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Highly textured $(Na_{1/2}Bi_{1/2})_{0.94}Ba_{0.06}TiO_3$ ceramics prepared by the screen-printing multilayer grain growth technique

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Abstract

The screen-printing multilayer grain growth (MLGG) technique was successfully applied to perovskite-structured lead-free piezoelectric ceramics. Highly textured $(Na_{1/2}Bi_{1/2})_{0.94}Ba_{0.06}TiO_3$ ceramics with (1 0 0) orientation were firstly fabricated by MLGG method with (or without) template particles. The MLGG approach using anisotropic $Bi_4Ti_3O_{12}$ templates resulted in >90% grain orientation, whereas the same approach without template particles resulted in high orientation degree. The grain orientation mechanism of MLGG using screen-printing was different form that of tape-casting and extrusion in templated grain growth (TGG) and reactive templated grain growth (RTGG) techniques. The interface between adjacent layers, which were formed by screen-printing, was the main mechanism for the texture development in MLGG technique. Compared with other grain orientation techniques, screen-printing was a simple, inexpensive and effective method to fabricate grain oriented lead-free piezoelectric ceramics.

Keywords: A. Grain growth; B. Interfaces; C. Piezoelectric properties; D. Perovskites; Screen-printing; Grain orientation

1. Introduction

In recent years, with the growing demands for global environmental protection, lead-free materials have gained much attention on an increasing degree. Sodium-bismuth titanate, $Na_{1/2}Bi_{1/2}TiO_3$ (abbreviated as NBT) is one of the most important lead-free piezoelectric materials with perovskite structure (ABO_3-type) discovered by Smolenskii et al. [1] in 1960. The NBT composition exhibits a strong ferroelectricity and high Curie temperature $T_C = 320\ ^{\circ}C$, it has been considered to be a good candidate to substitute lead-based materials (e.g., PZT), which have been widely used for various applications such as ultrasonic generators, actuators, filters and other electronic devices [2,3]. However, conventionally prepared NBT-based ceramics have low ferroelectric and piezoelectric properties for their randomly grain orientation.

Grain orientation is regarded as an effective way to enhance the piezoelectric properties of lead-free ceramics. It was reported that textured NBT-based ceramics had been prepared by templated grain growth (TGG) [4,5] and reactive templated grain growth (RTGG) techniques [6,7]. However, anisotropic templates are needed for both TGG and RTGG processes, which make the fabrication process quite expensive and complicated.

The screen-printing method has been widely used for fabricating thick-film electronic materials, such as superconductor, solar cell, ceramic films and so on [8–10]. It has been reported by our group that a BLSFs $CaBi_4Ti_4O_{15}$ piezoelectric ceramics with a high grain orientation of 94.3% was obtained by the MLGG technique [11]. However, no textured piezoelectric ceramics with a perovskite structure have been reported yet by the MLGG method up to now.

In this paper, the textured $(Na_{1/2}Bi_{1/2})_{0.94}Ba_{0.06}TiO_3$ (NBBT6) ceramics with (1 0 0) orientation were prepared by the MLGG technique with $Bi_4Ti_3O_{12}$ (BIT) templates. Meanwhile, the NBBT6 ceramics without templates were fabricated by the same method for the first time. The X-ray diffraction and electron microprobe microscopy analysis were employed to characterize the grain orientation and microstructure of the ceramics. The grain orientation mechanism of screen-printing was also discussed.

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2. Experimental procedure

2.1. Fabrication of textured NBBT6 ceramics from BIT templates

Plate-like BIT particles with an average diameter of 7.5 μm were prepared in a molten salt synthesis with NaCl–KCl, as shown in Fig. 1(a), as reported by Kimura and Yamaguchi [12]. Stoichiometrically required amounts of the oxides and carbonate powders 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 reaction schemes (1). The powders, templates and vehicles were well mixed in a ball mill for 15 min to obtain NBBT6 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 NBBT6 was supplied from the templates.

$$Bi_4Ti_3O_{12} + Bi_2O_3 + 3Na_2CO_3 + 0.77BaCO_3 + 9.77TiO_2 \rightarrow 12.77(Na_{1/2}Bi_{1/2})_{0.94}Ba_{0.06}TiO_3 + 3.77CO_2 \quad (1)$$

With a screen printer, the paste 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 were removed carefully from glass substrate and cut into 12mm × 12 mm, then, stacked in 60 layers, and pressed uniaxially at 400 MPa using a hydraulic pressing machine (769YP-24B, Keqi, Tianjin Keqi High & Technology Corporation, 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 sintered at a temperature between 1150 and 1180 °C for 2–10 h in air. The NBBT6 powders prepared by solid-state reaction method using the same starting materials were also prepared for comparison.

2.2. Fabrication of textured NBBT6 ceramics without templates

High purity Na_2CO_3, Bi_2O_3, $BaCO_3$, and TiO_2 (purity > 99%) powders were used as starting materials. Our preliminary experiments found that textured NBBT6 ceramics could not be obtained by mixing the starting powders directly for screen-printing. The textured NBBT6 ceramics without templates were, therefore, prepared by using a modified two-step mixing approach, in which plate-like $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ was synthesized by the conventional solid-state reaction, as shown in Fig. 1(b), and then blended with the complementary powders according to reaction schemes (2). The following screen-printing process was the same as that described in 2.1. The laminates were sintered at a temperature between 1180 and 1200 °C for 5–12 h in air.

$$Na_{0.5}Bi_{4.5}Ti_4O_{15} + 4.45Na_2CO_3 + 2.45Bi_2O_3 + 1.2BaCO_3 + 16TiO_2 \rightarrow 20(Na_{1/2}Bi_{1/2})_{0.94}Ba_{0.06}TiO_3 + 5.65CO_2 \quad (2)$$

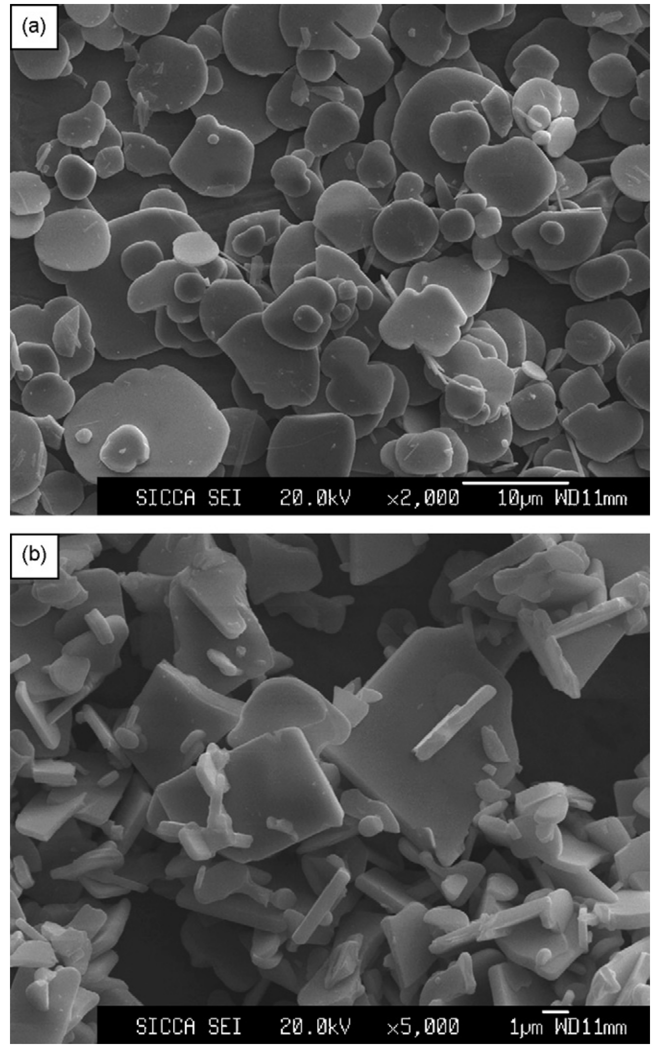

Fig. 1. The micrographs of (a) plate-like $Bi_4Ti_3O_{12}$ templates and (b) $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ particles.

2.3. Microstructural characterizations

The crystalline phase and the degree of grain orientation were determined by X-ray diffraction (XRD) analysis (D/max 2550 V, Rigaku, Tokyo, Japan) using Cu Kα radiation with a scan speed of 4° min^{-1} and a step width of 0.02° both on the major and side surfaces of the samples. The microstructure of sintered ceramics was observed using an electron microprobe microscopy analysis (JXA-8100, JEOL, Japan) on the etched surface perpendicular to the grain orientation direction.

3. Results and discussion

3.1. Texture development in NBBT6 ceramics with BIT templates

Fig. 2 shows the XRD patterns of two different samples, i.e., NBBT6 powders synthesized by solid-state reaction, one ceramic sample of the surface parallel and perpendicular to the screen-printing plane, as shown in Fig. 2(a). The textured sample was sintered at 1180 °C for 5 h. It can be seen that all

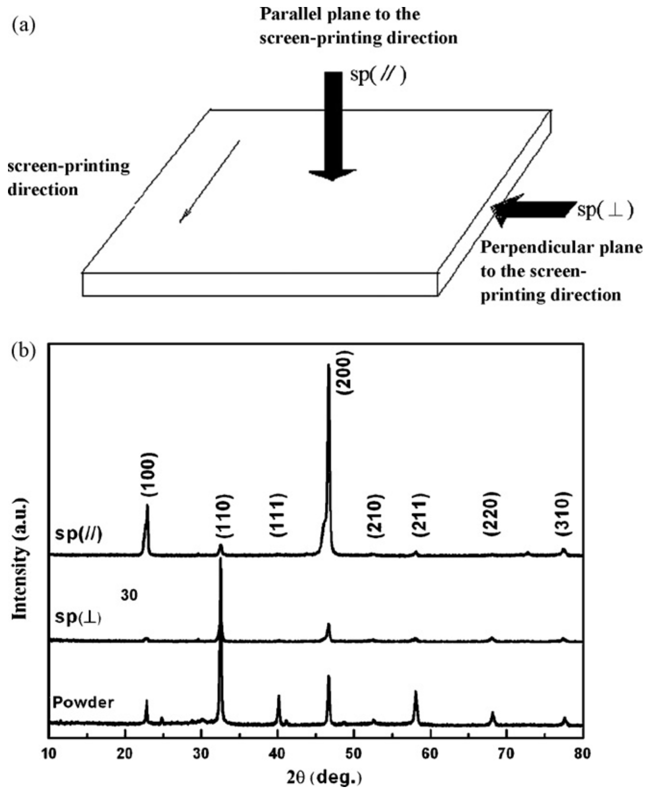

Fig. 2. The XRD patterns of the NBBT6 ceramics with BIT templates prepared by screen-printing method. (a) Schematic of screen-printed ceramics, illustrating the notation used in the text; (b) The XRD patterns of the sp (//) and sp (⊥) compared with the NBBT6 powders by solid-state reaction.

(h 0 0) reflections increase in the parallel plane, and decrease in the perpendicular plane compared with the NBBT6 powder diffraction patterns, as shown in Fig. 2(b). The (1 1 0) peak is the most intense peak of $Na_{1/2}Bi_{1/2}TiO_3$ powder, while it remarkably decreases for the screen-printed sample in its parallel plane.

The degree of grain orientation can be calculated by Lotgering factor f, which is defined as [13]:

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

where

$$p = \frac{\sum_i I_{(h\,0\,0)}}{\sum_i I_{(h\,k\,l)}}, \qquad p = \frac{\sum_i I^*}{\sum_i I^*_{(h\,k\,l)}}$$

and $\sum_i I_{(h\,0\,0)}$ is the sum of the XRD peak intensities for the parallel plane of the textured sample and $\sum_i I_{(h\,k\,l)}$ 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 orientation degree f is calculated from the above equation to be 91.5% for NBBT6 ceramics prepared by the MLGG method, which is competed with the same materials fabricated by TGG and RTGG techniques [14].

The microstructure of grain oriented NBBT6 ceramics with BIT templates sintered at 1180 °C for 5 h is shown in Fig. 3. 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 porous structure of textured ceramics is considered to affect the dielectric and piezoelectric properties.

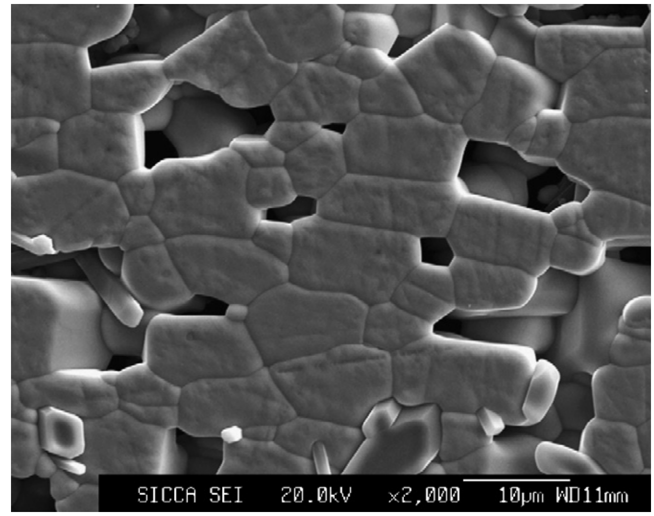

Fig. 3. The microstructure of grain oriented NBBT6 ceramics with BIT templates sintered at 1180 °C for 5 h.

3.2. Texture development in NBBT6 ceramics without templates

XRD patterns of textured NBBT6 ceramics without templates and powder samples are shown in Fig. 4. The most intense peak in the powder XRD pattern is (1 1 0). In the textured XRD pattern, however, the (2 0 0) peak is the most intense one, and the relative intensities of (1 0 0) peak also increase. It's clearly indicated that a high fraction of the sample grains are aligned along (1 0 0) for textured samples. The f value, calculated from the Lotgering method, was 32% for the specimens sintered at 1200 °C for 10 h.

Fig. 5 shows the microstructure of grain oriented NBBT6 ceramics without templates sintered at 1200 °C for 10 h. The

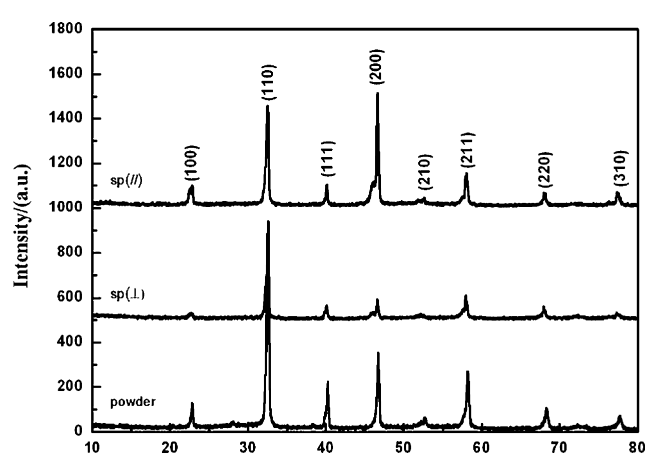

Fig. 4. The XRD patterns of the NBBT6 ceramics without templates prepared by screen-printing method on the sp (//) and sp (⊥) planes, compared with the NBBT6 powders by conventional processing.

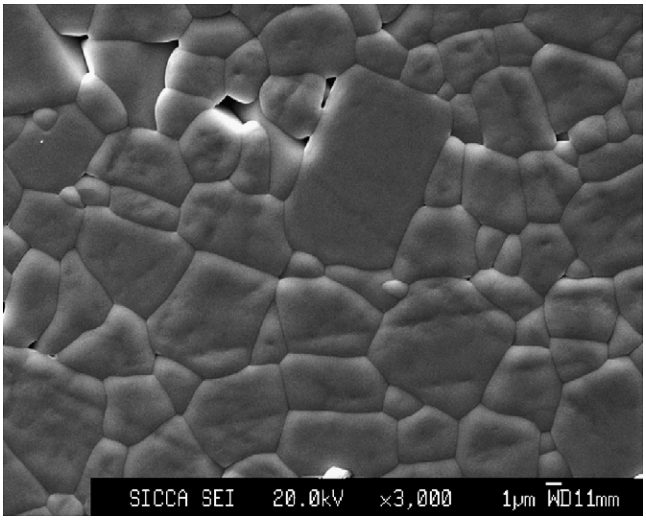

Fig. 5. The microstructure of grain oriented NBBT6 ceramics without templates sintered at 1200 °C for 10 h.

ceramic is partly grains oriented. There are several aligning directions in the sample, but the alignment angle of selected neighbor grains is small. Compared with NBBT6 ceramics with templates (as shown in Fig. 3), the NBBT6 ceramics without templates have higher density, which is 90% theoretical density that is determined by the Archimedes method.

3.3. Mechanism for grain orientation in MLGG

Highly textured NBBT6 ceramics can be prepared by MLGG method with and without templates. Our studies indicate that the grain orientation mechanism of MLGG method using screen-printing is different from tape-casting or extrusion in templated grain growth (TGG) and reactive templated grain growth (RTGG) techniques.

In MLGG method, the interface between adjacent layers, which were formed by screen-printing, was the main mechanism for the texture development. Because the thickness of screen-printed film was very small (less than 5 μm), the existence of such interface confined the grain growth in a single layer. At the initial stage, raw materials gradually formed target products (e.g., NBBT6) according to reaction (1) or (2), and the grains randomly oriented. When the grain growth took place, some grains, which were parallel to the interface, increased rapidly in particle size, while the growth of other grains was restricted by the interface. Hence, anisotropic grains parallel to the interface were formed. With the increasing temperature, the anisotropic grains grew larger with the consumption of smaller equiaxed particles, and then the grain oriented ceramics were obtained.

4. Conclusions

Screen-printing method was used to prepare textured perovskite-structure NBBT6 ceramics. Grain oriented NBBT6 ceramics without templates were fabricated by the MLGG technique for the first time. The highest orientation factor by this process was 32%. However, more than 90% grain orientation factor was achieved by using plate-like BIT templates. The SEM results showed strong preferred grain orientation. The mechanism for grain orientation in MLGG technique using screen-printing is different from that in templated grain growth (TGG) and reactive templated grain growth (RTGG) techniques by tape-casting or extrusion. In this method, the interface between adjacent layers played an important role in the texture development. Without the use of template particles and pressure densification process, the screen-printing is a simple approach to fabricate grain oriented piezoelectric ceramics.

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