



Synthesis and characterization of (001) oriented BaTiO₃ platelets through a topochemical conversion

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ABSTRACT

Micrometer-sized (001) oriented BaTiO₃ (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 NO₃⁻ 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.

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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 NaNbO₃ 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 KNbO₃ [8], Na_{0.5}Bi_{0.5}TiO₃ [9], SrTiO₃ [10], etc.

Anisometric BaTiO₃ (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})–PbTiO₃ 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 mm² × 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 Bi³⁺ ions will be released from Bi₂O₃ 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. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (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 ($\geq 99.0\%$) and TiO_2 ($\geq 99.0\%$) 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 ($\geq 99.5\%$); KCl ($\geq 99.5\%$) is 1:1 mol) at heating and cooling rates of $10^\circ\text{C}/\text{min}$. 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 ($\geq 99.0\%$) 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 $1000\text{--}1040^\circ\text{C}$ 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

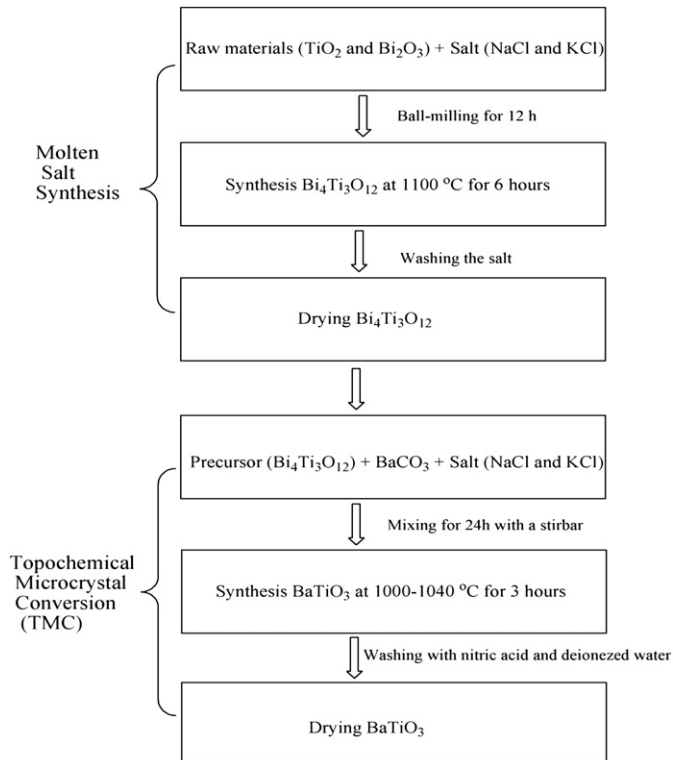


Fig. 1. The experimental procedure of synthesizing plate-like BT particles.

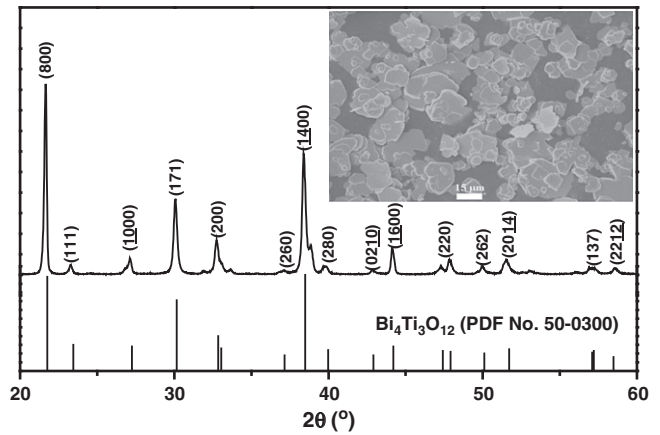


Fig. 2. XRD pattern of the BIT precursor synthesized at 1100°C for 6 h (inset is the corresponding SEM image).

examined by an X-ray diffractometer (XRD, D/Mx-rB, Rigaku, Japan) with $\text{Cu K}\alpha$ 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).

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: $2\text{Bi}_2\text{O}_3 + 3\text{TiO}_2 \rightarrow \text{Bi}_4\text{Ti}_3\text{O}_{12}$. 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 $10\text{--}20\ \mu\text{m}$ and a thickness of $0.5\text{--}1\ \mu\text{m}$ (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: $\text{Bi}_4\text{Ti}_3\text{O}_{12} + 3\text{BaCO}_3 \rightarrow 3\text{BaTiO}_3 + 2\text{Bi}_2\text{O}_3 + 3\text{CO}_2$. 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 ($\text{Ba} : \text{Ti} = 0.94:1$ in mol), but fine particles contain only Bi, Cl and O atoms ($\text{Bi} : \text{Cl} = 0.98:1$ 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 .

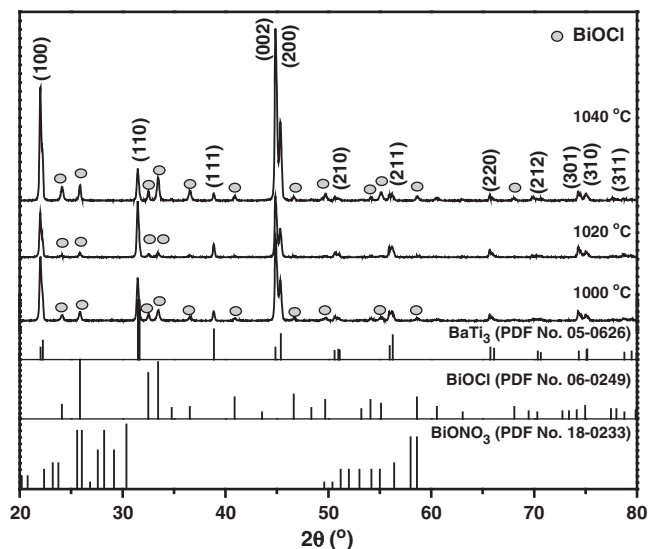


Fig. 3. XRD patterns of BT particles synthesized at 1000 °C, 1020 °C and 1040 °C for 3 h and washed by the “A” method.

Fig. 5 shows the XRD pattern of BT particles synthesized at 1020 °C for 3 h and washed by means of the “B” method. None of secondary phases can be detected. All diffraction peaks should belong to the perovskite-structured BT. Compared to the “A” method, the impurity phase such as BiOCl was completely inhibited by using the “B” method. The SEM photograph of the corresponding BT particles is shown in Fig. 6a. It can be seen that the topochemically converted BT particles exhibit clean surface as well as similar shape, size and aspect ratio to BIT precursor. Moreover, the EDS result of BT particles shows that there are only Ba, Ti, and O atoms (Fig. 6b). The atomic ratio of Ba to Ti is approximately 0.96:1, meaning that the product should be the stoichiometric BT composition if the measurement error is taken into account. There is no peak of Bi atom in the EDS, revealing that Bi^{3+} in BIT has been completely substituted by Ba^{2+} and also removed by washing.

4. Discussion

Whether the BT platelets are single crystals or strongly oriented polycrystalline aggregates can be directly evidenced by a transmission electron microscopy study. However, thinning of such a small BT particle for TEM observation is not an easy task and it is still too thick ($\sim 1 \mu\text{m}$) if it is not thinned. A useful suggestion was given in Ref. [27] that the roughness or smoothness of the particle surface could be taken as probable evidence of the polycrystalline or single crystal nature, respectively. Therefore, the rough surface of the as-prepared BT platelets (see Fig. 6) proves that they might be strongly oriented polycrystalline aggregates. This tendency seems increased with increasing synthesis temperature. As a result, the platelets become more easily split/exfoliate during reaction at higher temperatures, particularly during washing due to the leaching of Bi_2O_3 -rich boundary phases, leading to smaller particles [27].

As hot dilute HNO_3 solution was used as the washing medium, the above-mentioned byproducts will be dissolved. The following hydrolysis reaction may happen as the pH value of the solution is higher than 0 and 0.38, respectively [28,29]:

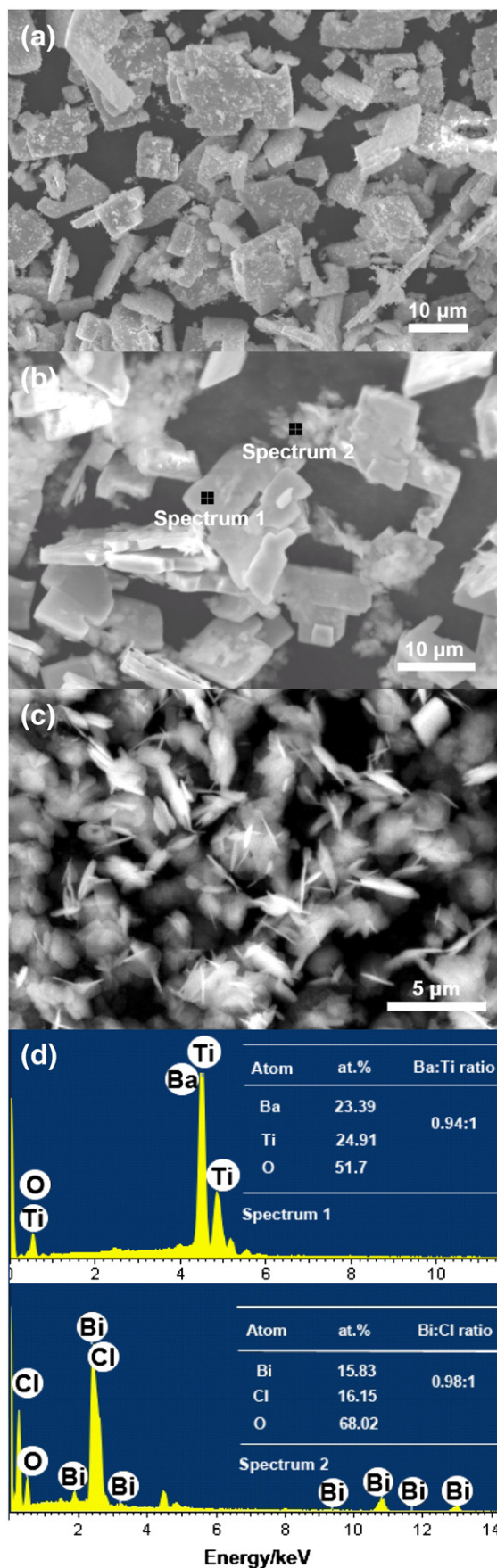
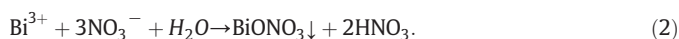


Fig. 4. SEM image of BT particles synthesized at (a) 1000 °C, (b) 1020 °C and (c) 1040 °C for 3 h and washed by the “A” method, and (d) EDS analysis of the corresponding powder synthesized at 1020 °C.

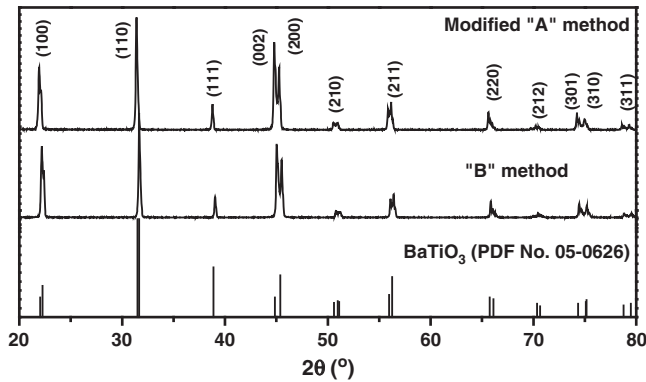


Fig. 5. XRD patterns of BT particles synthesized at 1020 °C for 3 h and washed by the modified "A" and "B" methods, respectively.

It is thus understood that the impurity phase of BiOCl was formed as the "A" method was used for washing (Fig. 3). As a small amount of HNO₃ was added, the following free ions such as Cl⁻, NO₃⁻, Bi³⁺, Ba²⁺, K⁺, Na⁺ and H⁺ would coexist in an acidic solution. As the above solution was added with a large quantity of warm de-ionized water, the above-mentioned hydrolysis reaction will progress to the right side of the reaction under nonacidic or weak acid environment. However, BiCl₃ hydrolyzes more easily and quickly than Bi(NO₃)₃ and tends to hydrolyze again once the acidity is weakened [28,29], but it is opposite for Bi(NO₃)₃ due to its higher solubility product ($K_{sp} \sim 2.82 \times 10^{-3}$) than BiOCl ($K_{sp} \sim 1.8 \times 10^{-31}$). As a result, only BiOCl was observed in Fig. 3 instead of BiONO₃. For comparison, a modified "A" washing method was proposed, i.e., hot dilute HNO₃ solution was first used for a few times. After each time, the upper clear solution was poured out. Then, the powder was washed using deionized water for a few time again. The XRD result of the corresponding powder is shown in Fig. 5. It can be seen that the BiOCl impurity disappeared in the final product. The addition of enough dilute HNO₃ solution effectively

inhibited the above hydrolysis reactions. At the same time, Bi³⁺ was almost cleared away. It is a pity that the modified "A" method may consume a large quantity of HNO₃ and cause pollution to the environment.

As to the "B" method, the use of a large amount of de-ionized water could make sure that Cl⁻ ions were completely removed before free Bi³⁺ was released from Bi₂O₃ as HNO₃ was added. As a result, the hydrolysis reaction (Eq. 1) was stopped. Then, excessive nitric acid was added for one time to react with the product until pH < 0.38 to avoid the hydrolysis reaction between NO₃⁻ and Bi³⁺ (Eq. 2). Finally, warm de-ionized water was adopted to get rid of the residual ions such as Cl⁻, Ba²⁺, etc. Compared to the modified "A" method, the "B" method is more effective as well as less pollutive.

In addition, it is worth to note that acidic washing can be very detrimental for the properties of BT particles because it determines the leaching of Ba ions from the near-surface region of the particles possibly with formation of a titania-rich layer [30–32]. This effect was weakened by reducing the time of acidic washing as much as possible in this study. Moreover, the addition of excessive BaCO₃ during the experiment could play a role in restraining the hydrolysis reaction of BT ($\text{BaTiO}_3 + \text{H}_2\text{O} = \text{Ba}^{2+} + \text{TiO}_2 + 2\text{OH}^-$). From EDS results (Ba: Ti = 0.96:1, see Fig. 6), it means that a slight leaching of Ba ions from BT surface region might happen.

5. Conclusions

The (001) oriented tabular BT particles with a mean diameter of 10–20 μm and a thickness of 0.5–1 μm were successfully synthesized using a modified two-step molten salt method. A particular attention was paid to the washing process during which some unexpected impurity phases are probably produced owing to the hydrolysis reaction. A comparative study on two kinds of washing techniques demonstrates that it is necessary to completely remove Cl⁻ before free Bi³⁺ was released from Bi₂O₃ using a large quantity of water or it is necessary to first use a large amount of HNO₃ to remove Bi³⁺ for the purpose to avoid the hydrolysis reaction of Bi³⁺, Cl⁻ and NO₃⁻. A less pollutive washing method was proposed in this work.

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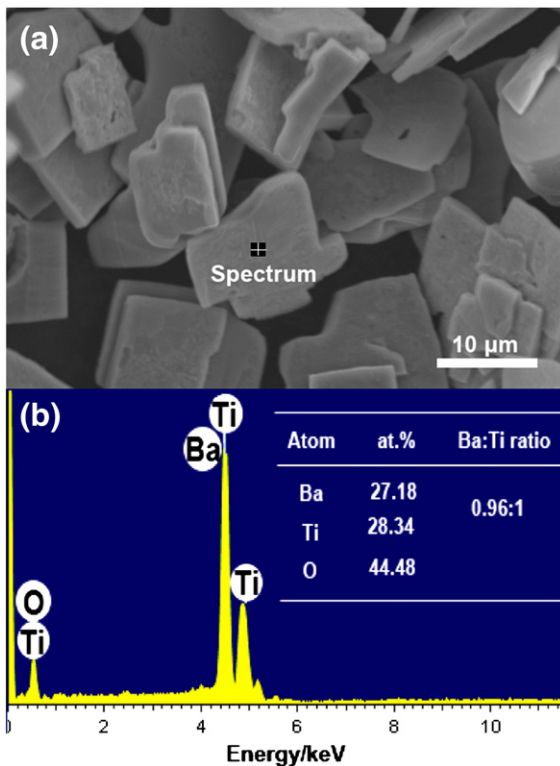


Fig. 6. SEM image (a) and EDS analysis (b) of BT powder synthesized at 1020 °C for 3 h and washed by the "B" method.

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