



## (Reactive) Templated Grain Growth of Textured Sodium Bismuth Titanate ( $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$ ) Ceramics—I Processing

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**Abstract.** Textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$  (5.5 mol%  $\text{BaTiO}_3$ ) ceramics with  $\langle 100 \rangle_{\text{pc}}$  (where pc denotes the pseudocubic perovskite cell) orientation were fabricated by Templated Grain Growth (TGG) and Reactive Templated Grain Growth (RTGG) using anisotropically shaped template particles. In the case of TGG, molten salt synthesized  $\text{SrTiO}_3$  platelets were tape cast with a  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol%BaTiO}_3$  powder and sintered at  $1200^\circ\text{C}$  for up to 12 h. In the RTGG approach,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) platelets were tape cast with a  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{BaCO}_3$  powder mixture and reactively sintered. The TGG approach using  $\text{SrTiO}_3$  templates resulted in  $>90\%$  texture along [001] whereas the RTGG approach using BiT templates resulted in 80% texture. The grain orientation distribution along the textured direction, as measured by X-ray rocking curve, showed a full width at half maximum of  $\sim 8^\circ$  and a texture fraction of 80%.

**Keywords:** texture, sodium bismuth titanate, ferroelectric, template, grain growth

### Introduction

Sodium bismuth titanate ( $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ) is an interesting non-lead based piezoelectric material with a high Curie temperature ( $T_c \sim 320^\circ\text{C}$ ) and remanent polarization ( $38 \mu\text{C}/\text{cm}^2$ ) [1]. In the [001] direction, a  $d_{33}$  coefficient as high as 450 pC/N [2] has been reported for flux grown single crystals at the morphotropic phase boundary with  $\text{BaTiO}_3$  (BT) (Fig. 1) [3]. (The phase diagram in Fig. 1 has been modified from Ref. [3] because controversial results have been reported in the literature about the high temperature crystal symmetry [4–10].) In contrast, the highest reported piezoelectric coefficient for polycrystalline  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  ceramics is 125 pC/N [1]. If the reported single crystal properties can be achieved in a textured ceramic, while simultaneously reducing the level of hysteresis [2], the resulting material would be an attractive alternative to lead-based piezoelectrics like lead zirconate titanate.

Grain oriented  $(\text{Na,K})_{1/2}\text{Bi}_{1/2}\text{TiO}_3$  (NKBT) ceramics were prepared by Tani et al. by a reactive templated grain growth method using plate-like  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  [11–13]. The plate-like  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  particles were aligned parallel to the tape casting direction to act as templates for oriented growth of NKBT. A Lotgering factor of 92% was achieved and improvements in the electrical properties like dielectric constant (9% increase to 644), planar coupling coefficient (46% increase to 0.43), and piezoelectric coefficient ( $d_{31}$ , 71% increase to  $-63$  pC/N), due to the increased crystallographic orientation, were reported [11–13].

The best material for seeding the phase formation of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  and to template its oriented growth would be  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ . However, anisotropically-shaped  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  particles are not available for templating. Alternative candidates include single crystals of other perovskites, which have the same crystal structure and a similar lattice parameter to  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ .

Preliminary experiments showed that  $\text{BaTiO}_3$  was unstable in a matrix of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  whereas  $\text{SrTiO}_3$  was able to template growth of oriented

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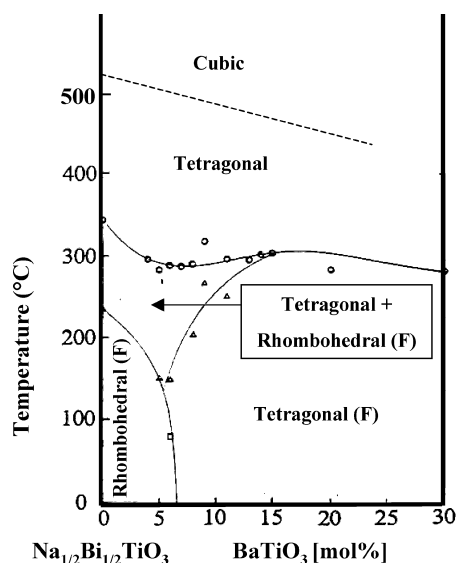


Fig. 1. The  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - $\text{BaTiO}_3$  phase diagram [3]. F = ferroelectric, AF = anti-ferroelectric, and P = paraelectric. The position of the boundary between the cubic and tetragonal regions is not known, and so is shown as a dashed line.

$(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  [14]. The objective of this study was to texture  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% $\text{BaTiO}_3$  solid solutions by either templated grain growth (TGG) using  $\text{SrTiO}_3$  (ST) templates or reactive templated grain growth using  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) templates. The composition close to the morphotropic phase boundary ( $\sim 5.5$  mol%  $\text{BaTiO}_3$ ) was specifically chosen because the electromechanical properties are reported to be the best at this composition. In part II the piezoelectric and dielectric properties of textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - $\text{BaTiO}_3$  are correlated to the texture quality and compared to those of single crystals.

## Experimental Procedure

### Template Synthesis

$\text{SrTiO}_3$  platelets were synthesized by a two-step process [15, 16]; in the first reaction, fumed  $\text{TiO}_2$  (P25, Degussa-Huls, Frankfurt-Main, Germany) and  $\text{SrCO}_3$  (Alfa Aesar 99% (1% Ba), Ward Hill, MA, USA) powders were reacted in a KCl (Alfa Aesar, Ward Hill, MA, USA) flux at  $1300^\circ\text{C}$  for 4 h to obtain  $\text{Sr}_3\text{Ti}_2\text{O}_7$  platelets. In the second reaction,  $\text{Sr}_3\text{Ti}_2\text{O}_7$  platelets were reacted with  $\text{TiO}_2$  at  $1200^\circ\text{C}$  for 4 h in a KCl flux to obtain  $\text{SrTiO}_3$  platelets with (100) major

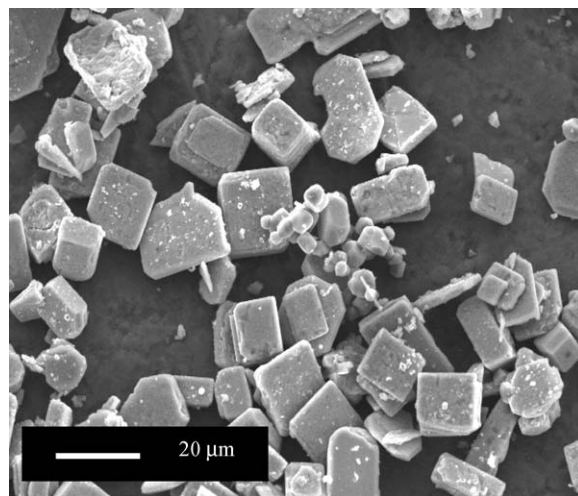


Fig. 2. Molten salt synthesized  $\text{SrTiO}_3$  particles.

faces. The reactions yield tabular  $\text{SrTiO}_3$  particles, (see Fig. 2). Residual KCl was removed from the platelets by repeated washing in deionized water. The  $\text{SrTiO}_3$  platelets have edge lengths of 10–20  $\mu\text{m}$  and thicknesses of 2–5  $\mu\text{m}$  to yield aspect ratios of 2–10. More details on the template synthesis are given in [15, 16].

Plate-like  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) particles were prepared by mixing equal weights of  $\text{Bi}_2\text{O}_3$  (Alfa Aesar 99.99%, Ward Hill, MA, USA) (79.5 wt%) and  $\text{TiO}_2$  (P25, Degussa-Huls, Frankfurt-Main, Germany) (20.5 wt%) powders with a eutectic mixture of NaCl (44 wt%) and KCl (56 wt%) in a sealed alumina crucible and by heating to  $1100^\circ\text{C}$ , which is above the eutectic temperature ( $645^\circ\text{C}$ ) of the salt [17, 18]. The mixture was heated at  $10^\circ\text{C}/\text{min}$  from room temperature, and held at  $1100^\circ\text{C}$  for 30 min, before slow cooling. It was then washed with warm deionized water to remove the salt. The  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  particles were 5–20  $\mu\text{m}$  in diameter and  $\sim 0.5$   $\mu\text{m}$  in thickness (Fig. 3).

### Sample Preparation

For TGG of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - $\text{BaTiO}_3$ , a mixture of pure  $\text{Na}_2\text{CO}_3$  (J.T. Baker Chemical Co., NJ, USA),  $\text{Bi}_2\text{O}_3$  (Alfa Aesar 99.99%, Ward Hill, MA, USA),  $\text{TiO}_2$  (P25, Degussa-Huls, Frankfurt-Main, Germany),  $\text{BaCO}_3$  (J.T. Baker Chemical Co 99.9%, NJ, USA) and  $\text{MnCO}_3$  (0.3 wt%, Alfa Aesar 99.9%, Ward Hill, MA, USA) powders, corresponding to a final stoichiometry of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol%  $\text{BaTiO}_3$ , were ball

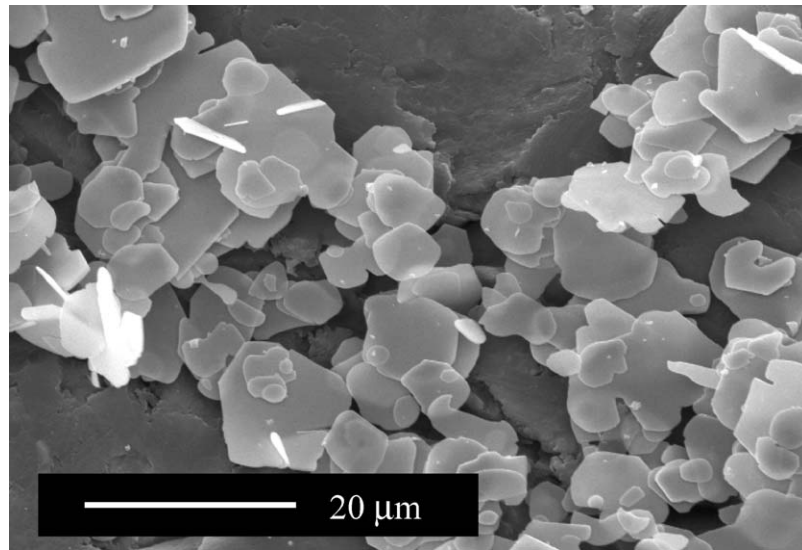


Fig. 3. Molten salt synthesized  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  platelets.

milled in isopropanol with 3 mm  $\text{ZrO}_2$  balls in a polyethylene bottle for 16 h. The mixture was calcined at  $800^\circ\text{C}$  for 2 h and then ball milled in isopropanol with 3 mm  $\text{ZrO}_2$  balls in polyethylene bottles for 16 h. The resulting milled powder was mixed with a commercial binder system (Ferro 73210, Ferro Corp., Cleveland, OH, USA) in toluene (J.T. Baker Chemical Co, NJ, USA) for tape casting.  $\text{SrTiO}_3$  ( $\rho_0 \approx 5.12 \text{ g/cm}^3$ ) platelets, corresponding to 5 vol% of the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-}5.5 \text{ mol\% BaTiO}_3$  ( $\rho_0 = 6 \text{ g/cm}^3$ ) powder, were added to the slurry.

For RTGG of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ , the chemicals mentioned above, i.e.  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{BaCO}_3$  and  $\text{MnCO}_3$ , were ball milled in isopropanol with 3 mm  $\text{ZrO}_2$  balls in polyethylene bottles for 16 h. The resulting milled powder mixture was mixed with a commercial binder system (Ferro 73305, Ferro Corp., Cleveland, OH, USA) in toluene for tape casting.  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  platelets, corresponding to 6 vol% of the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-}5.5 \text{ mol\% BaTiO}_3$  powder, were added to the slurry.

In both approaches, the slurry was cast with a doctor blade on a glass substrate with a blade opening of  $200 \mu\text{m}$  at a shear rate of  $\sim 200 \text{ s}^{-1}$ . The viscosity of the slurry was  $150 \text{ mPa}\cdot\text{s}$ . The dried tapes were cut into 1.5 cm by 2.5 cm pieces and 60 tapes were laminated at 80 MPa. The binder was burned out by heating at  $600^\circ\text{C}$  for 1 h with heating and cooling rates of  $0.86^\circ\text{C}/\text{min}$ . For TGG, the samples were heated in oxygen at  $10^\circ\text{C}/\text{min}$  to  $1200^\circ\text{C}$  and held for

up to 12 h. For RTGG, the sample was reacted between  $600$  and  $1000^\circ\text{C}$  for up to 4 h before sintering at  $1200^\circ\text{C}$ .

The Lotgering factor, rocking curves and X-ray pole figures were used to quantify texture. The Lotgering factor [19] is a semi-quantitative method and does not give any information about the grain orientation distribution. Crystallographic texture was characterized using X-ray based rocking curves [20] in order to obtain quantitative information about the grain orientation distribution. Rocking curve measurements were performed around the (002) peak (i.e.  $2\theta$ :  $46.6^\circ$ ) of NBT with a rocking curve in  $\omega$  of  $-20^\circ$  to  $+20^\circ$  using a standard X-ray diffractometer (Scintag, Inc., CA, PAD V, theta-2-theta goniometer, Si(Li) Peltier detector). The data were corrected to eliminate defocusing and absorption effects using a computer program developed by Vaudin [21]. The March-Dollase function, Eq. (1), was used to quantify the texture distributions from the rocking curve analysis [22].  $F(f, r, \omega)$  is given by

$$F(f, r, \omega) = f \left( r^2 \cos^2 \omega + \frac{\sin^2 \omega}{r} \right)^{-\frac{3}{2}} + (1 - f) \quad (1)$$

where  $\omega$  is the angle between the texture (orientation) axis and the scattering vector,  $r$  is the degree of orientation parameter, and  $f$  is the volume fraction of oriented material. The  $r$  parameter characterizes the width of the texture (orientation) distribution.  $r = 1$  for a random

sample and for a perfectly textured sample of tabular grains  $r = 0$ .

Pole figures were measured using a four-circle diffractometer and Cu  $K\alpha$  radiation. Pole figures were measured in steps of  $\Delta\alpha = 5^\circ$  and  $\Delta\beta = 5^\circ$  in the ranges of  $0^\circ \leq \alpha \leq 70^\circ$  and  $0^\circ \leq \beta \leq 360^\circ$ , with a measuring time of 10 seconds/point, where  $\alpha$  is the tilt angle and  $\beta$  is the azimuthal angle.

## Results and Discussion

### TGG of NBT using SrTiO<sub>3</sub> Template Particles

Figure 4 shows that 20  $\mu\text{m}$  of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> single crystal grows on a SrTiO<sub>3</sub> single crystal at 1200°C in 12 h. Based on orientation imaging microscopy  $\langle 001 \rangle_{\text{pc}}$  oriented  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> grows on  $\langle 001 \rangle_{\text{pc}}$  oriented SrTiO<sub>3</sub> [23], and the two are aligned in-plane.

For TGG of textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub>, 5 vol% molten salt synthesized SrTiO<sub>3</sub> templates were added to the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> matrix, which gave strong  $\langle 001 \rangle_{\text{pc}}$  texture.

Sakata and Masuda [24] determined the phase diagram of the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -SrTiO<sub>3</sub> system in the composition range of  $0 \leq x \leq 0.5$ , where  $x$  denotes the mol fraction of SrTiO<sub>3</sub>. They found that  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  and SrTiO<sub>3</sub> form a solid solution over this composition range. Therefore, the interaction of SrTiO<sub>3</sub> templates with the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> matrix was studied by electron microscopy. The Sr content in the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> matrix was determined to be  $<0.3 \text{ wt}\%$  6  $\mu\text{m}$  away from a SrTiO<sub>3</sub> template. Based on a microprobe compositional line scan from the template into the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -BaTiO<sub>3</sub> grown region, the Sr content in the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> matrix is constant and  $<0.3 \text{ wt}\%$ . Since, there is no Sr compositional gradient in the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> growth region, it can be inferred that there is relatively little Sr diffusion into the matrix from SrTiO<sub>3</sub> templates. Some evidence for limited Sr diffusion was obtained in permittivity measurements as a function of temperature. (Sr is known to decrease the  $T_{\text{max}}$  ( $-5.3^\circ\text{C}/\text{mol}\%$ ) of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  [25].) It is possible that the smallest of the SrTiO<sub>3</sub> template particles dissolve in the matrix.

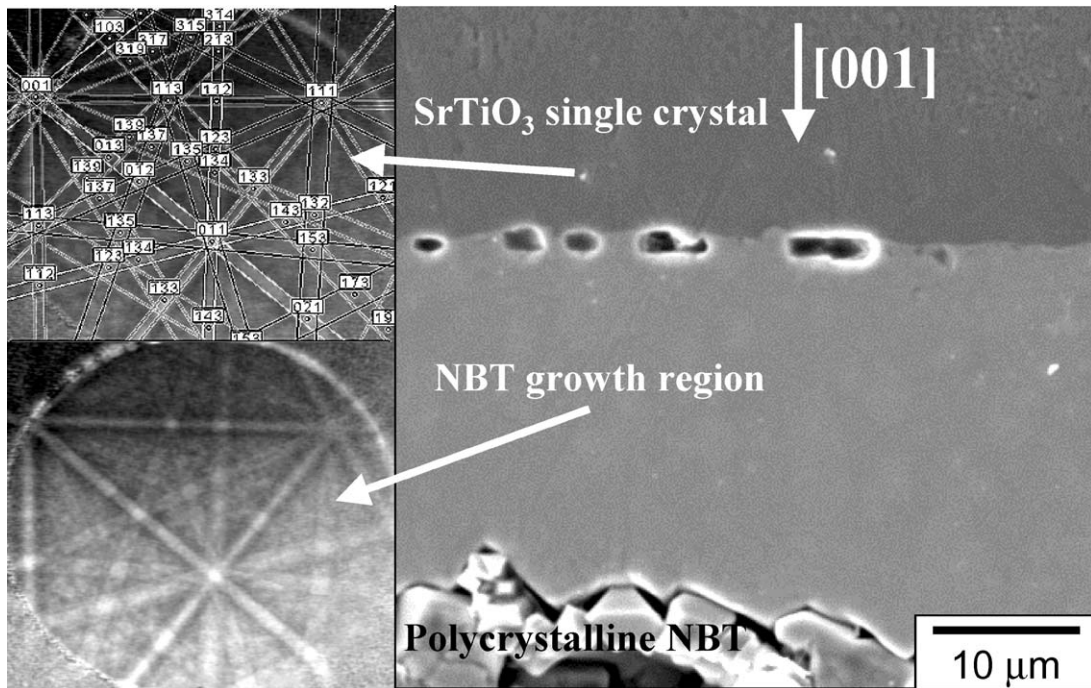


Fig. 4. Growth of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO<sub>3</sub> crystal on  $\langle 001 \rangle_{\text{pc}}$  single crystal SrTiO<sub>3</sub> at 1200°C.

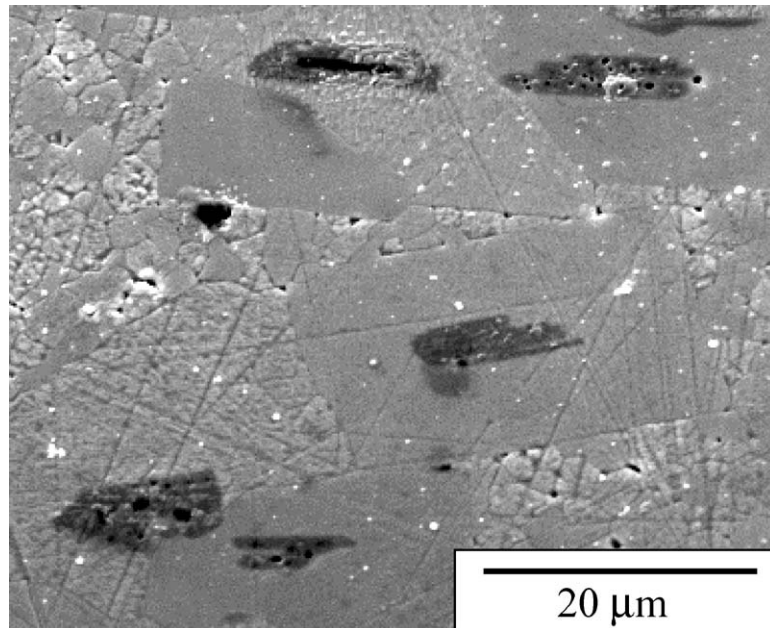


Fig. 5. Microstructure of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  ceramic heated at  $1200^\circ\text{C}$  for 12 h. Dark regions are  $\text{SrTiO}_3$  templates and the light regions are the matrix material.

#### Sintering and Microstructure

The microstructure of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  ceramic with 5 vol%  $\text{SrTiO}_3$  after heating at  $1200^\circ\text{C}$  for 12 h is shown in Fig. 5. The  $\text{SrTiO}_3$  templates can be easily distinguished from the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  matrix, i.e.  $\text{SrTiO}_3$  templates are darker than the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  matrix phase. All SEM images were taken in the tape casting direction, i.e. perpendicular to the sample normal. There is a  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  growth region on the templates. It appears that the amount of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  growth on each surface of the  $\text{SrTiO}_3$  templates is equal. This is because all of the  $\text{SrTiO}_3$  templates are largely bounded by  $\{100\}$  faces [15].

In Fig. 6, the texture fraction, as calculated from the Lotgering factor, is plotted as a function of heating time. It can be seen that  $f = 70\%$  after only one hour at  $1200^\circ\text{C}$ . The Lotgering factor increases slowly with longer sintering times. It takes about 12 h to reach a texture fraction of  $f = 94\%$ . These samples are  $\sim 98\%$  of the theoretical density. Random ceramics sintered at the identical conditions with no  $\text{SrTiO}_3$  templates were transparent (fully dense).

Texture evolves by dissolution of randomly oriented matrix grains and deposition on the oriented template particles. It should be noted that template growth does not occur until relatively high densities ( $>90\%$ ) are achieved [26]. The driving force for template growth comes from the size difference between the template particles and matrix grains, similar to Ostwald ripening. In the initial stage, the driving force for growth is large, and rapid growth takes place on the  $\text{SrTiO}_3$  templates at the expense of small matrix particles. Therefore,  $f = 70\%$  texture was obtained after 1 h at  $1200^\circ\text{C}$ . Coarsening of matrix particles also takes place during templated growth. As a result, the solubility difference between the relatively large, randomly oriented template grains and the matrix grains decreases thus slowing texture development at longer sintering times [27].

A second reason for the slowing of texture development is grain “impingement,” Fig. 6. Although  $\text{SrTiO}_3$  templates were well dispersed in the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  matrix powder, early grain impingement takes place between templates that are closer to each other. Further growth of these grains at the contact point is not expected, since these grains are at about the same size and grain boundary is flat. Therefore, there is significantly less driving force for grain boundary mobility.

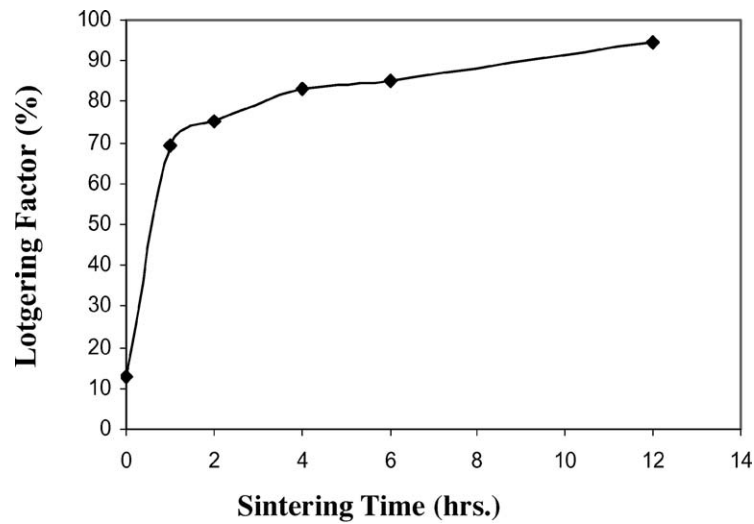


Fig. 6. Texture evolution as a function of sintering time at 1200°C, 5 vol% SrTiO<sub>3</sub> templated (Na<sub>1/2</sub>Bi<sub>1/2</sub>)TiO<sub>3</sub>-5.5 mol% BaTiO<sub>3</sub> samples.

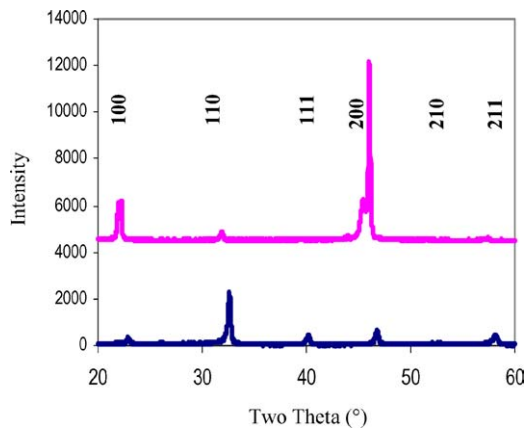


Fig. 7. XRD pattern of textured (Na<sub>1/2</sub>Bi<sub>1/2</sub>)TiO<sub>3</sub>-5.5 mol% BaTiO<sub>3</sub> ceramic using 5 vol% SrTiO<sub>3</sub> templates heated at 1200°C for 12 h (top), and powder of same chemical composition (bottom).

In Fig. 7, the XRD patterns of random and textured (Na<sub>1/2</sub>Bi<sub>1/2</sub>)TiO<sub>3</sub>-5.5 mol% BaTiO<sub>3</sub> ceramics after heating at 1200°C for 12 h are shown. In a randomly oriented ceramic, {110} is the main peak. In contrast, the {200} peak becomes the most intense one in SrTiO<sub>3</sub> templated (Na<sub>1/2</sub>Bi<sub>1/2</sub>)TiO<sub>3</sub>-5.5 mol% BaTiO<sub>3</sub>.

The rocking curve of the sample with a 5 vol% SrTiO<sub>3</sub> template concentration that was heated at 1200°C for 12 h is shown in Fig. 8. The March-Dollase [22] equation was used to model texture and is plot-

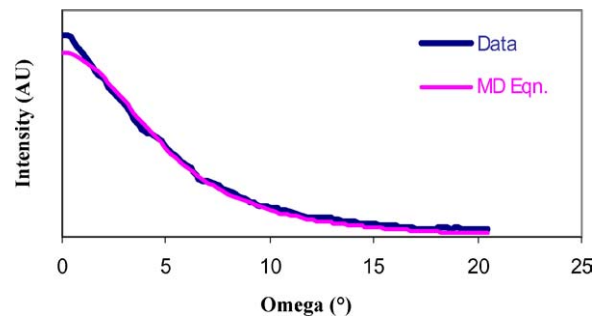


Fig. 8. Rocking curve of textured (Na<sub>1/2</sub>Bi<sub>1/2</sub>)TiO<sub>3</sub>-5.5 mol% BaTiO<sub>3</sub> ceramic using 5 vol% SrTiO<sub>3</sub> template heated at 1200°C for 12 h (MD Eqn. = March-Dollase equation).

ted in the same figure. The texture fraction  $f$  was determined to be 80% with an orientation parameter of  $r = 0.23$ . The width of the distribution was narrow, with a full width at half maximum (FWHM) of 8°. The texture fraction may be underestimated by a few percent, since the agreement between the experimental data and the March-Dollase fit is not as good at low  $\omega$  values.

Pole figures of the (002)<sub>pc</sub> and (111)<sub>pc</sub> planes are shown in Fig. 9. Both (002)<sub>pc</sub> and (111)<sub>pc</sub> pole figures are axisymmetric, i.e. the sample is fiber-textured and there is no in-plane preferential orientation. For the (111)<sub>pc</sub> pole figure, the intensity is a maximum at about 53° from the sample normal, which is very close to the angle between [001]<sub>pc</sub> and [111]<sub>pc</sub>.

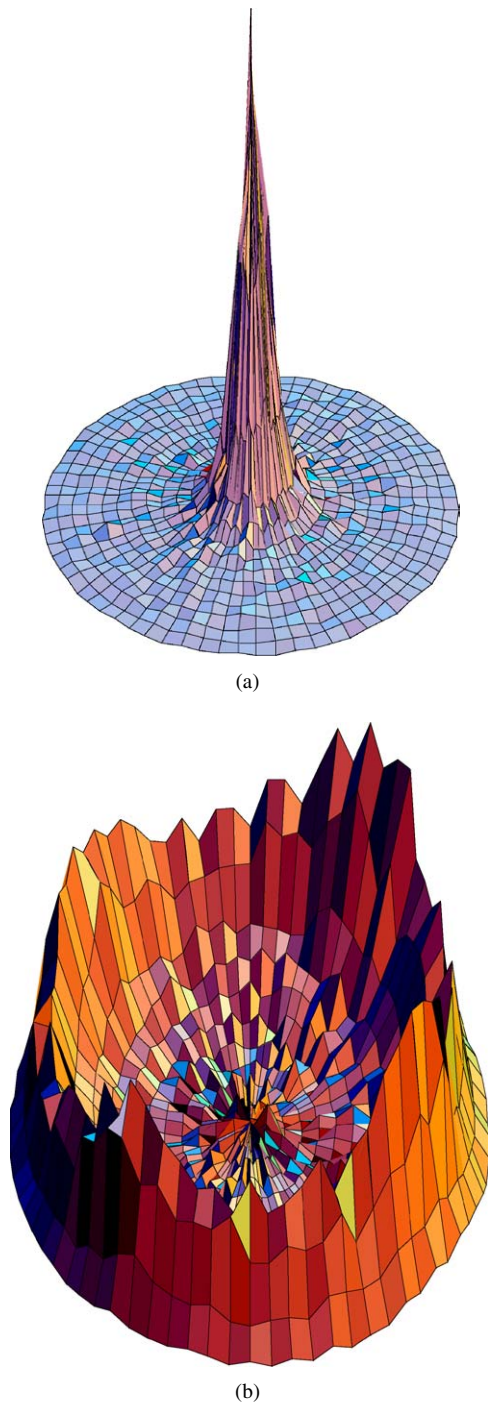


Fig. 9. (a) Pole figure of (002) planes of textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  ceramic using 5 vol%  $\text{SrTiO}_3$  templates heated at  $1200^\circ\text{C}$  for 12 h. (Tilt angle =  $70^\circ$ , Azimuthal angle =  $360^\circ$ ). (b) Pole figure of (111) planes of textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  ceramic using 5 vol%  $\text{SrTiO}_3$  templates heated at  $1200^\circ\text{C}$  for 12 h. (Tilt angle =  $70^\circ$ , Azimuthal angle =  $360^\circ$ .)

#### RTGG using $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Template Particles

$(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  ceramics were also textured using  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  platelets using the RTGG approach. The synthesized  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  platelets are single crystals (monoclinic at room temperature) with the  $c$ -axis perpendicular to the major surface, Fig. 3. Six vol% anisotropically shaped  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  platelets were aligned by tape casting in a reactive matrix powder. The prepared samples were either directly heated to the sintering temperature or pre-reacted at  $700$  or  $800^\circ\text{C}$  for 1 h before heating to the sintering temperature. These samples were also sintered at  $1200^\circ\text{C}$  for 12 h.

The pre-reaction at low temperature was found to be a key step in texture development. Samples that were pre-reacted at  $\geq 900^\circ\text{C}$ , or directly heated to the sintering temperature showed almost no evidence of texturing as measured by a Lotgering factor of  $f = 8\%$ , Fig. 10. However, if the samples were pre-reacted at  $700$  or  $800^\circ\text{C}$ , about  $f = 80\%$  texturing was achieved for both cases.

Potassium modified  $(\text{Na}_{0.85}\text{K}_{0.15})_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ceramics were textured via the RTGG approach by Tani et al. [11–13] using molten salt synthesized  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  template particles. Tani et al. observed *in situ* reactions by transmission electron microscopy (TEM). There was a rapid diffusion of Na and K atoms from the matrix into the BiT template particles, changing the layered perovskite to a regular perovskite. This *in-situ* reaction of the RTGG processing was regarded as topotactic in which the template itself changes structure [13]. It is also evident that the single crystallinity of the template particle does not change during this process. This is one of the major differences between the RTGG and TGG processes. In the TGG process, usually heteroepitaxial growth takes place on the template, as in the case of NBT-5.5 mol% BT ceramics textured using 5 vol%  $\text{SrTiO}_3$  templates.

The grain size of the textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$  using  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  templates and heated at  $1200^\circ\text{C}$  for 12 h was  $80\ \mu\text{m}$ . Interestingly, there was no evidence of morphological texture in this sample [23]. That is, a brick-wall microstructure was not obtained. In addition, the morphology and grain size were distinctly different than the BiT template size and morphology.

Both TGG and RTGG approaches resulted in  $\langle 001 \rangle_{\text{pc}}$  textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$  ceramics. In the RTGG approach, texture was strongly dependent on the pre-reaction temperature and a texture fraction of up to  $f = 80\%$  was achieved. The  $\text{SrTiO}_3$  templated



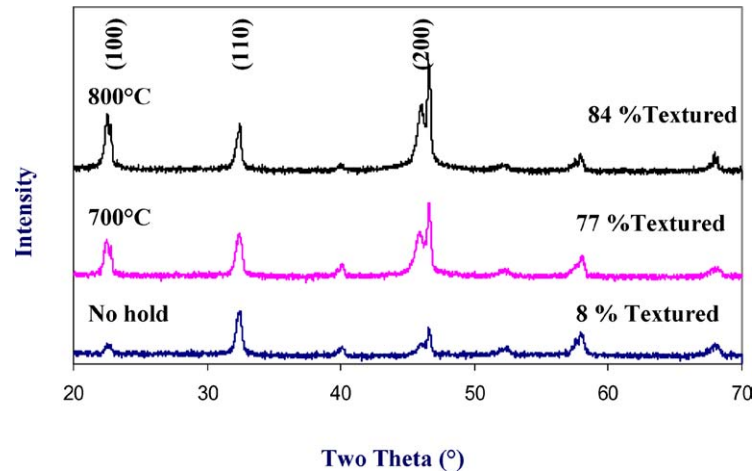


Fig. 10. XRD patterns of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol%  $\text{BaTiO}_3$  ceramics textured using  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  templates at different heat treatment conditions.

$(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  ceramics resulted in  $f = 94\%$  texture after sintering at identical sintering conditions.

The two approaches resulted in different microstructures.  $\text{SrTiO}_3$  templated ceramics had a narrow grain size distribution ( $<50\ \mu\text{m}$ ) with a brick-wall microstructure whereas  $\text{BiT}$  templated ceramics had a wide grain size distribution (up to  $80\ \mu\text{m}$ ) and no evidence of morphological texture. The number density of templates can control the final grain size. The higher the number density of template particles, the smaller the grain size would be. In this study 5 vol%  $\text{SrTiO}_3$  and 6 vol%  $\text{BiT}$  template particles were aligned in the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  matrix. Even though the volume of each  $\text{BiT}$  template particle ( $10 \times 10 \times 0.5\ \mu\text{m}^3$ ) was smaller than the volume of  $\text{SrTiO}_3$  template particle ( $15 \times 15 \times 5\ \mu\text{m}^3$ ) and therefore, there were a larger number (frequency) of  $\text{BiT}$  template particles per unit volume, the resultant grain size in the ceramic was larger than the grain size in the  $\text{SrTiO}_3$  templated samples. This suggests that not all of the  $\text{BiT}$  template particles act as templates [26]. One reason might be that  $\text{BiT}$  template particles are  $<0.5\ \mu\text{m}$  in thickness. The size difference between template particles and matrix powder is relatively small, and therefore the driving force for the template to grow is relatively small. Alternatively, it is possible that some of the  $\text{BiT}$  templates reacted with the matrix before nucleating oriented  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - $\text{BaTiO}_3$ .

The objective in studying the  $\text{BiT}$  templated NBT-BT ceramic was to compare the electrical properties to the NBT-BT textured using  $\text{SrTiO}_3$  templates. These properties are reported in part II [28].

## Conclusions

$(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol%  $\text{BaTiO}_3$  ceramics were textured using two kinds of template particles, i.e.  $\text{SrTiO}_3$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . Growth of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol%  $\text{BaTiO}_3$  on the  $\text{SrTiO}_3$  template surface was heteroepitaxial. A brick-wall microstructure resulted after sintering at  $1200^\circ\text{C}$ , with a  $\text{SrTiO}_3$  template grain located at the core of each NBT grain. 94% textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - $\text{BaTiO}_3$  ceramics, as measured by Lotgering factor, were obtained using 5 vol%  $\text{SrTiO}_3$  template particles. The FWHM of the texture distribution was  $8^\circ$ . Reproducible results were easily obtained with  $\text{SrTiO}_3$  templates using the TGG approach.

Reactive templated grain growth of  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol%  $\text{BaTiO}_3$  ceramics were fabricated using  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  template particles. A texture fraction of 80% was obtained as measured by the Lotgering factor. Pre-reaction at 700 or  $800^\circ\text{C}$  before heating the sample to the sintering temperature is critical, because samples directly heated to the sintering temperature did not show any evidence of texturing. During pre-reaction, all of [11–13] the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  templates were converted to  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol%  $\text{BaTiO}_3$  with the perovskite structure, so no residual  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  phase was expected in the grains.

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