

Processing and Morphology of (111) BaTiO₃ Crystal Platelets by a Two-Step Molten Salt Method

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The (111) oriented plate-like BaTiO₃ (BT) particles with a tetragonal perovskite structure and a stoichiometric composition were successfully synthesized by a two-step molten-salt synthesis method (MSS). The as-synthesized BT particles preserved the plate-like shape of precursor Ba₆Ti₁₇O₄₀ (B6T17) particles with (001) major crystalline face, and, however, had a preferred pseudo-cubic (111) orientation. BT particle with a high aspect ratio (10–20 μm in diameter and <1.5 μm in thickness) was achieved as the soaking temperature and time were optimized to be 1170°C and 5 h, respectively. Oriented particulate layer X-ray diffraction analysis revealed that the crystallographic (001) plane of B6T17 has a topotactic relation with the (111) plane of BT particles.

I. Introduction

SINGLE crystals have exhibited much higher piezoelectric properties than polycrystalline ceramics owing to the existing anisotropy in different crystallographic directions. Texturing techniques have produced significantly enhanced piezoelectric properties in polycrystalline ceramics by achieving aligned grain morphology with a desired orientation.^{1–3} Among these methods, (reactive) templated grain growth [(R)TGG] method mainly relies on the preferentially oriented growth of large, anisotropic template grains through consuming the matrix grains during densification. It has been demonstrated that the morphology, orientation, and composition of the template particles have a strong influence on the microstructure and properties of the final ceramics.⁴ Therefore, it is crucial to synthesize anisotropic template particles with required crystallographic orientation for fabricating high-performance textured piezoelectric ceramics.

BT particles with a perovskite structure have been used as ideal template seeds owing to their high chemical stability and good piezoelectric properties. Unfortunately, regular perovskite-structured materials typically grow as equiaxed particles. It is rather difficult to synthesize perovskite particles with high aspect ratios using conventional methods. Remeika fabricated (001) oriented tabular BT particles with a high chemical stability in KF solution.⁵ The corrosive KF molten salt was not eco-friendly and needed a costly platinum crucible. Kwon *et al.* have reported enhanced performances of Pb(Mg_{1/3}Nb_{2/3})–PbTiO₃ (PMN–PT) textured ceramics using Remeika BT templates^{6,7} and excess PbO. However, large Remeika BT templates (average diameters >75 μm) resulted in extremely coarse microstructure and thus too low mechanical strength for most applications. In addition, hot pressing was specially required to get dense ceram-

ics. The cost of hot pressing and the use of excess PbO nearly diminish the commercial potential of Remeika BT-templated PMN–PT ceramics. There is an urgent demand for finding templates with low lattice difference with matrix compositions, and particularly appropriate size and desired orientation. Saito *et al.* proposed a technique to synthesize plate-like NaNbO₃ particles using a topochemical microcrystal conversion (TMC) method.¹ This technique preserves and/or inherits the particle shape from an anisotropically shaped precursor to the objective compound particle through a topochemical, topotactic and/or pseudomorphic reaction. This method has been successfully applied to other perovskite-structured plate-like template particles such as KNbO₃,⁸ Na_{0.5}Bi_{0.5}TiO₃,⁹ SrTiO₃,¹⁰ BT¹¹ and so on. With regard to the synthesis of finer plate-like BT particles (5–10 μm in diameter and 0.5 μm in thickness), Liu *et al.*¹² synthesized BT platelets from BaBi₄Ti₄O₁₅ precursor by TMC method, and Ding *et al.*¹¹ also reported tabular BT prepared from Bi₄Ti₃O₁₂ precursor by the same method. All these BT particles exhibited plate-like morphology, but all with preferred pseudo-cubic (001) orientation. It is obvious that how to prepare BT particles with desired composition, morphology, size, and particularly with different crystallographic orientation is still a challenging task.

The purpose of this study was to synthesize finer plate-like BT particles with (111) orientation. Layer-structured Ba₆Ti₁₇O₄₀ (B6T17) was selected as precursor particles in the TMC method because it was reported to be a layer-structured material and has a structural similarity on the (001) plane of B6T17 and (111) plane of BT.^{13–15} Although (111) BT templates have been synthesized and used before,¹⁶ the processing details and influencing variables were not mentioned. Therefore, it would be of much interest to make a systematic study on the effect of processing parameters, such as soaking temperature and dwelling time on the morphology and size of B6T17 and BT particles. How the morphology and crystallographic orientation were correlated during TMC reaction is discussed.

II. Experimental Procedure

Plate-like BT particles were prepared through a double molten salt synthesis (MSS) method as shown in Fig. 1. BT powders were firstly synthesized from a mixture of BaCO₃ (≥99.0%) and TiO₂ (≥99.0%) at 1350°C for 3 h by a conventional mixed-oxide method. For the first-step MSS, plate-like B6T17 particles were prepared using the as-prepared BT powders and TiO₂ (≥99.0%) as raw materials. The as-prepared BT and TiO₂ were first mixed with a ball mill for 12 h. The molar ratio of BT:TiO₂ was 6:9. Excess Ba²⁺ was proposed to inhibit the formation of Ba₄Ti₁₃O₃₀.¹⁷ The mixture was homogenized thoroughly with NaCl in a weight ratio of 1:1 and heated 800°C for 1 h to melt NaCl and then at 1130°C–1170°C for several hours.

After the following reaction (6BT+11TiO₂→B6T17) was completed, flux NaCl was washed away using hot distilled

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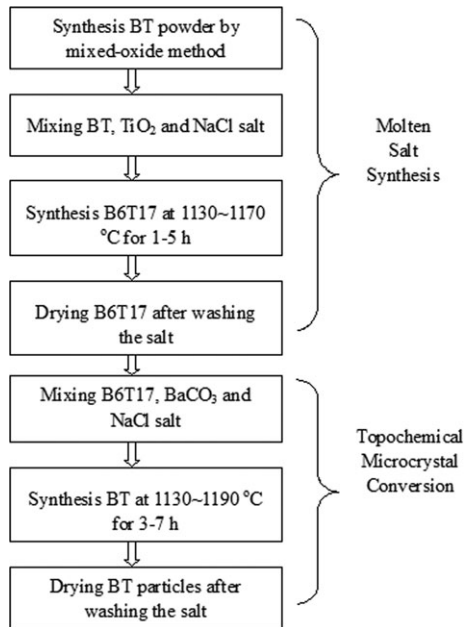


Fig. 1. Flow charts of preparing (111) BT particles through a two-step molten salt method.

water until there are no detectable chloride ions. Plate-like B6T17 precursor was then obtained. At the second step, the TMC reaction from B6T17 to BT in a molten NaCl solution happened by using the mixture of as-obtained B6T17 and BaCO₃ (the molar ratio of 1:11). The relevant reaction was described as $B6T17 + 11BaCO_3 \rightarrow 17BT + CO_2\uparrow$.

The crystal structure of the products was examined using an X-ray diffractometer (XRD; D/Mzx-rB, Rigaku, Tokyo, Japan) with CuK α radiation. To identify the largest developed planes of as-synthesized particles, the XRD patterns were obtained on the particles that were dispersed in the mixture of ethanol and 2-butanone and then cast on a glass substrate, which is called as oriented particulate layer XRD measurement technique (OPL-XRD).^{8,18} The morphology and chemical composition of the synthesized particles after each step were analyzed using a scanning electron microscope (SEM; SSX-550, Shimadzu, Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). The grain size was further analyzed by image processing software of Adobe Photoshop CS3 Extended.

III. Results and Discussion

Figure 2 shows the XRD pattern of BT powder prepared by a conventional mixed-oxide method. All the diffraction peaks could be readily indexed to a tetragonal phase of BT (JCPDS 05-0626), indicating that the obtained product is highly crystallized phase of pure BT. The prepared BT powder as raw material was used to synthesize plate-like B6T17 particles. The effects of processing temperatures on the morphology of the B6T17 particles are shown in Fig. 3. All the samples synthesized at different temperatures exhibited platelet morphology and were well-dispersed. When soaked at 1130°C, the size of B6T17 particle was relatively small and inhomogeneous because of low solubility and mobility of all the oxides in molten NaCl at a low temperature. With increasing temperature to 1150°C, the particles become large and relatively uniform (a mean diameter of 10–20 μ m and a thickness of 0.5–1 μ m, the aspect ratio of approximately 20–40, as shown in Table I). In addition, because fine B6T17 particles are gradually consumed by larger ones, the particle size distribution at higher temperature becomes more uniform. However,

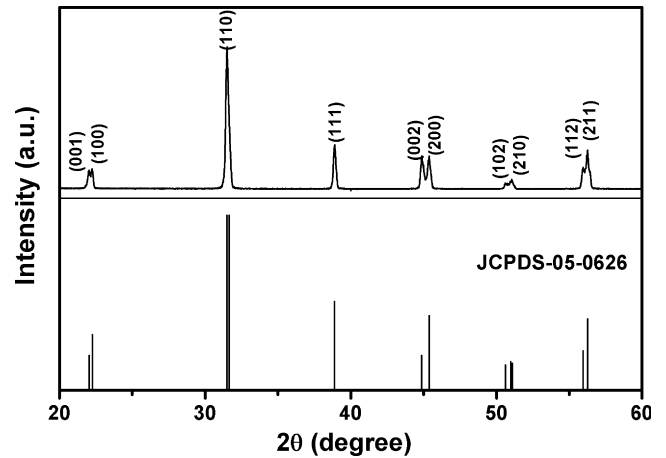


Fig. 2. XRD pattern of conventionally prepared BT powders compared with a standard diffraction pattern (JCPDS 05-0626).

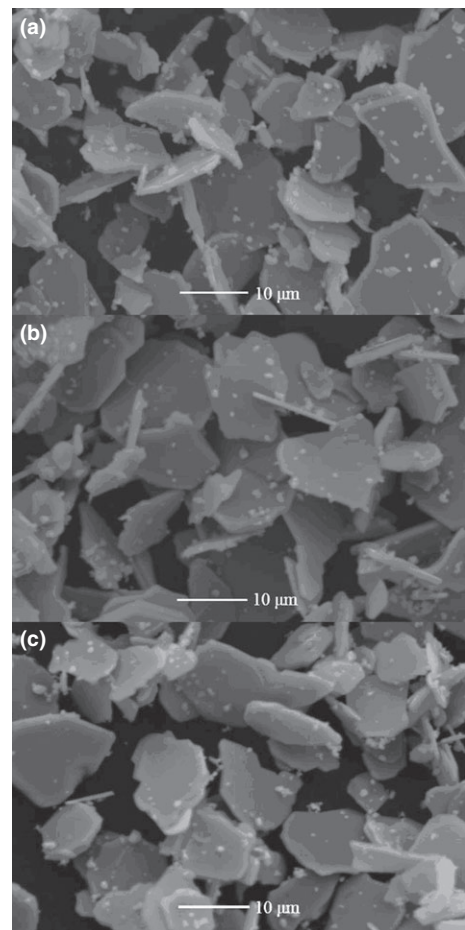


Fig. 3. SEM images of B6T17 particles synthesized in the molten salt at (a) 1130°C, (b) 1150°C, and (c) 1170°C for 1 h.

Table I. Statistical Analysis of B6T17 Particles Synthesized at Different Processing Conditions

Processing conditions	Diameter (μ m)	Thickness (μ m)	Aspect ratio
1130°C for 3 h	6–12	0.5–1	6–24
1150°C for 3 h	10–20	0.5–1	10–40
1170°C for 3 h	7–14	0.5–1	7–28
1150°C for 1 h	6–16	0.5–1	6–32
1150°C for 5 h	7–14	0.5–1	7–28

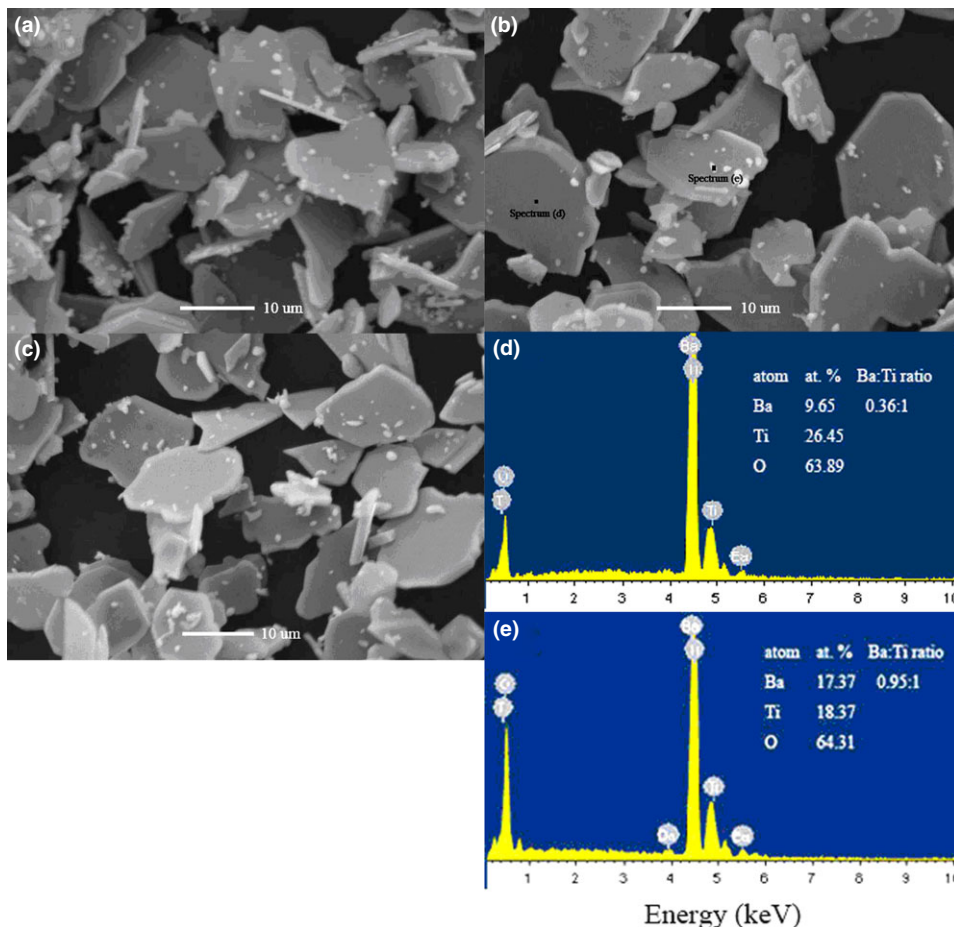


Fig. 4. SEM images of B6T17 particles synthesized in the molten salt at 1150°C for (a) 1 h, (b) 3 h, and (c) 5 h; (d) and (e) correspond to EDS analysis of big plate-like particles and small granule particles (white points) respectively as indicated in (b).

with further increasing the temperature to 1170°C, the aspect ratio of the B6T17 precursor particle decreased probably because the volatilization of NaCl reduces the amount of NaCl salt and thus decreases the solubility of the oxides and the growth space of B6T17 particles. The latter tends to cause an increase in the thickness owing to the confluent growth of neighboring particles. Moreover, higher temperature tends to cause the synthesized B6T17 particle to melt, leading to a slight reduction in the particle size.

Figure 4 displays the SEM micrographs and the compositional analysis of the B6T17 precursor synthesized at 1150°C. With increasing soaking time from 1 to 5 h (see Table I), the size and the aspect ratio of the B6T17 particles increased, and reached a maximum value at 3 h, and then decreased with further increasing time. The volatilization of NaCl was increased with prolonging the soaking time, and therefore the solubility of the oxides in molten NaCl was reduced. This is similar to the effect of the temperature (Fig. 3). EDS analysis was carried out at the platelet particles (spectrum 1) and fine particles (spectrum 2), respectively. The composition of the platelets as shown in Fig. 4(d) (0.36:1) is pretty close to the stoichiometry of B6T17 (0.353:1). In contrast, the chemical analysis of fine particles indicated that the Ba/Ti ratio was 0.95, approaching the value of BT if the measurement error was taken into account [Fig. 4(e)]. Such a small amount of BT particles probably come from the addition of excess BT, which was proposed to avoid the formation of Ba₄Ti₁₃O₃₀.¹⁷ The residual BT particle can be also confirmed by the following XRD result.

Figure 5 shows the XRD patterns of cast and non-cast B6T17 particles. The terms “cast” and “non-cast” are used to distinguish the powder deposited on a substrate by coating

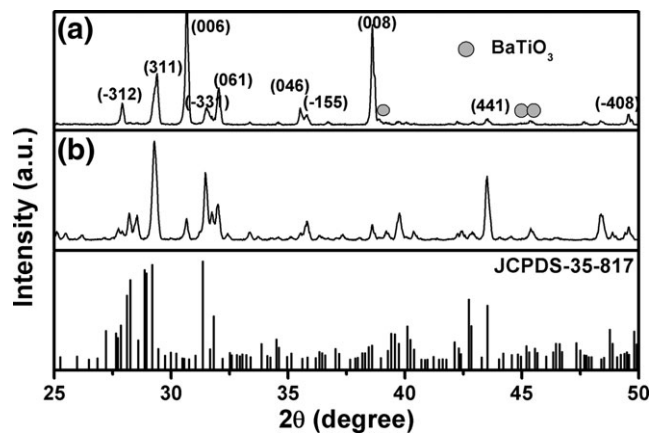


Fig. 5. XRD patterns of B6T17 precursor particles prepared by MSS at 1150°C for 3 h (a) with casting on a glass substrate and (b) without casting; a standard diffraction pattern was used for comparison.

with a suspension from the powder without any special treatment. The predominant diffraction peak intensity of such as (006) and (008) peaks has been obviously enhanced for the cast B6T17 particles, which indicates that the major face of the particles exhibits a crystallographic orientation of (001). All of major peaks can be assigned to a monoclinic phase of B6T17 (JCPDS 35-817). Moreover, a small amount of secondary phases indexed to BT was found from the XRD pattern. This result keeps good agreement with the above EDS analysis [Fig. 4(e)].

After the second-step MSS, XRD patterns, and morphology of as-synthesized BT platelets at different soaking temperatures for 3 h are shown in Fig. 6. It is indicated that pure BT phases were synthesized at these temperatures and synthesized particles had a plate-like shape, meaning that the TMC reaction was completed and simultaneously, the plate-like shape of B6T17 particles was preserved. Moreover, it can be seen that the products are all composed of large particles and a few small particles. When soaked at 1170°C, BT particles are relatively large and uniform.

In the MSS, crystal particles should nucleate and grow up through mass transportation in the liquid phase. The synthesis temperature can be adjusted to control the crystal shape and size. The lattice volume and the corresponding density of BT particles were calculated by fitting the diffraction peak profiles, as shown in Fig. 7. With increasing the soaking temperature from 1130°C to 1190°C, the cell volume increases, and reaches a maximum value at 1150°C, and then decreases with further increasing temperature. The density values exhibit an opposite tendency. This was believed to be due to the presence of lattice distortion as a result of a large number of barium vacancy formed during the reaction between BaCO₃ and B6T17 in the second-step MSS. High soaking temperatures tend to reduce the content of barium vacancy such that the cell volume becomes small. Compared with the cell volume value (64.41 Å³) calculated from a standard diffraction pattern (JCPDS 05-0626), the obtained values in our study seem a little higher, probably because of the

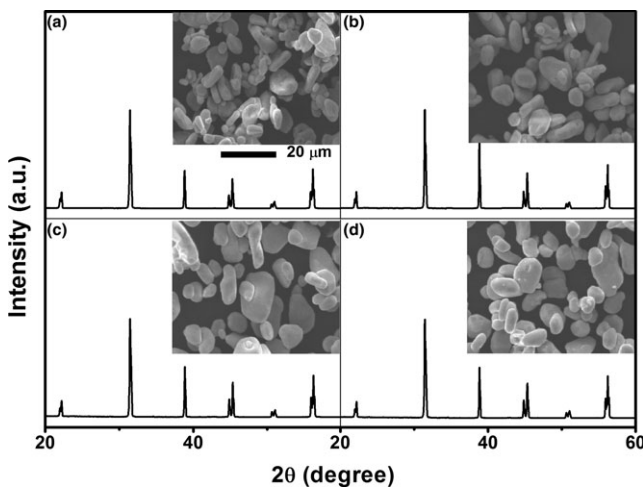


Fig. 6. XRD patterns of as-synthesized BT particles by MSS at (a) 1130°C, (b) 1150°C, (c) 1170°C, and (d) 1190°C for 3 h. The insets are their corresponding SEM images.

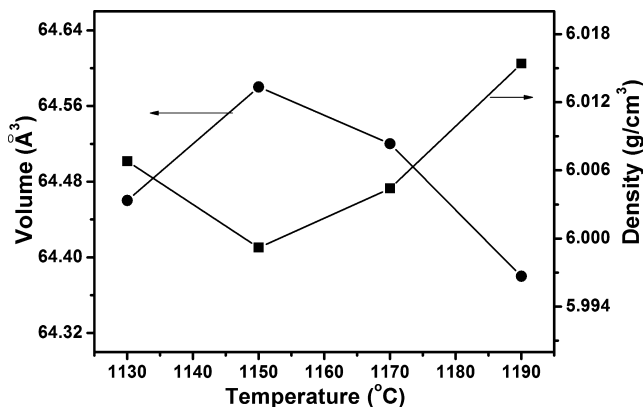


Fig. 7. Cell volumes and XRD density of BT particles as a function of the soaking temperatures.

presence of barium vacancy. As an example, by using the XRD profile, the crystallite size and microstrain of BT particles synthesized at 1170°C were calculated to be 585 (±8) nm and 0.1632(±0.00316)%, respectively. The crystallite size value is slightly smaller than the physical size (0.5–1 μm) of BT particles obtained from SEM pictures. This discrepancy and the microstrain value to a certain degree disclose the state of crystallographic perfection of two-step MSS driven BT platelets, which can be improved by further increasing the soaking temperature.

The SEM photographs of the BT particles synthesized at 1170°C with different soaking times are shown in Fig. 8. It can be seen that the TMC reaction tends to cause the plate-like morphology of B6T17 to change slightly such that the developed BT particle has a cobblestone-like morphology. However, with increasing the soaking time to 5 h, the TMC-transformed BT particle started to grow mainly in the radial direction. Further increase in soaking time did not obviously change the morphology of BT particles [Fig. 8(c)]. Irregular plate-like BT particles with a mean diameter of 10–20 μm

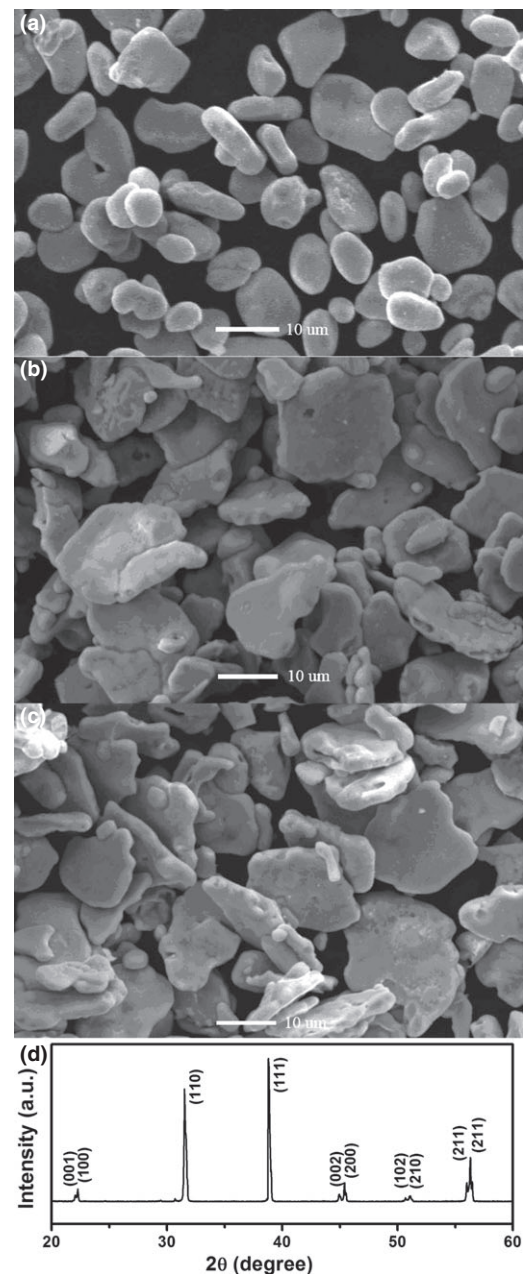


Fig. 8. SEM images of BT particles synthesized at 1170°C for (a) 3 h, (b) 5 h, and (c) 7 h; (d) the XRD pattern of BT particles (1170°C for 5 h) cast on a glass substrate.

and a thickness of $<1.5\ \mu\text{m}$ (the aspect ratio was approximately 7–14) were achieved as the soaking temperature and time are 1170°C and 5 h, respectively. The OPL-XRD pattern of BT particles (1170°C for 5 h) cast on the glass substrate is shown in Fig. 8(d). From the OPL-XRD, the strongest diffraction peak of MSS BT particles corresponds to the (111) lines, instead of (110) lines for the ordinary BT powder. These results indicate that the major face of as-synthesized plate-like BT particles lies in the (111) plane. It was reported that there is a topotactic relationship between B6T17 particle and BT particle ((001) of B6T17// (111) of BT).^{14,15} Moreover, if we compare Figs. 3 and 8, one may find that the major face of B6T17 particle is smooth, but the major face of BT is relatively rough, although BT particles were converted from B6T17 particles by means of TMC reaction. The reason could be that the surface energy of closely packed (001) plane of B6T17 has the lowest value. However, the surface energy of (111) plane of BT particle is higher than that of (100) plane, resulting in relatively rough surfaces. In addition, the rough surface suggests that the as-prepared BT platelets might be highly oriented polycrystalline aggregates rather than coherent single crystals.¹⁹ It was suggested in the study in ref. (19) that the loss of epitaxy and exfoliation during TMC would cause the originally formed microcrystals to be replaced by an aligned perovskite-phase aggregate. Although the formation of single crystals would be facilitated by a recrystallization process, yet it needs quite a long holding time.

IV. Conclusions

The (111) oriented tabular BT particles were successfully synthesized using the TMC method from plate-like precursor particles of layer-structured B6T17 in molten NaCl salt. TMC-synthesized BT particles preserved the shape of precursor particles, and had a high aspect ratio (10–20 μm in diameter and $<1.5\ \mu\text{m}$ in thickness) at 1170°C for 5 h. Moreover, OPL-XRD analysis revealed that during the TMC reaction, the crystallographic (001) plane of B6T17 was converted into the (111) plane of BT particles in spite of polycrystalline morphology.

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