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Densification and texture evolution of $Bi_4Ti_3O_{12}$ templated $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ ceramics: Effects of excess Bi_2O_3

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ABSTRACT

$0.94Na_{0.5}Bi_{0.5}TiO_3$–$0.06BaTiO_3$ lead-free ceramics were fabricated by templated grain growth method using 5 vol% platelet $Bi_4Ti_3O_{12}$ (BIT) templates. The effect of the addition of excess Bi_2O_3 on the densification and the texture evolution was investigated. A high degree of grain orientation ($f \sim 0.93$) and an excellent piezoelectric coefficient d_{33} of ~290 pC/N were obtained for undoped samples, however the texture was hardly developed for Bi_2O_3 doped samples whose densification behavior yet could be significantly improved. It was found that the Bi_2O_3 liquid phase can promote the particle rearrangement and mass transport, but simultaneously change the surface morphology of BIT templates and matrix grains from an atomically rough to smooth structure. The Ostwald growth was thus induced dominantly in the diametrical direction and little in the thickness direction of plate-like templates. The results provided a good reference for selecting the sintering aid in the fabrication of textured ceramics.

1. Introduction

$(Na_{1/2}Bi_{1/2})TiO_3$–$BaTiO_3$ (NBT–BT) ceramic is one of the most promising lead-free piezoelectric materials. The d_{33} value as high as 450 pC/N in the [0 0 1] direction has been reported for NBT–BT single crystals at the morphotropic phase boundary [1]. For polycrystalline NBT–BT ceramics, the piezoelectric response is however much lower because of the random orientation of the grains, which can be significantly improved by texturing process along a certain crystallographic direction. The templated grain growth method (TGG) has been widely used to make textured piezoelectric ceramics [2], which proves to be especially suitable for a material with a cubic symmetry, such as perovskite-structured materials. So far, textured NBT–BT ceramics have been manufactured using plate-like $Bi_4Ti_3O_{12}$ (BIT) [3–5] $SrTiO_3$ [3], $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ [6] and NBT [7] crystals as templates. BIT is an Arrhenius compound that consists of three perovskite-like units ($BiTiO_x$) separated by two $(Bi_2O_2)^{2+}$ layers along the c-axis [8]. Takeuchi et al. also reported that epitaxial single crystal layers of (0 0 1)-$PbTiO_3$ could grow on (0 0 1)-BIT platelets [9]. Furthermore, BIT thin film layer was used to template the epitaxial growth of various heterostructures of PZT in the [0 0 1] direction by pulsed laser deposition [10]. Therefore, (0 0 1)-faceted BIT seeds with layered perovskite structure can be utilized to make ⟨0 0 1⟩ oriented NBT–BT ceramics by a TGG method based on its crystal structure and morphology.

In addition, a magnetic stirring was usually used as a preferred method to mix templates seeds and the matrix composition, rather than long-term ball milling with ZrO_2 balls, to avoid destroying the flake-like morphology of crystal templates. As a result, the uniformity of the composition should be a problem in textured ceramics, compared to conventionally prepared ceramics. Moreover, textured ceramics are relatively difficult in sintering because they contain large-size templates. The expansion caused by in situ reaction between templates and the matrix grains also degrades the sintering kinetics [11]. An usual way was to add a few amount of sintering aids to promote the densification, and in some cases to achieve better epitaxial growth as well. According to the literature review, a few kinds of sintering aids were often chosen for different matrix compositions, for example, PbO, Bi_2O_3, CuO, Sb_2O_3 and V_2O_5 in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, NBT, $(K_{0.5}Na_{0.5})NbO_3$, $(K_{0.5}Na_{0.5})(Nb_{0.97}Sb_{0.03})O_3$ and $Sr_{0.4}Ba_{0.6}Nb_2O_6$, respectively [12–16]. These sintering aids could usually improve the densification by facilitating the mass transport, and simultaneously promote the evolution of the texture by enhancing the kinetics of template grain preferential growth [12,14–16]. However, cares were rarely taken of whether the sintering aids always play the same role as they did in the texture processing.

The objective of this work is thus to fabricate 0.94NBT–0.06BT textured ceramics by a TGG method using 5 vol% BIT templates. A special focus was placed on the effect of the addition of excess Bi_2O_3 on the texture evolution as well as the densification of the textured ceramics. A surprising result in this case was that the addition of excess Bi_2O_3 definitely benefited to the densification but obviously prevented the evolution of the grain orientation. A

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mechanism concerning how the texture evolution was influenced by the Bi_2O_3 liquid phase during sintering was put forward.

2. Experimental procedures

Plate-like BIT particles were prepared by a typical molten salt method [17]. According to the stoichiometry of $0.94Na_{0.5}Bi_{0.5}TiO_3$–$0.06BaTiO_3$, raw chemicals: Bi_2O_3 (≥99.0%), Na_2CO_3 (≥99.8%), $BaCO_3$ (≥99.0%), and TiO_2 (≥99.0%) were mixed by a planetary ball mill. Part of the calcined powder was added by 2 mol% Bi_2O_3 in excess. Slurry was made by first mixing the powder with solvents and dispersant, and then with plasticizers and binder. Subsequently, 5 vol% BIT template was added into the above slurry for 48 h using a magnetic bar. The slurry was finally tape casted into green tapes. The laminated green compacts were first burn-out in air at 600 °C for 15 h and then isostatically pressed under 250 MPa. Sintering was carried out in the temperature range of 1080 °C–1220 °C for 10 h. For comparison, 0.94NBT–0.06BT random ceramics were prepared by a conventional mixed oxide method.

The bulk density of sintered compacts was measured by the Archimedes method in deionized water. The crystal structure was examined by X-ray diffraction (XRD, D/Mzx-rB, Rigaku, Japan) using a Cu Kα radiation on the major surface of sintered ceramics (parallel to the tape casting base). The texture fraction was evaluated by the Lotgering factor (f) using the above XRD data [18]. The microstructure of the samples was observed on polished and thermally etched surfaces perpendicular to the tape casting base for textured samples and non-textured disk samples by a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). Before electrical measurements, silver paste was coated on major surfaces and then fired at 550 °C for 30 min. The electric poling was performed at 25 °C in a silicone oil bath by applying a dc field of 4–5 kV/mm for 15 min. The piezoelectric constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China).

3. Results and discussion

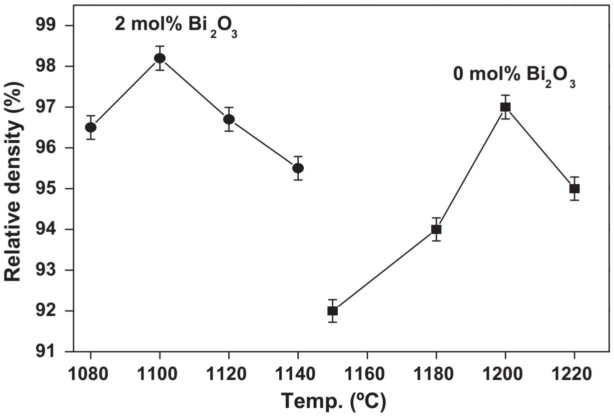

Fig. 1. Influence of excess Bi_2O_3 on the densification behavior of 0.94NBT–0.06BT powder compacts containing 5 vol% BIT templates.

Fig. 1 shows the effect of the addition of excess Bi_2O_3 on the densification behavior of 0.94NBT–0.06BT samples with 5 vol% BIT templates. It can be seen that both samples exhibited high density of >96% theoretical density (TD) at the optimum sintering temperature, although large-size template seeds tend to cause poor densification. The possible reason may be attributed to the relatively low content of template seeds used in this study, compared to the value (6 vol%) in the literature [3]. Moreover, it is obvious that excess Bi_2O_3 significantly improved the densification and reduced the optimum sintering temperature by ∼100 °C.

Fig. 2 shows the microstructure of the polished and etched cross section (perpendicular to the tape casting plane) of the sintered 0.94NBT–0.06BT samples. It can be seen that the amount of Bi_2O_3 produced an extremely different effect on the grain morphology. For the sample without excess Bi_2O_3, the template seeds grow mainly in the thickness direction at the expense of smaller matrix grains. The driving force for the grain growth should mainly come from the difference in the surface free energy of large templates

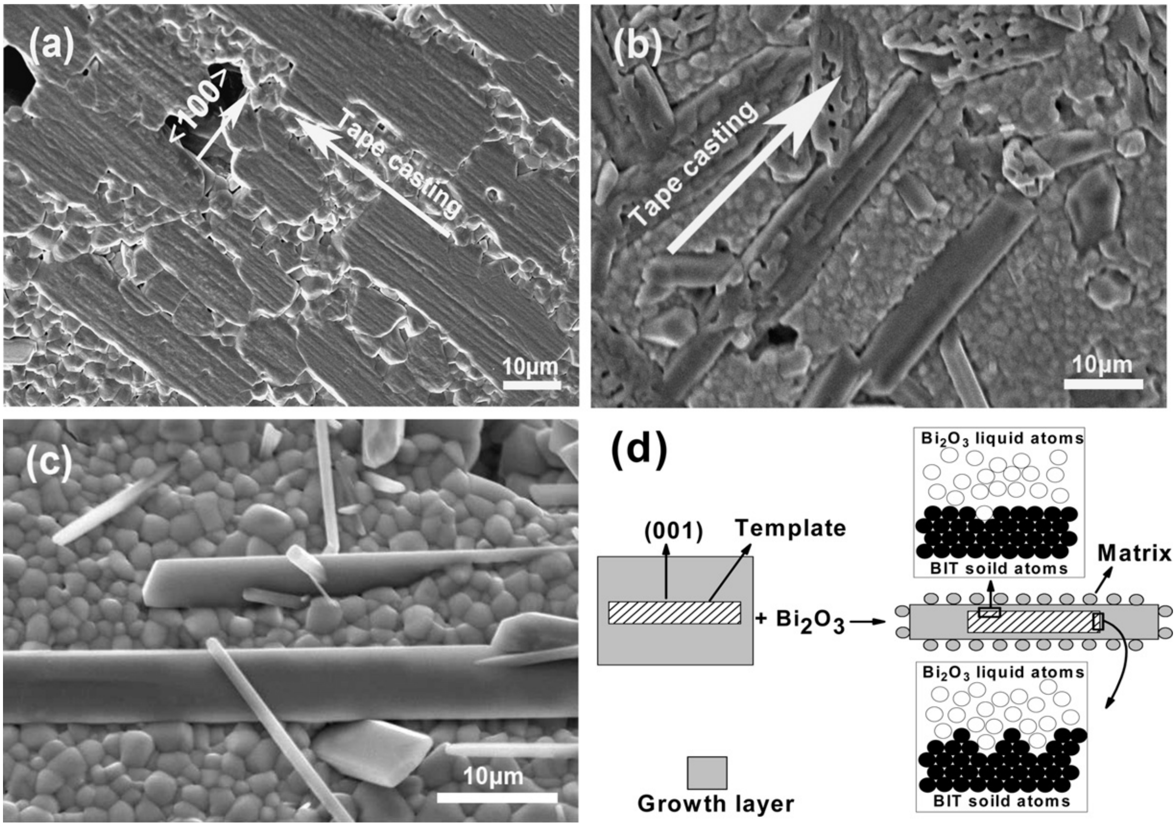

Fig. 2. SEM morphology of the polished and etched cross section of 5% BIT templated 0.94NBT–0.06BT ceramics: (a) 0 mol% Bi_2O_3, sintered at 1180 °C for 10 h, (b) excess 2 mol% Bi_2O_3, sintered at 1100 °C for 10 h and (c) excess 2 mol% Bi_2O_3, sintered at 1180 °C for 10 h; and (d) schematic illustration showing how excess Bi_2O_3 affects the interfacial atomic structure of the BIT template.

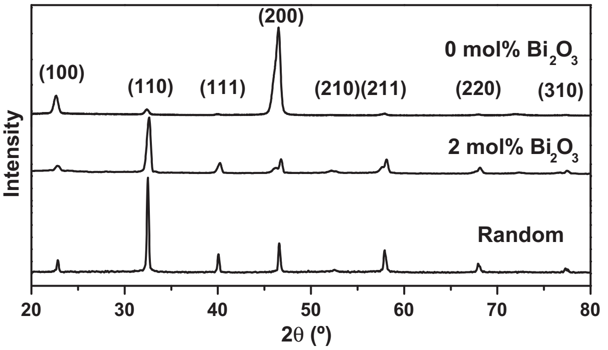

Fig. 3. X-ray diffraction patterns of conventionally prepared 0.94NBT–0.06BT random ceramics and 5% BIT templated 0.94NBT–0.06BT ceramics with 0 mol% and 2 mol% Bi_2O_3 in excess.

and fine matrix particles. The Ostwald growth would continue till each templated grain almost impinges together and even all small matrix grains disappear if the holding time is long enough. As a result, a densified and perfectly textured "brick-wall" microstructure was developed as the sample was sintered at its optimum sintering temperature (1180 °C) (Fig. 2(a)). However, the counterpart sample with excess Bi_2O_3 sintered at 1100 °C for 10 h hardly developed any texture even if the density reached the maximum value (~98% TD, see Fig. 1), as shown in Fig. 2(b). No improvement of the texture can be seen even if the sintering temperature was increased up to 1180 °C (Fig. 2(c)). It seems that most matrix grains were not consumed because the template seeds grew mainly along the diametical direction.

The difference in grain morphology can be also distinguished by means of the XRD measurement, as shown in Fig. 3. For clear comparison, the XRD result for the ceramic sample without BIT template and excess Bi_2O_3 was also included (named as random ceramics). As can be seen, undoped ceramic samples (f ~ 93%) were much better oriented than the counterpart samples with excess Bi_2O_3 (f ~ 0%), as evaluated by the Lotgering method. For well-textured samples, the (2 0 0) peaks were obviously enhanced instead of (1 1 0) peaks, compared to either non-textured or random ceramics. It is indicated that the (h 0 0) planes became the main crystal planes parallel to the sample surface for the measurement. Similar results were reported in BIT textured NBT ceramics where the texture degree was significantly reduced as the amount of Bi_2O_3 becomes much more [13]. Unfortunately, no explanations were given about it. In fact, the obtained texture degree was rather low as can be seen from their XRD and SEM data.

The piezoelectric and electromechanical properties of random and textured 0.94NBT–0.06BT ceramics are compared in Table 1. It can be seen that the kind of template seeds has an obvious effect on the orientation degree and piezoelectric properties, probably because of the deviation from the stoichiometry caused either by the compositional inhomogeneity or by the hetero-composition of the template. Furthermore, the poorly-textured ceramic samples prepared by adding 2 mol% Bi_2O_3 as a sintering aid show almost one half the d_{33} values of the well-textured ceramics without excess Bi_2O_3, but are similar to the completely non-textured ceramic samples in electrical properties. The difference in piezoelectric properties also reflects a surprising role of excess Bi_2O_3 playing in BIT templated NBT–BT systems.

The addition of excess Bi_2O_3 was originally expected to act as a sintering aid to improve the densification of textured samples. In most cases, this kind of sintering additives was also anticipated to promote the epitaxial growth of matrix grains on the aligned templates [13]. However, we wonder that why Bi_2O_3 in this work promoted the densification, but did not benefit to the formation of the texture. Bi_2O_3 can form liquid phases during sintering owing to its low melting point (~824 °C) [13], and thus promotes the densification by speeding up the mass transport. In addition, liquid phase can induce particle rearrangement at the early stage of sintering and the relieved internal stress around large size templates may also contribute to the sintering behavior.

In addition, the ability of a growing interface to attach atoms mainly depends on whether the boundary structure is an atomically smooth or rough [19,20]. For an atomically rough grain boundary, the atomic attachment to it has a negligible energy barrier, such that grains can grow quickly through a diffusion-controlled process. However, the movement of an atomically smooth boundary can only be realized by screw dislocations or two-dimensional nucleation with a certain thermodynamic barrier for overcoming the step-edge energy. As a result, as atoms attach to a smooth interface, grains can grow slowly by an interfacial-reaction-controlled process [20]. The boundary of the matrix grains and template seeds in un-doped 0.94NBT–0.06BT samples (0% Bi_2O_3 in excess) are usually atomically rough to varying degrees because of energy fluctuation and thus template seeds would grow at the expense of small matrix grains in the thickness direction, due to a larger driving force caused by a bigger difference of the boundary sizes (main plane and side plane size of the template in comparison to the matrix grain boundary size). However, the existence of excess Bi_2O_3 would change the growth habit of the BIT template seed to be mainly in its diametrical direction instead of the thickness direction, as schematically shown in Fig. 2(d). This is because the (0 0 1) main crystal face of the BIT template is closely packed with rare pit defects, meaning an approximately atomically smooth structure. Therefore, the main crystal faces tend to be changed into an atomically smooth structure through adsorbing impurity atoms to fill limited pit defects as the liquid phase of Bi_2O_3 is present. Furthermore, the (0 0 1) planes of BIT templates are closely packed and have larger inter-planar spacing, which results in a slow growth rate because of a low specific surface energy and a weak atomic absorbability. By comparison, the side planes of the template would keep an atomically rough structure throughout the growth process due to more atomic pit defects and higher surface roughness. As a result, the growth rate in the diametrical direction of template seeds becomes much higher as excess Bi_2O_3 is present. Moreover, it is reasonable to speculate that the matrix grain boundary might also be changed into an atomically smooth structure, based on the fact that the addition of Bi_2O_3 tends to inhibit the grain growth in random NBT based ceramics [21–23]. Under these circumstances, the template seeds would preferably grow in the direction perpendicular to their side crystal faces (diametrical direction), leading to a poor texture owing to less matrix grains consumed during densification. Therefore, sintering

Table 1
Processing methods and electrical properties of random and textured NBT–BT ceramics.

Matrix	Template	Method	ρ (%)	f (%)	d_{33} (pC/N)
0.94NBT–0.06BT [7]	NBT	TGG	94	87	299
0.945NBT–0.055BT [24]	$SrTiO_3$	TGG	~98	94	~200
0.94NBT–0.06BT + 0 mol% Bi_2O_3 (this study)	$Bi_4Ti_3O_{12}$	TGG	97	93	290
0.94NBT–0.06BT + 2 mol% Bi_2O_3 (this study)	$Bi_4Ti_3O_{12}$	TGG	98.2	~0	150
Random 0.94NBT–0.06BT (this study)	–	Conventional	98	0	140

aids could relieve the difficulty in sintering of textured ceramics. However, the promotion to the formation of the texture is uncertain, mainly depending on whether or how the liquid phase formed during sintering influences the interfacial structure and morphology. Of course, the effect may also be related to the amount of the sintering aids. This is also the reason why a slight texture [13] can be still seen in BIT textured NBT ceramics in which a little amount of Bi_2O_3 only has an ignorable effect on the interfacial structure and morphology.

4. Conclusions

The templated grain growth method was applied to make 0.94NBT–0.06BT piezoelectric ceramics using 5 vol% of BIT template seeds. It was indicated that un-doped samples have a high degree of grain orientation ($f \sim 0.93$), and an excellent piezoelectric coefficient ($d_{33} \sim 290$ pC/N) while excess Bi_2O_3 doped samples exhibit improved densification but hardly develop any texture. It was considered that the addition of excess Bi_2O_3 promotes the Ostwald grain growth preferably in the diametrical direction of the template rather than in the thickness direction (for undoped samples) by changing the grain boundary atomic structure, ultimately leading to less consumption of matrix grains and poorer texture development. The results demonstrated that the sintering aid should match with the template and the matrix as it is used in the fabrication of textured ceramics.

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