Journal of Alloys and Compounds 509 (2011) L203–L207

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Letter

Preparation of textured $K_2BiNb_5O_{15}$ ceramics with rod-like templates by the screen-printing technique

Yali Li[a], Chun Hui[b], Yongxiang Li[c,*], Youliang Wang[c]

[a] Research Institute of Micro/Nano Science and Technology, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai 200030, PR China
[b] School of Life Sciences and Biotechnology, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai 200030, PR China
[c] The Key Lab of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

ARTICLE INFO

Article history:
Received 20 December 2010
Received in revised form 18 March 2011
Accepted 18 March 2011
Available online 27 March 2011

Keywords:
Ceramic
Anisotropy
Crystal growth
Dielectric response
Screen-printing

ABSTRACT

This work focuses on the fabrication of textured ceramics with rod-like templates using screen-printing technique. Rod-like $K_2BiNb_5O_{15}$ (KBIN) crystals with an aspect ratio of 10:1 were synthesized by the reaction of K_2CO_3, Bi_2O_3 and Nb_2O_5 in molten KCl flux at 1100 °C for 2 h. The KBIN templates were mixed with equiaxed powder of the same composition and oriented through the screen-printing reactive templated grain growth (SP-RTGG) technique. By printing onto a flexible polymer substrate and repeating the process of printing and drying, thick films with a thickness of several hundred micrometers were produced, then subsequently removed from the substrate, stacked layer by layer together and pressed into pieces. Textured KBIN ceramics were successfully obtained by this method. SEM and XRD were performed to study the grain growth and orientation degree. The textured $K_2BiNb_5O_{15}$ ceramics showed an orientation degree (Lotgering factor) of 42% along ⟨0 0 1⟩ direction. The analysis of the dielectric properties of the textured $K_2BiNb_5O_{15}$ ceramics revealed obvious anisotropies.

1. Introduction

Recently, in the field of electronic materials research, much attention has been focused on tungsten bronze structure as they exhibit ferroelectric, piezoelectric, pyroelectric, nonlinear optical and electro-optic properties [1–3]. As one of the most representative materials, barium sodium niobate ($Ba_2NaNb_5O_{15}$, abbreviated as BNN) has been widely researched [4–6]. $K_2BiNb_5O_{15}$ (KBIN) exhibits the same tungsten bronze type structure as BNN and possesses large piezoelectric properties in both the longitudinal and transverse directions, the polar axis is along ⟨0 0 1⟩ with only one phase transition (~420 °C). The crystal structure of KBIN is orthorhombic at room temperature and has first-order ferroelectric phase transition with no relaxor character [7]. Sugai and Wada synthesized a single crystal of KBIN, stated on the basis of the result of X-ray powder diffraction that it has a tungsten bronze type of structure, and measured the dielectric properties ε_{11} and ε_{33} with the changes of temperatures [8]. Iwai and Takuchi prepared KBIN ceramic and obtained the highest value of dielectric constant at 350 °C [9], and Filip'ev et al. found that the system $K_2BiNb_5O_{15}$–$K_3Li_2Nb_5O_{15}$ is soluble in entire range [10]. However, one of the drawbacks is that KBIN and BNN single crystals easily crack during the cooling process due to thermal stress, and there are many difficulties in producing large size single crystals, which are also quite costly. For random grain oriented ceramics, their electrical properties are unsatisfactory for most practical applications.

In recent years, the technology of textured ceramics has developed quite rapidly, with an increasing number of ceramics with anisotropic properties, such as KNN-based ceramics, $Ba_{0.60}Sr_{0.4}TiO_3$, and $Sr_{0.53}Ba_{0.47}Nb_2O_6$ [11–13]. The techniques reported for fabricating these materials have included templated grain growth (TGG) and/or reactive templated grain growth (RTGG). In TGG/RTGG process, anisotropic templates (plate-like or rod-like) are oriented in matrix powder slurry by tape-casting technique or extrusion technique, which have been explored extensively and used in production of textured ceramics.

Screen-printing is another high volume technique employed for fabricating thick-film electronic materials such as superconductors, solar cells, and so on, yet, has remained relatively neglected for processing textured ceramics. Screen-printing has numerous advantages over tape-casting or extrusion, which include the realization of polymorphism and streamline production [14]. The use of screen-printing multilayer grain growth of texturing ceramics was proposed by Zeng et al. for textured bismuth layer-structured ferroelectrics (BLSFs) $CaBi_4Ti_4O_{15}$ (CBT) in 2005 [15], and later on used successfully for the perovskite structure $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ (NBBT) lead-free piezoelectric ceramics with a grain orientation of 92% [16,17]. All reported textured ceramics via screen-printing methods were used with plate-like templates. To date, texturing

* Corresponding author.: +86 21 52411066; fax: +86 21 52413122.
E-mail address: yxli@mail.sic.ac.cn (Y. Li).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2011.03.115

ceramic utilizing rod-like templates via screen-printing has not been reported.

In the present paper, we report our research on the preparation of high-purity and rod-like KBIN templates via molten salt synthesis (MSS), and the screen-printing technique has been successfully applied to texturing the anisotropic KBIN ceramics. The process of screen-printing templated grain growth is described in detail, and the degree of grain orientation and the anisotropic property of textured KBIN ceramics obtained through screen-printing are also discussed.

2. Experimental

K_2CO_3 (>99.5%, Shanghai Jinghua Co., China), Nb_2O_5 (>99.8%, Shanghai Jinghua Co., China), Bi_2O_3 (>99.7%, SCRC, China), and KCl (99%, Shanghai Jinghua Co., China), were used as starting materials for the preparation of rod-like KBIN templates by molten salt synthesis at a weight ratio of oxides to salt = 1:1. K_2CO_3, Nb_2O_5, and Bi_2O_3 were mixed at mole ratios of $K_2BiNb_5O_{15}$, to which the same mass of KCl was later added. After being milled, dried, and ground, the mixtures were placed into an Al_2O_3 crucible covered with a flat Al_2O_3 lid, and heated to 1100 °C at a heating rate of 10 °C/min in order to minimize the evaporation of Bi, held for 3 h at the temperature, and then cooled to room temperature naturally. The product was washed with hot de-ionized water several times to remove the residual salt until no chloride ions were detected by silver nitrate.

Textured KBIN ceramics were fabricated by the screen-printing technique. The matrix powders of KBIN ceramics were prepared by ball milling of appropriate amounts of K_2CO_3, Nb_2O_5, and Bi_2O_3 for 4 h in ethanol, which were then calcined at 850 °C for 3 h. The calcined matrix powders were mixed with ethyl-cellulose and α-terpineol organic vehicle in a ball mill for 2 h, then the KBIN rod-like templates were added with 10 wt.% of the total amount. The powders, templates and vehicles were well mixed in a ball mill for 30 min to obtain aiming ink for the subsequent screen-printing process. The obtained ink was composed of 30 wt.% of the inorganic powders and 70 wt.% of the organic vehicles. A standard 200 mesh screen was employed in the screen printing process subsequently.

The ink was screen-printed into a film with a thickness of 2–3 μm on the mylar pasted on a glass substrate, and then dried at 80 °C. The process was repeated many times until the thickness of the multilayered sheets was close to 150 μm. The sheet was cut into 12 mm × 12 mm squares and removed from the substrate, then stacked, and laminated to fabricate green compacts. After burning out the binder at 650 °C, the samples were treated with cold-isostatic pressing (CIP) at 250 MPa for densification. The samples were sintered at 1150 °C for 10 h in air at a heating rate of 10 °C/min. Silver paste was painted on the two parallel surfaces of the tablets, and fired at 700 °C for 30 min. The KBIN powders prepared by the solid-state reaction method using the same starting materials were also prepared for comparison.

The crystal phase and texture of samples were characterized using X-ray diffraction (D/max 2550 V, Rigaku, Japan) using Cu-Kα radiation, and the degree of grain orientation was calculated by Lotgering method. Electron probe microanalysis (EPMA-8705QH2, Shimadzu, Japan) was employed to examine the microstructure morphology. The temperature dependence of dielectric constant and dissipation factor were measured with an HP 4284A precision LCR meter (Agilent Technology Co. Ltd., USA) at several frequencies from 100 Hz to 1 MHz.

3. Results and discussion

3.1. Synthesis of rod-like KBIN templates

The X-ray diffraction pattern of the powders synthesized via MSS is shown in Fig. 1. The products are single-phase KBIN ($a \approx b$ = 17.8676 Å and c = 7.8451 Å), which well resembles with the $K_2BiNb_5O_{15}$ JCPDF data card (no. 46-0317). Fig. 2 shows SEM micrograph of the synthesized KBIN powders. It can be seen that the synthesized powders are rod-like single crystals of about 1–2 μm in diameter and 10–20 μm in length.

3.2. Grain orientation with rod-like template with screen-printing process

Fig. 3 shows schematic of the screen printing technique and the orientation of the samples with $SP_{\parallel}$, $SP_{\perp}$-1, and $SP_{\perp}$-2 planes in an ideal case (f = 100%). Under the shear force of the squeegee, the rod-like seeds could be pushed through the openings of the screen. On the Mylar, the seeds could remain aligned parallel to the direction of squeegee plane, which is (0 0 l) direction in KBIN single crystal. In this screen-printing technique, the thickness of each screen-printed ceramic film (~4 μm) is comparable to the diameter of the rod-like templates, which confine the grain growth in a single layer. Furthermore, the existence of the interface between adjacent layers make almost all seeds "lie" flat in the $SP_{\parallel}$ plane, which is beneficial to the textured evolution.

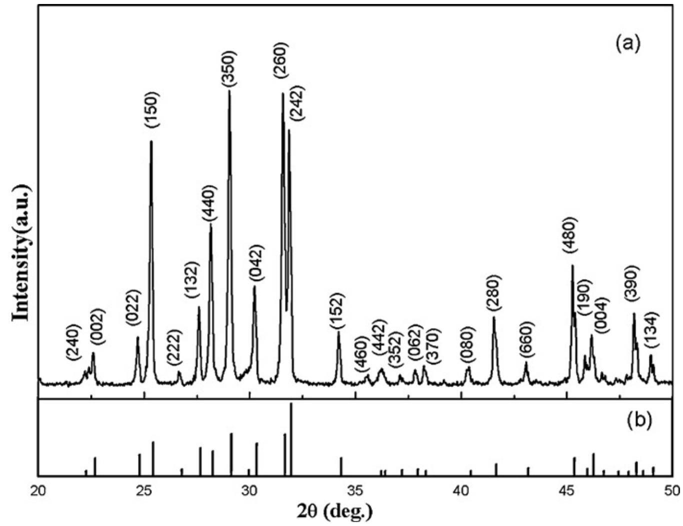

Fig. 1. (a) XRD pattern of the powders synthesized by the reaction of K_2CO_3, Bi_2O_3 and Nb_2O_5 in molten KCl at 1100 °C for 3 h, (b) JCPDS data of $K_2BiNb_5O_{15}$.

3.3. Microstructure analysis of KBIN ceramics

The degree of grain orientation in the textured ceramics was examined by X-ray diffraction. The degree of c-axis texturing achieved in the printed samples was determined by calculating the Lotgering factor. The degree of orientation f, which was defined as [18]:

$$f = \frac{P - P_0}{1 - P_0}$$

where

$$P_0 = \frac{\sum_i I(0\ \ 0\ \ l)}{\sum_i I(h\,k\ \ l)}, \quad P = \frac{\sum_i I^*(0\ \ 0\ \ l)}{\sum_i I^*(h\ \ k\ \ l)}$$

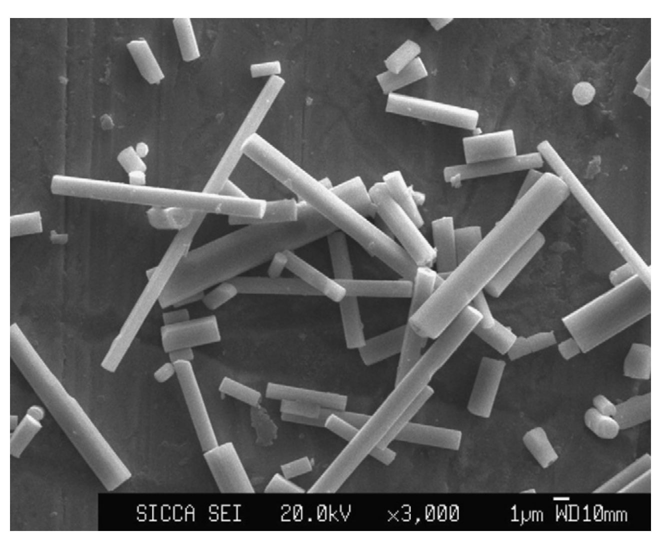

Fig. 2. SEM micrograph of the synthesized KBIN particles by the reaction of K_2CO_3, Bi_2O_3 and Nb_2O_5 in molten KCl at 1100 °C for 3 h.

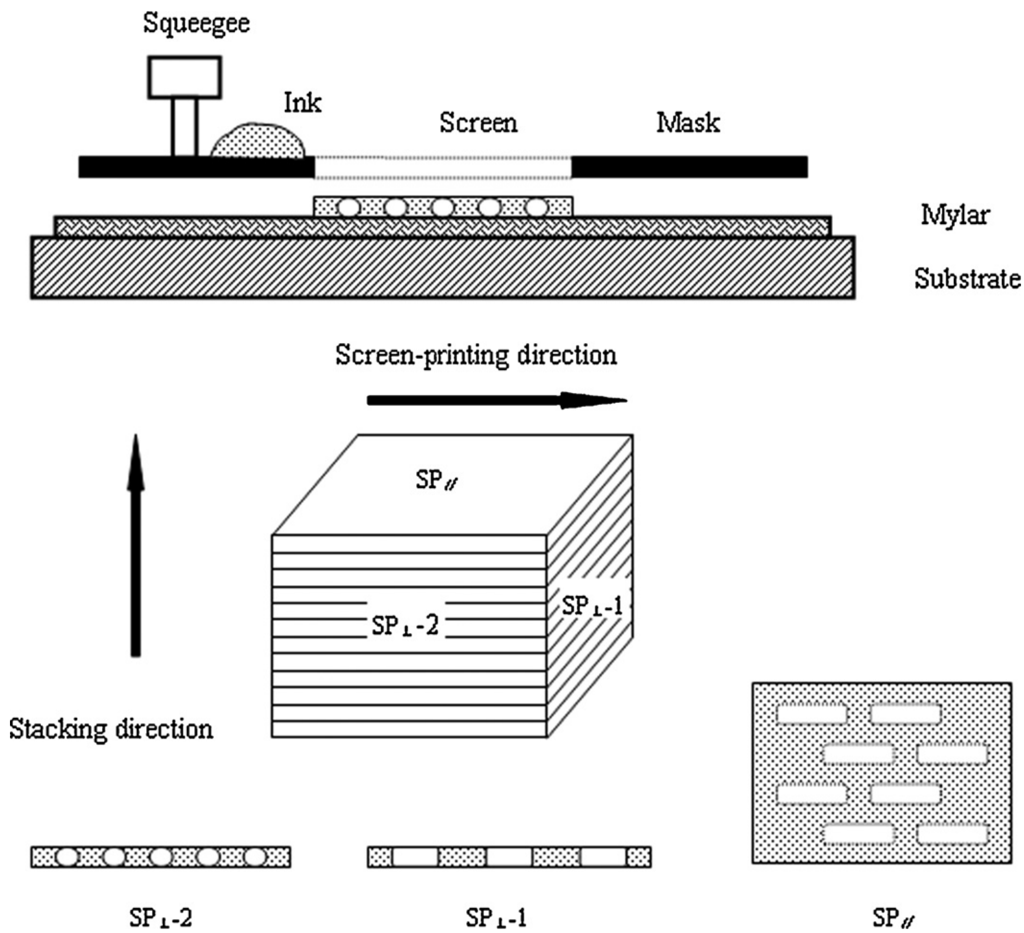

Fig. 3. Schematic of the screen printing technique and the orientation of the samples with the $SP_{\parallel}$, $SP_{\perp}$-1, and $SP_{\perp}$-2 planes.

and $\sum I^*$ is the sum of the XRD peak intensities for the $SP_{\perp}$-2 plane of the textured sample, and $\sum I$ is the sum of peak intensities in the powder diffraction pattern. The diffraction peaks between $2\theta = 20^{\circ}$ and 50° were used for the calculation.

Fig. 4 shows that X-ray diffraction patterns of the textured KBIN ceramics in three directions are anisotropic, the X-ray diffraction patterns of the KBIN powders prepared by the solid-state reaction method are shown for comparison. After sintering at a temperature of 1150 °C for 10 h, tungsten bronze structure was clearly observed. The ($h\,k\,0$) peaks corresponding the planes parallel to c-axis were the most prevalent and the ($0\,0\,l$) peaks are hardly to find in Fig. 4(b) and (c), while in Fig. 4(a) the ($0\,0\,l$) peaks become increasingly dominant, with the relative peak–intensity ratio of ($0\,0\,l$) to ($h\,k\,0$) increasing remarkably. This will exert positive effect on anisotropic property of textured ceramics. The degree of grain orientation in ⟨0 0 1⟩ direction shows a value of 42% by calculating the Lotgering factor with the XRD data in Fig. 4(a) and (d).

The surface microstructure of the three planes in KBIN ceramics fabricated by screen-printing method is shown in Fig. 5 which corresponds to SP_{Vert}, $SP_{\perp}$-1, and $SP_{\perp}$-2 planes as indicated in Fig. 3, respectively. Fig. 5(b) shows that most of the rod-like grains are aligned along the screen-printing direction, since the templates grew at the expense of fine-grained matrix grains, while in Fig. 5(a) and (c) the grains were found to be not well oriented. The reason can be explained as follows: during the screen-printing process, all rod-like seeds will maintain parallel to (0 0 1) direction in the ideal case. In fact, due to various factors, such as the difference in length of rod-like seeds, the size of mesh, the viscosity of ink, and so on, it is very difficult to make the seeds align ideally as shown in Fig. 3.

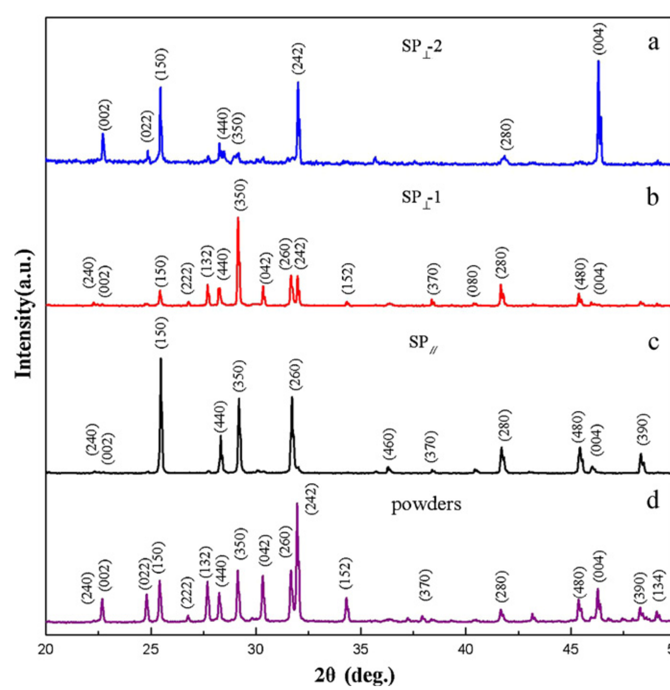

Fig. 4. XRD patterns of $SP_{\parallel}$, $SP_{\perp}$-1, and $SP_{\perp}$-2 planes of the KBIN ceramics with rod-like templates prepared by screen-printing method and powders by solid-state method.

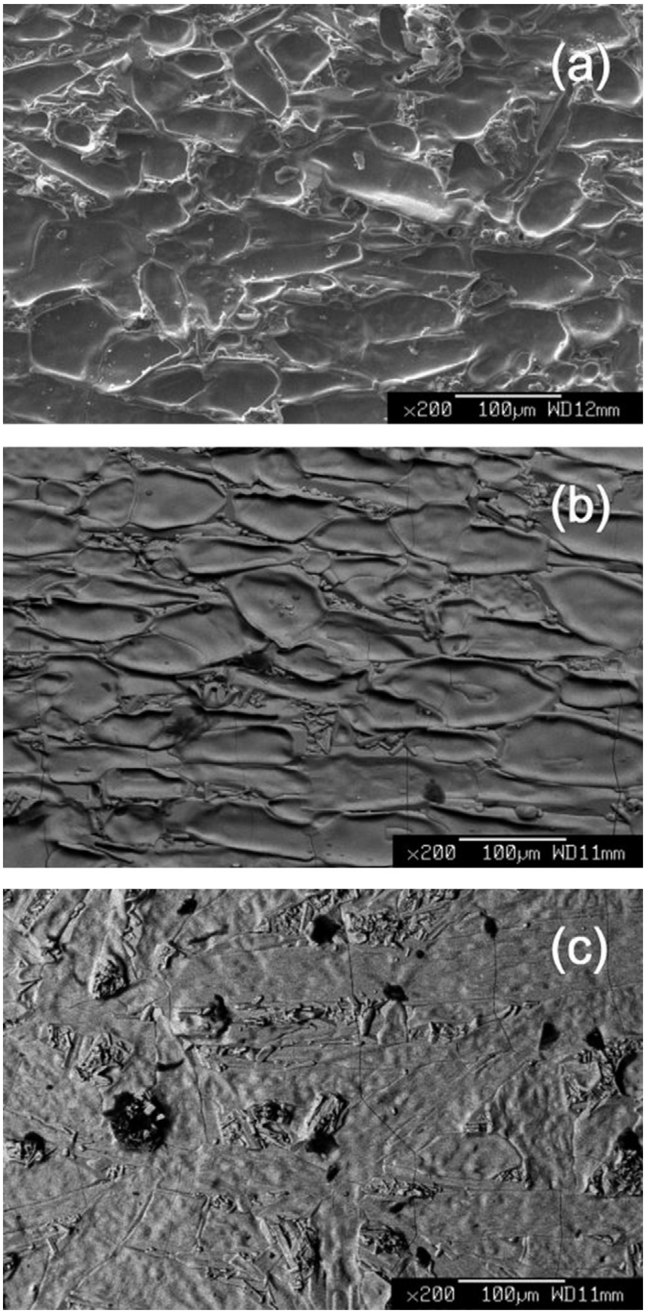

Fig. 5. SEM micrographs of the three planes in textured KBIN ceramics prepared by screen-printing method. (a) $SP_{\perp}$-2 plane, (b) $SP_{\perp}$-1 plane, and (c) $SP_{\parallel}$ plane.

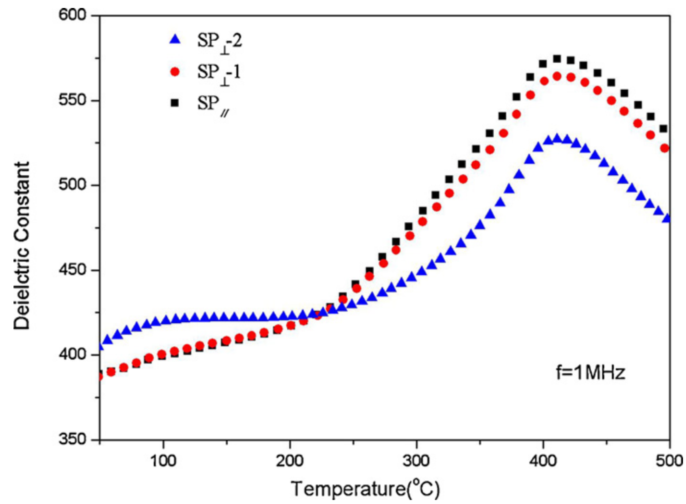

Fig. 6. Temperature dependence of dielectric constant for KBIN ceramics on $SP_{\perp}$-2, $SP_{\perp}$-1, and $SP_{\parallel}$ planes.

There are some rod-like templates which "lie" randomly in the $SP_{\parallel}$ plane, which has led to the similar dielectric properties on $SP_{\parallel}$ and $SP_{\perp}$-1 planes.

3.4. Anisotropy of dielectric properties

Fig. 6 shows the temperature dependences of dielectric constant measured on $SP_{\parallel}$, $SP_{\perp}$-1, and $SP_{\perp}$-2 planes of specimens at 1 MHz. The dielectric spectra measured at frequencies less than 100 kHz did not show obvious anomalous peaks, thus the temperature dependence of capacitance was measured at a frequency of 1 MHz for all samples, and the dielectric loss measured on $SP_{\parallel}$, $SP_{\perp}$-1, and $SP_{\perp}$-2 planes of specimens show values of 0.039, 0.042, 0.047 at 1 MHz at room temperature, respectively. From Fig. 6, it can be seen that the textured KBIN ceramics have only one phase transition above room temperature. At the Curie temperature of 410 °C, the dielectric constants in three directions exhibit anomalies. In particular, the dielectric constant on $SP_{\perp}$-2 plane was different with those on $SP_{\parallel}$ and $SP_{\perp}$-1 planes. The dielectric properties of textured KBIN ceramics prepared by screen-printing technique are obvious anisotropic, compared to those of traditional randomly oriented KBIN ceramics (T_c = 350 °C) and KBIN single crystals (T_c = 420 °C) reported in literatures [7,9,19]. The T_c value diversification of KBIN ceramics fabricated by screen-printing method is mainly owing to the composition variation of KBIN ceramics caused by the volatility of Bi and K during high temperature sintering, and the high reactivity with moisture. The temperature dependences of dielectric constant along $SP_{\parallel}$ and $SP_{\perp}$-1 planes are found to be very close, and different from that along $SP_{\perp}$-2 plane. This just corresponds well to the results of the XRD and SEM.

4. Conclusions

The rod-like $K_2BiNb_5O_{15}$ templates with a diameter of 1–2 μm and a thickness of 10–20 μm were synthesized via MSS. The anisotropic $K_2BiNb_5O_{15}$ ceramics were successfully fabricated by the screen-printing templated grain growth technique. As the grain orientation degree of $K_2BiNb_5O_{15}$ ceramics is just 42%, further work is needed to improve it through changing experimental conditions and parameters. We have highlighted that by taking a new approach that utilizes screen-printing TGG or RTGG techniques textured ceramics with rod-like templates can be fabricated.

Acknowledgments

This work was supported by the Ministry of Sciences and Technology of China through 973-Project (2009CB623305), The Major Program of the National Natural Science Foundation of China (50932007), and The Science & Technology Commission of Shanghai Municipality (10XD1404700, 08JC1420500). The authors would like to thank Dr. Adrian Trinchi of CSIRO Materials Science & Engineering, Clayton, VIC, Australia, for his kind help and discussions.

References

[1] Y. Bai, X.L. Zhu, X.M. Chen, X.Q. Liu, J. Am. Ceram. Soc. 93 (2010) 3573–3576.
[2] Z.P. Yang, R. Gu, L.L. Wei, H.M. Ren, J. Alloys Compd. 504 (2010) 211–216.
[3] T. Watanabe, J. Hayashi, T. Matsuda, T. Ifuku, B.Y. Lee, T. Iijima, H. Funakubo, H. Yu, N. Kumada, J. Ceram. Soc. Jpn. 118 (2010) 717–721.

[4] Y.F. Yang, Y.Y. Liu, M.G. Jian, Y. Huan, Y.N. Wu, J. Alloys Compd. 453 (2008) 401–406.
[5] Y. Takahashi, N. Fujie, M. Osada, H. Masai, R. Ihara, T. Fujiwara, J. Appl. Phys. 108 (2010) 103519.
[6] M.E. Torres, A.A. Kaminskii, C. Gonzalez-Silgo, J.G. Platas, Onzalez, D. Jaque, A. Rodenas, I.R. Martin, V. Lavin, J. Alloys Compd. 451 (2008) 198–200.
[7] R.R. Neurgaonkar, W.K. Cory, J.R. Oliver, E.J. Sharp, G.L. Wood, G.J. Salamo, Ferroelectrics 142 (1993) 167–188.
[8] T. Sugai, M. Wada, Jpn. J. Appl. Phys. 11 (1972) 1863–1864.
[9] Y. Iwai, H. Takuchi, Trans. Mater. Res. Soc. Jpn. 29 (2004) 1129–1130.
[10] V.S. Filip'ev, R.U. Devlikanova, V.G. Kryshtop, V.P. Zav'yalov, Z.V. Bondarenko, Fesenko, Neorg. Mater. 19 (1983) 1383.
[11] Y. Saito, H. Takao, J. Electroceram. 24 (2010) 39–45.
[12] H. Xue, Z.X. Xiong, J. Alloys Compd. 467 (2009) 338–341.
[13] C. Duran, S. Trolier-McKinstry, G.L. Messing, J. Mater. Res. 17 (2002) 2399–2409.
[14] M.R. Winter, C.B. DiAntonio, P. Yang, M.A. Rodriguez, J.R. Michael, T.P. Chavez, B.B. McKenzie, J. Am. Ceram. Soc. 93 (2010) 1922–1926.
[15] J.T. Zeng, Y.X. Li, Q.B. Yang, X.Z. Jing, Q.R. Yin, J. Eur. Ceram. Soc. 25 (2005) 2727–2730.
[16] M.J. Wu, Y.X. Li, D. Wang, J.T. Zeng, Q.R. Yin, J. Electroceram. 22 (2009) 131–135.
[17] M.J. Wu, Y.X. Li, D. Wang, Q.R. Yin, Ceram. Int. 34 (2008) 753–756.
[18] F.K. Lotgering, J. Inorg. Nucl. Chem. 9 (1959) 113–123.
[19] M. Shimazu, Y. Tanokura, S. Tsutsumi, Jpn. J. Appl. Phys. 28 (1989) 1877–1881.