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Influence of different templates on the textured $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ piezoelectric ceramics by the reactive templated grain growth process

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Abstract

One-dimensional TiO_2 whiskers were used first time as templates to fabricate grain-oriented $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ ($x = 0.15$) (BNKT) piezoelectric ceramics with the reactive templated grain growth process. The influences of sintering temperature and the template concentration on the orientation of BNKT were investigated. The orientation factor along ($h\,0\,0$) direction was only 26.41% since the fibrous TiO_2 particles on the surface were aligned along the extrusion direction while many randomly oriented particles were in the middle of the rods. The reaction and crystal formation of BNKT ceramic from fibrous TiO_2 templates is a dissolution–recrystallization process on its surface and the dissolution of fibrous TiO_2 templates is detrimental to the grain orientation. The orientation factor of more than 70% was obtained successfully when the plate-like $Bi_4Ti_3O_{12}$ was used as the templates using a tape casting process. The reaction and crystallization of the two kinds of templates in the whole sintering process were discussed and the grain orientation mechanism was also elucidated in this paper.

Keywords: $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$; Lead-free piezoelectric ceramics; TiO_2 whisker; Plate-like $Bi_4Ti_3O_{12}$; RTGG

1. Introduction

In recent years, the investigations of lead-free piezoelectric ceramics have been desired due to environmental concerns. But compared with the conventional used PZT piezoceramics, present lead-free ceramics showed poor piezoelectric properties, which has restricted the applications of the lead-free piezoceramics. There are two approaches to enhance the piezoelectric properties of lead-free ceramics, one is to search for new compositions [1], and the other is to tailor the microstructure of ceramics with known composition. For the latter, grain orientation is an important technique to improve ceramic performance. Due to the randomly oriented grains in the ferroelectric polycrystal ceramics, the spontaneous polarization can not be all aligned along the poling direction as that of single crystals even under ideal conditions. Therefore, it is expected that enhanced piezoelectric properties reach to its single crystals could be obtained through the grain orientation processes.

At present, successful results have been reported for the textured ceramics with anisotropic crystal structure such as bismuth layer-structured ferroelectrics [2,3]. But the preparation of dense and highly textured polycrystal ceramics was limited for one kind of important materials with perovskite structure due to its high crystal symmetry. However, the excellent piezoelectric properties of their single crystals suggested that the textured bulk polycrystals could exhibit high performances with a low production cost.

Bismuth sodium potassium titanate ($Bi_{0.5}(Na_{1-x}K_x)_{0.5}$-$TiO_3$, BNKT) ceramic is an attractive solid solution as a lead-free piezoelectric with the perovskite structure [4]. Tani et al. proposed the reactive templated grain growth (RTGG) method to prepare grain oriented BNKT ceramics [5]. In his study, green sheets were prepared by tape-casting of a mixture of Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2, and plate-like $Bi_4Ti_3O_{12}$ (BIT), and then sintered. Plate-like BIT particles align parallel to the casting direction and act as templates for the grain-oriented BNKT. Significant improvement of piezoelectric properties by the alignment of dipoles was also reported [6].

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In the present study, one-dimensional TiO_2 whiskers were used as templates to fabricate grain-oriented BNKT ceramic with RTGG method for the first time. The influences of sintering temperature and template concentration on the orientation of BNKT were investigated. Meanwhile, the plate-like $Bi_4Ti_3O_{12}$ was also used as templates and the different effects of the two kinds of templates were discussed. The reaction and crystal structure formation in the entire sintering process were discussed. The X-ray diffraction and scanning electron microscopy were employed to characterize the grain orientation and microstructure of the ceramics. The grain orientation mechanisms were also discussed.

2. Experimental

2.1. Fabrication of textured BNKT ceramics from TiO_2 whisker templates

Fibrous TiO_2 particles were prepared from potassium tetratitanate (Hongjie Co., Wuxi, China), which possesses fibrous morphology prepared by a kneading–drying–calcining process. Ten gram of the $K_2Ti_4O_9$ powder was suspended in 200 cm^3 of 1 M HCl for 3 days at room temperature, and the acid solution was changed everyday in order to remove alkaline completely from the compound. The powder was filtrated and washed with deionized water several times until the pH value of the effluent was 6–7. The resulting product was dried in air at 80 °C overnight and then heated to 550 °C for 2 h. The fibrous TiO_2 with length of 2–15 μm and diameter of 0.2–2 μm was shown in Fig. 1a.

Analytical grade Bi_2O_3, TiO_2, Na_2CO_3, and K_2CO_3 were used as raw materials. Firstly, the raw materials mixed with ethanol and ball milled for 24 h. The fibrous TiO_2 was then added and mixed for another 0.5 h and dried. The mixture was further mixed with an ethanol solution of poly(vinyl butyral) and kneaded by roll mixer. Then, they were extruded through a die having a hole with a diameter of 1 mm. After drying, they were cut into rods with 10 mm long and compacted. The rods compacts were heated at 600 °C for 5 h to remove the binder and further sintered at various temperatures 1000–1200 °C in air.

2.2. Fabrication of textured BNKT ceramics from plate-like BIT templates

Plate-like BIT particles were prepared from Bi_2O_3 and TiO_2 using molten salt synthesis at 1050 °C for 1 h with NaCl–KCl mixture in the molar ratio 1:1 (weight ratio of oxides to salt = 1:1) [7]. The product was washed with deionized water more than 20 times to remove NaCl and KCl. The plate-like BIT particles with an average diameter of 5 μm and a thickness <0.5 μm were obtained (as shown in Fig. 1b).

The textured BNKT ceramics were prepared by tape casting according to literature [6]. The plate-like BIT (supplied 20% titanium) was mixed with raw materials. Polyvinyl and plasticizer were added to the starting mixtures and green sheets were prepared by tape-casting. Several green sheets were stacked and heated at 700 °C for 3 h to remove organic ingredients and further sintered at high temperatures in air.

2.3. Microstructural characterizations

The crystal structure and grain orientation were determined by the X-Ray Diffractometer (XRD) on the major surfaces of sintered ceramics. The analysis was performed at 40 kV and 100 mA with Ni-filtered Cu-K_α radiation (Rigaku D/max 2550V), 2θ in the range of 20–60° with a step of 0.02°. The microstructure of sintered ceramics was studied by a Field Emission Scanning Electron Microscopy (FE-SEM, JSM-6700F) on fracture surfaces perpendicular to the major face and parallel to the oriented direction.

3. Results and discussion

3.1. Influence of the sintering temperatures

The dimensional shrinkages (containing 20 mol% of the template) in length (parallel to the extrusion direction) and width direction (vertical to the extrusion direction) are shown in Fig. 2. It can be seen that the first largest volume appeared at 600 °C due to the evacuation of organic additives. So the samples were heat-treated at 600 °C to remove the organic

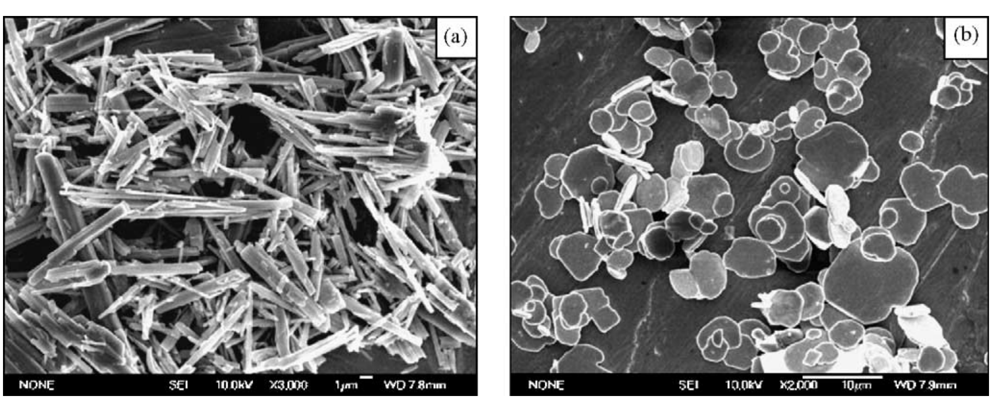

Fig. 1. The micrographs of (a) TiO_2 whisker and (b) plate-like BIT.

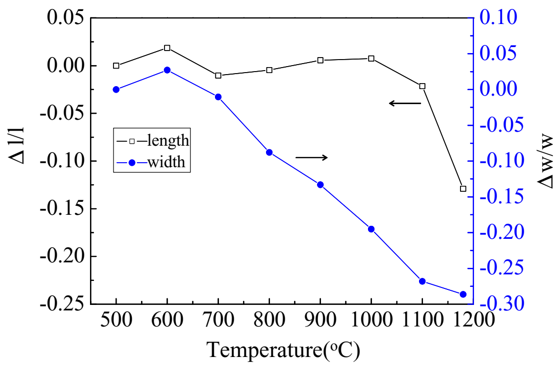

Fig. 2. The shrinkages of the ceramic in length and width directions during sintering process.

binders in the green compacts. Then, the sample shrank in both length and width directions until 700 °C. The XRD results showed that the BNKT phase was formed during this stage. The sample exhibits anisotropic shrinkages in length and width at the temperatures of 700–1000 °C. This is the evident that fibrous TiO_2 particles were initially aligned along extrusion direction in the green body. The anisotropic grains came from fibrous TiO_2 templates grew with the reaction and consumption of small matrix particles above 1000 °C. The shrinkages in both directions were increased fast above 1000 °C, which indicated that the ceramic sintering takes place. Therefore, the sintering temperature of the ceramic was determined in the range of 1100–1160 °C.

The degree of grain orientation against the sintering temperatures is shown in Fig. 3. It can be seen that relative intensities of (1 0 0) and (2 0 0) peaks of the pseudo-cubic perovskite structure increased with the increasing of the sintering temperatures. The orientation factor F along (h 0 0) direction was calculated by Lotgering's definition [8]:

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

$$P = \frac{\sum I(h\,0\,0)}{\sum I(h\,k\,l)}, \qquad P_0 = \frac{\sum I_0(h\,0\,0)}{\sum I_0(h\,k\,l)}$$

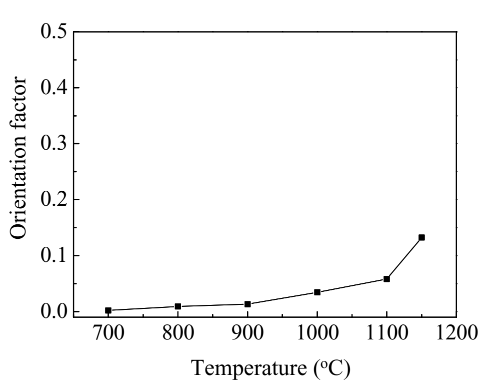

Fig. 3. The orientation factor along (h 0 0) direction against different sintering temperatures for 2 h.

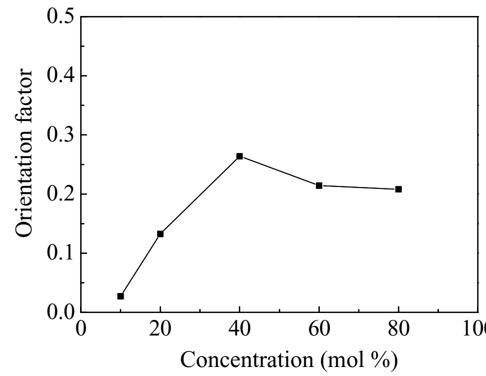

Fig. 4. The orientation factor along (h 0 0) dependence on the template concentrations at 1160 °C for 5 h.

where I and I_0 are the peak heights of the grain oriented and the randomly orientated BNKT ceramics, respectively. The F-values increased from 0 to 13.25% when the temperature increased from 700 to 1160 °C.

3.2. Influence of the template concentrations

In order to improve the orientation factor of BNKT ceramics, high concentration templates of TiO_2 fibrous in the green body were investigated. It is believed that the inter-particle interactions can influence the orientation during tape-casting process. The texture should scale inversely with the spacing between particle surfaces in the slurry [2]. It seems also fit for extrusion processing. Since the spacing of anisotropic particles depends on the template loading, the template concentration was studied as follows.

The F-value dependence on the template concentrations is shown in Fig. 4. The F-value increased from 2.73 to 26.41% when the template concentration increased from 10 to 40%. Then, the orientation factor was decreased slightly at higher concentrations. This maybe resulted from that higher volume fraction leads to lower spacing of anisotropic particles. At lower template loading, the orientation factor increased, but at higher template loading, the orientation factor has no large improvement.

3.3. Comparison with two types of templates

It is questionable that higher orientation factor cannot be obtained using fibrous TiO_2 templates. In order to elucidate the different effects of the templates, the plate-like BIT was used. Fig. 5 shows the XRD patterns of BNKT ceramics prepared from different templates. The higher orientation factor along (h 0 0) direction of more than 70% was obtained using plate-like BIT as template. The microstructure of the fracture surfaces of sintered ceramic is shown in Fig. 6. When fibrous TiO_2 was used as template, only a small part of grains aligned along the extrusion direction and many randomly oriented grains were surrounding them. On the contrary, from the microstructure of the ceramic from plate-like BIT

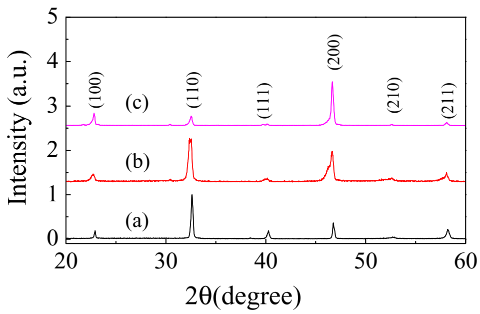

Fig. 5. XRD patterns of BNKT ceramics from different templates: (a) without template; (b) TiO_2 whisker; (c) plate-like BIT at 1160 °C for 5 h.

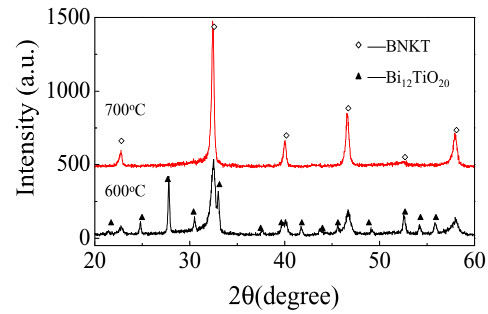

Fig. 7. XRD patterns of the specimen from fibrous TiO_2 template calcined at different temperatures.

as template, nearly all the grains are elongated and aligned themselves along the casting direction face-to-face.

3.4. Different reactions during the sintering process

The reaction and crystallization of BNKT ceramics from two kinds of templates during the entire sintering process was investigated. The XRD results are shown in Figs. 7 and 8. When using fibrous TiO_2 as template, $Bi_{12}TiO_{20}$ and BNKT phases were formed at 600 °C, and pure BNKT single phase was formed completely at 700 °C. This transition process is similar to that of the hydrothermal synthesis [9]. No obvious orientation can be observed at this sintering temperature. However, in the case of BIT as template, there is no other intermediate phase appeared in the sintering process rather than original BIT and resulted BNKT structures. Dominant BNKT phase was not formed until 800 °C, and the single phase was formed at above 900 °C. Obvious crystal orientation was observed at this temperature as shown in Fig. 8.

As mentioned above, BNKT crystal formation during sintering process in the system using fibrous TiO_2 as template is proposed as follows:

$$TiO_2\ (\text{fibrous}) + 6Bi_2O_3 \rightarrow Bi_{12}TiO_{20} \tag{1}$$

$$Bi_{12}TiO_{20} + 23TiO_2 + 6(1-x)Na_2CO_3 + 6xK_2CO_3 \rightarrow 24Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3 + 6CO_2 \tag{2}$$

$$4TiO_2\ (\text{raw material}) + Bi_2O_3 + (1-x)Na_2CO_3 + xK_2CO_3 \rightarrow 4Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3 + CO_2 \tag{3}$$

where fibrous TiO_2 reacted firstly with Bi_2O_3 and formed $Bi_{12}TiO_{20}$. Then, it reacted and converted into BNKT with the fibrous morphology. The reaction (3) formed equiaxed BNKT grains.

In the case of plate-like BIT template, BNKT was formed by the following reactions:

$$BIT + 2(1-x)Na_2CO_3 + 2xK_2CO_3 + 5TiO_2 \rightarrow 8Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3 + 2CO_2 \tag{4}$$

$$4TiO_2\ (\text{raw material}) + Bi_2O_3 + (1-x)Na_2CO_3 + xK_2CO_3 \rightarrow 4Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3 + CO_2 \tag{5}$$

Reaction (4) formed plate-like BNKT particles with the crystallographic ⟨1 0 0⟩ direction perpendicular to the plate face and no intermediate phase was formed. Reactions (3) and (5) were the same and formed equiaxed BNKT grains with random orientation.

3.5. Orientation mechanism

Compared with BIT, in the system containing fibrous TiO_2 template, no obvious crystallographic orientation can be observed when the single BNKT phase formed. This

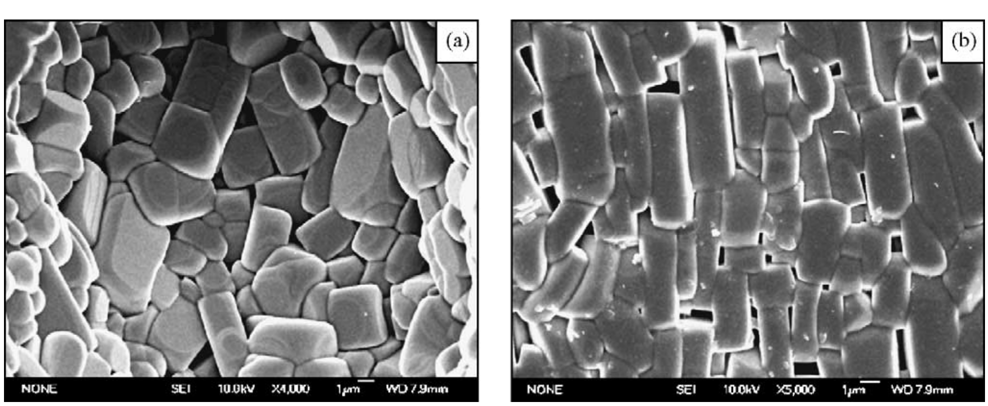

Fig. 6. The fracture micrographs of the BNKT ceramics from (a) TiO_2 whisker, and (b) plate-like BIT as template sintered at 1160 °C for 5 h.

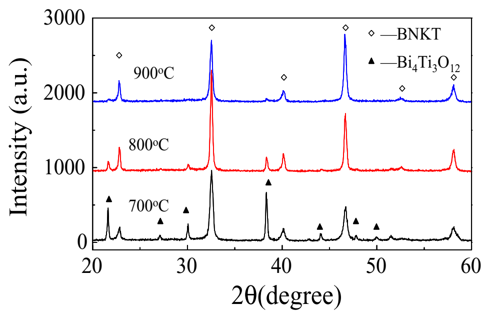

Fig. 8. XRD patterns of the specimen from plate-like BIT template calcined at different temperatures.

may be explained by the appearance of $Bi_{12}TiO_{20}$ phase. This indicated that the process of BNKT formation is a dissolution–recrystallization process. At low temperature, $Bi_{12}TiO_{20}$ phase was formed first because of lower titanium solubility. This process could result in the dissolution of fibrous TiO_2 template, which is detrimental to the grain orientation growth. Even though the template concentration was increased to 80%, no evident increase of grain orientation was seen. Due to the larger particle size of the template (compared with the raw materials), dissolution–recrystallization process mainly occurred on its surface. In the inner of TiO_2 template, BNKT was formed through in-situ transformation process at higher temperature. Hence, anisotropic grain was formed and grew larger with the consumption of smaller equiaxed particles at higher temperature. But because of the dissolution, only lower crystallographic orientation can be achieved.

Owing to the low reactivity of BIT, no dissolution of BIT was occurred at low temperature and no intermediate phase was formed. Moreover, because of the similarity between structures of BIT and BNKT, the grain orientation can start by the solid phase heteroepitaxy growth, followed by the topotactic conversion of BIT into BNKT at the interface. Hence, the orientation factor increased with the growth of the oriented grains and the effect on adjacent grains.

It can be concluded that the template selection should match following rules: (1) large anisotropic dimension compare to the raw materials; (2) low reactivity that ensure no dissolution process occurring at low temperature; (3) crystallographic similarity with the final product that ensure the solid phase heteroepitaxy and topotactic transformation.

4. Conclusion

One-dimensional TiO_2 whiskers were used as template to fabricate grain-oriented BNKT with RTGG method for the first time. The highest orientation factor by this process was only 26.41%. However, more than 70% orientation factor was achieved by using plate-like BIT templates. The reaction and crystal formation of BNKT ceramic from fibrous TiO_2 templates is a dissolution–recrystallization process on its surface. The dissolution of fibrous TiO_2 templates is detrimental to the grain orientation growth. However, in the case of BIT templates, the grain orientation starts with the solid phase heteroepitaxy and follows with the topotactic growth convert BIT into BNKT at the grain interface. Finally, it is proposed that the suitable template to get highly textured piezoceramics should possess the following characters: (1) large anisotropic dimension compare to the raw materials; (2) low reactivity to ensure no dissolution process occurring at mediate sintering temperature; (3) similar crystal structure with the final ceramic.

Acknowledgements

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