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Paisan Setasuwon & Suphakan Kijamnajsuk

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# Synthesis of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ anisotropic particles with grain orientation by conversion of $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ crystals

Paisan Setasuwon\*, Suphakan Kijamnajsuk

*National Metal and Materials Technology Center, 114 Paholyothin Road, Pathumthani, Thailand*

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## Abstract

A novel method for synthesizing  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (BNT) anisotropic particles with grain orientation is reported. Anisotropically shaped particles of BNT were prepared by conversion of  $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT15) single crystals. Platelet NBT15 was produced by molten-salt synthesis. They were converted to BNT by second molten-salt synthesis at 800–1200 °C. NBT15 single-crystal platelets were transformed into platelet particles of polycrystalline BNT. The reaction is topotaxial, those recrystallized BNT were oriented with (*h* 0 0) plane parallel to the platelet. The use of converted BNT particles as seed was confirmed by performing templated grain growth (TGG) of BNT with 5% grain-oriented, anisotropic particles of BNT.

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**Keywords:**  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ;  $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ ; Templated grain growth; Conversion; Seeds; Topotaxial reaction

## 1. Introduction

Commercial piezoelectric materials at the present are of lead zirconium titanate family, they exhibit a range of useful properties with low cost. However, with growing concern on health and safety worldwide, a requirement for environmentally benign piezoelectrics is continually increasing.  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (BNT) ceramic is a promising piezoelectric material without the lethal element, lead. This material and its variations are now being investigated intensively. Improvement in piezoelectric characteristics is the main aim, employing various techniques [1–7].

Templated grain growth (TGG) is a technique used to utilize the better piezoelectric properties along certain crystallographic directions, it uses seeds with anisotropic shape to arrange them with shear forces into orientation. Platelet and needle are typical shapes of seeds. Single-crystal seeds are produced by molten-salt synthesis, the shape of molten-salt-synthesized crystals is the characteristics of their crystal structure. However, seeds are not

needed to be single crystal, anisotropic particles with grain orientation could also be the candidates.

BNT crystal structure is rhombohedral at room temperature, tetragonal and cubic at 260 and 520 °C, approximately [8]. However, the rhombohedral and tetragonal structure of BNT is very close to cubic, resulting in symmetrical crystal shape [1]. Therefore, TGG techniques for BNT with seeds of the same material have not been reported in any literatures, only  $\text{SrTiO}_3$  seeds were used instead [1,9]. Nevertheless, the addition of poor-piezoelectric  $\text{SrTiO}_3$  seeds would in effect reduce the increase in piezoelectric properties with TGG. If anisotropic BNT seeds were available, piezoelectric properties of polycrystalline BNT could be very close to those of single crystal via TGG.

As seeds of BNT with anisotropic shape are not available, an innovative method is needed to make anisotropic BNT particles with orientation. Anisotropic  $\text{SrTiO}_3$  crystal seeds were prepared by epitaxially growing  $\text{Sr}_3\text{Ti}_2\text{O}_7$  crystals in molten salt [10]. It might be possible to obtain anisotropic BNT seeds from intermediate templates. Reaction of needle-shaped  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$  particles with excessive  $\text{NaCO}_3$  yielded polycrystalline BNT needle particles with no orientation in particle [11]. Therefore,  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$  is not the appropriate template.

\*Corresponding author. Tel.: +66 2 564 6500; fax: +66 2 564 6447.

E-mail address: [paisan@mtcc.or.th](mailto:paisan@mtcc.or.th) (P. Setasuwon).

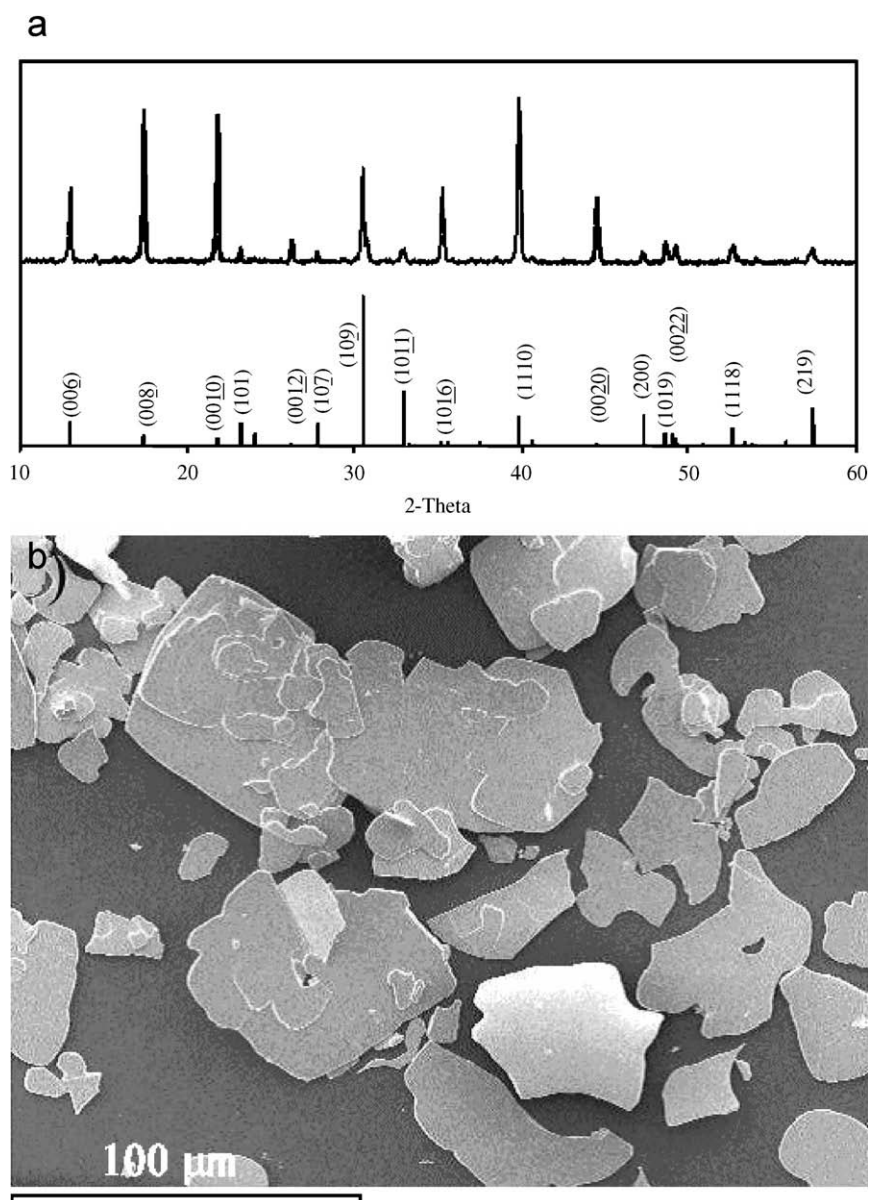


Fig. 1. (a) X-ray diffraction pattern of NBT15 crystals grown at 1100 °C for 6 h with NBT15 JPDF No. 74-1316 and (b) SEM micrograph of NBT15 crystals.

$\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT15) was identified as suitable intermediate template. The crystal structure of NBT15 is tetragonal with  $a = 0.384 \text{ nm}$  and  $c = 4.08 \text{ nm}$  [12]. Near-cubic BNT has unit cell parameter of  $0.389 \text{ nm}$  [13]. (001) plane of NBT15 is occupied by common constituent elements and has similar lattice parameters to those of BNT. The conversions of NBT15 to BNT were studied. TGG of BNT was performed to investigate the usability of synthesized BNT particles.

## 2. Experimental procedures

### 2.1. Molten-salt synthesis of $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ (NBT15)

$\text{Na}_2\text{CO}_3$  (Fluka, 99%),  $\text{Bi}_2\text{O}_3$  (Fluka, 98%) and  $\text{TiO}_2$  (Fluka, 99%) were used as starting materials. They were

mixed in the proportion to yield NBT15. NaCl (AnalaR, 99.5%) was added at 85 vol %. The mixture was put in the alumina crucible and the lid was sealed with alumina cement. The synthesizing temperature was 1100 °C for 6 h with cooling rate of 180 °C/min. Salt was washed out with hot water several times.

### 2.2. Molten-salt conversion for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (BNT)

NBT15 crystals produced earlier were subjected to second molten-salt synthesis.  $\text{Na}_2\text{CO}_3$  and  $\text{TiO}_2$  were added to give the total composition of BNT. Again, 85 vol% NaCl was added. The sealed crucible were heated at temperature of 800–1200 °C for 4 h with cooling rate of 180 °C/h. Salt was washed out with hot water several times. The size and shape of synthesized particles were

investigated with SEM (JEOL, JSM-6301F). X-ray diffraction analysis was performed for phase identification. The degree of orientation was determined with Lotgering factors [14]. The Lotgering factor can be calculated as follows:

$$f = (P - P^0)/(1 - P^0),$$

where  $P$  and  $P^0$  are  $\Sigma I(00l)/\Sigma I(hkl)$  in the textured and random cases, respectively.

### 2.3. Templated grain growth of BNT

Simple tape casting of calcined powder of BNT with 5% BNT seed particles was performed. BNT seed particles were the product of conversion at 1000 °C. Tape slurry was prepared by adding 10 g of attrition-milled BNT powder with 15 g of deionised water, 1.6 g of Duramax B-1000 binder and 0.2 g Duramax D3005 dispersant (Rohm and Haas). The mixture was stirred by magnetic stirrer for 2 h before 0.5 g of BNT seed particles were added. The stirring continued for another half an hour before the slurry was cast through doctor blade gap of 600 µm on running silicone-coated mylar sheet. Tape was dried and cut into small rectangles. They were fired at 1080 °C for 4 h (the sintering temperature of attrition-milled BNT powder [15]). X-ray diffraction analysis was performed for detection of preferred orientation.

## 3. Results and discussion

### 3.1. Molten-salt synthesis of $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ (NBT15)

NBT15 crystals were successfully grown at 1100 °C for 6 h (Fig. 1). The X-ray diffraction pattern (Fig. 1(a)) shows preferred orientation of (001) planes in crystals packed in sample holder slot, comparing with standard pattern [12]. The preferred orientation could be the result of in-packing arrangement of particles with very high aspect ratio, the platelet crystals of NBT15 were large and thin (Fig. 1(b)). The diameters of some crystals were larger than 50 µm and just a few micron thin. It is possible that smaller particles were broken pieces of complete crystals.

### 3.2. Molten-salt conversion for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (BNT)

Fig. 2(a) shows the X-ray diffraction pattern of product of NBT15 crystals with  $\text{TiO}_2$  and  $\text{Na}_2\text{CO}_3$  in NaCl at 800 °C for 4 h. Both starting NBT15 and BNT phases coexisted, more time would be required for complete reaction. Raising temperature to 900 °C, the reaction was complete and only BNT was obtained (Fig. 2(b)). Figs. 2(c)–(e) are the X-ray diffraction patterns of reactions at 1000, 1100 and 1200 °C, respectively. Only the relative intensity in the pattern at 1200 °C is similar to that of powder diffraction pattern [13] (Fig. 2(f)). X-ray diffraction patterns at 900–1100 °C all show preferred orientation with the (h00) plane. The Lotgering factor for (h00) plane were

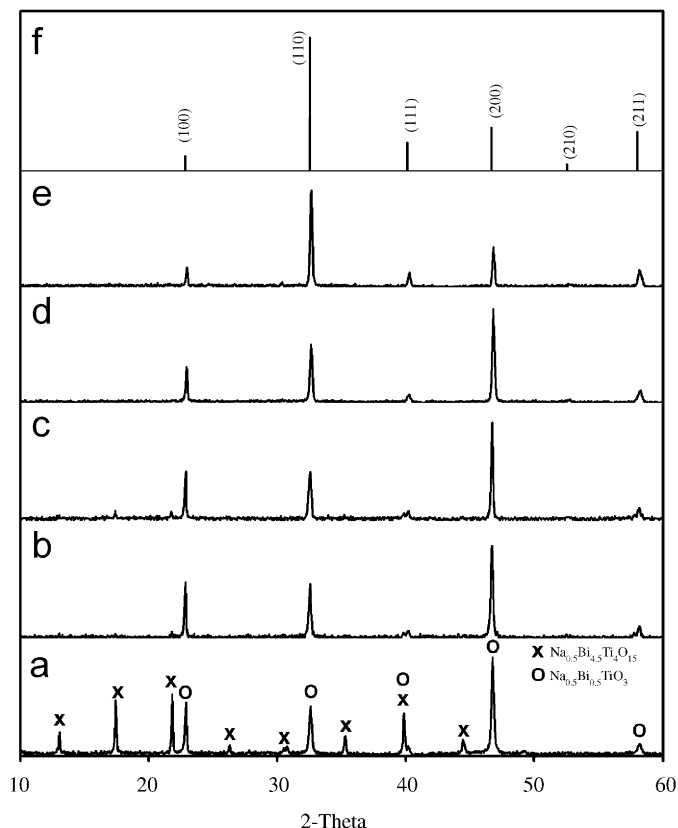


Fig. 2. X-ray diffraction patterns of conversion of NBT15 crystals at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C and (f) BNT JPDF No. 89-3109.

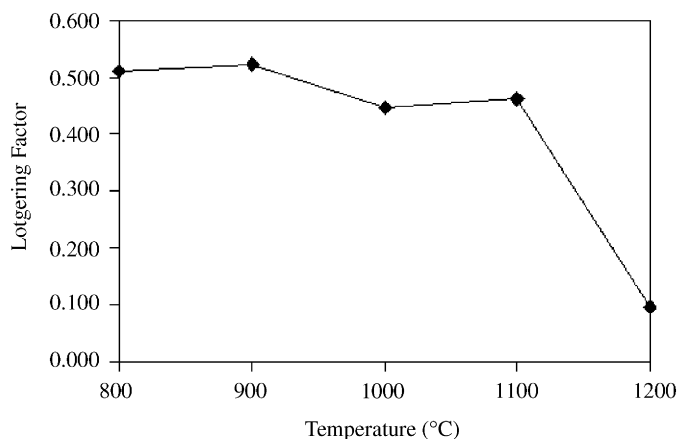


Fig. 3. Lotgering factor for (h00) plane for various conversion temperatures.

calculated and plotted in Fig. 3. It clearly demonstrates the high degree of orientation in particles by conversion at 800–900 °C, and the degree of orientation decreased with increasing temperature. The preferred orientation in the in-packing-arranged particles indicates that the conversion of NBT15 crystal yielded BNT with (h00) orientation in particle.

SEM micrographs of converted BNT particles at 800–1200 °C for 4 h are shown in Figs. 4(a)–(h). The converted products composed of large particles similar in

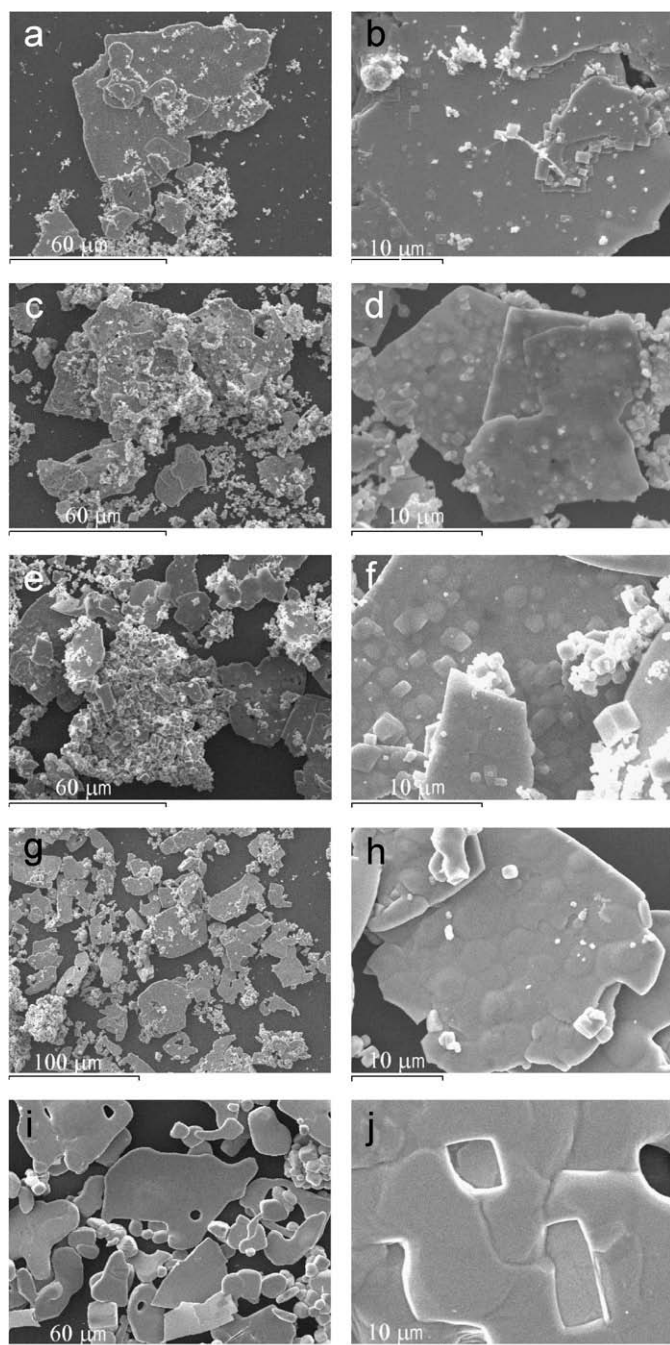


Fig. 4. SEM micrograph of conversion product at (a,b) 800 °C, (c,d) 900 °C, (e,f) 1000 °C, (g,h) 1100 °C and (i,j) 1200 °C.

shape and size to original NBT15 high aspect-ratio platelet, and many small particles whose size is less than a few microns. At 1000 °C, some small particle grew large and displayed cubic shape (Fig. 4(f)), typical to BNT crystal morphology. The most prominent features were numerous tiny squares observable on the surface of platelet particles (Fig. 4(b)). These square features were getting larger with increasing temperature (Figs. 4(d) and (f)). At 1200 °C, the square features behaved as grain rounding when edges of adjoining grains met the other during grain growth. It is likely that those square features are BNT grains growing

on the original NBT15 platelet particle. Therefore, the conversion of NBT15 to BNT is not that of epitaxial growth. It was recrystallization of BNT, therefore, single crystal of NBT15 platelets were transformed into platelet particles of polycrystalline BNT. Fortunately, those recrystallized BNT crystals were topotaxially oriented along ( $h00$ ) plane as determined by X-ray diffraction (Figs. 2(b)–(e)). The orientation is possibly the result of structural compatibility between NBT15 (001) and BNT ( $h00$ ). At 1200 °C, the X-ray diffraction pattern was similar to that of powder or randomly oriented polycrystalline BNT. This could be explained that thicker, more rounded and agglomerated particles (Fig. 4(i)) do not have the in-packing rearrangement of particles as high aspect-ratio platelet particles do.

### 3.3. Templated grain growth of BNT

Preliminary test of converted BNT particles as seed in TGG of BNT was performed. The 1000 °C BNT particles were used by washing again several times to remove small particles, which remained floating in the water. Green tape of calcined BNT powder with 5 vol% of seed was cast with doctor blade gap of 600 μm. Dried tape was cut and fired at 1080 °C for 4 h. X-ray diffraction pattern of the sintered tape is shown in Fig. 5. The relative intensity for ( $h00$ ) plane is clearly dominated with the Lotgering factor of 0.3318. Although the degree of orientation of sintered tape is not very high but this simple experiment has demonstrated that the converted BNT particles could be used as seed for TGG of BNT material. It is also proved that seeds for TGG are not limited to single crystals. Optimizing the tape preparation should increase the value substantially; in the next work optimization of the whole process for TGG will be carried out to achieve the best piezoelectric properties from total BNT composition.

## 4. Conclusion

BNT anisotropic particles with grain orientation are synthesized by conversion of NBT15 single crystals. It is

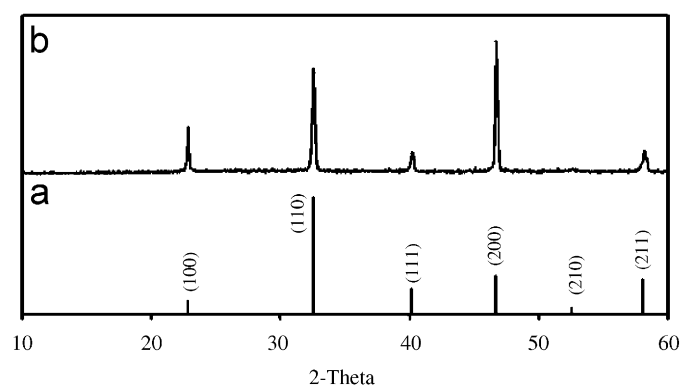


Fig. 5. X-ray diffraction patterns of (a) BNT JPDF No. 89-3109 and (b) tape-cast sintered BNT with 5% seed.

the first time that TGG of BNT material was performed with seed of the same material. The theoretical advantage is no deterioration of piezoelectric properties from the inclusion of seeds with poorer piezoelectric characteristics. Optimizing seed synthesis and orientation will give the ability to utilize TGG of BNT to its full potential for future commercialization of this material.

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