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Synthesis and characterization of (001) oriented $BaTiO_3$ platelets through a topochemical conversion

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ABSTRACT

Micrometer-sized (001) oriented $BaTiO_3$ (BT) platelets with a perovskite structure, a stoichiometric composition and a high aspect ratio (10–20 μm in diameter and 0.5–1 μm in thickness) were synthesized through a modified two-step molten salt method by means of a typical topochemical microcrystal conversion. The results indicated that it is necessary to prevent Bi^+ and Cl^- or NO_3^- from coexisting under nonacidic or weakly acid environment. A less pollutive washing method and the corresponding principle were summarized in combination with the hydrolysis reaction process. The effect of synthesis temperatures on the formation of BT platelets was discussed.

1. Introduction

Single crystals usually exhibit higher piezoelectric performance but cost much more than random ceramics. In order to improve the piezoelectric properties of ceramics, much attention has been paid to the textured ceramics in the last decades. A few grain orientation methods were developed such as directional solidification technology [1], hot forging [2], multilayer grain growth technology [3], templated grain growth (TGG) [4], reactive templated grain growth (RTGG) [5] and so on. Among these methods, (R)TGG proves to be suitable particularly for materials with a cubic symmetry, for example, perovskite-structured materials. The template particles needed should have a suitable morphology, a desirable crystallographic orientation and a high aspect ratio, so that they can be mechanically oriented under an applied shear force during tape casting. Moreover, the template particles should also have lattice parameter mismatch of <15% with the matrix to be textured [4], such that the matrix composition could relatively easily nucleate and epitaxially grow on oriented templates at elevated temperature. Considering the structure similarity, perovskite-structured templates would be the best for perovskite ceramics. However, most of perovskite ceramics own isometric particle morphology [6], so it is relatively difficult to synthesize their particles with high aspect ratios using conventional methods. A technique was proposed to synthesize plate-like perovskite-structured $NaNbO_3$ particles using topochemical microcrystal conversion (TMC) method [7], through which the morphology of anisometrically shaped precursors can be maintained and simultaneously the precursors can be transformed into objective compound particles with required chemical formulation and crystal structure by a topochemical, topotactic and/or pseudomorphic reaction. Most importantly, this method has provided the possibility to synthesize other perovskite-structured template seeds such as $KNbO_3$ [8], $Na_{0.5}Bi_{0.5}TiO_3$ [9], $SrTiO_3$ [10], etc.

Anisometric $BaTiO_3$ (BT) particle with a tetragonal perovskite structure [11] is one of the most important template seeds for texturing some perovskite systems and has been used in $Pb(Mg_{1/3}Nb_{2/3})$–$PbTiO_3$ textured ceramics [12,13] owing to both similar structures and chemical stability at high temperature and under PbO liquid environment [13]. Nanometer-sized spherical, cuboidal or dendritic BT particles were usually synthesized by hydrothermal method [14–16] and micrometer-sized BT fibers and platelets were prepared through an ion-exchange reaction by means of molten salt, hydrothermal and solid-state processes [17–22]. Millimeter-scaled (001)-oriented BT crystal platelets (~1.0 $mm^2 \times 0.4$ mm) were synthesized by the Remeika process utilizing a molten salt method [23,24]. However, the employment of such big template particles resulted in coarsened microstructure and compromised the mechanical strength of the textured ceramics [12,25]. Liu et al. [26] synthesized micrometer-scaled BT platelets by a three-step molten salt method, but the residual Bi was not effectively removed. It is obvious that the preparation of BT template particles with desired composition, morphology, crystallographic orientation and so on is still a challenging task. How to completely remove the impurity phases such as Bi-containing precipitates seems critical because they tend to affect the densification behavior, the formation of the texture and electrical properties of textured ceramics. Therefore, particular attention should be paid to the washing process because Bi^{3+} ions will be released from Bi_2O_3 when nitric acid is added and becomes

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easy to be hydrolyzed with Cl^- and NO_3^- in nonacidic or weakly acidic environment.

In this work, micrometer-scaled tabular BT particles with a high aspect ratio (10–40) were synthesized using a modified two-step molten method through a TMC process. $Bi_4Ti_3O_{12}$ (BIT) particle was prepared as precursor because of its platelet morphology and similar structure. Two kinds of washing methods were proposed as well as the effect of synthesis temperatures in the TMC reaction. The composition, morphology and crystal structure of as-synthesized BT particles were investigated in detail.

2. Experimental

The experimental procedure of synthesizing tabular BT particles was illustrated in Fig. 1. Plate-like BIT particles were prepared using Bi_2O_3 (≥99.0%) and TiO_2 (≥99.0%) as raw materials by a conventional molten salt method. The powder mixture was heated at 1100 °C for 6 h in mixed molten salt (NaCl (≥99.5%): KCl (≥99.5%) is 1:1 mol) at heating and cooling rates of 10 °C/min. The weight of the salt was half of the total amount of the powder mixture. Subsequently, the product was washed with warm de-ionized water for several times until no free Cl^- ions could be detected as confirmed using $AgNO_3$ solution. The as-prepared BIT precursor and excessive $BaCO_3$ (≥99.0%) in a molar ratio of 1:10 were carefully mixed by magnetic stirring to avoid destroying the morphology of BIT. After drying, the mixture was placed in a sealed alumina crucible and heated at 1000–1040 °C for 3 h. Two kinds of washing methods were adopted to remove the residual impurity in the final product. The first one was that 6 mol/L HNO_3 was used for just one time and then de-ionized water were used for washing for a few times (named as "A" method); the second one was that the product was first washed using de-ionized repeatedly, then using HNO_3 for one time and finally using de-ionized again for a few times (named as "B" method).

The pH value of the solution was determined by a digital pH meter (FE20, METTLER TOLEDO). The crystal structure of the product was examined by an X-ray diffractometer (XRD, D/Mzx-rB, Rigaku, Japan) with Cu Kα radiation. The morphology and chemical composition of the synthesized particles were analyzed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS).

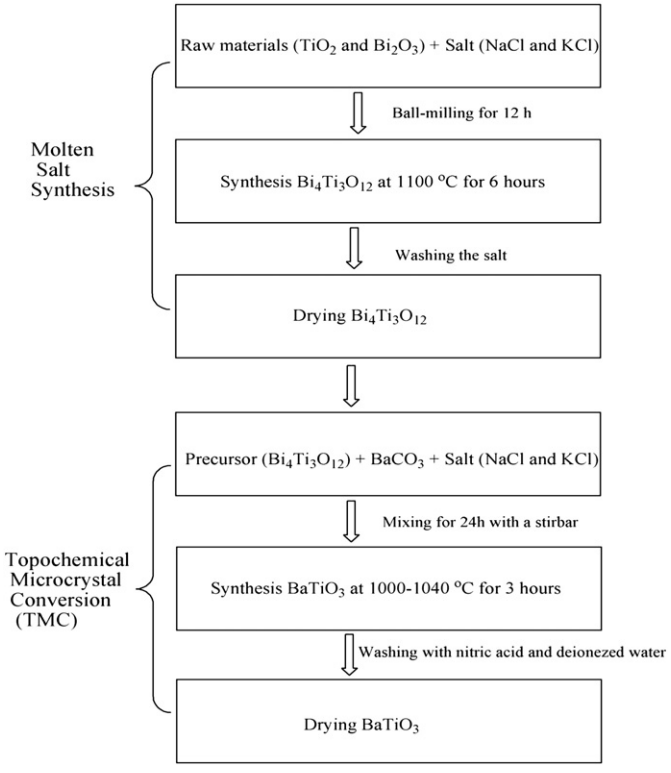

Fig. 1. The experimental procedure of synthesizing plate-like BT particles.

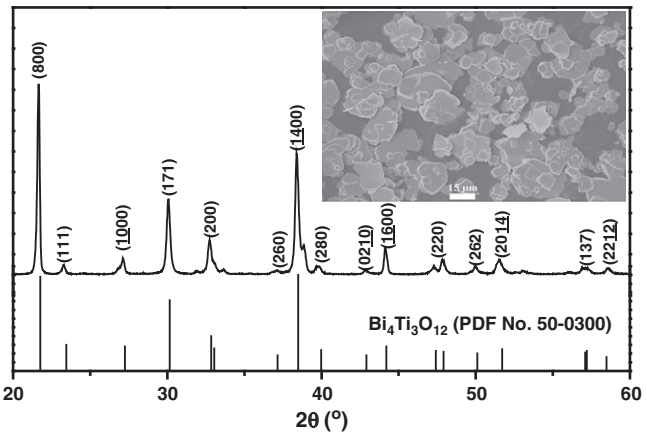

Fig. 2. XRD pattern of the BIT precursor synthesized at 1100 °C for 6 h (inset is the corresponding SEM image).

3. Results

As shown in Fig. 2, single-phase BIT precursor was obtained as synthesized at 1100 °C for 6 h via the first-step molten salt process. The corresponding chemical reaction was written as follows: $2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12}$. According to the standard PDF card, it can be seen that all diffraction peaks could be assigned to the BIT phase. Moreover, the (h00) diffraction peaks were enhanced, especially for (800) peaks. The SEM image of BIT particles (inset in Fig. 2) indicates plate-like grain morphology with a mean diameter of 10–20 μm and a thickness of 0.5–1 μm (the aspect ratio was approximately 20–40). Therefore, it can be concluded that the as-prepared BIT powder should be (h00) faceted because the major face of lamellar particles are likely to lie on the platform during the sample preparation for XRD examination. These results further demonstrate that the as-prepared BIT precursor could meet the requirement for synthesizing platelet BT owing to its desired dimension, phase-purity as well as similar crystal structure.

The above-mentioned BIT platelets were used for the second-step molten salt process, during which the following chemical reaction occurs: $Bi_4Ti_3O_{12} + 3BaCO_3 \rightarrow 3BaTiO_3 + 2Bi_2O_3 + 3CO_2$. Fig. 3 shows the XRD patterns of the synthesized powder washed using the "A" method. It can be seen that perovskite-structured phases are dominant in all three samples, although a few amount of secondary phases are also visible. According to the standard PDF card, the secondary phase can be assigned to the impurity of BiOCl. Moreover, it is obvious that (h00) diffraction peaks were enhanced to some extent, compared to the strongest (110) peak usually for random BT powder, suggesting that the as-synthesized BT particles exhibit preferable (h00) orientation. This result indicates that the crystal orientation of BIT platelets was inherited after the TMC process. Fig. 4 shows the particle morphology of all three samples as mentioned in Fig. 3. It can be found that a lot of fine impurity phases are attached to large platelets. EDS analysis was carried out at fine particles (spectrum 1) and big particles (spectrum 2), respectively, as shown in Fig. 4(b and d). The EDS results indicate that big platelets only contain Ba, Ti and O atoms (Ba : Ti = 0.94:1 in mol), but fine particles contain only Bi, Cl and O atoms (Bi : Cl = 0.98:1 mol), keeping good consistency with the XRD result (Fig. 3). By comparison, it can be also seen that the BT powders synthesized at 1020 °C for 3 h own a relatively high aspect ratio and a relatively uniform particle size (Fig. 4b). The BT particle size decreases with increasing temperature to 1040 °C.