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Effect of different templates on microstructure of textured $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ ceramics with RTGG method

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Abstract

One-dimensional needle-like $KSr_2Nb_5O_{15}$ (KSN) and two-dimensional plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) particles were used as templates to fabricate grain-oriented $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ (NBTBT) ceramics by reactive-templated grain growth. The effects of the template concentration on the microstructure and orientation of NBTBT ceramics were investigated, and the mechanism of grain growth was discussed. The results show that NBTBT textured ceramics cannot be obtained with KSN template, since the needle-like KSN particles were aligned randomly along the tape casting direction. Ceramics contain perovskite NBTBT and tungsten–bronze-type KSN phase. Some cucurbit-like KSN grains resulted from the defects of needle-like KSN templates were detected. Textured ceramics with orientation factor more than 60% were obtained successfully when the plate-like BNN was used as templates. The results show that the texture fraction of NBTBT textured ceramics increase with increasing the content of BNN. The textured ceramics exhibited $\{h\,0\,0\}$ preferred orientation have brick wall microstructure with strip-like grains aligning in the same plane as the casting plane. The reaction and crystal formation of textured NBTBT ceramics with plate-like BNN templates are by diffusion–recrystallization process. Finally the selecting rules of suitable templates are proposed.

Keywords: Lead-free ceramics; Tape casting; Grain growth; Texture; Piezoelectrics; (Na, Bi) TiO_3; $BaTiO_3$

1. Introduction

Most widely used piezoelectric materials are lead-based ceramics including Pb(Ti, Zr)O_3 (PZT). However, it is very important to use lead-free piezoelectric materials for environmental protections.[1,2] $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ (NBTBT) ceramic, which is an attractive solid solution with the perovskite structure, is considered an excellent candidate for lead-free piezoelectric ceramics to replace the lead-based piezoelectric materials.[3,4]

But compared with the conventional PZT piezoelectric ceramics, NBTBT ceramics still show poor piezoelectric properties, which has restricted the applications of material. One of the approaches to enhance the piezoelectric properties of lead-free ceramics is to control the microstructure of ceramics by grain orientation.[5,6] Reactive-templated grain growth (RTGG) method has been used successfully to form crystallographically textured ceramic such as bismuth layer-structured ferroelectrics.[7,8] Tani et al. have reported that the grain-oriented (Na, K)$_{0.5}Bi_{0.5}TiO_3$ ceramics were prepared by plate-like $Bi_4Ti_3O_{12}$ particles aligned parallel to the casting direction and piezoelectric properties were improved.[9] In RTGG method, the first step is to prepare particles with shape anisotropy, such as plate-like particles, needle-like particles. The second is to align particles with shape anisotropy in green compacts by tape casting. Then textured ceramics are formed after sintering with specific crystal axis of grains aligned in one direction, and high electrical properties are expected.

In the present study, one-dimensional needle-like $KSr_2Nb_5O_{15}$ (KSN) and two-dimensional plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) template particles were synthesized by the NaCl–KCl molten salt process, and textured $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ (NBTBT) ceramics were fabricated by RTGG in combination with tape casting. The effects of template content on the grain orientation and microstructure of NBTBT ceramics were investigated. And the different effects of the two kinds of templates on the mechanism of grain growth were discussed.

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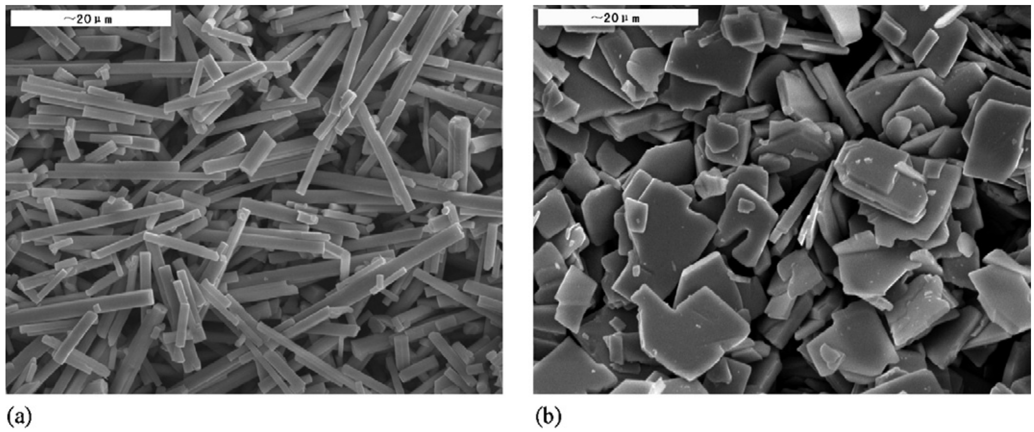

Fig. 1. SEM micrographs of template particles. (a) $KSr_2Nb_5O_{15}$ template particle and (b) $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ template particle.

2. Experimental procedure

2.1. Preparation of templates

Needle-like $KSr_2Nb_5O_{15}$ (KSN) and plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) template particles were prepared by NaCl–KCl molten salt synthesis (MSS).[10] Reagent-grade K_2CO_3, Na_2CO_3, $SrCO_3$, Nb_2O_5, Bi_2O_3, NaCl, and KCl were used as starting materials. Firstly, needle-like KSN template particles were synthesized by a two-step process. In the first reaction, $SrCO_3$ and Nb_2O_5 were ball milled and reacted at 1050 °C for 2 h to obtain $SrNb_2O_6$. In the second reaction, $SrNb_2O_6$ powder was reacted with K_2CO_3 at 1250 °C for 2 h in KCl flux to obtain KSN template. In separate experiment, an equal weight of NaCl–KCl mixture and Bi_2O_3, Na_2CO_3, Nb_2O_5 were ball milled in ethanol for 12 h and calcined in a sealed alumna crucible at 1100 °C for 2 h to obtain BNN. After slowly cooling down to room temperature, the reaction product was washed with hot deionized water for twenty times until no free Cl^- ions were detected with the use of $AgNO_3$ solution. KSN and BNN template particles were obtained by drying at 80 °C for 10 h. As shown in Fig. 1, $KSr_2Nb_5O_{15}$ particles have needle-like shape with 10–20 μm in length and 1–2 μm in diameter, $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ powder is formed by plate-like particles with average diameter of ~6 μm and a thickness of ~1 μm, which can meet the needs of RTGG method.

2.2. Fabrication of textured NBTBT ceramics by RTGG

The general formula of the material studied was $0.92Na_{0.5}Bi_{0.5}TiO_3$–$0.08BaTiO_3$ (abbreviated as NBTBT). The samples were prepared by reactive-templated grain growth (RTGG) in combination with tape casting. Reagent-grade Bi_2O_3, TiO_2, Na_2CO_3, $BaCO_3$ powders and solvent, binder, plasticizer were mixed and ball milled for 48 h. The solvents were ethanol and xylcne. The binder and plasticizer were polyvinyl alcohol (PVA) and glycerin, respectively. After completion of the ball milling process for the slurry, needle-like KSN or plate-like BNN template particles were added respectively and mixed with the slurry for 4 h. The samples with 10 wt%, 15 wt%, 20 wt%, 30 wt% KSN and BNN templates are numbered as K1, K2, K3, K4, B1, B2, B3, and B4 in sequence. Then the slurry was degassed under vacuum and tape cast on a plated steel surface with a blade gap of 200 μm. The green tapes were cut into pieces of 100 mm × 100 mm and laminated at a pressure of 100 MPa for 15 min. After the laminated samples were cut into 10 mm × 10 mm square, the binder and plasticizer were burned out at 500 °C for 2 h with a heating rate of 1 °C/min. Then the samples were sintered at 1100–1250 °C for 2 h.

2.3. Microstructure characterization

The crystal structure and grain orientation were determined by intensity of X-ray diffraction (XRD; model Panalytical X'Pert PRO, Holland) on the major surfaces of sintered ceramics, 2θ in the range of 20–70° with a step of 0.02°. Microstructure was observed by a scanning electron microscopy (SEM; Model Hitachi S-570, Japan) on polished surfaces perpendicular to the tape casting direction and parallel to the major face.

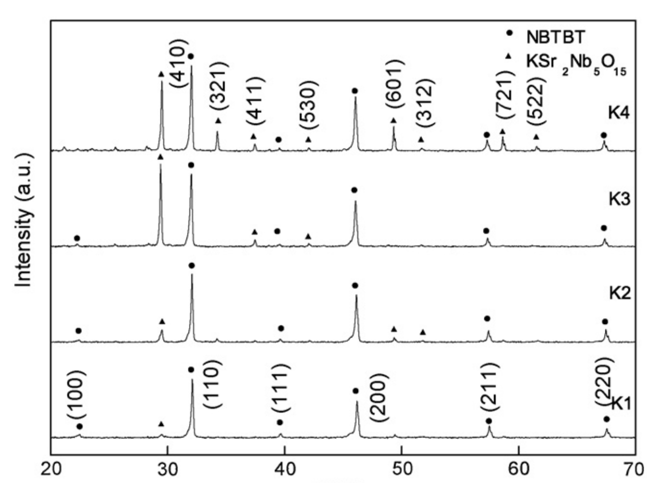

Fig. 2. XRD patterns of NBTBT ceramics with different content of KSN.

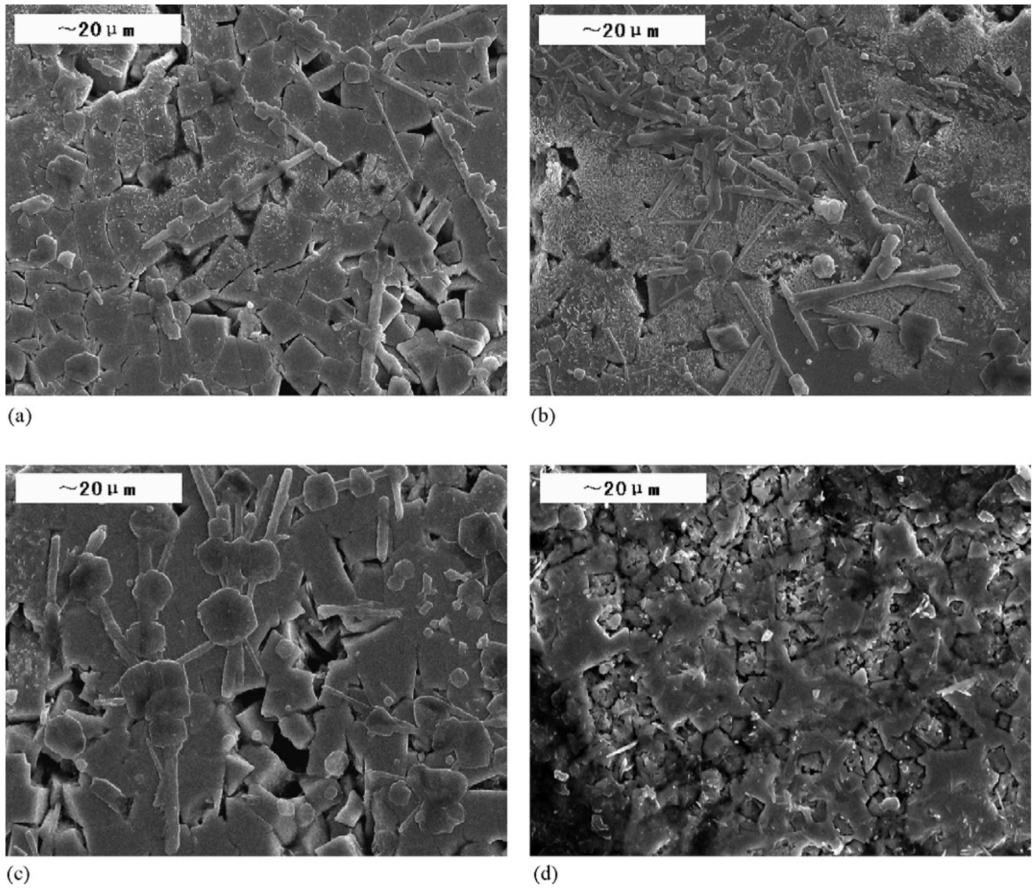

Fig. 3. SEM micrographs of NBTBT ceramics with different content of KSN (1250 °C). (a) NBTBT-10wt%KSN, (b) NBTBT-15wt%KSN, (c) NBTBT-20wt%KSN, and (d) NBTBT-30wt%KSN.

3. Results and discussions

To determine whether NBTBT ceramics would be textured or not, X-ray diffraction was taken on ceramics plane parallel to the tape casting direction. Fig. 2 shows XRD patterns of NBTBT ceramics with different content of KSN template. It is found that perovskite NBTBT phase and tungsten–bronze-type KSN phase coexisted, no other phases could be detected. The main intense peak (4 1 0) of KSN phase enhances with rising content of KSN. Comparing to (4 1 0) peak, (1 1 0) peak of perovskite NBTBT phase is the most intense one in K1 and K2 ceramics. But (4 1 0) peak is high enough to be the most intense peak in the XRD patterns of K3 ceramics. The results indicate that NBTBT textured ceramics cannot be obtained using needle-like KSN template.

Fig. 3 is the SEM micrographs of NBTBT ceramics with different content of KSN sintered at 1250 °C for 2 h. It is observed that the samples are all well sintered and are composed of two types of grains. One type was irregularly shaped grains, which are NBTBT matrix grains. There was no remarkable change in matrix grain sizes with rising the content of KSN. Besides the matrix grains, the needle-like grains observed in ceramics were randomly oriented. It is concluded that the needle-like KSN template grains were randomly oriented in the middle of the tapes along the tape casting direction.

What is more, it is interesting that KSN grain with irregular cucurbit-like morphology was distinctly different from that of KSN template. The growth of KSN single crystal particles was governed by two-dimensional nucleation starting at crystal surfaces centers or corners. Fig. 4 sketches the growth mechanism of KSN template particles might be.[11] The stepwise surface is resulted from the multiple nucleation of KSN on the crystal surface. The KSN crystal growth does not depend on the horizontal-orientation growing of the sidesteps, but directly longitudinal stacks on crystal lattice randomly and some defects appeared in the needle-like KSN template particles. It is well known that defect on boundary is the easiest position for grain growth. Therefore, the growing of roughness interface is faster than that of boundary without defects. Some of the KSN templates grow longitudinal from the defects position and the grain morphology come into being like the cucurbit, as shown in Fig. 5.

It is illuminated that needle-like KSN used as templates of NBTBT ceramics can show a little extent inducement of orientation on the growing of matrix grains, and the distribution in the matrix is aligned randomly in the main plane, which resulted in unsuccessful textured ceramics. No obvious crystallographic orientation can be observed in the NBTBT ceramics.

Fig. 6 shows XRD patterns of NBTBT ceramics with different content of BNN template. It is revealed that two phases

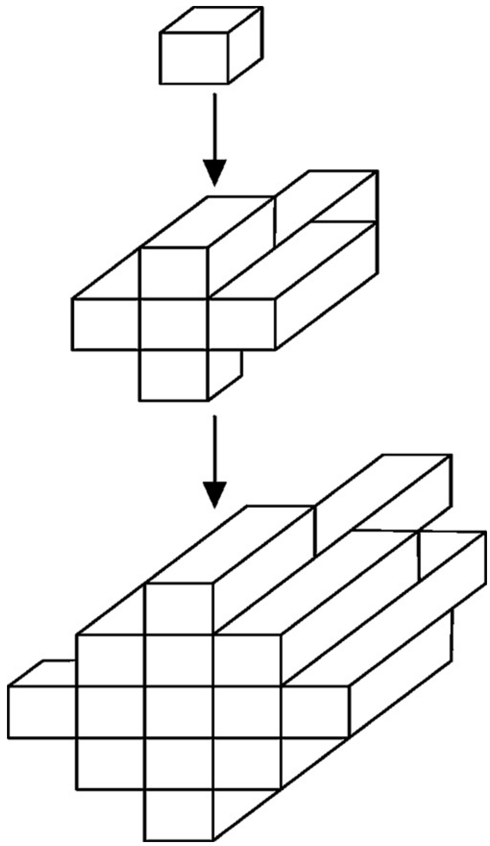

Fig. 4. The sketch map of the growth KSN particles.

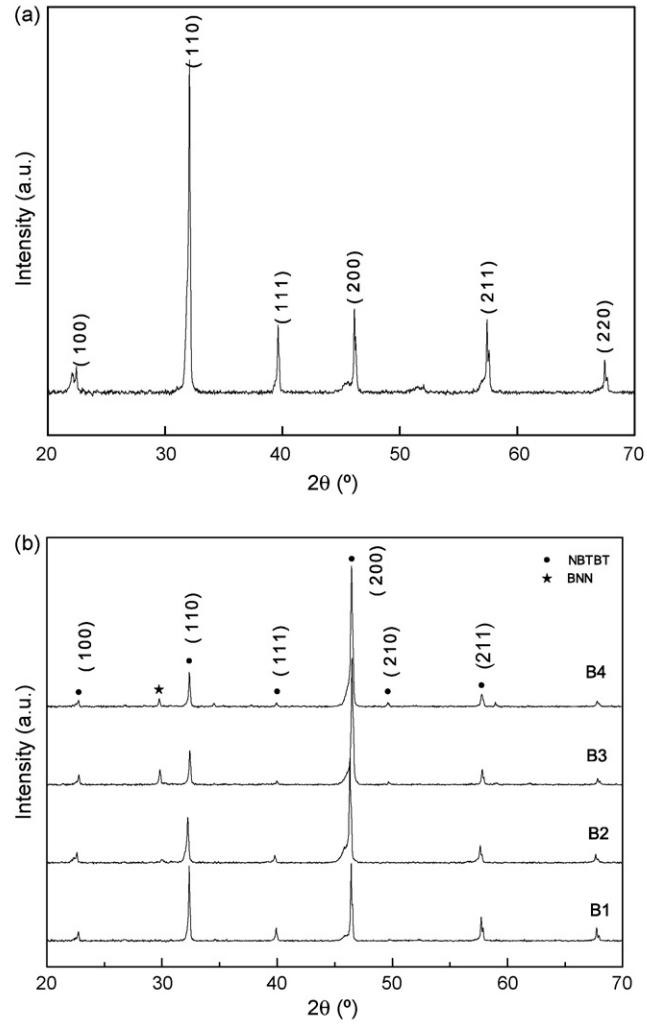

Fig. 6. XRD patterns of NBTBT textured ceramics with different content of BNN. (a) NBTBT ceramic with random orientation grains and (b) NBTBT textured ceramics.

coexisted in the ceramics, one is NBTBT with perovskite structure, the other is BNN with Bi-layer structure. The (1 1 0) peak is main intense peak in the pure NBTBT ceramics with randomly oriented grains, as shown in Fig. 6(a). While the intensities of the (1 0 0) and (2 0 0) peaks increase, the intensities of others decrease as the content of BNN increased. And the (2 0 0) peak is the most intense one in the textured NBTBT ceramics. The results indicate that (h 0 0) texture is formed in the NBTBT ceramics prepared by RTGG method. The texture fraction (f) is calculated by Lotgering method, as the following equations shown[12,13]:

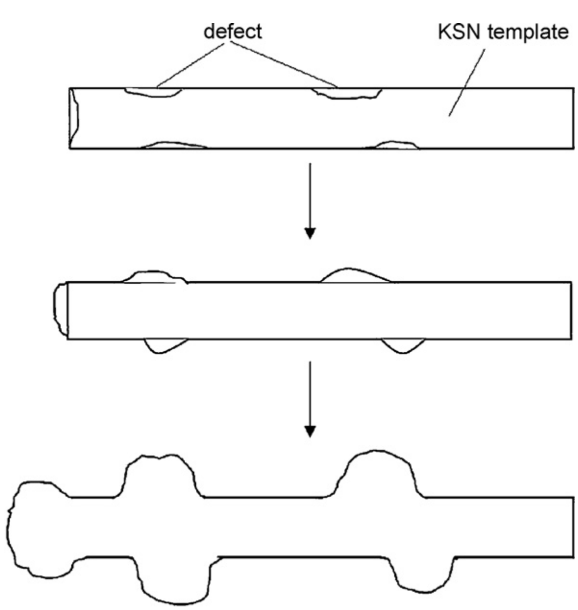

Fig. 5. The sketch map of the KSN grain growth in NBTBT ceramics.

$$f = \frac{P - P_0}{1 - P_0} \quad (1)$$

$$P = \frac{\sum I_{\{h00\}}}{\sum I_{\{hkl\}}} \quad (2)$$

$$P_0 = \frac{\sum I_{0\{h00\}}}{\sum I_{0\{hkl\}}} \quad (3)$$

where I and I_0 are the peak intensities of the sintered compacts and randomly oriented NBTBT, respectively. $\{h\,0\,0\}$ and $\{h\,k\,l\}$ are Miller indexes. The diffraction lines between $2\theta = 20^{\circ}$ and $2\theta = 70^{\circ}$ are used to calculate P and P_0.

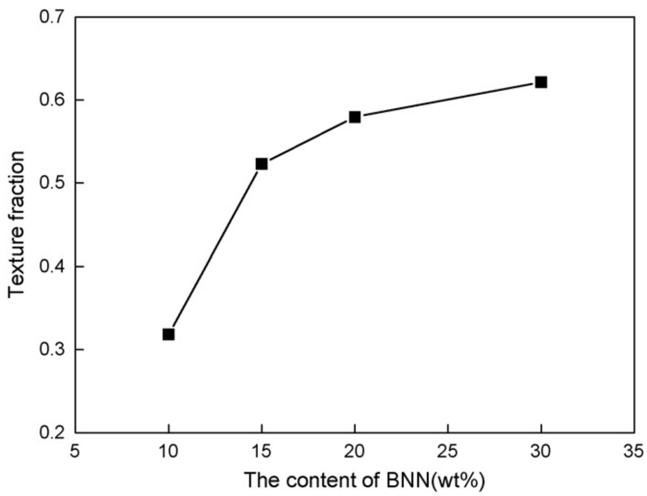

Fig. 7. Texture fraction of NBTBT textured ceramics with different content of BNN.

Fig. 7 shows the effect of BNN on the degree of orientation for NBTBT ceramics. The texture fraction is small (0.32) when the content of BNN is 10 wt%, then increases as the content of BNN increases and the largest volume appears at 30 wt% where *f* amounts to 0.62. It is indicated a textured material, which has significant grain orientation.

Fig. 8 shows the microstructure of NBTBT ceramics with polished plane perpendicular to the tape casting direction. It is obvious that NBTBT ceramics is well sintered at 1185 °C. The size and uniformity of the grains are manifested obviously with the increasing of the templates, at the same time the grains grow with orientation apparently. All specimens are composed of two types of NBTBT grains. One is strip-like grain, which originated from plate-like BNN particles. The other is fine, equiaxed shaped grain. They are called oriented and matrix grains, respectively. There are few oriented grains in the NBTBT ceramics with 10 wt% BNN. It indicates that 10 wt% BNN templates which are added in the matrix for reaction is insufficient.

Most of the grains grow along the existing interface of templates by spontaneous nucleation. Therefore, the size of the strip-like grain grows bigger gradually with increasing content of BNN. It is revealed that a brick wall microstructure with grain size up to 20 μm in length and ~5 μm in thickness was obtained in the NBTBT ceramics, as shown in Fig. 8(c) and (d). In addition, a non-polygon curved grain boundary appeared in samples, as shown in Fig. 8(c), it can be deduced that a liquid phase formed in ceramics during sintering.

To comparing how does the anisotropy verify, the anisotropy degree is proposed as follows:

$$A_d = \frac{L}{t} \quad (4)$$

where A_d means the anisotropy degree, L stands for length size and t is thickness of strip-like grain in textured ceramics. The larger the A_d value is, the larger the anisotropy degree is. And there will be the more differences between the length size and the thickness of grains. The strip-like grain sizes are measured and the results are shown in Table 1. It reveals that both the length and the thickness of strip-like grain increase with the increasing of the BNN templates. What is more, the anisotropy degree of strip-like grain is from 2.81 to 2.98, which is much smaller than that of BNN templates. And the anisotropy degree decreases with the increasing of the BNN templates. The results indicate that the grains grow not only along the length (a–b plane) direction, but also grow along the thickness direction (a–c plane).

Table 1
Strip-like grain size of textured NBTBT ceramics

Samples	L_{max} (μm)	L_{aver} (μm)	t_{aver} (μm)	A_d
B1	7.64	7.27	2.44	2.98
B2	16.73	10.00	3.34	2.99
B3	18.18	10.55	3.61	2.92
B4	19.98	11.64	4.15	2.81

L_{max}, the maximum value of length for strip-like grain; L_{aver}, the average length of strip-like grain; t_{aver}, the average thickness of strip-like grain.

Textured microstructures evolve by dissolution of randomly oriented matrix particles and precipitation on the oriented template particles. The driving force for grain growth comes from the size difference between the template particles and matrix particles. In the sintering stage, because the grain size and the specific grain boundary area differ from the equiaxed and the plate-like grains, the small matrix grains tend to be consumed by the large oriented grains during sintering in order to reduce the grain boundary area and the internal energy of the system.[13] The plate-like grains oriented parallel to the (h 0 0) planes form low-energy grain boundaries, and are difficult to be consumed. Some of them can grow large and eventually remain in the final product. In contrast, the fine matrix grains misaligned form high-energy grain boundaries and are easily consumed not only by the oriented grains but also by the larger matrix grains. As a result, the volume fraction of the randomly oriented grains in the sample is reduced, and the degree of grain orientation increases with BNN increase.

Textured ceramics cannot be prepared using needle-like KSN templates, but can be obtained successfully with plate-like BNN templates. One of the most important reasons is that the lattice structure of the BNN template has a perovskite cell between the two $Bi_2O_2^{2+}$ layers, which is similar to the perovskite crystal structure of NBTBT, and results in good extension grain growth relationship. Seno and Tani[14] prepared textured $(Na, K)_{0.5}Bi_{0.5}TiO_3$ ceramics by plate-like $Bi_4Ti_3O_{12}$ particles and observed that there was a rapid diffusion of Na and K atoms from the matrix into the $Bi_4Ti_3O_{12}$ template particles, changing the layered perovskite to a regular perovskite. It is deduced that the reaction and crystal formation of textured NBTBT ceramics with plate-like BNN templates is diffusion–recrystallization process. Because of the similarity between crystal structure of BNN and NBTBT, the grain orientation can start by ion diffusion at the interface. Once two-dimensional nucleation is formed on the BNN crystal surface, the crystal will grow along the interface. The texture fraction increases with the growth of the oriented grains and the effect on adjacent grains, finally

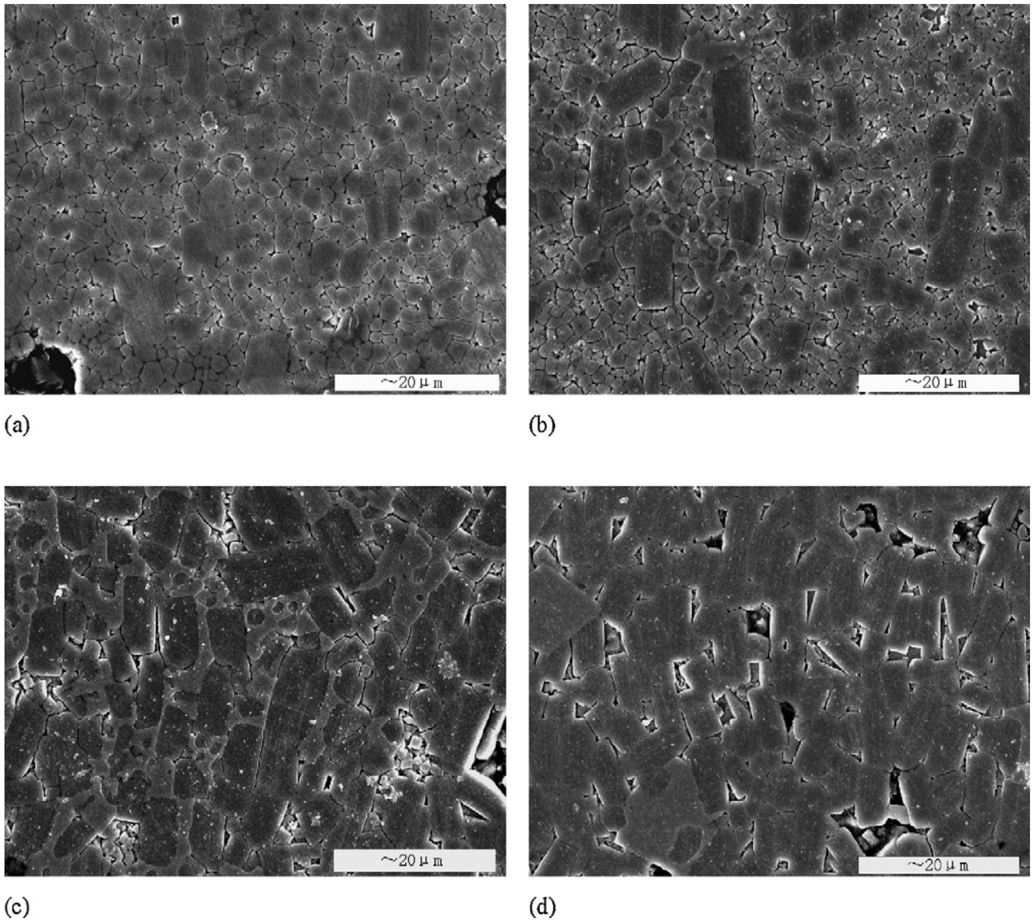

Fig. 8. Microstructure of NBTBT textured ceramics sintered at 1185 °C. (a) NBTBT-10wt%BNN, (b) NBTBT-15wt% BNN, (c) NBTBT-20wt% BNN, and (d) NBTBT-30wt% BNN.

brick wall morphology is obtained. But tungsten–bronze-type KSN template used is a different phase from the matrix, and the elements of composition are not involved in the matrix NBTBT composition, so heteroepitaxical growth will take precedence at the defects of the templates and form cucurbit-like grains.

In addition, the formation of well-textured ceramics is related to the shape of the template grains and the fabrication process. Fig. 9 is the sketch map of the templates distributing in the base particulate. Under the ideal condition, the templates disperse along horizontal direction, other particles well-distributed around. But this kind of arrangement cannot be achieved in reality, because it is impossible that the size of templates become regular and ideal uniform in the synthesis process. The average size of the templates is assumed as L, while T is the gap between the blade and steel plate. When $T \gg L$, the templates are distributed in tapes randomly, the texture fraction of the ceramic dives to 0. When $T > L$ and the inequality between them is not obvious, the templates distribution in tapes is parallel to the tape casting direction, and textured ceramics formed after sintering.

The tape-casting direction is perpendicular to the c axis. In a–b plane, the plate-like BNN templates can arrange with orientation easily, while the needle-like KSN templates arrange randomly, as shown in Fig. 9(b) and (c). The degree of freedom for needle-like templates is greater than that of the plate-like templates. At sintering stage, texture ceramics is formed in NBTBT ceramics using plate-like BNN templates while obtained unsuccessfully using needle-like templates. Therefore, the plate-like template is suitable for the tape-casting process to obtain texture ceramics.

In summary, the template selection for texture ceramics should obey following rules:

(1) Template with large anisotropy dimension should be easy prepared. Compared to needle-like template, plate-like template is much better to obtain texture ceramics.
(2) The elements of templates composition should be involved in the composition of matrix ceramics.
(3) Lattice structure of templates should be similar to that of matrix ceramics.
(4) Templates should have high reactivity or diffusion with matrix particle to ensure a single phase.
(5) The morphology and the size of template should be uniform for tape casting.

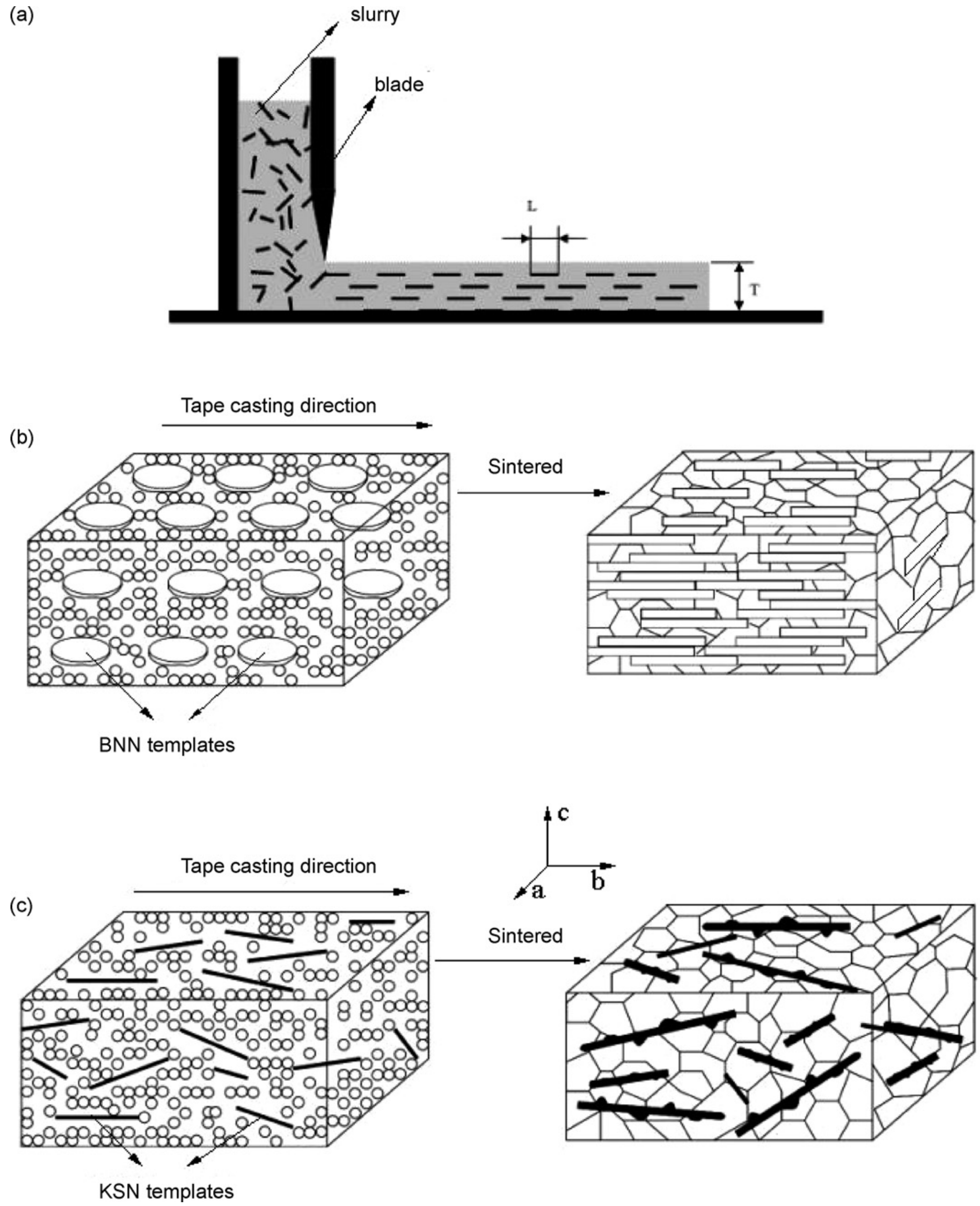

Fig. 9. The sketch map of templates arranged in matrix. (a) Arranging state of templates in tape casting, (b) plate-like template, and (c) needle-like template.

4. Conclusions

Textured $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ ceramics were fabricated by RTGG method with needle-like $KSr_2Nb_5O_{15}$ (KSN) and plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) template particles. The results show that NBTBT textured ceramics cannot be obtained with KSN template, since the needle-like KSN particles were aligned randomly along the tape casting direction. Ceramics constitute perovskite NBTBT and tungsten–bronze-type KSN phase. Some cucurbit-like KSN grains which resulted from the defects of needle-like KSN templates were detected. Textured ceramics with orientation factor more than 60% were obtained successfully with plate-like BNN templates. The results show that textured ceramics exhibited $\{h00\}$ preferred orientation have brick wall microstructure with strip-like grains aligning in the direction parallel to the casting plane. The texture fraction of NBTBT textured ceramics increase with increasing the content of BNN. The reaction and crystal formation of textured NBTBT ceramics with plate-like BNN templates is diffusion–recrystallization process. Finally the rules of chosen templates to get highly textured ceramics are proposed as following: (1) Template with large anisotropy dimension can be easily prepared. (2) The elements of templates composition should be involved in the composition of matrix ceramics. (3) Lattice structure of templates should be similar to that of matrix ceramics. (4) Templates should have high reactivity or diffusion with matrix particle to ensure a single phase. (5) The morphology and the size of template should be uniform for tape casting.

Acknowledgements

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