ABS-064: Grain oriented $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ piezoceramics prepared by the screen-printing multilayer grain growth technique

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Abstract The texture control of polycrystalline ceramics is an important and effective way to improve the piezoelectric properties of lead-free ceramics without drastically changing the composition of the ceramics. The screen-printing multilayer grain growth (MLGG) technique is now successfully applied to perovskite-structured lead-free piezoelectric ceramics. Grain oriented $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ (NBBT) ceramics with (100) orientation were fabricated. The influences of sintering time, heating rate, and pre-reaction at low temperature on grain orientation were studied. Highly textured NBBT ceramics ($f{\sim}92\%$) were obtained with a high heating rate. The interface between adjacent layers, which was formed by screen-printing, was the main mechanism for the texture development in MLGG technique. Compared with other grain orientation techniques, screen-printing is a simple and effective method to fabricate grain oriented lead-free piezoelectric ceramics.

Keywords Sodium bismuth titanate · Grain orientation · Screen-printing

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1 Introduction

In recent years, with the growing concern for global environmental protection, lead-free materials have gained much attention increasingly. Sodium–bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (abbreviated as NBT) is one of the most important lead-free piezoelectric materials with perovskite structure (ABO_3-type) discovered by Smolenskii et al. in 1960 [1]. The NBT composition with a strong ferroelectricity and high Curie temperature $T_c=320$ °C has been considered to be a promising candidate to substitute lead-based materials, e.g. PZT, which have been widely used for ultrasonic generators, actuators, filters and other electronic devices [2–4]. However, the piezoelectric performance of NBT-based lead-free ceramics is inferior to that of lead containing ceramics, and thus microstructure control as well as composition design is required to develop ceramics with excellent piezoelectric properties, which are comparable to those of lead-based ceramics. Although there have been continuous efforts to develop new lead-free piezoelectric ceramics systems for years, no effective alternatives to PZT ceramics have been found yet [5–8].

Texture control of polycrystalline ceramics is an important approach to improve the piezoelectric properties of lead-free materials without drastically changing the composition of the ceramics [9–12]. Formation of solid solution often improves the room temperature piezoelectric properties of lead-free ceramics, while it generally lowers Curie temperature T_c and therefore limits the applications. Texture control, on the other hand, hardly affects T_c as long as the ceramics retain their original compositions. Meanwhile, textured ceramics have additional advantages over single crystals in terms of composition flexibility and uniformity in a wide range of solid solutions besides lower production costs.

The screen-printing method has been widely used for fabricating thick-film electronic materials, such as superconductor, solar cell, ceramic films and so on [13, 14]. It has been reported by our group that BLSFs CaBi$_4$Ti$_4$O$_{15}$ lead-free piezoelectric ceramics with a high grain orientation of 94.3% were obtained by the screen-printing multilayer grain growth (MLGG) technique [15].

In this paper, textured (Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$Ba$_{0.06}$TiO$_3$ (NBBT) ceramics with (100) orientation were prepared by the MLGG technique by using plate-like Bi$_4$Ti$_3$O$_{12}$ (BIT) templates. The X-ray diffraction and electron probe microanalysis were employed to characterize the grain orientation and microstructure of the ceramics. The effects of sintering time, heating rate, and pre-reaction at low temperature on grain orientation were studied. The mechanism for grain orientation in MLGG technique using screen-printing was also discussed.

2 Experimental procedure

2.1 Synthesis of Bi$_4$Ti$_3$O$_{12}$ templates

Plate-like BIT particles were prepared from Bi$_2$O$_3$ (99.7%, SCRC, China) and TiO$_2$ (99.99%, P25, Degussa, Germany) via molten salt synthesis at 1100 °C for 30 min, using a NaCl–KCl mixture in the molar ratio 1:1 (weight ratio of oxides to salt=1:1), as reported by Kimura and Yamaguchi [16]. The product was washed with warm de-ionized water more than ten times to remove the residual salt. The BIT particles obtained were of plate-like shape, with an average diameter of 7.5 μm and thickness of 0.4 μm, as shown in Fig. 1.

2.2 Preparation of NBBT samples

NBBT ceramics were prepared by the screen-printing technique. Stoichiometrically required amounts of the oxide and carbonate powders, i.e., Bi$_2$O$_3$ (99.7%, SCRC, China),
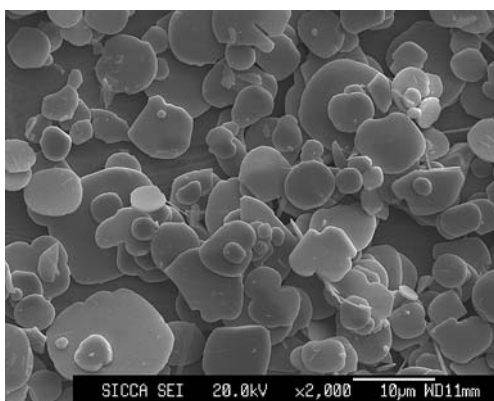

Fig. 1 The micrograph of molten salt synthesized Bi$_4$Ti$_3$O$_{12}$ platelets

TiO$_2$ (99.99%, P25, Degussa, Germany), Na$_2$CO$_3$ (99.8%) and BaCO$_3$ (99.0%, Shanghai Jinghua Scientific and Technological Research Institute, China) were thoroughly mixed with alcohol in a ball mill for 4 h, then dried and ground. The resulting milled powders were first mixed with ethyl-cellulose and α-terpineol organic vehicle in a ball mill for 2 h, and then the BIT templates were added according to the following reaction scheme:

$$Bi_4Ti_3O_{12} + Bi_2O_3 + 3Na_2CO_3 + 0.77BaCO_3 \qquad (1)$$
$$+ 9.77TiO_2 \rightarrow 12.77NBBT + 3.77CO_2$$
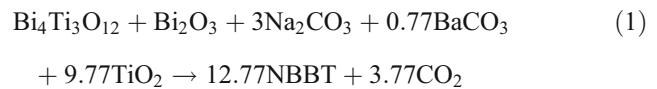
The powders, templates and vehicles were well mixed in a ball mill for 15 min to obtain NBBT slurry with a suitable viscosity and rheology for the subsequent screen-printing process. The amount of BIT particles was fixed so that 20% of the total titanium of NBBT was supplied from the template. The obtained slurry was composed of 30.5 wt% of the inorganic powders and 69.5 wt% of the organic vehicles.

With a screen printer, the slurry was forced by a blade through the open pattern in a stencil screen and deposited onto a glass substrate and then dried at 100 °C. Repeat the process 30 times until the multilayered thick film to be about 150 μm. The films was cut into 12×12 mm^2 and removed carefully from the glass substrate, then, stacked in 30–60 layers, and pressed with a pressure of 1,500–2,000 kg/cm^2 into laminates of 3–10 mm in thickness using a hydraulic pressing machine (769YP-24B, Keqi, Tianjin Keqi high-tech Co., Tianjin, China). The binder was burned out by heating at 650 °C in air for 2 h with a heating rate of 0.625 °C/min and a cooling rate of 0.8 °C/min. The laminates were then sintered at a temperature between 1150 and 1200 °C for 0.5–10 h in air. The NBBT powders prepared by the solid-state reaction method using the same starting materials were also prepared for comparison.

2.3 Characterizations

The crystalline phase and grain orientation degree were determined by X-ray diffraction (XRD) analysis (D/max 2,550 V, Rigaku, Japan) using Cu-Kα radiation with a scan speed of 4°/min and a step width of 0.02° both on the major and side surfaces of the samples. The degree of grain orientation can be calculated by Lotgering factor f, which is defined as [17]:

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

where, $p_0 = \dfrac{\sum_i I(h00)}{\sum_i I(hkl)}$, $p = \dfrac{\sum_i I^*(h00)}{\sum_i I^*(hkl)}$, and $\sum I^*$ is the sum of the XRD peak intensities for the parallel plane of the

textured sample and $\sum I$ is the sum of peak intensities in the powder diffraction pattern. The diffraction peaks between $2\theta=20$ and $60°$ were used for the calculation. The microstructure of sintered ceramics was observed using an electron probe microanalyser (JXA-8100, JEOL, Japan) on the thermal etched surface perpendicular to the oriented direction.

3 Results and discussion

3.1 Effect of sintering time on the grain orientation

Figure 2 shows the effect of sintering time on the degree of grain orientation at 1180 °C. A large degree of orientation ($f=62\%$) was obtained after soaking only 30 min. The orientation degree increased rapidly with the sintering time from 30 min to 2 h, and then slowly reached the highest value for sintering 5 h. Further increase of sintering time for more than 5 h did not increase the orientation degree.

It is known that the driving force for texture development comes from the size difference between the templates and the equiaxed grains [18]. In the initial stage, the driving force for grain growth is large, and rapid grain growth takes place. Therefore, an orientation degree of 62% was obtained after 30 min at 1180 °C. However, coarsening of equiaxed grains also occurs during the texture development. The decrease in size difference between the templates and the equiaxed grains results in a slow texture development at longer sintering times.

3.2 Effect of heating rate on the grain orientation

The orientation degree, as calculated from the Lotgering method, is plotted as a function of heating rates, as shown
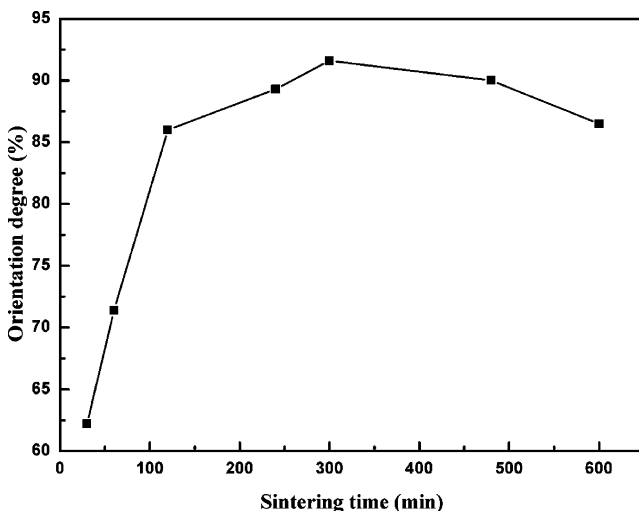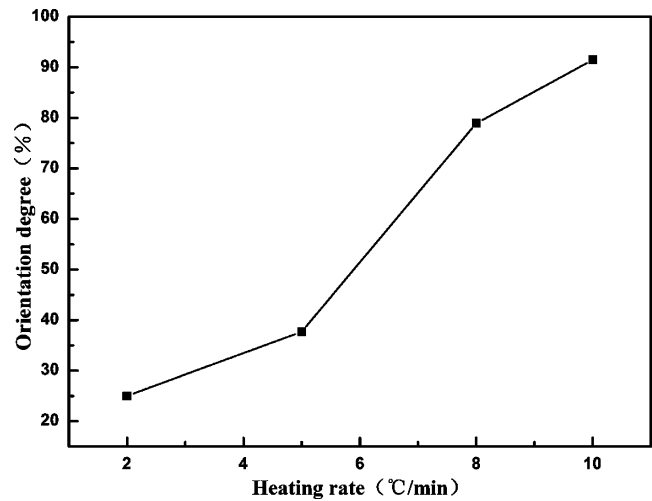

Fig. 3 The degree of grain orientation as a function of heating rates for NBBT ceramics sintered at 1180 °C for 5 h

in Fig. 3. The samples were sintered at 1180 °C for 5 h. The orientation degree increased approximately linearly as the increase of heating rates. Samples that were sintered with heating rate of 2 or 5 °C/min showed a low degree of grain orientation. However, the orientation degree sharply increased with a heating rate more than 8 °C/min.

It is generally known that the origin of the texture development is partly attributed to the growth of template grains at the expense of small equiaxed grains in the templated grain growth (TGG) and reactive templated grain growth (RTGG) processes [18, 19]. It is also the same as in the MLGG technique. Since the driving force of grain growth is the difference in grain sizes, the relative grain growth rates of templates and equiaxed grains are key factors for texture development. If the heating rate is low, the equiaxed NBT grains gradually increases in particle size, while the particle size of plate-like NBT grains changes a
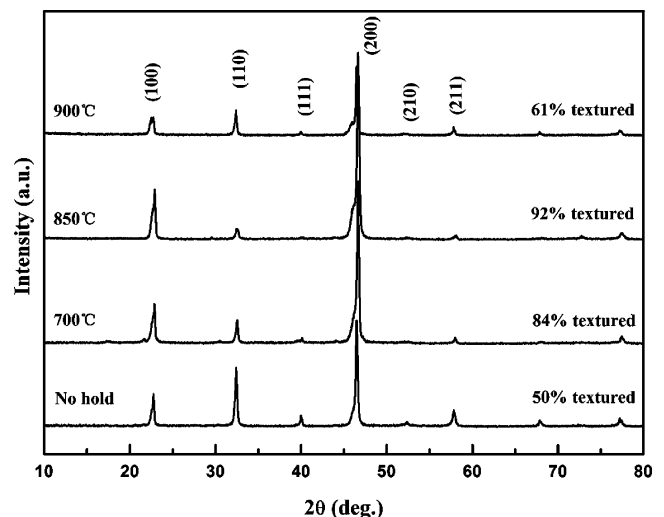

Fig. 2 The degree of grain orientation as a function of sintering time for NBBT ceramics sintered at 1180 °C

Fig. 4 XRD patterns of sintered NBBT ceramics at different pre-reaction temperature
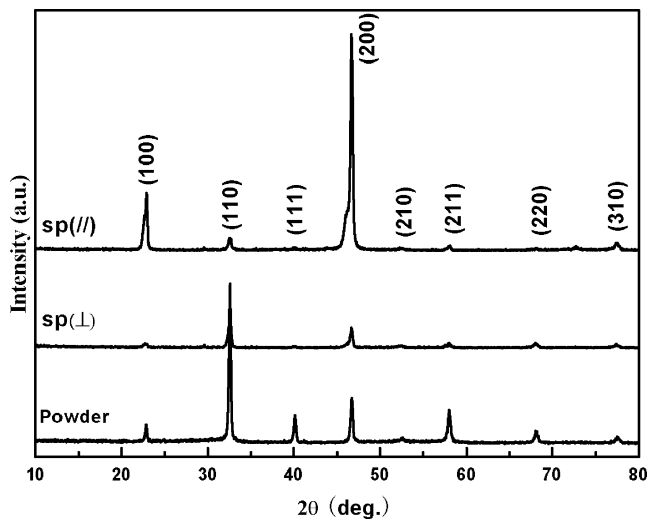
Fig. 5 The XRD patterns of the NBBT ceramics prepared by the screen-printing technique on the parallel (*sp//*) and perpendicular (*sp⊥*) to the screen-printing plane, compared to the XRD pattern of the NBBT powders prepared by the conventional solid state reaction

little. Thus, the driving force for texture development slows down, resulting in a low degree of grain orientation.

3.3 Effect of pre-reaction at low temperature

To investigate the effect of pre-reaction at low temperature on the grain orientation, the NBBT samples were either directly heated to the sintering temperature or per-reacted at 700–900 °C for 8 h before heating to the sintering temperature. These samples were then sintered at 1180 °C for 5 h. Figure 4 shows the effect of pre-reaction at low temperature on the grain orientation. Samples that were directly heated to the sintering temperature, or pre-reacted at 900 °C showed a low orientation degree. However, if the samples were pre-reacted at 700 or 850 °C, a large orientation degree about f=90% was obtained. Thus, the pre-reaction at low temperature was found to be a key step for grain orientation. The same phenomenon was also reported by Messing et al. [18].

As described in the experimental procedure, the green laminates contained the aligned BIT templates and complementary compound particles. After binder burn-out process, the compact was heated at various pre-reacted temperatures to form NBBT in the laminate. During this reaction, two kinds of particles, e.g., plate-like NBT and equiaxed NBBT were formed, as reported in the BNKT composition [19, 20]. For the soaking time at pre-reaction temperature is long (8 h), if the pre-reaction temperature is too high, e.g., 900 °C, the growth of equiaxed NBT grains increases rapidly in particle size, while the growth of plate-like NBT grains is relatively low. The decreasing difference between the plate-like and the equiaxed grains results in a decrease in the driving force for texture

development. Thus, an orientation degree of only 61% was obtained for the samples pre-reacted at 900 °C. For the samples without soaking at low temperature, no plate-like NBT particles were formed, so it was difficult for the texture development.

3.4 Analysis of grain oriented NBBT ceramics

Highly textured NBBT ceramics can be obtained by optimizing the processing parameters. Figure 5 shows the XRD patterns of two different samples, i.e., NBBT powders synthesized by solid-state reaction and a textured NBBT ceramic sample of the surface parallel and perpendicular to the screen-printing plane. The textured sample was sintered at 1180 °C for 5 h. It can be seen that all the (h00) reflections increased in the parallel plane, and decreased in the perpendicular plane compared with the NBBT powder diffraction patterns. The (110) peak was the most intense peak of $Na_{0.5}Bi_{0.5}TiO_3$ powders, while it remarkably decreased for the screen-printed sample in its parallel plane. The orientation degree f was calculated from the Lotgering method to be 91.6% for NBBT ceramics prepared by the MLGG technique, which was competed with the same materials fabricated by TGG and RTGG methods [18, 21–22].

The microstructure of grain oriented NBBT ceramics sintered at 1180 °C for 5 h is shown in Fig. 6. It can be seen that the textured ceramics give brick-layer-like quadrangular grains, which elongate and align parallel to the screen-printing plane. The density of textured NBBT ceramics was 90% theoretical density, which was measured from the Archimedes method. The porous structure of textured ceramics can be mainly attributed to the high weight percentage of organic vehicle (69.5 wt%) in the slurry and high volume percentage of BIT template particles. During the binder burn-out process, although low heating and cooling rates were applied, the organic vehicle was still volatile heavily, lefting pores in the green laminate. On the
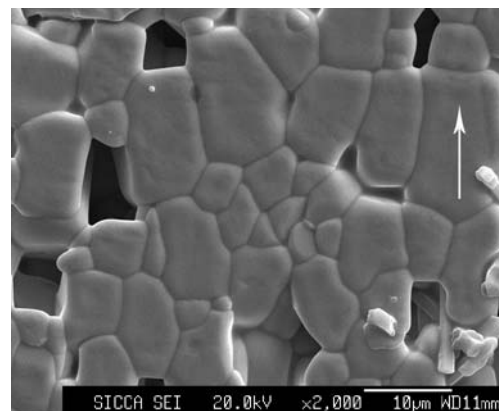

Fig. 6 The microstructure of grain oriented NBBT ceramics sintered at 1180 °C for 5 h. The *arrow* shows the screen-printing direction

other hand, a high volume fraction of BIT template particles, which hindered well packing due to tangling, also made the textured NBBT ceramics difficult to be densified.

3.5 Mechanism for grain orientation in MLGG technique

Highly textured NBBT ceramics can be prepared by the MLGG technique. Our studies indicate that the grain orientation mechanism for MLGG technique using screen-printing is different from tape-casting or extrusion in TGG and RTGG techniques.

In the MLGG technique, the interface between adjacent layers, which is formed by screen-printing, is the main mechanism for the texture development. Since the thickness of each screen-printed film (~5 μm) is comparable to or even thinner than that of the template particles, the existence of such interface confines the grain growth in a single layer. Furthermore, owning to the existence of surface of each screen-printed film and the effect of surface tension, the templates should have their major surface align parallel to the screen-printing plane, which is beneficial to the texture development.

At the initial stage, raw materials gradually formed target products (e.g. NBBT) according to reaction 1, and the grains randomly oriented. When the grain growth took place, some grains which was parallel to the interface, increased rapidly in particle size, while the growth of other grains was restricted by the interface. Thus, anisotropic grains parallel to the interface were formed. With the increasing temperature, the anisotropic grains grew larger with the consumption of smaller equiaxed grains, and then the grain oriented ceramics were obtained.

4 Conclusions

A perovskite structured NBBT piezoelectric ceramics with a high grain orientation of 91.6% were obtained by the MLGG technique. The XRD patterns of the textured ceramics showed prominent differences in two directions of parallel and perpendicular to the screen-printing direction. The degree of grain orientation increased with the sintering time. The heating rate and pre-reaction at low temperature were found to be crucial factors to the textured development. Higher orientation degree can be obtained by pre-reacting at 700–850 °C with a high heating rate. The mechanism for grain orientation in the MLGG technique using screen-printing is different from that in TGG and

RTGG techniques by tape-casting or extrusion. In this method, the interface between adjacent layers played an important role in the texture development. Compared to hot forging, TGG and RTGG methods, the screen-printing multilayer grain growth (MLGG) technique is a simple and effective method to fabricate high quality textured piezo-electric ceramics.

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