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# Fabrication and electrical properties of 0.94Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>–0.06BaTiO<sub>3</sub> textured ceramics by RTGG method using micrometer sized BaTiO<sub>3</sub> plate-like templates

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#### 1. Introduction

Textured NBT–BT ceramics have been often reported using different templates. So far, plate-like Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BIT) [1–3], SrTiO<sub>3</sub> [1], Bi<sub>2.5</sub>Na<sub>3.5</sub>Nb<sub>5</sub>O<sub>18</sub> [4] and Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> [5] crystals have been synthesized and successfully used as templates in texturing of NBT–BT ceramics. Moreover, BT crystal ( $a_0 = 3.992$  Å,  $c_0 = 4.036$  Å at room temperature) [6] was often chosen as templates for some perovskite systems such as Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)–PbTiO<sub>3</sub> textured ceramics [7,8] owing to both similar structures, and chemical stability at high temperature and under PbO liquid environment [8]. Unfortunately, it was never successfully applied in texturing NBT–BT ceramics although it seems to be an ideal candidate template as far as its composition and structure are concerned. Messing et al. have reported that BT seeds were unstable in a matrix of NBT [1], but no explanation was given.

Nanometer-sized spherical, cuboidal or dendritic BT particles were usually synthesized by hydrothermal method [9–11] and micrometer-sized (001)-oriented BT fibers were prepared through an ion-exchange reaction by molten salt and hydrothermal methods [12,13]. Millimeter-scaled (001) oriented BT crystal platelets ( $\sim$ 1.0 mm<sup>2</sup> × 0.4 mm) were synthesized utilizing a molten salt method by Remeika [14,15]. However, the employment of such big template particles resulted in coarsened microstructure and compromised the mechanical strength of the textured ceramics [7,16]. Liu et al. [17] synthesized micrometer-scaled BT platelets by means

## ABSTRACT

Two-step molten salt driven micrometer-scaled tabular (100) BaTiO<sub>3</sub> (BT) template seeds were used for the first time to make (100) textured 0.94Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-0.06BaTiO<sub>3</sub> (NBT-BT) piezoelectric ceramics. The use of platelet Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> powders instead of Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> as raw chemicals would not only benefit to the alignment of BT templates during tape casting, but also avoid the dissolution of BT seeds in liquid Bi<sub>2</sub>O<sub>3</sub> during sintering. The results also proved that a pre-reaction procedure at a low temperature is unnecessary during reactive templated grain growth owing to the structure similarity between BT seeds and target compound. Well-textured NBT-BT lead-free piezoelectric ceramics ( $f \sim 91\%$ ) show excellent dielectric and piezoelectric properties of dielectric constant  $\varepsilon_r \sim 1300$  and piezoelectric charge constant  $d_{33} = 260$  pC/N.

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of a three-step molten salt process, but the residual Bi still existed. Therefore, how to synthesize pure and fine BT crystals with desired crystallographic orientation is still a challenging task.

In this study, phase-pure and micrometer-scaled tabular (001) faceted BT particles (6 mol%) with a high aspect ratio (10–40) were firstly synthesized using a modified two-step molten method, and then used as template seeds to texture 0.94NBT–0.06BT ceramics by means of an RTGG method. Considering the fact that the instability of crystal seeds in matrix compositions at elevated temperatures is usually the result of corrosive oxide liquids such as PbO [18,19] and Bi<sub>2</sub>O<sub>3</sub>. Plate-like BIT powders were conventionally synthesized and used as raw chemicals instead of Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Moreover, the similar particle morphology of BIT powders and BT seeds would be beneficial to the alignment of particles along the tape casting direction. The influence of pre-reaction at low temperature on the densification and the texture formation was investigated together with a study on anisotropic electrical properties in the parallel and perpendicular cuts of textured 0.94NBT–0.06BT ceramics.

#### 2. Experimental procedures

The (100) faceted BT seeds were synthesized by a modified two-step molten salt method. The first step was to synthesize plate-like BIT particles using Bi<sub>2</sub>O<sub>3</sub> ( $\geq$ 99.0%) and TiO<sub>2</sub> ( $\geq$ 99.0%) as raw materials. The second step was to prepare plate-like BT template particles by mixing as-prepared BIT precursor, excessive BaCO<sub>3</sub> ( $\geq$ 99.0%) (BIT:BaCO<sub>3</sub> is 1:10 in mol) and NaCl salt (NaCl:(BIT+BaCO<sub>3</sub>)=1:1 in weight), and then heating at 1020 °C for 3 h in a sealed alumina crucible. The detailed procedures could be referred to elsewhere [20]. To avoid the existence of single Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> ( $\geq$ 99.0%) and TiO<sub>2</sub> ( $\geq$ 99.0%) were reacted into BIT compound by a conventional mixed oxide method. The purpose to do so was to avoid staying of BT template seeds in Bi<sub>2</sub>O<sub>3</sub> liquid at high temperature. The as-prepared BIT powders were milled again to reduce the particle size for better densification. Finally, BIT powders, Na<sub>2</sub>CO<sub>3</sub>

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Fig. 1. XRD pattern of the BT seeds synthesized at 1020 °C for 3 h (inset is the corresponding SEM image).

 $(\geq 99.8\%)$  and TiO\_2 were homogeneously mixed with 6 mol% BT templates according to the following equation:

 $0.94(Bi_4Ti_3O_{12} + 2Na_2CO_3 + 5TiO_2) + 8(0.06BaTiO_{3(T)})$ 

 $\rightarrow 8(0.94Na_{0.5}Bi_{0.5}TiO_3-0.06BaTiO_3) + 1.88CO_2$ 

where BaTiO<sub>3(T)</sub> denotes BT template. After drying, these powders were mixed with solvents and dispersant, then with plasticizers and binder. The slurry was tape casted at a speed of 6.25 cm/s with a blade opening of 250  $\mu$ m. The laminated green compacts were firstly heated in air at 600 °C for 15 h to remove organic additives and then isostatically pressed again under 250 MPa to increase the green density. The samples were either pre-reacted at 800 °C for 4 h and then sintered at 1180–1220 °C for 15 h, or directly sintered at 1180–1220 °C for 15 h. The sintered samples were cut parallel (//) and perpendicular ( $\perp$ ) to the tape casting direction, respectively, in order to characterize the anisotropic electrical properties. For comparison, 0.94NBT–0.06BT ceramics without BT templates were prepared through a conventional solid-state method.

The bulk density of sintered compacts was measured by the Archimedes method. The crystal structure and the texture fraction were examined by an X-ray diffractometer (XRD, D/Max-rB, Rigaku, Japan) using a Cu K $\alpha$  radiation and evaluated by the Lotgering factor (f) [21]. Silver paste was coated and then fired on both sides of the sintered samples at 550 °C for 30 min. The electric poling was performed at 40 °C in a silicone oil bath by applying a dc field of 4–5 kV/mm for 15 min.

The microstructure and chemical composition of the samples were analyzed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, Santa Clara, CA). Polarization versus electrical field (P-E) loops were measured by a ferroelectric measuring system (Precision LC, Radiant Technologies Inc., Albuquerque, NM). The piezoelectric charge constant ( $d_{33}$ ) was directly measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China).

### 3. Results and discussion

Fig. 1 shows that phase-pure BT template particles were obtained via the two-step molten salt method as sintered at 1020 °C for 3 h. The chemical reactions in these two steps were accordingly written as follows:  $2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12}$  and  $Bi_4Ti_3O_{12} + 3BaCO_3 \rightarrow 3BaTiO_3 + 2Bi_2O_3 + 3CO_2$ . According to the standard PDF card (No. 05-0626), it can be seen that all diffraction peaks could be assigned to the perovskite-structured BT phase. Moreover, it can be found that the (h00) diffraction peaks were enhanced to some extent, indicating that the as-prepared BT seeds should be (h00) faceted and tabular. The SEM image of BT particles (see the inset in Fig. 1) indicates a plate-like particle morphology with a mean diameter of  $10-20\,\mu m$  and a thickness of  $1-1.5\,\mu m$ (the aspect ratio was approximately 7-20). It can be believed that the as-prepared BT template might be suitable for texturing 0.94NBT-0.06BT system owing to its desired dimension, phasepurity as well as the same perovskite structure to the target compound.



**Fig. 2.** XRD patterns of conventionally prepared 0.94NBT–0.06BT random ceramics and textured 0.94NBT–0.06BT ceramics either pre-sintered at 800 °C for 4 h, and then sintered at 1200 °C for 15 h or directly sintered at 1200 °C for 15 h (// and  $\perp$ ).

The XRD patterns of random and textured 0.94NBT-0.06BT ceramic samples are shown in Fig. 2. It can be seen that all samples show a single perovskite phase. Compared to conventionally prepared random ceramics, specimens containing BT templates own significantly enhanced (100) diffraction lines no matter whether a pre-reaction procedure was taken or not. The results indicate that a pre-reaction at a relatively low temperature is unnecessary since homogeneous solid solution together with a high orientation degree (f=91%) could be formed by directly heating to the sintering temperature. For different cuts, the parallel cuts show much better orientation along (100) direction than the perpendicular cuts (f=19%). This is possible because not all templates were perfectly aligned during tape casting. BT template acts as part of target compound and owns the same crystal structure to the matrix, making it easy to form the final solid solution with desired stoichiometry, similar to NaNbO<sub>3</sub> template textured (K,Na)NbO<sub>3</sub> [22,23]. Moreover, a well textured NBT-BT ceramics were obtained using BIT compound as raw chemicals instead of Bi<sub>2</sub>O<sub>3</sub>. This means that a preferred crystallographic orientation of BaTiO<sub>3</sub> template was maintained and inherited during epitaxial growth and diffusion between BT and complementary compounds (i.e., Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, TiO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>), forming homogeneous solid solution with a preferential orientation finally. Otherwise, a preferential orientation solid solution was not obtained due to breakdown of preferential orientation of BT template, meeting with matrix. It indicated that BT template was stable and plays its role successfully indirectly.

The grain morphology on the cross section of textured 0.94NBT-0.06BT samples is shown in Fig. 3. It can be seen that major grains have been elongated along the tape casting direction, showing good texture. This keeps good agreement with the XRD data in Fig. 2. It can be found that BT templates grow at the expense of smaller matrix grains by the difference in surface free energy, showing good chemical stability. As a result, a well-densified, welltextured "brick-wall" microstructure was finally formed by the Ostwald growth. Moreover, EDS analysis was carried out either at residual fine matrix grains (spectrum 1) or big "brick" grains (spectrum 2) developed from template grains, as shown in Fig. 3(b). The EDS results indicate that both kinds of grains only contain Ba, Bi, Na, Ti and O atoms. Atomic ratios of Ba:Bi:Na:Ti are nearly equal (1:8.2:7.3:17.3 for small grains and 1:7.1:8.2:15.8 for big grains), revealing that the composition distribution after sintering is homogeneous. The stoichiometry of the ceramic samples was almost kept close to the desired one (Ba:Bi:Na:Ti = 1:7.83:7.83:16.7) if the measurement error was taken into account. This result suggests that BT templates used have completely interdiffused into the matrix and formed a single perovskite solid solution.

Fig. 4 shows the variation of the dielectric constant  $\varepsilon_r$  of random 0.94NBT-0.06BT ceramics and textured counterparts of different

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