)})$$
$$\rightarrow 8(0.94Na_{0.5}Bi_{0.5}TiO_3{-}0.06BaTiO_3) + 1.88CO_2\uparrow$$

where $BaTiO_{3(T)}$ denotes BT template. After drying, these powders were mixed with solvents and dispersant, then with plasticizers and binder. The slurry was tape casted at a speed of 6.25 cm/s with a blade opening of 250 μm. The laminated green compacts were firstly heated in air at 600 °C for 15 h to remove organic additives and then isostatically pressed again under 250 MPa to increase the green density. The samples were either pre-reacted at 800 °C for 4 h and then sintered at 1180–1220 °C for 15 h, or directly sintered at 1180–1220 °C for 15 h. The sintered samples were cut parallel (//) and perpendicular (⊥) to the tape casting direction, respectively, in order to characterize the anisotropic electrical properties. For comparison, 0.94NBT–0.06BT ceramics without BT templates were prepared through a conventional solid-state method.

The bulk density of sintered compacts was measured by the Archimedes method. The crystal structure and the texture fraction were examined by an X-ray diffractometer (XRD, D/Max-rB, Rigaku, Japan) using a Cu Kα radiation and evaluated by the Lotgering factor (f) [21]. Silver paste was coated and then fired on both sides of the sintered samples at 550 °C for 30 min. The electric poling was performed at 40 °C in a silicone oil bath by applying a dc field of 4–5 kV/mm for 15 min.

The microstructure and chemical composition of the samples were analyzed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, Santa Clara, CA). Polarization versus electrical field (P–E) loops were measured by a ferroelectric measuring system (Precision LC, Radiant Technologies Inc., Albuquerque, NM). The piezoelectric charge constant (d_{33}) was directly measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China).

3. Results and discussion

Fig. 1 shows that phase-pure BT template particles were obtained via the two-step molten salt method as sintered at 1020 °C for 3 h. The chemical reactions in these two steps were accordingly written as follows: $2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12}$ and $Bi_4Ti_3O_{12} + 3BaCO_3 \rightarrow 3BaTiO_3 + 2Bi_2O_3 + 3CO_2$. According to the standard PDF card (No. 05-0626), it can be seen that all diffraction peaks could be assigned to the perovskite-structured BT phase. Moreover, it can be found that the (h 0 0) diffraction peaks were enhanced to some extent, indicating that the as-prepared BT seeds should be (h 0 0) faceted and tabular. The SEM image of BT particles (see the inset in Fig. 1) indicates a plate-like particle morphology with a mean diameter of 10–20 μm and a thickness of 1–1.5 μm (the aspect ratio was approximately 7–20). It can be believed that the as-prepared BT template might be suitable for texturing 0.94NBT–0.06BT system owing to its desired dimension, phase-purity as well as the same perovskite structure to the target compound.

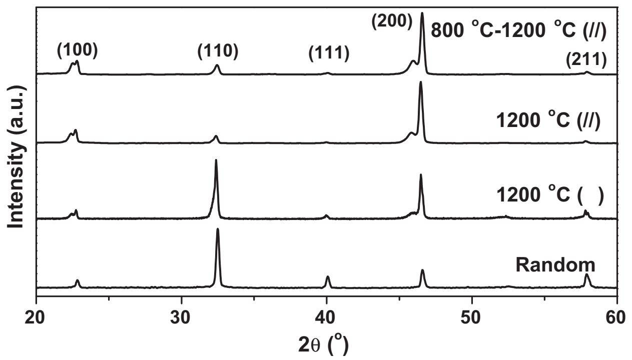
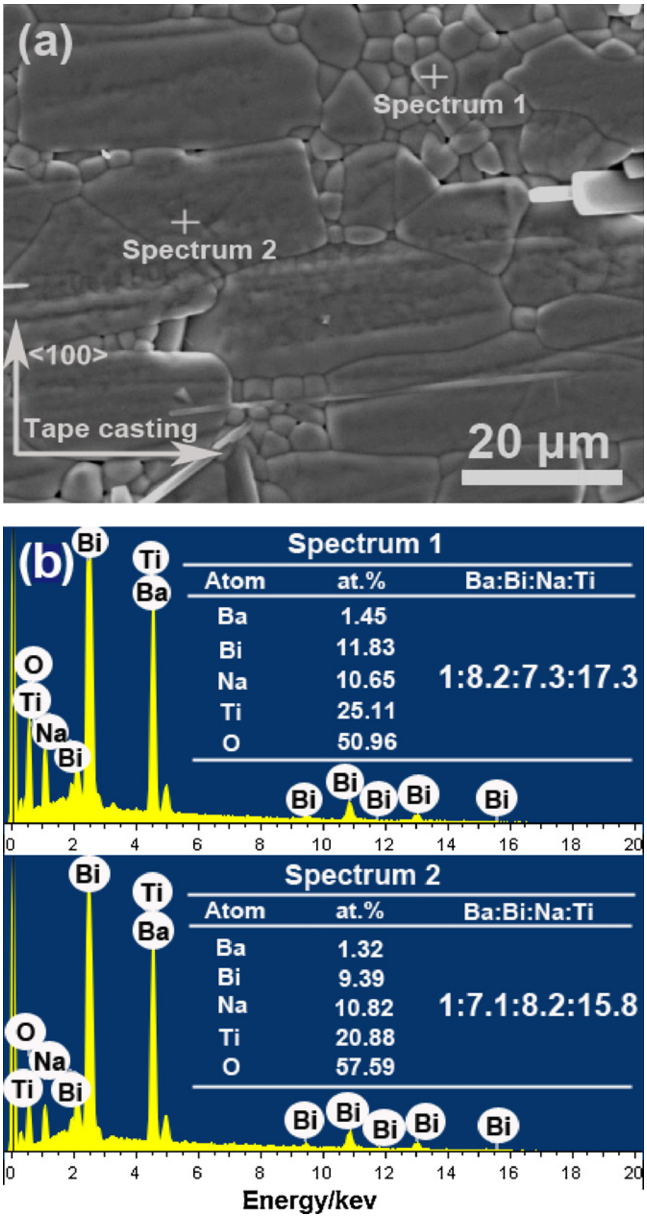


Fig. 2. XRD patterns of conventionally prepared 0.94NBT–0.06BT random ceramics and textured 0.94NBT–0.06BT ceramics either pre-sintered at 800 °C for 4 h, and then sintered at 1200 °C for 15 h or directly sintered at 1200 °C for 15 h (// and ⊥).

The XRD patterns of random and textured 0.94NBT–0.06BT ceramic samples are shown in Fig. 2. It can be seen that all samples show a single perovskite phase. Compared to conventionally prepared random ceramics, specimens containing BT templates own significantly enhanced (1 0 0) diffraction lines no matter whether a pre-reaction procedure was taken or not. The results indicate that a pre-reaction at a relatively low temperature is unnecessary since homogeneous solid solution together with a high orientation degree (f = 91%) could be formed by directly heating to the sintering temperature. For different cuts, the parallel cuts show much better orientation along (1 0 0) direction than the perpendicular cuts (f = 19%). This is possible because not all templates were perfectly aligned during tape casting. BT template acts as part of target compound and owns the same crystal structure to the matrix, making it easy to form the final solid solution with desired stoichiometry, similar to $NaNbO_3$ template textured (K,Na)NbO_3 [22,23]. Moreover, a well textured NBT–BT ceramics were obtained using BIT compound as raw chemicals instead of Bi_2O_3. This means that a preferred crystallographic orientation of $BaTiO_3$ template was maintained and inherited during epitaxial growth and diffusion between BT and complementary compounds (i.e., $Bi_4Ti_3O_{12}$, TiO_2 and Na_2CO_3), forming homogeneous solid solution with a preferential orientation finally. Otherwise, a preferential orientation solid solution was not obtained due to breakdown of preferential orientation of BT template, meeting with matrix. It indicated that BT template was stable and plays its role successfully indirectly.

The grain morphology on the cross section of textured 0.94NBT–0.06BT samples is shown in Fig. 3. It can be seen that major grains have been elongated along the tape casting direction, showing good texture. This keeps good agreement with the XRD data in Fig. 2. It can be found that BT templates grow at the expense of smaller matrix grains by the difference in surface free energy, showing good chemical stability. As a result, a well-densified, well-textured "brick-wall" microstructure was finally formed by the Ostwald growth. Moreover, EDS analysis was carried out either at residual fine matrix grains (spectrum 1) or big "brick" grains (spectrum 2) developed from template grains, as shown in Fig. 3(b). The EDS results indicate that both kinds of grains only contain Ba, Bi, Na, Ti and O atoms. Atomic ratios of Ba:Bi:Na:Ti are nearly equal (1:8.2:7.3:17.3 for small grains and 1:7.1:8.2:15.8 for big grains), revealing that the composition distribution after sintering is homogeneous. The stoichiometry of the ceramic samples was almost kept close to the desired one (Ba:Bi:Na:Ti = 1:7.83:7.83:16.7) if the measurement error was taken into account. This result suggests that BT templates used have completely interdiffused into the matrix and formed a single perovskite solid solution.

Fig. 4 shows the variation of the dielectric constant ε_r of random 0.94NBT–0.06BT ceramics and textured counterparts of different



Spectrum 1

Atom	at.%	Ba:Bi:Na:Ti
Ba	1.45	1:8.2:7.3:17.3
Bi	11.83	
Na	10.65	
Ti	25.11	
O	50.96	

Spectrum 2

Atom	at.%	Ba:Bi:Na:Ti
Ba	1.32	1:7.1:8.2:15.8
Bi	9.39	
Na	10.82	
Ti	20.88	
O	57.59	

Fig. 3. (a) SEM micrograph on the cross section of textured 0.94NBT–0.06BT ceramics sintered at 1200 °C for 15 h and (b) EDS analysis at two places as indicated.

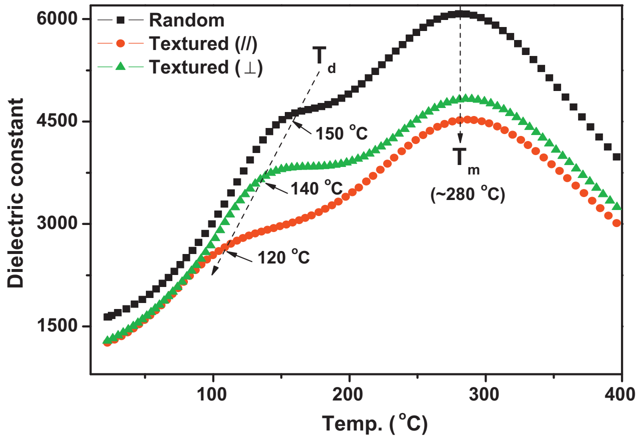


Fig. 4. Temperature dependence of dielectric constant at 10 kHz for random and textured 0.94NBT–0.06BT ceramics (// and ⊥).

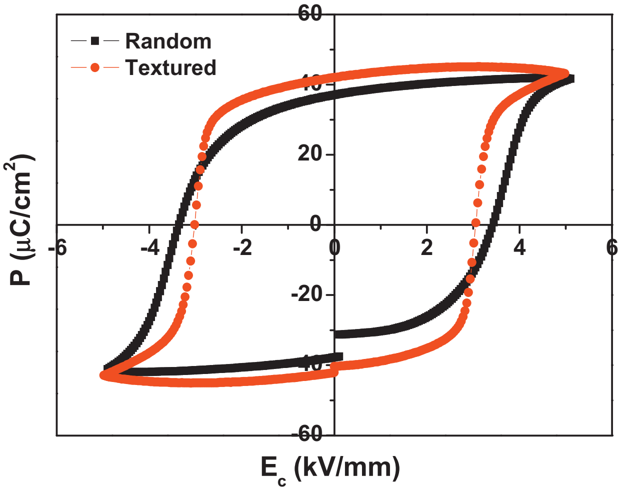


Fig. 5. *P–E* hysteresis loops of random and textured 0.94NBT–0.06BT ceramics (//).

cuts (measured at 10 kHz). On the one hand, the textured samples exhibit relatively low ε_r than random samples. Moreover, the phase transition temperature between ferroelectric and antiferroelectric phases (T_d) was slightly reduced for textured samples but the temperature for the maximum dielectric constant (T_m) was nearly the same. The inhibition of dielectric constant of textured ceramics relative to the random materials can be attributed to a preferential orientation, the relatively low density, compositional homogeneity and internal stresses due to the presence of big template particles. On the other hand, there is anisotropy in the variation of the dielectric constant with temperature for parallel and perpendicular cuts of textured ceramics. The parallel cuts show lower T_d and ε_r values than the perpendicular cuts. Furthermore, it is to be noted that T_d moves to lower temperature and at the same time the phase transition becomes more broadening. It seems that the thermal stability of ferroelectric phases in NBT–BT ceramics is orientation-dependent. It is known that the crystallographic orientation dependence of dielectric constant should be attributed to the difference in energy of thermal fluctuation of polar microregions and difficulty of macro–micro domains switching in different orientations. Moreover, the difference of internal stresses in two directions (// and ⊥) might make additional contribution.

Fig. 5 shows *P–E* hysteresis loops of random and textured 0.94NBT–0.06BT ceramics (//). For the textured ceramics, its ferroelectric properties seem to be enhanced and superior to random counterparts. After texturing, its remnant polarization (P_r) increased from 37 μC/cm^2 to 42 μC/cm^2, but its coercive field value (E_c) decreased from 33.7 kV/cm to 30.2 kV/cm, which is probably caused by the crystal-like characteristics of the textured ceramic. It is known that the coercive field of a single crystal is usually lower than that of random ceramics with the same composition.

The piezoelectric properties of random and textured NBT–BT ceramics prepared using different methods are compared in Table 1. It can be seen that the highest orientation (f ∼ 96%) and largest d_{33} value (299 pC/N) were obtained for 0.94NBT–0.06BT textured ceramics prepared using 7.8 mol% BIT templates by RTGG method and 5 vol% NBT templates by TGG method, respectively. In this study, 0.94NBT–0.06BT textured ceramics (//) with a high texture degree (f = 91%) as well as excellent piezoelectric properties (d_{33} = 260 pC/N) were successfully prepared by RTGG method using only 6 mol% BT templates. The densification behavior (96% theoretical density) and high texture degree would lead to high P_r (42 μC/cm^2), low E_c (30.2 kV/cm) and good piezoelectric constant for parallel-cut textured ceramics using (0 0 1) BT template. The piezoelectric properties of textured 0.94NBT–0.06BT ceramics

Table 1
Processing methods and electrical properties of random and textured NBT–BT ceramics.

Matrix	Template	Method	ρ (%)	$f_{(100)}$ (%)	d_{33} (pC/N)
0.945NBT–0.055BT (//) [24]	$SrTiO_3$	TGG	~96	94	200
0.94NBT–0.06BT (//) [5]	$Na_{0.5}Bi_{0.5}TiO_3$	TGG	94	87	299
0.94NBT–0.06BT (//) [2]	$Bi_4Ti_3O_{12}$	RTGG	~96	~96	241
0.94NBT–0.06BT (this study) (//)	$BaTiO_3$	RTGG	~96	~91	260
0.94NBT–0.06BT (this study) (⊥)	$BaTiO_3$	RTGG	~96	19	150
Random 0.94NBT–0.06BT (this study)	–	Conventional	98	0	140

of different cuts are better than those of random samples because of a preferred crystallographic orientation. The d_{33} value of NBT templated NBT–BT textured ceramics is slightly better than that of BT, possibly because of TGG method used. NBT–BT textured ceramics using NBT or BT templates show better piezoelectric properties than those using $SrTiO_3$ and BIT templates where the chemical composition was unavoidably altered.

4. Conclusions

The (1 0 0) oriented micrometer scaled BT templates were successfully applied for the first time to make well-textured 0.94NBT–0.06BT ceramics. The use of platelike $Bi_4Ti_3O_{12}$ instead of single Bi_2O_3 as raw powders for texturing not only benefits to the alignment during tape casting, but also effectively avoids the contact between BT template and Bi_2O_3 liquid phase at elevated temperature. The results indicate that a pre-reaction at a low temperature was not necessary as far as the developed texture fraction is concerned, probably because of the structure similarity between BT template and target compound. A high orientation ($f \sim 91\%$) and good piezoelectric coefficient ($d_{33} = 260$ pC/N) were obtained by directly heating the sample to 1200 °C for 15 h.

Acknowledgments

This work was financially supported by a project of Natural Science Foundation of Anhui Province (1108085J14), the National Natural Science Foundation of China (50972035) and a Program for New Century Excellent Talents in University, State Education Ministry (NCET-08-0766).

References

[1] H. Yilmaz, G.L. Messing, S. Trolier-Mckinstry, J. Electroceram. 11 (2003) 207–215.
[2] Y.K. Yan, H.P. Zhou, W. Zhao, D. Liu, J. Electroceram. 21 (2008) 246–250.
[3] M.J. Wu, Y.X. Li, D. Wang, J.T. Zeng, Q.R. Yin, J. Electroceram. 22 (2009) 131–135.
[4] F. Gao, R.Z. Hong, J.J. Liu, Y.H. Yao, C.S. Tian, J. Electroceram. 24 (2010) 145–152.
[5] W. Zhao, J. Ya, Y. Xin, L.E.D. Zhao, H.P. Zhou, J. Am. Ceram. Soc. 92 (2009) 1607–1609.
[6] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.
[7] E.M. Sabolsky, A.R. James, S. Kwon, S. Trolier-McKinstry, G.L. Messing, Appl. Phys. Lett. 78 (2001) 2551–2553.
[8] E.M. Sabolsky, G.L. Messing, S. Trolier-Mckinstry, J. Am. Ceram. Soc. 84 (2001) 2507–2513.
[9] L. Zhao, A.T. Chien, F.F. Lange, J.S. Speck, J. Mater. Res. 11 (1996) 1325–1328.
[10] I.J. Clark, T. Takeuchi, N. Ohtori, D.C. Sinclair, J. Mater. Chem. 9 (1999) 83–91.
[11] Y.G. Wang, G. Xu, L.L. Yang, Z.H. Ren, X. Wei, W.J. Weng, P.Y. Du, G. Shen, G.R. Han, Mater. Lett. 63 (2009) 239–241.
[12] Y. Ohara, K. Koumoto, H. Yanagida, J. Am. Ceram. Soc. 68 (1985) 108–109.
[13] Y. Hayashi, T. Kimura, T. Yamaguchi, J. Mater. Sci. 21 (1986) 757–762.
[14] J.P. Remeika, J. Am. Chem. Soc. 76 (1954) 940–941.
[15] R.C. Devries, J. Am. Ceram. Soc. 42 (1959) 547–558.
[16] E.M. Sabolsky, S. Trolier-McKinstry, G.L. Messing, J. Appl. Phys. 93 (2003) 4072–4080.
[17] D. Liu, Y.K. Yan, H.P. Zhou, J. Am. Ceram. Soc. 90 (2007) 1323–1326.
[18] S. Kwon, E.M. Sabolsky, G.L. Messing, S. Trolier-McKinstry, J. Am. Ceram. Soc. 88 (2005) 312–317.
[19] Y.K. Yan, K.H. Cho, S. Priya, J. Am. Ceram. Soc. 94 (2011) 1784–1793.
[20] S. Su, R.Z. Zuo, D.Y. Lv, J. Fu, Powder Technol. 217 (2012) 11–15.
[21] F.K. Lotgering, J. Inorg. Nucl. Chem. 9 (1959) 113–123.
[22] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Nature 432 (2004) 84–87.
[23] H. Takao, Y. Saito, Y. Aoki, K. Horibuchi, J. Am. Ceram. Soc. 89 (2006) 1951–1956.
[24] H. Yilmaz, S. Trolier-Mckinstry, G.L. Messing, J. Electroceram. 11 (2003) 217–226.