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Fabrication and electrical properties of textured $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ ceramics by reactive-templated grain growth

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Abstract The <001> fiber-textured $Na_{1/2}$ $Bi_{1/2}TiO_3$-$BaTiO_3$ (6 mol% $BaTiO_3$) ceramics were fabricated by reactive-templated grain growth (RTGG), using plate-like $Bi_4Ti_3O_{14}$ (BiT) particles prepared by a molten salt method as templates. The effects of sintering conditions on texture development and microstructure evolvement were both studied, and the mechanisms of grain orientation and densification were discussed. High Lotgering factor (≥96%) and high density (≥96% theoretic density) textured $Na_{1/2}$ $Bi_{1/2}TiO_3$-6$BaTiO_3$ ceramics were prepared by using the max templates concentration supplying 100% Bi in the final product, and sintering at 1200 °C for 10 h. The NBT-6BT obtained exhibited good piezoelectric performance with piezoelectric coefficient d_{33}=241pC/N, and electro-mechanical coupling factor k_p=41.2%, k_t=66.5% at room temperature.

Keywords Templated grain growth · Texture · $Na_{1/2}$ $Bi_{1/2}TiO_3$-$BaTiO_3$ · Piezoelectric

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1 Introduction

Sodium bismuth titanate ($Na_{1/2}Bi_{1/2}TiO_3$)-based solid solution is one of promising lead-free or low-lead piezoelectric materials [1, 2]. Along the <001> direction, single crystals of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ (NBT-BT) solid solution system at the morphotropic phase boundary (MPB) have extremely high piezoelectric coefficient (d_{33} as high as 450 pC/N) [3]. Compared with the single crystals, NBT-BT ceramics have much lower piezoelectric responses (d_{33}= 125 pC/N, d_{31}=40 pC/N, k_{33}=0.55, and k_{31}=0.19) [1] because the grains are randomly oriented in polycrystalline ceramics. Texture development is a convenient method to improve properties of polycrystalline ceramics by tailoring microstructure of materials, and it has been shown that ferroelectric/ piezoelectric ceramics with a high degree of texture exhibited good performance [4, 5].

Reactive-templated grain growth (RTGG) is a ceramic process for producing textured ceramics, highly textured NBT-base ceramics have been prepared by this method [6, 7]. The RTGG process is dependent on the formation of oriented grains by the in-situ reaction between precursor particles with aligned shape anisotropy templates (the oriented plate-like NBT grain formed by the Na^+ diffusion into BiT and the Bi^{3+} diffusion out of BiT in the BNT case) [5]. In some cases, however, it hardly develops texture: one is degradation of the desired anistropically shape of templates during the diffusion reaction [8, 9]. Another case is limitation of the growth of oriented grains because of a high growth rate of matrix grains. Increasing the amount of templates is one effective method to solve the problem [5].

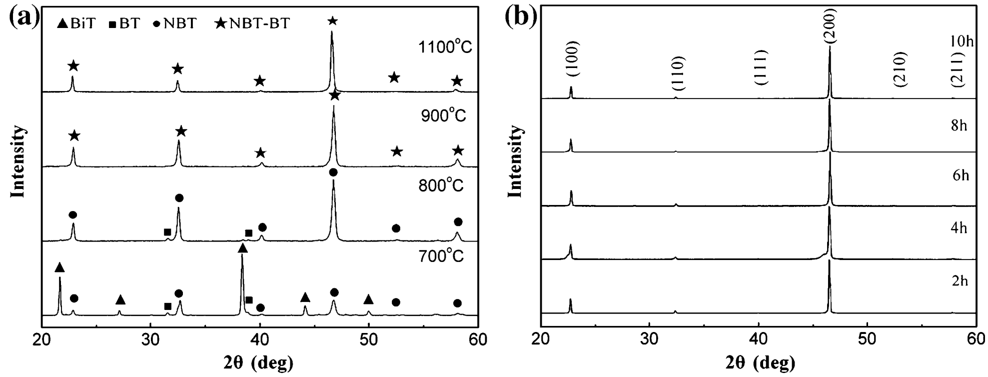

Fig. 1 XRD patterns of NBT-6BT specimens sintered (**a**) at various temperatures for 2 h; (**b**) at 1200 °C for different soaking time

In NBT-6BT case, the amount of BiT templates was designed by the experiment. The overall reaction is expressed by the following equation.

$$
\begin{aligned}
0.94\{xBi_4Ti_3O_{12(T)} &+ 2(1-x)Bi_2O_3 + 2Na_2CO_3 \\
&+ (8-3x)TiO_2\} + 8(0.06BaTiO_3) \\
&\xrightarrow{\Delta} 8\{0.94Na_{1/2}Bi_{1/2}TiO_3 - 0.06BaTiO_3\} \\
&+ 1.88CO_2\uparrow
\end{aligned}
$$

Where $Bi_4Ti_3O_{12\ (T)}$ denotes BiT template; x (0~1) is the percentage of BiT supplying Bi in the final product. The more templates are added, the higher textured degree can be obtained. In this work, Bi in the final product was supplied wholly by BiT templates (x=1).

2 Experimental procedure

2.1 Preparation of textured ceramics

For slurry preparation, Na_2CO_3, Bi_2O_3, TiO_2, and $BaTiO_3$, according to the reaction equation above, were first mixed with solvents and dispersant by ball-milling for 12 h; then plasticizers and binder were added and mixed for another 12 h to obtain the slurry; the slurry organic additives system was as followings: the solvents were the azeotropic mixture of ethanol and butanone, the dispersant was castor oil, the binder

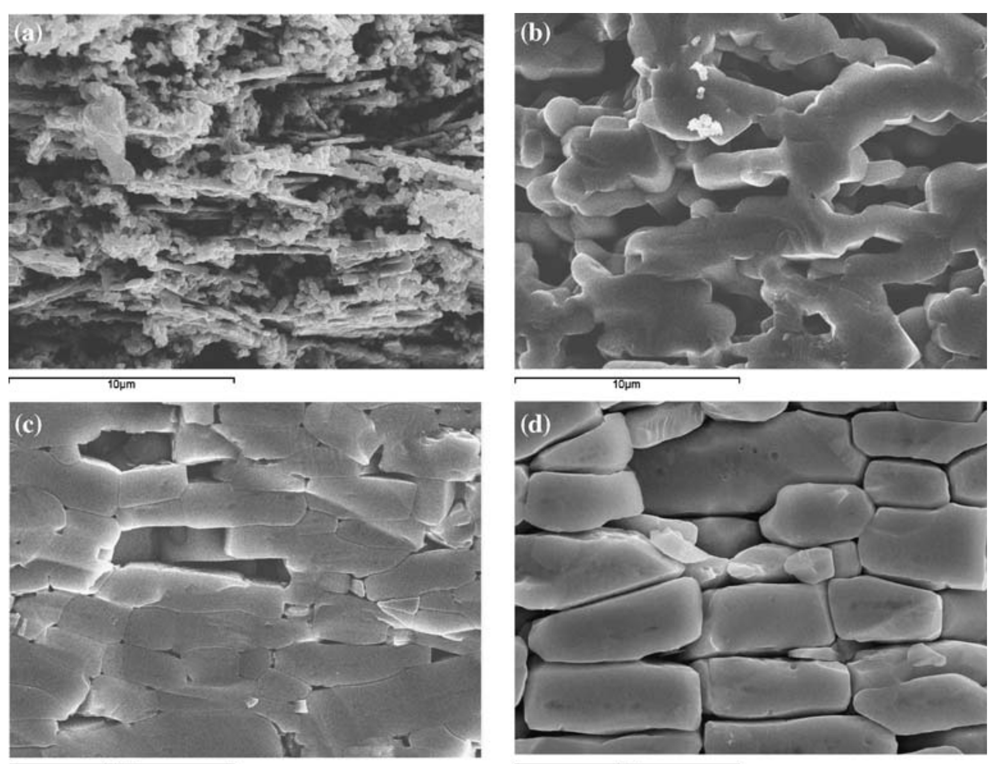

Fig. 2 Microstructure of the NBT-6BT ceramics sintered at (**a**) 900 °C for 2 h; (**b**) 1100 °C for 2 h; (**c**) 1200 °C for 2 h; (**d**) 1200 °C for 10 h

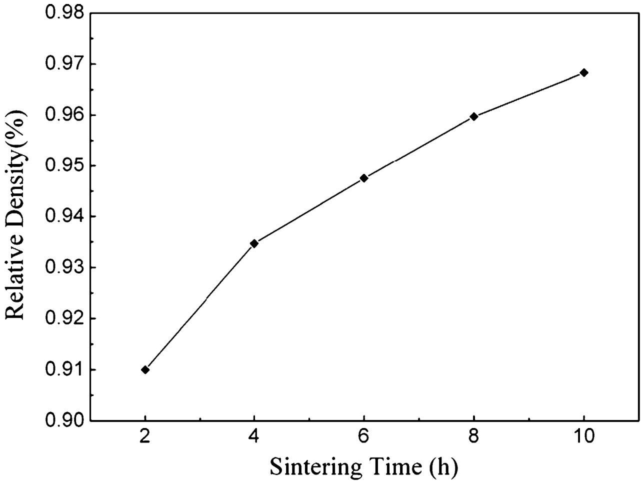

Fig. 3 Effect of soaking time on the density of NBT-6BT specimens sintered at 1200 °C

was polyvinyl butyral (PVB), and the compatible plasticizers were dibutyl phthalate (DBP) and polyethylene glycol (PEG).

For template preparation, plate-like $Bi_4Ti_3O_{12}$ (BiT) particles were prepared from Bi_2O_3 and TiO_2 by molten salt synthesis at 1100 °C for 30 min in the eutectic NaCl/KCl flux; The BiT particles obtained were ~15 μm in diameter and ~0.5 μm in thickness.

The plate-like BiT template particles with a high aspect ratio, according to the reaction equation above, were added and mixed in the slurry with a stir bar. The slurry was tape-cast with a blade opening of 160 μm. The tapes obtained were dried, cut, and then laminated into a multilayer sheet approximately 2 mm thick under a pressure of 40 MPa at 80 °C for 15 min. The laminated green compacts blanked into discs with a diameter of 12 mm. Then the green samples obtained were heated in air at 600 °C for 1 h to remove organic additives, at a heating rate of 0.6 °C/min. After the samples were pre-reacted at 700 °C for 2 h to form the NBT perovskite phase, the samples were sintered at 1200 °C for 10 h.

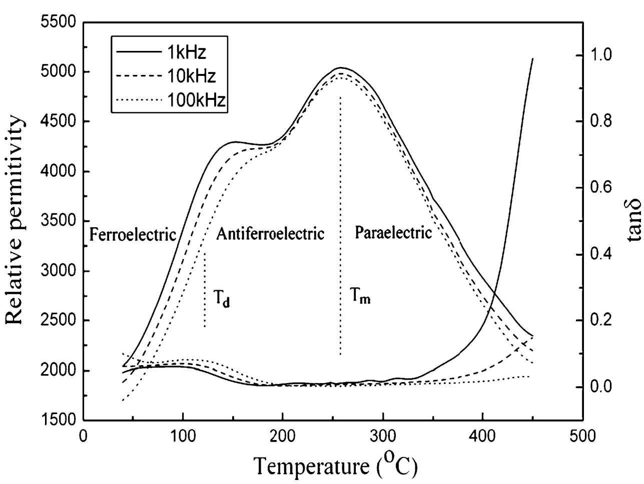

Fig. 4 Temperature dependence of dielectric constant and dissipation factor of NBT-6BT ceramics at different frequencies

2.2 Characterization

The densities of the sintered samples were measured by the Archimedes method. The crystalline phases and degree of textured development were determined by X-Ray Diffraction (XRD) patterns between 2θ=20° and 60°, and evaluated using the Lotgering factor (F) as described in [10]. The microstructures of the sintered samples were observed by a scanning electron microscope. Silver paste was fired on both faces of the discs at 800 °C as electrodes. The samples for the measurement of the piezoelectric properties were poled in silicone oil at 50°C under 4 kV/mm for 15 min. The resonance and anti-resonance frequencies were measured using an impedance/gain phase analyzer (HP-4194A). The thickness and planar coupling coefficients (k_t, k_p respectively) were calculated based on the Onoe's formulas [11]. The piezoelectric constant d_{33} was measured by a ZJ-3A quasistatic d_{33}-meter based on Berlincourt method. The temperature dependence of the dielectric constant and the dissipation factor of the unpoled samples was measured between 40 and 450 °C at a step of 2 °C in a temperature-programmable tube furnace at different frequencies (1 kHz, 10 kHz, 100 kHz respectively) using a impedance analyzer (HP-4192A).

3 Results and discussion

3.1 Texture development

The RTGG process is dependent on the formation of oriented particles by in-situ reaction between precursor particles with aligned shape anisotropy templates. Figure 1 shows the XRD patterns of NBT-BT specimens sintered at various temperatures from 700 to 1100 °C for 2 h and at 1200 °C for different soaking times. A small fraction of oriented NBT was formed after heat treatment at 700 °C and BiT remained was well oriented with all pseudotetragonal {001} crystallographic planes parallel to the sheet plane. The NBT formation reaction was completed at 800 °C for 2 h; NBT and BT were present as separate phases at this stage, and

Table 1 Piezoelectric properties of nontextured and textured NBT-6BT ceramics.

NBT-6BT	Nontextured [1, 13]	Textured	Ratio
d_{33}(pC/N)	125	241	1.93
k_p	0.29	0.412	1.42
k_t	0.40	0.665	1.67

NBT showed a distinct preferred orientation. The solid solution formation was finished at 900 °C for 2 h. This character that oriented grains formation by in-situ reaction and solid solution formation reaction take place separately at different temperature is very important to the texture development [7].

After solid solution formation reaction finished at 900 °C, Texture developed rapidly with increasing sintering temperature. It can be seen that the Lotgering factor reach 96% at 1200 °C for only 2 h, and the Lotgering factor increases slowly with further prolonging soaking time. The effect of sintering condition and the mechanisms of grain orientation to the texture development will be discussed in detail at microstructure evolvement.

3.2 Microstructure evolvement

Figure 2 shows the microstructures of the NBT-6BT ceramics evolved in heat treatment. The plate-like template particles were well oriented with plate plane parallel to the sheet plane under the shear force of doctor blade. During the pre-reaction, oriented NBT particles formed by in-situ reaction between precursor particles with aligned shape anisotropy BiT templates. After BT solid solution into NBT, texture developed by oriented NBT-BT epitaxial growth and densification with increasing sintering temperature and soaking time.

Figure 2(a) shows the SEM image of the sample sintered at 900 °C for 2 h, the anisotropic shape of the oriented template grains maintained during the oriented NBT particles formation by in situ reaction and solid solution reaction with BT, which is a key for the reactive-templated grain growth. Combining with Fig. 1(a), it indicates that the oriented plate-like NBT grains and fine equiaxed grains as matrix formed by the Na^+ diffusion into BiT and the Bi^{3+} diffusion out of BiT. Texture developed by epitaxial growth in <001> direction from the surface of oriented NBT-BT grains by consuming the fine matrix as shown in Fig. 2(b).

After sintered at 1200 °C for 2 h, the oriented NBT-BT grains grew completely and obtained the brick-wall microstructure as shown in Fig. 2(c), this resulting microstructure has strong crystallographic texture. Figure 3 shows the relative density of the sample sintered at 1200 °C for different soaking time, the samples densified rapidly and obtained about 97% of the theoretical density with prolonging sintering time. Figure 2(d) shows the microstructure of the final high density and highly textured NBT-BT ceramics sintered at 1200 °C for 10 h.

3.3 Dielectric and piezoelectric properties

Figure 4 shows the temperature dependence of dielectric constant ε_r and dissipation factor tanδ of the unpoled textured NBT-6BT ceramics at different frequencies (1 kHz, 10 kHz. 100 kHz), Comparing with the results reported by Takenaka [12], samples were also characterized by the existence of three phases of ferroelectric, anti-ferroelectric and paraelectric states in different temperature ranges. Here, T_d refers to the temperature of the transition between the ferroelectric phase and anti-ferroelectric phase, and T_m stands for the temperature corresponding to the maximum value of dielectric constant. No obvious changes in T_d and Tm were observed. Furthermore, the dielectric constant and dissipation factor increased which can be attributed to the porosity and internal stresses, which is one common problem in (R)TGG process because it is difficult for compact with strong anisotropy and large difference of grain sizes to obtain high density product.

Table 1 shows the piezoelectric properties of textured NBT-6BT ceramics and nontextured NBT-6BT ceramics prepared by the conventional ceramic method. The textured NBT-6BT ceramics exhibited good performance with piezoelectric constant d_{33}=241 pC/N, and electromechanical coupling factor k_p=41.2%, k_t=66.5% at room temperature, which were nearly two times as much as those of nontextured ceramics reported in the literature[1, 13]. This enhanced electromechanical properties of <001> textured NBT-6BT ceramics can be attributed to domain or crystallographic engineering.

4 Conclusions

The <001> fiber-textured $Na_{1/2}$ $Bi_{1/2}TiO_3$-$BaTiO_3$ (6 mol% $BaTiO_3$) ceramics were fabricated by reactive-templated grain growth (RTGG), using plate-like $Bi_4Ti_3O_{14}$ particles prepared by a molten salt method as templates. Anisotropic shape of oriented templates maintained during formation of the oriented NBT particles by in-situ reaction and solid solution reaction with BT. The high Lotgering factor (~96%) and high density (~97% theoretic density) $Na_{1/2}$ $Bi_{1/2}TiO_3$-6$BaTiO_3$ ceramics obtained exhibited good performance with piezoelectric constant d_{33}=241 pC/N, and electro-mechanical coupling factor k_p=41.2%, k_t=66.5% at room temperature.

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