

Grain growth kinetics of textured $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ — 0.08BaTiO_3 ceramics by tape casting with $\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18}$ templates

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Abstract Plate-like $\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18}$ particles were used as templates to fabricate grain-oriented $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ — BaTiO_3 (NBTBT) ceramics by reactive-templated grain growth. The effects of sintering conditions on the grain orientation and microstructure of the textured NBTBT ceramics were investigated, and the kinetic mechanism of grain growth is discussed. The results show that textured ceramics were successfully obtained with orientation factor more than 0.6. NBTBT specimens are composed of strip-like grains and equiaxed shaped grains. The textured ceramics have a microstructure with strip-like grains aligning in the direction parallel to the casting plane and exhibit an $\{h00\}$ preferred orientation. The degree of grain orientation increases initially, then decreases with increasing sintering temperature and soaking time. The maximum texture fraction is 0.69 when sintered at 1185 °C for 6 h. The kinetic exponent n and activation energy Q of the two types of grain in textured NBTBT ceramics were calculated. The results show that the grain growth mechanism of oriented grains is controlled not only by grain lattice diffusion, but also by grain boundary diffusion. The grain growth mechanism of matrix grains is mainly controlled by the grain boundary curvature.

Keywords Lead-free ceramics · Tape casting · Grain growth · Texture

1 Introduction

The most widely used piezoelectric materials are lead titanate zirconate ceramics $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$ (PZT). However, it is important to use lead-free piezoelectric materials to avoid environmental pollutions [1]. Some lead-free materials have been reported, such as ferroelectric ceramics with perovskite structure, tungsten bronze-type oxides, and Bi-layer structure oxides [2–5]. Among these materials, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ — BaTiO_3 (NBT) ceramic, which is an attractive solid solution with perovskite structure, is considered an excellent candidate for lead-free piezoelectric ceramics to replace the lead-based piezoelectric materials [6–7].

But compared with the conventional PZT piezoelectric ceramics, NBT ceramics still show poor piezoelectric properties, which has restricted the applications of the material. It is well known that the crystallization process is of technological importance in the manufacture of ceramics. The physico-chemical properties of the ceramics largely depend on the microstructure, phase structure and the morphology of the crystalline phases, etc. Controlled crystallization makes it possible to obtain ceramic materials with the desired properties [8–9]. As an alternative to techniques such as hot pressing and hot forging, reactive-templated grain growth (RTGG) offers the possibility of fabricating grain-oriented polycrystalline ceramics. The RTGG method has been used successfully to form textured lead-free ceramics [10–12]. A detailed kinetic understanding of the grain-orientation process is therefore fundamental to design the conditions for controlled crystallization and to regulate the morphology and microstructure of the materials. But the kinetic mechanism of grain growth in textured lead-free piezoelectric ceramics is seldom reported.

Because $\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18}$ (BNN) template particles were easy prepared, and the BNN powder is formed of plate-like

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particles with size anisotropy, which is suitable for preparing texture ceramics by the RTGG method. What is more, the lattice structure of the BNN template has a perovskite cell between the two $\text{Bi}_2\text{O}_2^{2+}$ layers, which is similar to the perovskite crystal structure of $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ — 0.08BaTiO_3 (NBTBT), and results in good extension grain growth relationship. Based on above reasons, BNN was chosen as template particles for RTGG.

In the present study, plate-like BNN template particles were synthesized by the NaCl—KCl molten salt process, and textured NBTBT ceramics were fabricated by RTGG in combination with tape casting. The effects of sintering conditions on the grain orientation and microstructure of the NBTBT ceramics were investigated. The kinetic exponent n and activation energy Q of the two types of grain in textured NBTBT ceramics were calculated and the kinetic mechanism of grain growth is discussed.

2 Experimental procedure

2.1 Preparation of plate-like BNN templates

Plate-like BNN template particles were prepared by NaCl—KCl molten salt synthesis (MSS) [13]. Reagent-grade Bi_2O_3 , Na_2CO_3 , Nb_2O_5 , NaCl, and KCl were used as starting materials. An equal weight of NaCl—KCl mixture and reagent-grade oxides were ball milled in ethanol for 12 h and calcined in a sealed alumina crucible at 1100 °C for 2 h. After slowly cooling to room temperature, the reaction product was washed 20 times with hot deionized water until no free Cl^- ions were detected using AgNO_3 solution. The BNN templates were obtained by drying at 80 °C for 10 h. As shown in Fig. 1, the BNN powder is

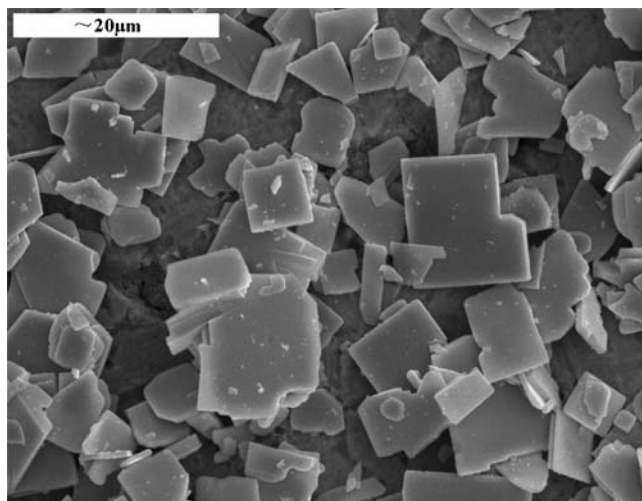


Fig. 1 SEM micrograph of BNN template particle

formed of plate-like particles with an average diameter of $\sim 5 \mu\text{m}$ and a thickness of $1 \mu\text{m}$, which can meet the needs of the RTGG method.

2.2 Fabrication of textured NBTBT ceramics by RTGG

The general formula of the material studied was $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ — 0.08BaTiO_3 (abbreviated as NBTBT). The samples were prepared by 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 xylene. The binder and plasticizer were polyvinyl alcohol and glycerin, respectively. After completion of the ball milling process on the slurry, 30 wt.% plate-like BNN template particles were added and mixed with the slurry for 4 h. 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 $100 \times 100 \text{ mm}$ and laminated at a pressure of 100 MPa for 15 min. After the laminated samples were cut into $10 \times 10 \text{ mm}$ squares, 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 1100–1200 °C for 2 h.

2.3 Microstructure characterization

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

3 Results and discussions

The densities of NBTBT ceramics sintered at different temperatures are shown in Fig. 2. It was found that the density increased quickly in the temperature range from 1100 °C to 1140 °C. Then the rate of increase was slower in the range 1140–1170 °C. The maximum density, 5.315 g/cm^3 , was achieved at 1170 °C. When the sintering temperature was higher than 1170 °C, the density decreased with rising sintering temperature. The results indicate the narrow temperature range of well sintered NBTBT ceramics (1155–1185 °C).

Figure 3 shows XRD patterns of textured NBTBT ceramics. It is seen that two phases coexist in the ceramics, one is NBTBT with perovskite structure, and the other is BNN with Bi-layer structure. The main peak of BNN becomes weaker with rising sintering temperature, which

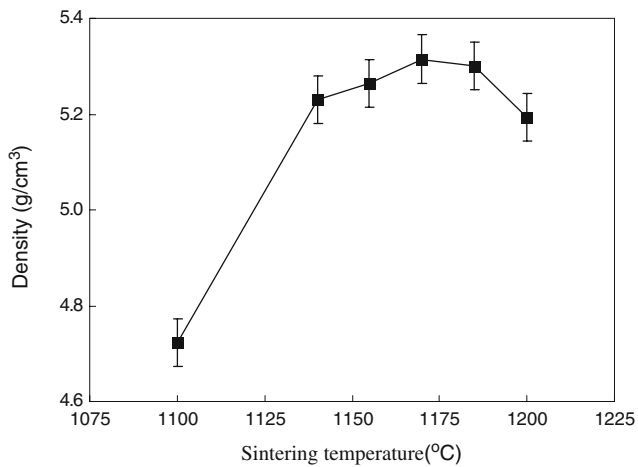


Fig. 2 Density of NBTBT textured ceramics sintered at different temperatures

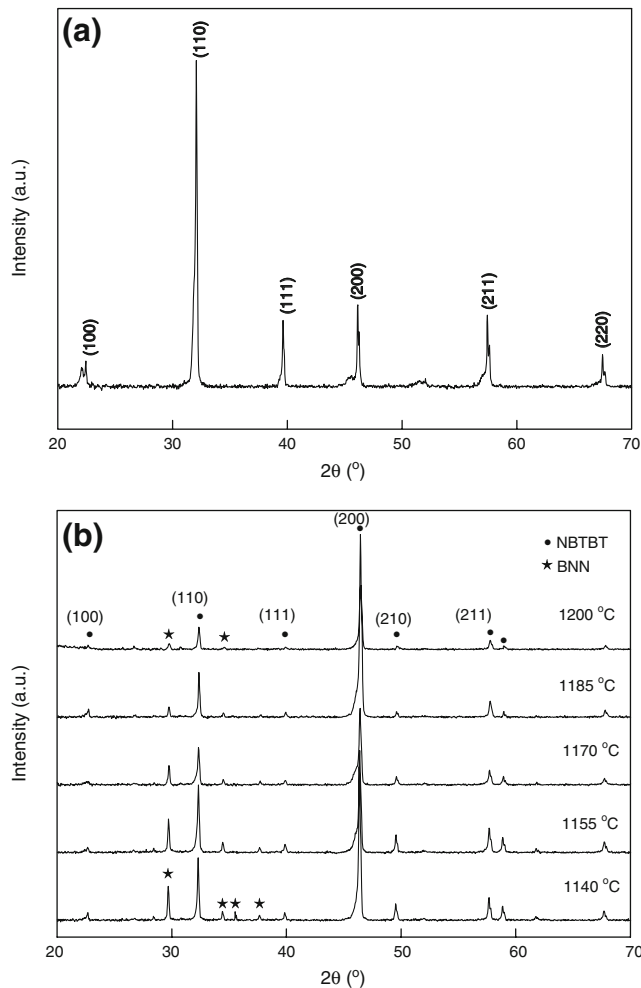


Fig. 3 XRD patterns of NBTBT ceramic with random orientation grains (a) and NBTBT textured ceramics sintered at different temperatures (b)

means that the BNN templates react with the original powder to form texture grains and the content of BNN decreases with increasing temperature. The (110) peak is the main intense peak in the pure NBTBT ceramics with randomly oriented grains, as shown in Fig. 3(a). While the intensity of the (200) peak increases, that of (110) goes from the biggest to the smallest in the order: 1155, 1140, 1185, 1170, 1200 °C. The whole trend of (110) intensity is become smaller as the sintering temperature rising. The results indicate that (h00) texture is formed in the NBTBT ceramics prepared by RTGG. The texture fraction (*f*) is calculated by the Lotgering method, as the following equations show [14]:

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

$$P = \frac{\sum I_{\{h00\}}}{\sum I_{\{hkl\}}} \tag{2}$$

$$P_0 = \frac{\sum I_{0\{h00\}}}{\sum I_{0\{hkl\}}} \tag{3}$$

where *I* and *I*₀ are the peak intensities of the sintered compacts and randomly oriented NBTBT, respectively. {*h00*} and {*hkl*} are Miller indexes. The diffraction lines between 2θ=20° and 2θ=70° are used to calculate *P* and *P*₀.

Figure 4 shows the effect of sintering temperature on the degree of orientation for NBTBT ceramics. The degree of orientation was small (0.18) in the samples sintered at

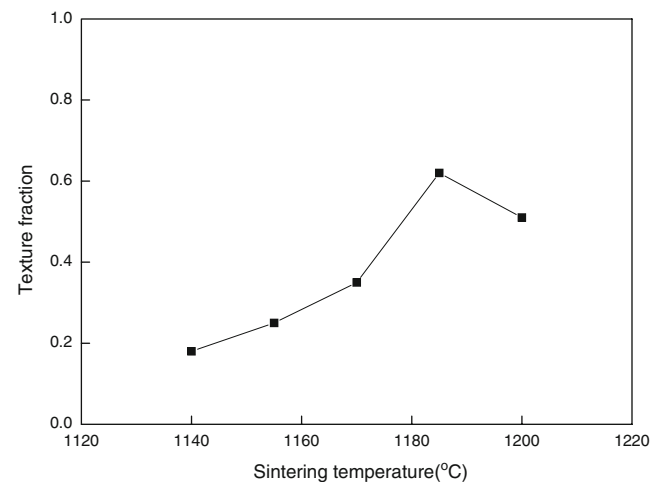


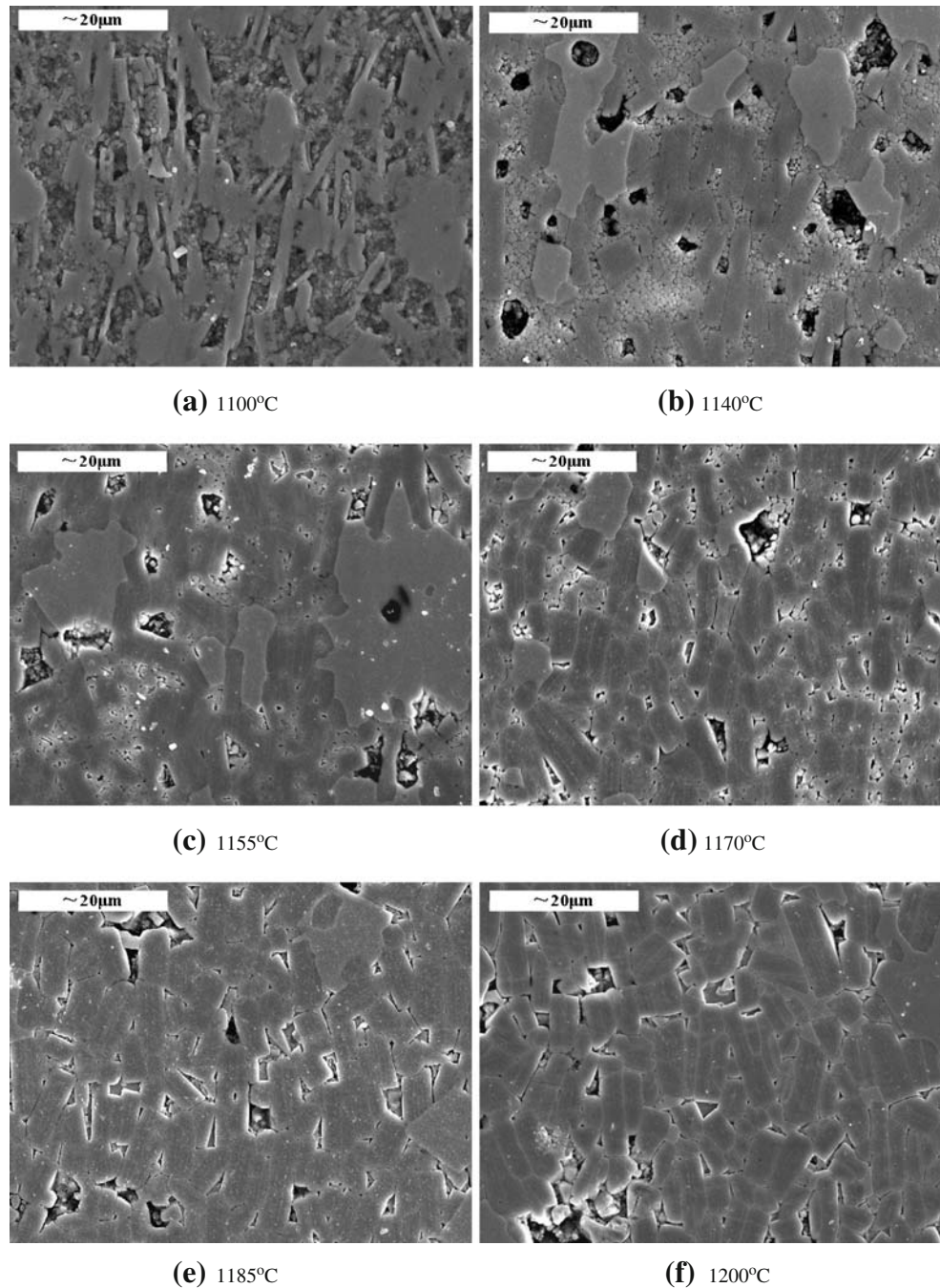
Fig. 4 Texture fraction of NBTBT textured ceramics

1140 °C. But f increases as the sintering temperature increases and the largest volume (0.62) is present at 1185 °C. A more textured material is present with increasing sintering temperature from 1140 °C to 1185 °C, and NBTBT ceramics sintered at 1185 °C have significant grain orientation.

Figure 5 shows the microstructure of NBTBT ceramics with polished plane perpendicular to the tape casting direction. All specimens are composed of two types of NBTBT grains. One is a strip-like grain, which originates

from plate-like BNN particles. It can be seen that the plate face is parallel to the casting plane, and the thickness is larger than that of the original BNN templates. The other is a fine, equiaxed shaped grain. These two grain types are called oriented and matrix grains, respectively. It is clear that NBTBT ceramics are not well sintered at 1100 °C, and many pores are present in the microstructure, as shown in Fig. 5(a). The thickness of the oriented grains increases as the sintering temperature increases. The matrix grains also grow and their shapes change to cubic above 1155 °C. It is

Fig. 5 Microstructure of NBTBT textured ceramics sintered at different temperatures (a–f)



revealed that NBTBT ceramics are well sintered at 1185 °C. The size and uniformity of the grains are clearly seen with increasing temperature, and at the same time, the grains grow with apparent orientation.

In our early research, the effects of the BNN template concentration (10 wt.%, 15 wt.%, 20 wt.%, 30 wt.%) on the orientation of NBTBT ceramics have been investigated. The results showed that the texture fraction of NBTBT textured ceramics increase with increasing the content of BNN. Textured ceramics with the maximum orientation factor were obtained when the content of plate-like BNN was 30 wt.%. For BNN template particles, Bi³⁺ and Na⁺ are involved in the composition of matrix ceramics. Only Nb⁵⁺ is extra ion and will result in composition fluctuation. EDS was taken for the matrix grain and the results show that the Nb content in the matrix phase is 10.16% (Atomic%). So we deduced that some of the BNN were dissolved into the matrix phase. Most of the grains grow by spontaneous nucleate along the existing interfaces of the templates. It is found that a brick-wall microstructure with grain size up to 13 μm in length and 4 μm in thickness was obtained in the NBTBT ceramics, as shown in Fig. 5(e) and (f).

Figure 6 shows XRD patterns of NBTBT textured ceramics sintered at 1185 °C with different soaking times. It is seen that NBTBT and BNN phases coexist in the ceramics. The (200) peak is the main intense peak in the ceramics. Although an 8 h soaking time is longer enough, BNN templates are not consumed completely. The results show that increasing the soaking time cannot eliminate the BNN phase. Figure 7 shows the effect of soaking time on the degree of orientation of NBTBT ceramics. The degree of orientation increases as the soaking time increases and the largest volume is 0.69 at 6 h.

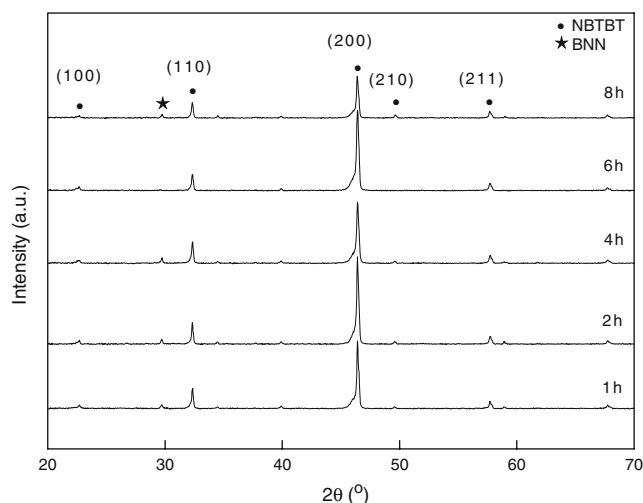


Fig. 6 XRD patterns of NBTBT textured ceramics with different soaking times

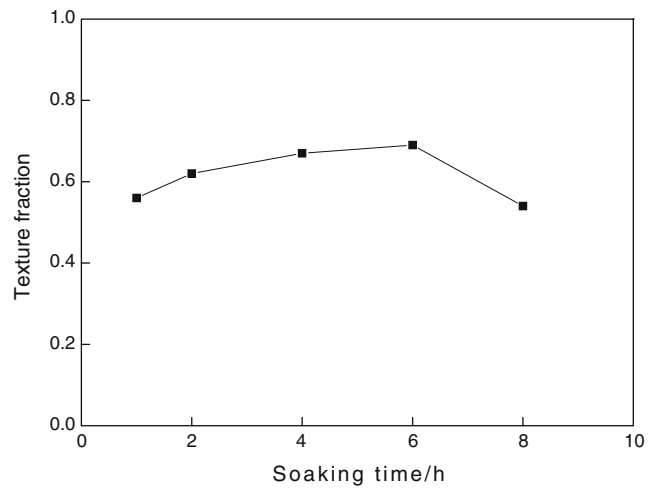


Fig. 7 Texture fraction of NBTBT textured ceramics with different soaking times

The crystallization of ceramics is a complex process that may proceed in several stages. These stages can consist of nucleation and crystal growth which are controlled by short-range diffusion or chemical reaction interface or by phase separation, structural relaxation or long-range diffusion and viscous flow, etc. In a strict sense, the real kinetics of these processes can only be fully described on the basis of a fundamental understanding of the respective elemental processes. It is usually difficult to describe such simultaneous processes separately. Conventionally, Burke and Turnbull proposed the parabolic law of grain growth to describe the grain growth characteristics of metallic materials, but it is limited to the temperature range near the melting point [15]. So, a general grain growth equation was then developed as follow:

$$G_t^n - G_0^n = k_0 t \exp\left(-\frac{Q}{RT}\right) \tag{4}$$

where G_t is the grain size, G_0 is the original particle size, n is the grain growth exponent, t is the sintering time, Q is the grain growth activation energy, k_0 is the grain growth rate constant, and R is the general gas constant. The values of n and Q are the most important two factors in the grain growth kinetic formula. Equation 4 can be transformed into Eq. 5 by logarithmizing the two sides.

$$\ln(G_t^n - G_0^n) = \ln k_0 + \ln t - \frac{Q}{RT} \tag{5}$$

Because G_0 is always much smaller than G_t , Eq. 5 is simplified as Eq. 6 by omitting G_0 .

$$\ln(G_t^n) = \ln k_0 + \ln t - \frac{Q}{RT} \tag{6}$$

Table 1 The average grain size of matrix grain and strip-like grain in textured NBTBT ceramics.

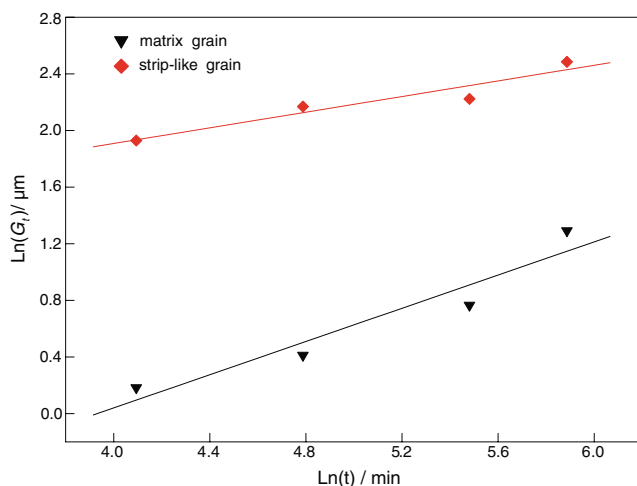
Sintering temperature/°C	Texture fraction	Matrix grain size/ μm	Oriented grain size/ μm	
			Length	Thickness
1100	/	0.77	8.24	1.53
1140	0.18	0.87	9.44	2.80
1155	0.25	1.07	9.74	3.76
1170	0.35	1.24	10.87	3.88
1185	0.62	2.30	12.90	4.16
1200	0.51	2.96	12.33	3.42

In order to determine the values of n and Q , Eq. 6 is described by the following equation:

$$\ln(G_t) = \frac{1}{n} \bullet \ln t + \frac{1}{n} \ln k_0 - \frac{Q}{nRT} \quad (7)$$

From Eq. 7, $\ln G_t$ is linearly proportional to $\ln t$ when sintering temperature T is determined. The n value can be acquired from the slope ratio. The grain growth exponent n stands for the grain growth mechanism. An n value equal to 2 indicates that grain growth is controlled by the grain boundary curvature mechanism, an n value equal to 3 indicates that grain growth is controlled by the lattice diffusion mechanism, and, an n value equal to 4 indicates that grain growth is controlled by the grain boundary diffusion mechanism [15].

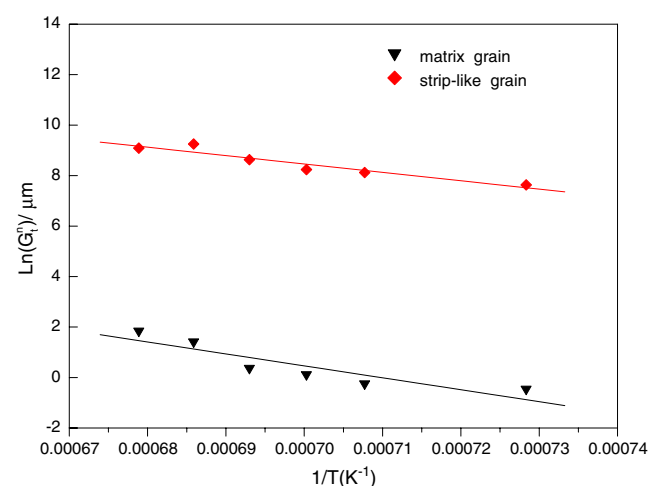
Textured NBTBT ceramics are composed of strip-like grains and matrix grains. The kinetics of the two different types of grain should be discussed separately. The average grain sizes were measured from 30 grains taken from at least three SEM micrographs from the same sample, as shown in Table 1. It was found that the matrix grain sizes

**Fig. 8** Plots of $\ln G_t$ versus $\ln t$ for NBTBT textured ceramics**Table 2** Kinetic exponent n and activate energy Q of matrix grain and strip-like grain.

	Matrix grain	Strip-like grain
n	1.71	3.62
Q (KJ/mol)	393.4	276.3

increased from 0.77 to 2.96 μm with rising sintering temperature. The length and thickness of the strip-like grains have the same trend. It is interesting to see that the length and thickness of the strip-like grains decreased at 1200 °C where the texture fraction also decreased to 0.51. $\ln G_t$ and $\ln t$ were calculated and Fig. 8 shows the function of $\ln G_t$ versus $\ln t$. It is obvious that either matrix grains or oriented grains show a linear relationship of $\ln G_t$ and $\ln t$. The n values of matrix grains and oriented grains were therefore calculated, and are listed in Table 2. As for the matrix grains, the n value is approximately equal to 2, indicating that the grain boundary curvature mechanism controls grain growth. Correspondingly, the n value of oriented grains is situated between 3 and 4, indicating a mixture-controlled mechanism of grain boundary diffusion and lattice diffusion.

Y. Seno and T. Tani [16] prepared textured $(\text{Na}, \text{K})_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics with plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ particles and observed that there was a rapid diffusion of Na and K atoms from the matrix into the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ template particles, changing the layered perovskite to a regular perovskite. Our research work from grain growth kinetics demonstrated that the crystal formation of textured NBTBT ceramics with plate-like templates is a diffusion–recrystallization process. Because of the similarity between the crystal structure of BNN and NBTBT, the grain orientation can start by ion diffusion at the interface. Once two-dimensional nucleation

**Fig. 9** Plots of $\ln(G_t^n)$ versus $1/T$ for NBTBT textured ceramics

has 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 the adjacent grains, finally a brick-wall morphology is obtained.

Equation 6 can also be expressed as the following equation:

$$\ln(G_t^n) = \ln k_0 t - \frac{Q}{R} \cdot \frac{1}{T} \quad (8)$$

If the y -axis is set to be $\ln(G_t^n)$, and the x -axis to be $1/T$, the linear relationship of the two functions is established, in which $\ln k_0 t$ and $-Q/R$ correspond to the interceptive space and slope ratio, respectively. As shown in Fig. 9, $\ln(G_t^n)$ of the matrix grains and oriented grains were shown to be linearly proportional to $1/T$ at temperatures from 1373 K to 1473 K. The activation energy Q values of the two types of grains were calculated to be 393.4 kJ/mol and 276.3 kJ/mol, respectively. The Q value of the matrix grains is much higher than that of the oriented grains. It is suggested that the oriented grains are easier to grow. The driving force for grain growth comes from the size difference between the template particles and the matrix particles. In the sintering stage, the plate-like grains oriented parallel to the (h00) planes form low-energy grain boundaries, and are not easily consumed. Some of them can grow to a large size and eventually remain in the final product. In contrast, the fine matrix grains are misaligned and 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.

Therefore, the grain growth kinetic formula of the matrix grains is given by:

$$G_t^{1.71} = k_0 t \exp\left(-\frac{393.4}{RT}\right) \quad (9)$$

The kinetic equation of the strip-like grains is established as:

$$G_t^{3.62} = k_0 t \exp\left(-\frac{276.3}{RT}\right) \quad (10)$$

4 Conclusions

Textured NBTBT ceramics were fabricated by the RTGG method with plate-like BNN template particles. The results show that textured ceramics were successfully obtained with an orientation factor of more than 60%. NBTBT

specimens are composed of strip-like grains and equiaxed shaped grains. The textured ceramics have a microstructure with strip-like grains aligned in the direction parallel to the casting plane and exhibit an {h00} preferred orientation. The degree of grain orientation increases initially, then decreases with increasing sintering temperature and soaking time. A sintering temperature of 1185 °C and soaking time of 6 h are the optimal sintering conditions, where the maximum texture fraction of 0.69 is obtained. The kinetic exponent n and activation energy Q of the two types of grain in textured NBTBT ceramics were calculated. The n and Q values of matrix grains and strip-like grains are 1.71 and 3.62, 393.4 kJ/mol and 276.3 kJ/mol, respectively. The grain growth mechanism of oriented grains is controlled by grain lattice diffusion and grain boundary diffusion. The mechanism of matrix grain growth is mainly controlled by the grain boundary curvature. Finally, the kinetic equations for strip-like grains and matrix grains have been established.

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