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# Synthesis and characterization of $Na_{0.5}Bi_{0.5}TiO_3$ platelets with preferred orientation using Aurivillius precursors

Chao Jiang, Kechao Zhou, Xuefan Zhou, Zhiyou Li, Dou Zhang*

*State key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China*

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**Abstract**

Plate-like $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) templates with perovskite structure were successfully synthesized by a topochemical microcrystal conversion (TMC) method from Aurivillius precursors, $Bi_4Ti_3O_{12}$ (BIT) and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBIT) platelets. Both NBT platelets and their precursors showed a high aspect ratio between an average size of 10–20 μm and thickness of 0.5–1.0 μm. The clear lattice fringe and the diffraction spots of BIT, NBIT and NBT platelets obtained from high-resolution transmission electron microscopy (HRTEM) indicated good crystallinity. The NBT platelets showed a high degree of preferred pseudocubic [001] orientation with a large Lotgering factor of 0.87 which exhibited good potential as suitable templates for synthesizing textured lead free piezoelectric ceramics, e.g. $Na_{0.5}Bi_{0.5}TiO_3$–$x$$BaTiO_3$, via the templated grain growth process.


*Keywords:* Aurivillius precursors; High aspect ratio; Good crystallinity; Preferred orientation

## 1. Introduction

Lead-free piezoelectric materials have attracted great interest because of their potential to replace lead based piezoelectric materials. Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$, is considered to be an excellent candidate as a key material of lead-free piezoelectric applications [1–3]. However, the piezoelectric properties of NBT based ceramics are not good enough for practical applications [4]. Texture control of polycrystal is an important approach for enhancing piezoelectric properties. Among various texture methods, the (Reactive) Templated Grain Growth ((R)TGG) is one of the most convenient processes. Anisotropic platelets or templates play a crucial role in the grain orientation process [5–8].

Plate-like $SrTiO_3$ [5,6] and $Bi_4Ti_3O_{12}$ [6,7] particles have been widely used as templates to prepare textured NBT based piezoelectric ceramics. However, both $SrTiO_3$ and $Bi_4Ti_3O_{12}$ [9,10] are not ideal templates because their crystal structures are different with the matrix which will reduce the piezoelectric properties. The best material for seeding the phase formation of NBT based ceramics and to template the oriented grain growth is NBT itself [11,12]. Recently, soft chemical methods including the molten-salt method and topochemical microcrystal conversion method have been used to prepare anisotropic NBT platelets [12,13]. Topochemical synthesis involves replacing or modifying the interlayer cations but retaining the morphological and structural features of plate-like, layered perovskite precursors by ion exchange and intercalation reactions at low temperatures. The layer-structured BIT and NBIT can be transformed into a perovskite NBT in the topochemical reaction. Zhao et al. [14] reported the preparation of large plate-like NBT templates from bismuth layer structured ferroelectric (BLSF) compound $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBIT). In most papers [11–17], NBT platelets were prepared by a two-step synthesis method. NBT platelets were synthesized using BIT or NBIT as precursors. The properties of NBT platelets and their precursors were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Which was the better method to synthesis NBT platelets, using BIT as precursors or using NBIT as precursors? Controlled experiment had been designed to answer

*Corresponding author. Tel./fax: +86 731 88877196.
*E-mail address:* dzhang@csu.edu.cn (D. Zhang).

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this question in this paper, and high-resolution transmission electron microscopy (HRTEM) was used to characterize microstructures of NBT platelets and precursors for the first time.

In this paper, two technique routes were used to prepare high-aspect-ratio NBT platelets. Route one was to synthesis NBT platelets using Aurivillius-structured BIT platelets as precursors. Anisotropic BIT platelets were obtained by reaction of $Bi_2O_3$ and $TiO_2$. Route two was to synthesis NBT platelets using Aurivillius-structured NBIT platelets as precursors. Anisotropic NBIT platelets were synthesized using $Na_2CO_3$, $Bi_2O_3$ and $TiO_2$ as raw materials. The microstructure and morphology characterizations of BIT, NBIT and NBT were investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The chemical composition of final NBT platelets was confirmed by inductively coupled plasma (ICP).

## 2. Experimental procedure

### 2.1. Preparation of NBT platelets

The raw materials were chemically pure powders of $Bi_2O_3$ (Sinopharm Chemical Reagent Co., Ltd), $TiO_2$ (rutile) (Tianjin Kermel Chemical Reagent Co., Ltd.), $Na_2CO_3$ (Sinopharm Chemical Reagent Co., Ltd) and NaCl (Sinopharm Chemical Reagent Co., Ltd).

BIT precursors were prepared from $Bi_2O_3$ and $TiO_2$ via molten salt synthesis (MSS) at 1100 °C for 4 h according to the reaction formula (formula (1)). Then perovskite NBT was achieved by the TMC method (formula (2)). The raw materials including BIT, $Na_2CO_3$ and $TiO_2$ were mixed by magnetic stirring on a hot disk to avoid destroying the plate-like shape of BIT. The synthesizing temperature was maintained at 950 °C for 6 h. The salt in the as-synthesized product was washed out with hot deionized water several times and NBT platelets were obtained.

Platelet NBIT was prepared at 1050 °C for 4 h by MSS using reagent-grade $Bi_2O_3$, $Na_2CO_3$ and $TiO_2$ as raw materials (formula (3)). NBIT particles were used as precursors to synthesize NBT platelets by the TMC method (formula (4)). NBIT platelets, $Na_2CO_3$ and $TiO_2$ were mixed with a magnetic stir bar in ethanol medium, and an equal weight of NaCl salt was added. The slurry was dried and subsequently heated at 950 °C for 6 h. NBT seeds were separated by washing with hot deionized water.

$$2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12} \quad (1)$$

$$Bi_4Ti_3O_{12} + 2Na_2CO_3 + 5TiO_2 \rightarrow 8Na_{0.5}Bi_{0.5}TiO_3 + 2CO_2\uparrow \quad (2)$$

$$Na_2CO_3 + 9Bi_2O_3 + 16TiO_2 \rightarrow 4Na_{0.5}Bi_{4.5}Ti_4O_{15} + CO_2\uparrow \quad (3)$$

$$Na_{0.5}Bi_{4.5}Ti_4O_{15} + 2Na_2CO_3 + 5TiO_2 \rightarrow 9Na_{0.5}Bi_{0.5}TiO_3 + 2CO_2\uparrow \quad (4)$$

### 2.2. Characterization of NBT platelets and precursors

The crystal phase and orientation of the particles were determined using X-ray diffraction (XRD) analysis with Cu-Kα radiation (D-max/2550PC, Rigaku Inc., Japan) at a scan speed of 10°/min and a step width of 0.02°. It should be noted that, all the template particles including BIT, NBIT and NBT laid down with the *c* axis aligning along the vertical direction during the sample preparation for the XRD analysis.

In general, the degree of orientation for seed crystal can be estimated by the Lotgering factor *f*, which is given as follows:

$$f = (p - p_0)/(1 - p_0) \quad (5)$$

$$p = \sum I(00l)/\sum I(hkl) \quad (6)$$

$$p_0 = \sum I_0(00l)/\sum I_0(hkl) \quad (7)$$

where *I* is the relative intensity of the diffraction peak, and $p_0$ is the value of *p* for a randomly oriented sample. *f* varies from 0 for a randomly oriented sample to 1 for a completely oriented sample [18].

The morphology and microstructure were observed by a scanning electron microscope (SEM, model JMS 6460LV, JEOL, Tokyo, Japan) and high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F, Japan). The chemical composition of final NBT platelets was confirmed by inductively coupled plasma (ICP).

## 3. Results and discussion

### 3.1. Phase evaluation and crystal orientation

Fig. 1(a) shows the BIT particles are of single phase with all the diffraction peaks attributed to a layered structure, assigned to JCPDS card no. 35-0795. The (00*l*) peaks become stronger as compared with the standard powder diffraction pattern, in particular for (040), (060), (080), (0100), and (0140) peaks. The increased intensities of these (00*l*) peaks indicate that the BIT particles are parallel to (001) plane. The BIT platelets show a high degree of preferred orientation and give a large Lotgering factor of 0.89, which is calculated according to the formulas (5)–(7). Fig. 1(b) shows XRD data of NBT templates prepared by the topochemical conversion method using BIT precursors, in comparison with JCPDS pattern of NBT powders

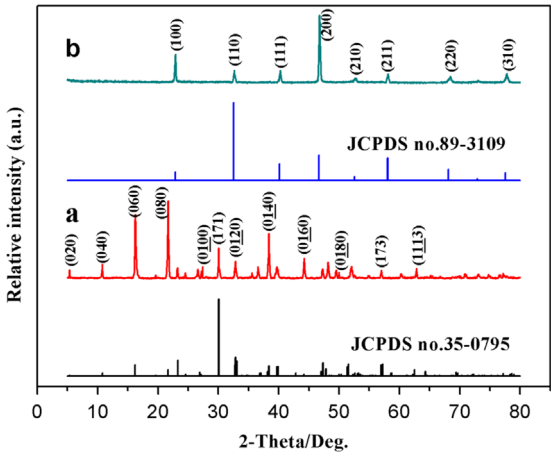


Fig. 1. (a) X-ray diffraction pattern of BIT crystals grown at 1100 °C for 3 h with JCPDS no. 35-0795 and (b) X-ray diffraction pattern of NBT crystals grown at 950 °C for 6 h using BIT as precursor with JCPDS no. 89-3109.