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Fabrication of $(BiNa)_{0.5}TiO_3$–$BaTiO_3$ textured ceramics by tape casting

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Abstract The textured $(BiNa)_{0.5}TiO_3$–$BaTiO_3$ ceramic with a preferred ⟨*h*00⟩ orientation was fabricated by tape casting with the plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BINN5) particles as template. Effects of processing parameters and the content of template on the microstructure and the texture fraction of NBT-based ceramics were investigated. The results show that the texture fraction increases with increasing sintering temperature and the increasing content of BINN5. The increased sintering temperature and BINN5 content result in the grain size and the grain shape changing from irregular to plate like. These factors were responsible for the increased degree of orientation. The texture fraction had a maximum value when the sintering temperature is 1225 °C and the optimal content of template is 20 wt.%.

Introduction

It is imperative under the situation of increasing environmental protection worldwide that investigating of lead-free piezoelectric ceramics to replace traditional piezoelectric ceramics has become a subject with significant social and commercial value. However, the key issue in this research field is that how to improve the piezoelectric properties of the ceramics. There are two approaches to develop lead-free ceramics with excellent piezoelectric properties. The first approach is to search for new compositions. The second approach is to improve the microstructure of ceramics with known compositions [1]. Even though single crystal displays high electrical and electromechanical performance the cost is very high. If low-cost lead-free piezoelectric textured ceramics with anisotropic property could be prepared by physical design, which made the ceramic grains grow along the preferred orientation, the excellent piezoelectric property which is similar to the single crystal could be expected.

Reactive-templated grain growth (RTGG) method uses the mixture of precursor particles with shape anisotropy and equiaxed particles that react with the precursor to form the object material. The template selection for texture ceramics should obey the following rules: (1) Template with large anisotropy dimension should be easily 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. The improvement of piezoelectric properties by grain orientation has been reported in the literature [2–8]. In recent years, $(BiNa)_{0.5}TiO_3$ sodium bismuth titanate has been widely attracting attention of researchers, which is one of the most important candidate materials to replace lead-based piezoelectric ceramics.

In this article, the textured $(BiNa)_{0.5}TiO_3$–$BaTiO_3$ ceramic was prepared using RTGG method. Plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BINN5) was chosen as template particle as it perfectly obeyed the rules for selecting template. BINN5 was prepared by NaCl–KCl molten salt synthesis (MSS). The ferroelectric and piezoelectric $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ ceramics was fabricated by tape casting. Effects of

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processing parameters and the content of template on the microstructure and the texture fraction of NBT-based ceramics were investigated.

Experimental procedure

The general formula of the material studied was $0.92(BiNa)_{0.5}TiO_3$–$0.08BaTiO_3$ (NBT-BT). Reagent-grade Na_2CO_3, $BaCO_3$, Bi_2O_3, and TiO_2 were adopted as raw materials. The plate-like BINN5 particles with shape anisotropy were prepared by KCl–NaCl MSS. Figure 1 shows the scanning electron microscopy (SEM) and XRD patterns of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ powders. The microstructure of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ particles with 10 μm in radial dimensions and 1 μm in thickness are shown in Fig. 1a. From Fig. 1b, there is only a spot of Nb_2O_5 phase existed in the staple and the main phase is BINN5, after MSS. NBT-BT powder was synthesized first. All the powder was mixed and ball milled for 12 h and then calcined at 880 °C for 2 h. The organic solvent, binder, plasticizer, and surface active agent were added after second ball milling. BINN5 (template) was mixed into the slurry for tape casting after 60 h of ball milling with the mixture. The content of BINN5 was 10, 15, 20, and 30 wt.% designated as N1, N2, N3, and N4, respectively. Tape casting was performed on a plated steel surface with blade gap of 30 μm. After 24 h of drying at room temperature, the green tapes were cut, laminated, and pressed to prepare a green compact of 12 × 12 mm^2 with 1.5 mm in thickness. The green compact was heated at about 500 °C for binder burn-out, then sintered at 1170–1250 °C. Figure 2 shows the sketch map of NBT-based ceramics which were prepared by tape-casting process; the direction of *b*-axis parallel to the tape-casting direction was the orientation of the template particles in matrix.

The crystal structure and the texture fraction were confirmed by X-ray diffraction analysis (XRD, X'pert MPD PRO, Holland). The microstructure of the polished and thermally etched samples was observed by SEM (JEM5800).

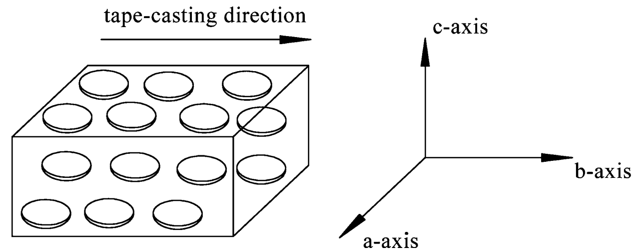
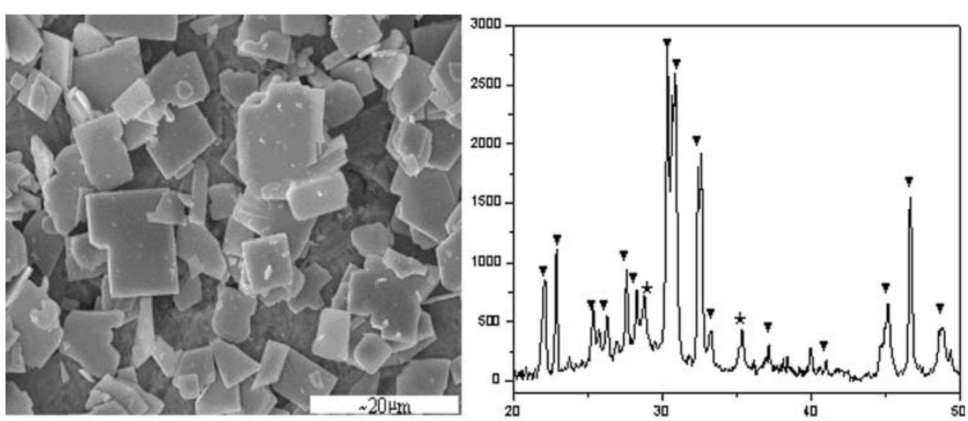


Fig. 2 The sketch map of NBT-based ceramics

Results and discussion

Influence of sintering temperature on microstructure

Figure 3 shows the effect of sintering temperature on the microstructure of textured NBT ceramics (N3) heated at 1170–1250 °C. The specimen sintered at 1170 °C was composed of two types of NBT grains: one was plate-like grains and the other was fine, irregularly shaped grains. The orientation of the crystal axis of these fine grains was random. These two types of grains are called oriented and matrix grains, respectively. The thickness of oriented grains increased as the sintering temperature increased. The matrix grains also grew and their shape changed to plate like above 1200 °C, which originated from plate-like BINN5. When the sintering temperature is above 1200 °C, the matrix grains started to react with template grain. On the other hand, the NBT ceramics needs high sintering temperature, more than 1200 °C, to obtain a dense body. Figure 3c shows the plate-like grains that had grown gradually with obvious orientated growth tendency and the descending porosity. At 1250 °C, the grains changes to equiaxed grains, orientated growth tendency descends compared to the condition at 1225 °C, and the density also descends.



(a) SEM micrographs (×2000) **(b)** XRD patterns

Fig. 1 SEM micrographs and XRD patterns of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ powders

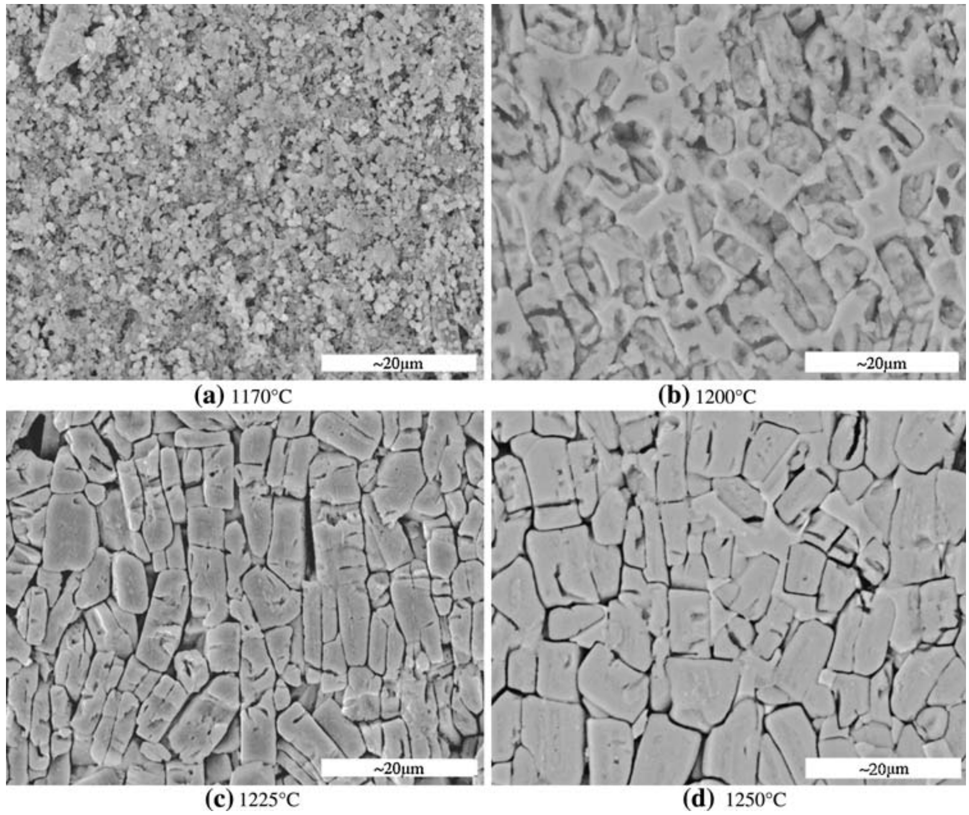


Fig. 3 SEM micrographs of textured NBT ceramics sintered at different temperatures (×2000)

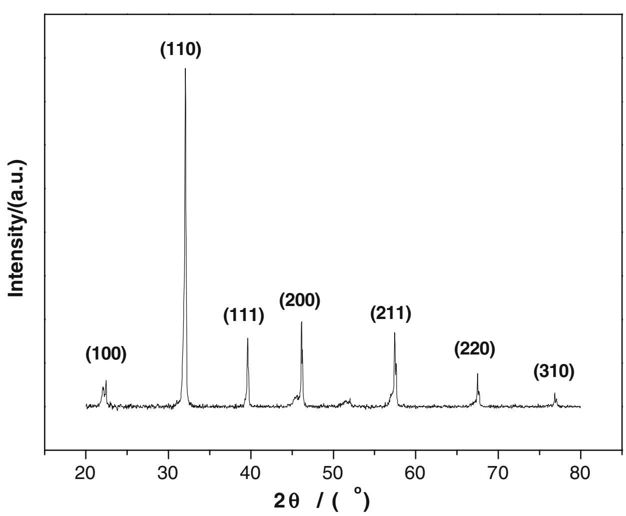


Fig. 4 XRD patterns of pure NBT-BT ceramics

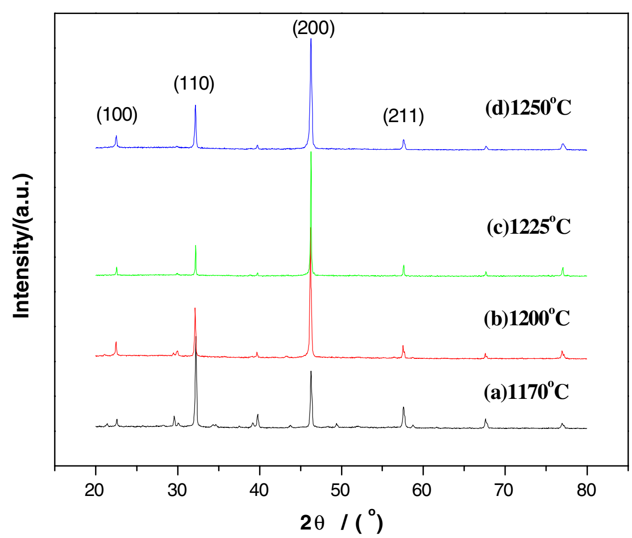


Fig. 5 XRD patterns of N3 ceramics with different sintering temperatures

Figure 4 shows the XRD pattern of pure NBT-BT-based ceramics; the structure of NBT-BT-based ceramics is perovskite and the most intense peak is (110) peak. Figure 5 shows the XRD patterns of N3 ceramics at different sintering temperatures. At 1170 °C, the subsequences of the main peak and the second main peak are opposite compared to the samples that sintered at other temperatures. The intensity of (110) peak drops down when the temperature steps up. The (200) peak becomes the most intense one when the sintering temperature is higher than 1200 °C; therefore, it is proved from the texture with different stages shown in NBT-based ceramics at sintering temperatures 1170–1250 °C that the orientation of the grains is (*h*00). Table 1 shows the relative intensity of the (100), (200), and (110) peaks of N3 ceramic prepared at different sintering temperatures. It is obvious that the relative intensity of (200) peak at 1170 °C is 61.4%, which is

Table 1 Relative intensity of XRD peaks of NBT ceramics sintered at different temperatures

Peaks	1170 °C	1200 °C	1225 °C	1250 °C	Unoriented NBT ceramics
(100)	8.40	11.84	7.77	10.19	10.51
(110)	100.00	41.05	25.38	38.36	100.00
(200)	61.40	100.00	100.00	100.00	26.32

much higher than that of the unoriented NBT ceramics (26.32%). It means that some grains have been oriented in the matrix at 1170 °C and (*h*00) preferred orientation was formed. At 1225 °C, the preferred orientation of the textured ceramic is the highest. In XRD patterns, other peaks are very low except (100), (110), and (200) peak, which are abnormally high.

Generally, texture fraction of ceramics can be evaluated by Lotgering factor *f* using the following equations [9]:

$$f = \frac{p - p_0}{1 - p_0} \tag{1}$$

$$p = \frac{I_{(100)} + I_{(200)}}{\sum I_{(hkl)}} \tag{2}$$

$$p_0 = \frac{I_{0(100)} + I_{0(200)}}{\sum I_{0(hkl)}} \tag{3}$$

where I corresponds to the intensity of the XRD peak relatively and p_0 is the p value of randomly oriented ceramic. The span of f is from 0 to 1. The bigger the f is the higher is the orientation degree of the ceramic.

Lotgering factor is calculated with 2θ from 20° to 80°. The results are shown in Fig. 6. The texture fraction of NBT ceramic increases rapidly with increasing sintering temperatures. At 1225 °C, the texture fraction comes to the

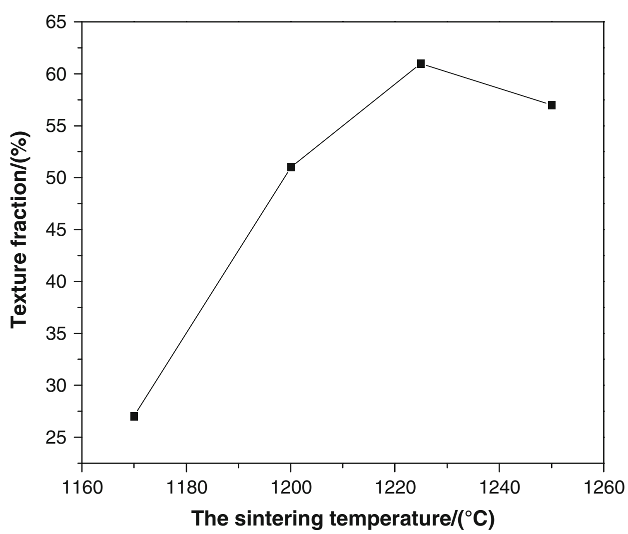


Fig. 6 Texture fraction of NBT ceramics with different sintering temperatures

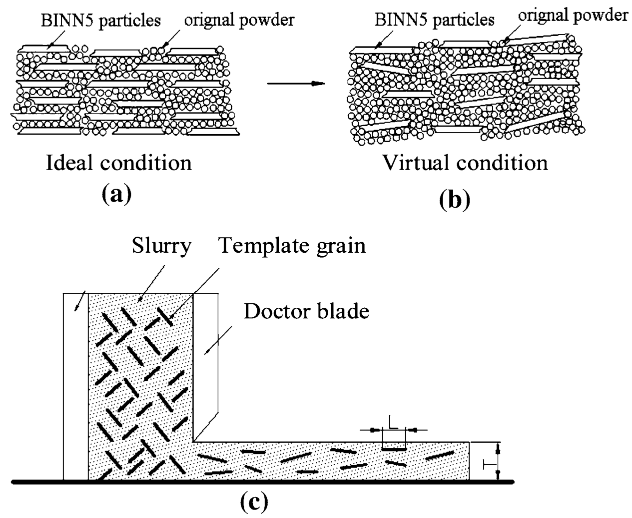


Fig. 7 Distribution state of the crystal template in bulk

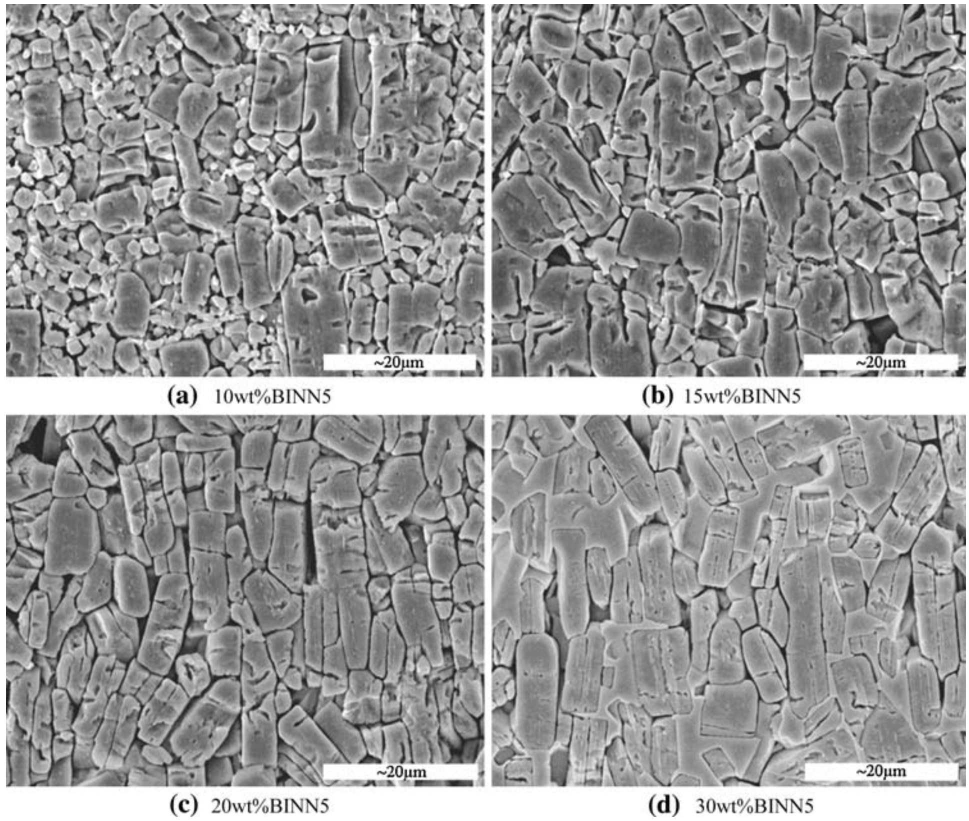
maximum value (~0.61) but it drops when the sintering temperature is higher.

Figure 7 shows the arrangement of BINN5 template grains in the matrix. Figure 7a shows the ideal condition with the template grains dispersed along the horizontal direction and other particles well-distributed around. But this kind of arrangement cannot be achieved in reality, because it is impossible for the size of template grains to become regular in the synthesis process. Figure 7b shows the virtual arrangement of the template grain. Figure 7c shows the distribution of template grain in tape casting. The average size of the template grains is assumed as L, while T is the gap between the blade and steel plate. When $T \gg L$, the template grains are distributed randomly in the tapes, the texture fraction of the ceramic drops to 0. When $T > L$ and the inequality between them is not obvious, the template grains distribution in tapes is as shown in Fig. 7b, and the textured ceramics are formed after sintering. The optimal sintering temperature of the textured NBT ceramic is 1225 °C.

Influence of template grains content on microstructure

Figure 8 shows the microstructure of NBT ceramics on *a–c* face with different BINN5 content. Figure 8a–d correspond to N1–N4, respectively. Strip-like grains are observed in all the four compositions obviously. At 1225 °C, every composition with different BINN5 content access to the growing period rapidly. A great amount of equiaxed grains with small size are present in N1 sample (Fig. 8a). It shows that 10 wt.% BINN5 template grains which are added to the matrix for reaction is deficient. The size and uniformity of the grains are manifested obviously with the increasing

Fig. 8 SEM micrographs of NBT ceramics with different BINN5 content (×2000)



template grains content, at the same time, the grains grow with orientation apparently (Fig. 8b–d). The grains with larger size in matrix are resulted from the content of BINN5 template grains, and most of the grains grow along the existing interface of template grains besides the grains spontaneously nucleating themselves. Therefore, the grains grow larger in size gradually.

Figure 9 shows the XRD patterns of NBT ceramic with different BINN5 content when sintered at 1225 °C for 2 h. The most intense peak of NBT ceramic is (200) when BINN5 template grains are added. Compared to Fig. 4, the preferred orientation of the grains are shown, the intensity of (200) peak increases when the BINN5 content increases, while (110) peak decreases when the content of BINN5 is more than 20 wt.%.

The texture fraction is calculated and shown in Fig. 10; it increases gradually (from 0.41 to 0.61) with increasing

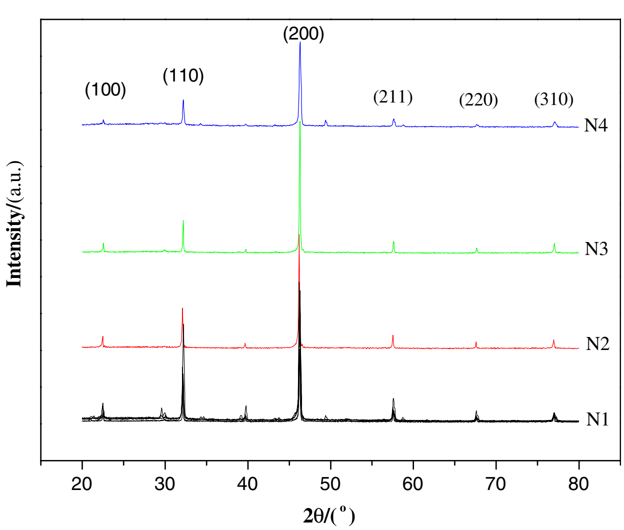


Fig. 9 XRD patterns of NBT ceramics with different BINN5 content

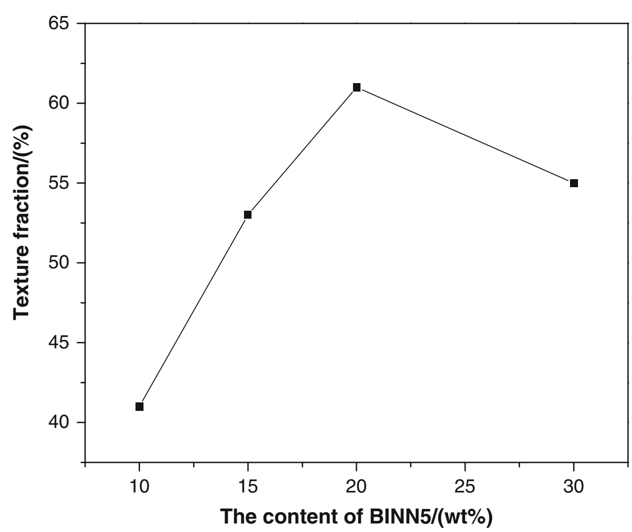


Fig. 10 Texture fraction of NBT ceramics with different BINN5 content

BINN5 content from 10 to 20 wt.%. When the template content is 30 wt.%, the texture fraction reduces to 0.57, because the excessive volume fraction of template grains prohibit the preferential growth of the matrix grains. To summarize, the optimal content of BINN5 template grains is 20 wt.%.

Conclusions

The textured $(BiNa)_{0.5}TiO_3$–$BaTiO_3$ lead-free piezoelectric ceramics was prepared successfully by tape casting with the plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BINN5) particles as template. With increasing sintering temperature, the density and the size of the grains also increase. The texture fraction of NBT-based ceramics first increased then decreased when the temperature is higher than 1225 °C. The texture fraction of NBT ceramics were first increased then decreased with the increasing content of BINN5. The texture fraction has a maximum value (0.61) at the sintering temperature of 1225 °C and the optimal content of template is 20 wt.%.

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