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Effect of treatment conditions and titanium source on the hydrothermal synthesis of bismuth titanate particles

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Abstract

Hydrothermal synthesis of bismuth titanate particles was performed using various titanium sources. Uniform particles of titanium hydroxide, hydrous titania, and anatase were prepared respectively as starting materials. They were treated hydrothermally with bismuth nitrates in NaOH aqueous solution. The obtained crystal phases depended strongly upon the phase of the titanium source. Plate-like bismuth titanate particles were obtained at high-treatment temperatures when hydrous titania was used as the starting material. Spherical particles with a spherulite-like structure were obtained at low temperatures and for long treatments.

Keywords: Powders-chemical preparation; $BaTiO_3$ and titanates; Hydrothermal

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) is a typical bismuth layer-structured ferroelectric (BLSF) material that has excellent ferroelectric, piezoelectric, electro-optic, and fatigue properties.[1–3] Consequently, BIT is anticipated for use in many applications such as capacitors, high-temperature piezoelectric devices, random access memories, and electro-optical devices. BIT crystals are well known to grow in a plate-like shape. The higher components of spontaneous polarization are parallel to the plane of the platelets.[4–9] Using plate-like BIT particles, grain-oriented BIT ceramics of many kinds were prepared to obtain single-crystal-like properties.[4–7] An important problem is that BIT crystal shows high electrical conductivity anisotropy in the same plane as the polarization. For that reason, BIT ceramics with randomly oriented small grains and starting particles suitable for preparing them are also required.[8–11] When BIT ceramics are prepared using a conventional solid-state reaction, they require high reaction temperatures, resulting in the excess coarsening of BIT particles.[8–15] For lowering the processing temperature of BIT ceramics, various procedures for preparing fine BIT particles have been investigated and reported, such as co-precipitation method and sol–gel method.[8–10,12–16] Hydrothermal synthesis is a typical procedure for preparing BIT particles.[17–24] This procedure presents advantages for preparing fine particles with high crystallinity at low-treatment temperatures. For hydrothermal synthesis of BIT particles, bismuth sources of many kinds have been used, but direct addition of bismuth nitrate to the mineralizer aqueous solution is a typical procedure.[17,20,22–24] Titanium sources of many kinds have also been used as starting materials: titanium hydroxide (prepared by hydrolyzing titanium alkoxide or titanium chloride), hydrous titania ($TiO_2 \cdot nH_2O$), and anatase particles. The crystalline phases of the obtained particles depend strongly on the titanium source.[17,20] However, effects of the titanium sources on the morphology of hydrothermally formed particles and the BIT particles' formation mechanism have not been described in detail. For this study, titanium sources of three kinds were prepared. Their respective morphologies were made as similar as possible to compare effects of the source material phases. Uniform spherical hydrous titania particles were prepared by hydrolysis of titanium alkoxide in an acetonitrile/butanol mixed solution in the presence of ammonia.[25,26] Crystalline anatase particles were prepared by heat treatment of the spherical hydrous titania particles. Titanium hydroxide particles were also prepared by adding titanium butoxide directly to the NaOH aqueous solution.

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Using the prepared titanium source particles, hydrothermal synthesis of BIT particles was performed and the effects of hydrothermal conditions and titanium sources on the phase and morphology were examined in detail.

2. Experimental procedures

2.1. Preparation of titanium sources

Reagents used for starting materials were titanium *n*-butoxide (Acros Organics BVBA, Belgium), bismuth nitrate pentahydrate, ethanol, butanol, acetonitrile, ammonia, triethanolamine, and sodium hydroxide (Wako Pure Chemical Industries, Ltd., Japan). The water used in this study was purified by reverse osmosis and electrodeionization (Elix System, Millipore, USA).

Hydrous titania particles were prepared as follows[25,26]: first, a mixed solvent of butanol and acetonitrile was prepared (butanol:acetonitrile = 1:1 (v/v)). Then, titanium butoxide was dissolved to the mixed solvent. A mixed solution of butanol and acetonitrile containing water and ammonia was also prepared. Before starting the reaction, both solutions were preheated at 80 °C using a water bath. Then, a hydrolysis reaction of titanium butoxide was started by mixing equal volumes of solutions under continuous agitation and aging them at 80 °C for 2 h. The final concentrations of the solutes after mixing all solutions were as follows: titanium butoxide, 0.05 M; ammonia, 0.10 M; water, 0.50 M. After aging was completed, the sample was centrifuged and the supernatant solution was removed. The remaining precipitate was washed by centrifugation: three times with ethanol and three times with water. After washing, the obtained particles were dispersed in water again and freeze-dried. The amount of hydration in the hydrous titania was quantified using thermogravimetry. Anatase particles were prepared by heat treatment of the prepared hydrous titania at 500 °C for 1 h. Titanium hydroxide particles were prepared by adding titanium butoxide directly to the 3 M NaOH (mineralizer for the synthesis of bismuth titanate) aqueous solutions. The prepared titanium hydroxide suspension was used directly for BIT particle synthesis. To verify the crystalline structure and morphology of the prepared titanium hydroxide, samples that had been washed three times by centrifugation with water and freeze-dried were also prepared.

2.2. Preparation of bismuth titanate particles

Bismuth titanate particles were prepared by hydrothermal processing. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) and titania source particles were added to 3 M NaOH aqueous solution and were dispersed ultrasonically when hydrous titania or anatase was used as the titanium source. Titanium butoxide was added directly to 3 M NaOH aqueous solution when titanium hydroxide was used. Then, bismuth nitrate pentahydrate was added and dispersed ultrasonically. The standard concentrations of Bi^{3+} ion and Ti^{4+} ion were, respectively, 1.0×10^{-3} and 7.5×10^{-4} M. The amounts of the hydrous titania particles were adjusted according to their water contents. The prepared suspensions were treated hydrothermally in a PTFE-lined autoclave without stirring. After hydrothermal treatment, the prepared particles were washed three times by centrifugation using purified water.

2.3. Characterization

The crystalline phases were identified using X-ray diffractometry (XRD, M18X-HF-SRA; Mac Science Ltd., Japan) using Cu Kα radiation with a monochromator. The samples' morphology was observed using scanning electron microscopy (SEM, JSM-6330F; JEOL, Japan). Water contents of hydrous titania were determined using thermogravimetry (TG8120; Rigaku Corp., Japan). The obtained particles' composition was measured using an energy dispersive X-ray fluorescence spectrometer (MiniPal 2; PANalytical B.V., The Netherlands).

3. Results and discussion

Using XRD measurements, it was confirmed that prepared hydrous titania particles and titanium hydroxide particles were amorphous. The results of thermogravimetry measurements of the prepared hydrous titania proved that its composition was $TiO_2 \cdot 1.5H_2O$. Using heat treatment at 500 °C for 1 h, hydrous titania particles were crystallized to anatase. Fig. 1 shows SEM images of the prepared titania sources. Monodispersed, spherical hydrous titania particles were prepared using hydrolysis of titanium butoxide in butanol/acetonitrile solvent under the existence of ammonia. Even after the heat treatment, anatase particles retained their original shape. The titanium hydroxide particles prepared only by addition of titanium oxide directly to the mineralizer solution mutually aggregated; their morphology was not uniform. Although the aggregation of the titanium hydroxide might affect the reactivity, we used these titanium hydroxide particles as one titanium source because their primary particles' diameter was similar to those of hydrous titania and anatase particles.

Fig. 2 shows XRD patterns of hydrothermally prepared samples using various titanium sources at 160 °C for 24 h. The starting composition of Bi:Ti was set at 4:3, which corresponds to the stoichiometric ratio of BIT. At this condition, single-phase BIT was not obtained. In fact, $Bi_{12}TiO_{20}$ was the main phase when anatase or titanium hydroxide particles were used as the titanium source. The BIT was the main phase and α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$ and $Bi_{12}TiO_{20}$ phases were also identified when hydrous titania particles were used. In the XRD patterns shown in Fig. 2(b), the possible presence of $Bi_2O_2CO_3$ cannot be disregarded. However, assignment to $Bi_2O_2CO_3$ was not conducted because almost all of their diffraction peaks coincide with those of BIT, α-Bi_2O_3, and $(BiO)_4CO_3(OH)_2$.[27,28] Actually, $(BiO)_4CO_3(OH)_2$ is known to form when α-Bi_2O_3 reacts with an aqueous solution containing NaOH and Na_2CO_3.[28] The water used for this study was prepared using reverse osmosis and electrodeionization, but no special treatment for removing carbon dioxide was conducted. In addition, handling of NaOH aqueous solutions was performed in air atmosphere. For that reason, a certain amount of carbon dioxide might have dissolved in the reaction solution, thereby forming $(BiO)_4CO_3(OH)_2$. Fig. 3 shows SEM images of hydrothermally treated samples using

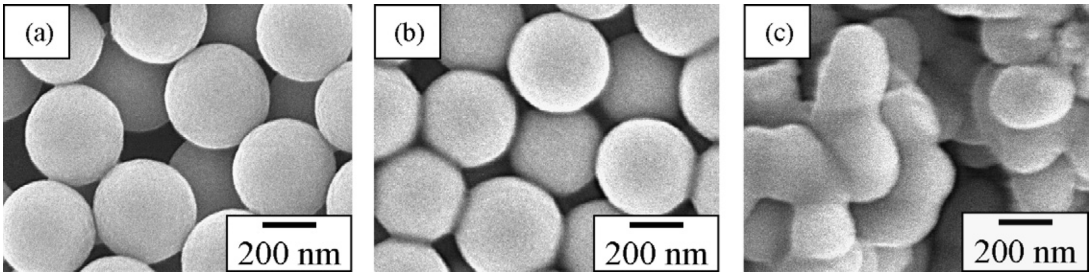

Fig. 1. SEM images of prepared titanium source particles: (a) anatase, (b) hydrous titania, and (c) titanium hydroxide.

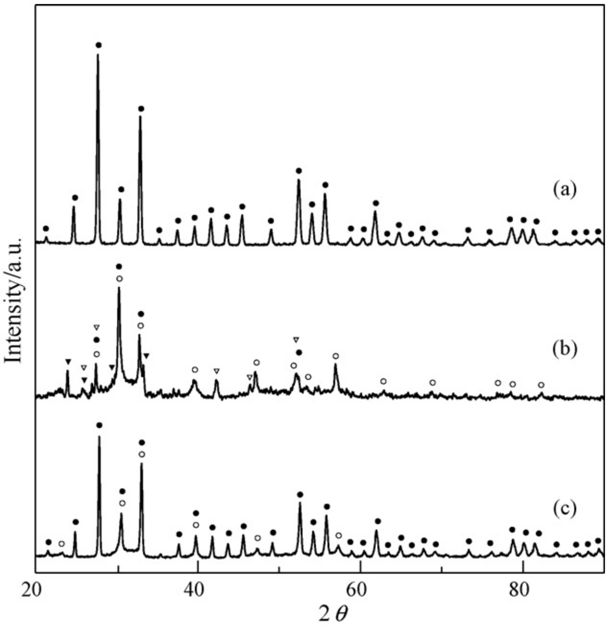

Fig. 2. XRD patterns of hydrothermally prepared samples using (a) anatase, (b) hydrous titania, and (c) titanium hydroxide (Bi:Ti = 4:3, hydrothermally treated at 160 °C for 24 h): (◯) $Bi_4Ti_3O_{12}$, (●) $Bi_{12}TiO_{20}$, (▽) α-Bi_2O_3, and (▼) $(BiO)_4CO_3(OH)_2$.

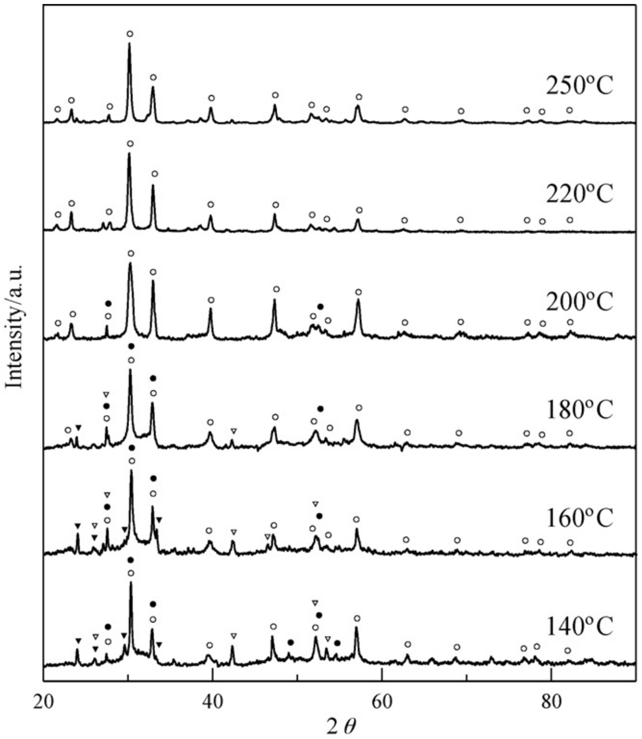

Fig. 4. XRD patterns of hydrothermally prepared samples with various temperatures for 24 h (Bi:Ti = 4:3): (◯) $Bi_4Ti_3O_{12}$, (●) $Bi_{12}TiO_{20}$, (▽) α-Bi_2O_3, and (▼) $(BiO)_4CO_3(OH)_2$.

various titania sources at 160 °C for 24 h. Only tetrahedral particles were obtained when anatase particles were used as the titanium source (Fig. 3(a)). This tetrahedral shape typically signifies hydrothermally prepared $Bi_{12}TiO_{20}$ particles.[29] However, spherical particles, tetrahedral particles, and plate-like particles were observed when hydrous titania was used as the titanium source (Fig. 3(b)). The spherical particles had a spherulite-like structure comprising fine primary crystals.[30–33] Both incomplete tetrahedral particles and spherical particles were observed when titanium hydroxide was used (Fig. 3(c)). Comparing the results obtained with each titanium source, a hydrous titania titanium source was selected for BIT particle preparation.

Hydrothermal treatment conditions were varied to obtain single-phase BIT particles. Figs. 4 and 5 respectively show XRD patterns and SEM images of samples prepared hydrothermally at

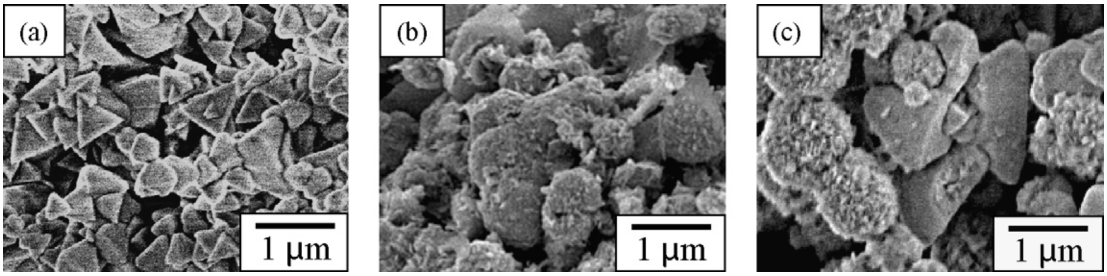

Fig. 3. SEM images of hydrothermally prepared samples using (a) anatase, (b) hydrous titania, and (c) titanium hydroxide (Bi:Ti = 4:3, hydrothermally treated at 160 °C for 24 h).

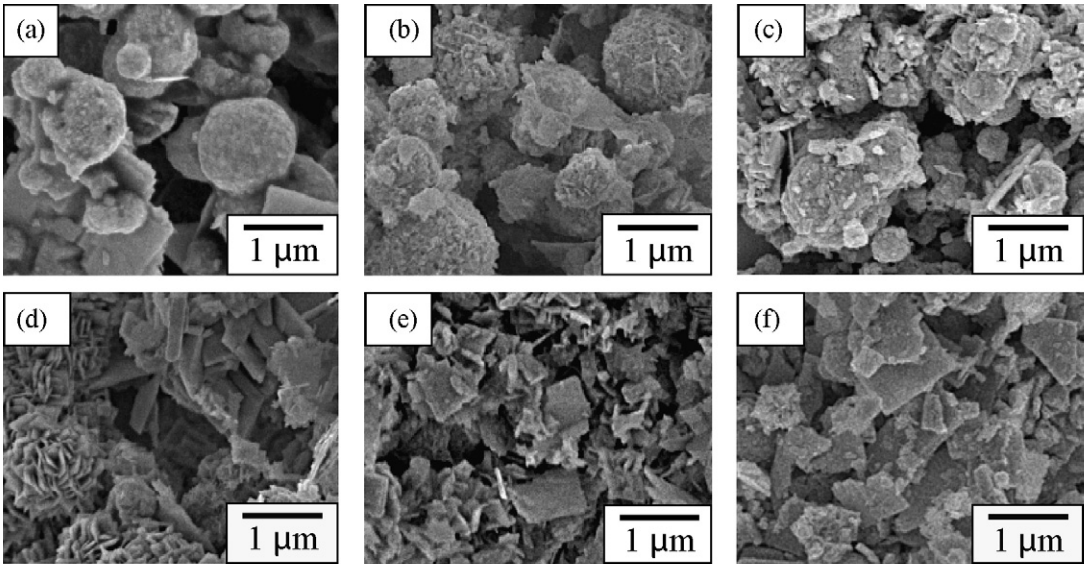

Fig. 5. SEM images of hydrothermally prepared samples with various temperatures for 24 h (Bi:Ti = 4:3): (a) 140 °C, (b) 160 °C, (c) 180 °C, (d) 200 °C, (e) 220 °C, and (f) 250 °C.

various temperatures for 24 h. The starting composition of Bi:Ti was 4:3. When the treatment temperature was low, BIT phase was identified, but α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$ and $Bi_{12}TiO_2$ phases were also observed. The by-product amount decreased with increased treatment temperature. The sample prepared at lower temperature (140–180 °C) comprised spherical particles with a spherulite-like structure and large plate-like particles (Fig. 5(a)–(c)). In this lower temperature range, the plate-like particles decreased with increased treatment temperature. Therefore, considering XRD measurement results, spherical particles with a spherulite-like structure must be of BIT phase. At 200 °C, the primary crystals of the spherical particles were grown to large platelets (Fig. 5(d)). Single-phase BIT was obtained when the treatment temperature was 220 °C or higher. At this high temperature range, BIT particles became plate-like and their size was increased with increased treatment temperature. (Fig. 5(e) and (f)). This plate-like BIT particle seems to be suitable for preparing a grain-oriented sintered body.

To suppress the formation of α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$, and $Bi_{12}TiO_{20}$ phases and to obtain single-phase BIT particles at low temperature, the starting composition ratio of Ti to Bi was increased. The starting composition of Ti to Bi was controlled by decreasing the amount of bismuth nitrate because the starting material concentrations become too high when their composition is controlled by increasing the titanium source amount. Figs. 6 and 7 respectively show the XRD patterns and SEM images of the hydrothermally prepared samples with various starting compositions. The treatment conditions were set at 180 °C for 24 h. By increasing the molar ratio of hydrous titania, only the diffraction peaks of BIT-phase were observed. This result demonstrated that an increased concentration ratio of titanium inhibits the formation of α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$ and $Bi_{12}TiO_{20}$ phases. The morphology of the obtained particles prepared with excess titanium source was spherical with a spherulite-like structure. Fluorescence X-ray spectroscopy of the particles prepared with starting compositions of Bi:Ti = 4:3 and 4:6 were conducted to elucidate the particles' composition. Consequently, the samples prepared with various starting compositions retained a starting ratio of Bi to Ti after hydrothermal treatment, washing, and drying. Using XRD measurements, apparent diffraction peaks attributed to the excess titanium source were not observed. However, after calcining at 800 °C for 1 h, the diffraction peaks of $Bi_2Ti_2O_7$ were observed beside that of BIT only on the sample prepared with the excess titanium source. Therefore, excess titanium might exist within the particle as amorphous phase. Using this result, it is acknowledged that formation of α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$ and $Bi_{12}TiO_{20}$ phases

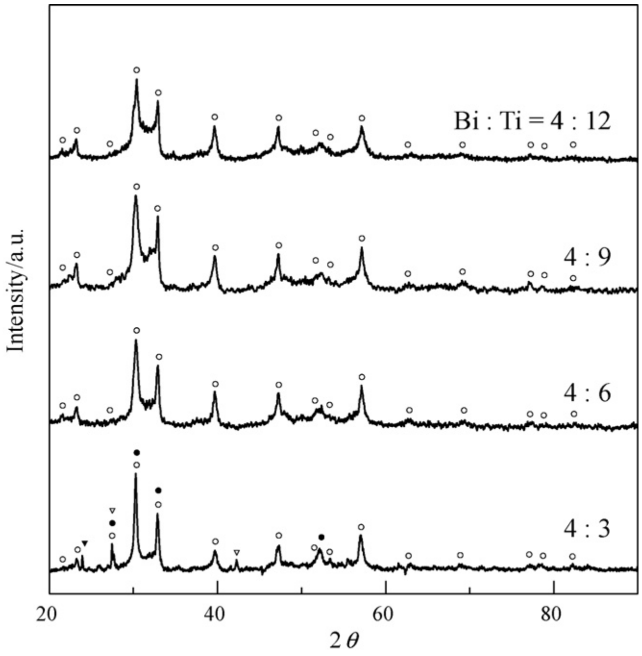

Fig. 6. XRD patterns of hydrothermally prepared samples with various starting compositions (hydrothermally treated at 180 °C for 24 h): (○) $Bi_4Ti_3O_{12}$, (●) $Bi_{12}TiO_{20}$, (▽) α-Bi_2O_3, and (▼) $(BiO)_4CO_3(OH)_2$.

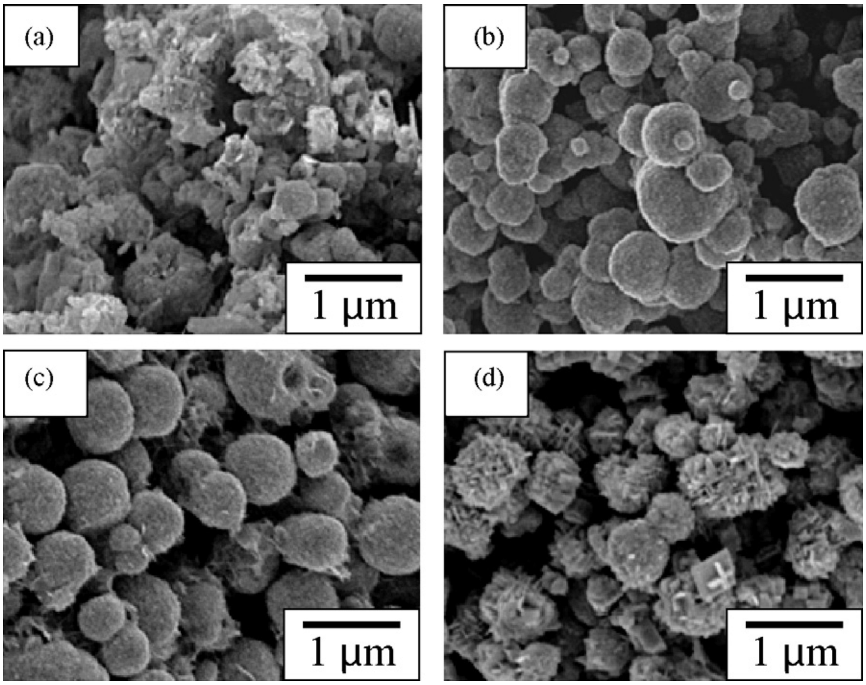

Fig. 7. SEM images of hydrothermally prepared samples with various starting compositions (hydrothermally treated at 180 °C for 24 h): (a) Bi:Ti = 4:3; (b) Bi:Ti = 4:6; (c) Bi:Ti = 4:9; and (d) Bi:Ti = 4:12.

is attributed to low concentration of titanium species. Therefore, the effect of the titanium source (Figs. 2 and 3) might arise from a difference in dissolution properties of each particle. It creates differences in local concentrations of the titanium species in the solution.

Figs. 8 and 9 respectively show XRD patterns and SEM images of samples that were prepared hydrothermally at 180 °C with various heat treatment times. The starting composition of Bi:Ti was set at 4:3. The diffraction peaks of α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$ and $Bi_{12}TiO_{20}$ phases were observed beside that of BIT phase when the treatment time was 24 h or less. With increasing treatment time, the peak intensity ratio of BIT increased; single-phase BIT phase was obtained when the treatment time was 72 h. Plate-like particles and spherical particles coexisted when the treatment time was short. The plate-like particles became fewer with increasing treatment time. Therefore, plate-like particles must be the α-Bi_2O_3 or $(BiO)_4CO_3(OH)_2$ phase, neither of which is stable at this treatment temperature. The primary crystals of the spherical particles treated for a long time (Fig. 9(d)–(f)) were slightly larger than those with short treatment time (Fig. 9(a)–(c)). With increasing treatment time, the bismuth-rich compounds might gradually dissolve and be deposited as BIT, mainly on the primary crystals of the initially formed spherical BIT particle. When the treatment time was 72 h, almost all particles were spherical; most plate-like particles had disappeared. Spherical particles with randomly aligned primary crystals are apparently suitable for preparing a sintered body with randomly oriented small grains at low temperatures.

In fact, α-Bi_2O_3, $(BiO)_4CO_3(OH)_2$, and $Bi_{12}TiO_{20}$ phases observed on the sample with low temperature or short treatment time conditions might arise from bismuth species which were unable to react with sufficient titanium species at the initial stage of the reaction. As presented in Fig. 9(a), spherical particles of hydrous titania used as the starting material had disappeared completely, even when the reaction time was 1 h. Therefore, the crystallization of BIT in this reaction condition

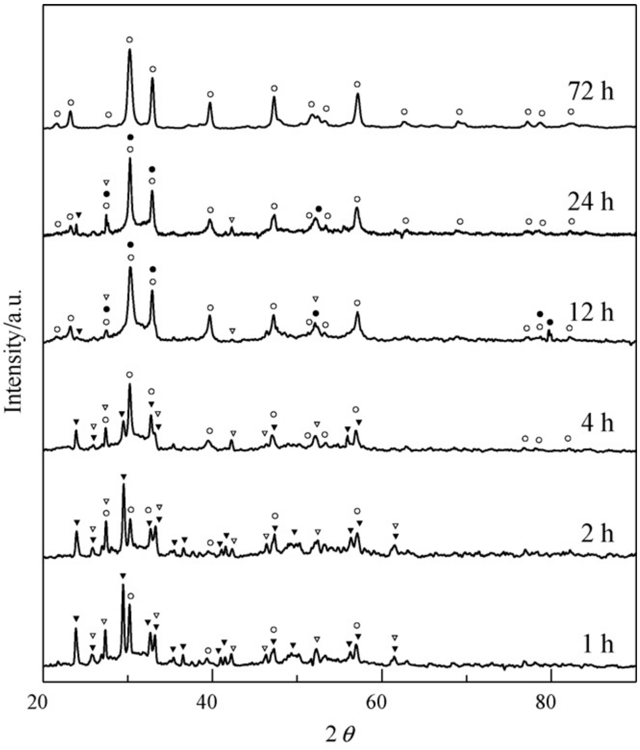

Fig. 8. XRD patterns of hydrothermally prepared samples with various hydrothermal treatment times (hydrothermally treated at 180 °C): (○) $Bi_4Ti_3O_{12}$, (●) $Bi_{12}TiO_{20}$, (▽) α-Bi_2O_3, and (▼) $(BiO)_4CO_3(OH)_2$.

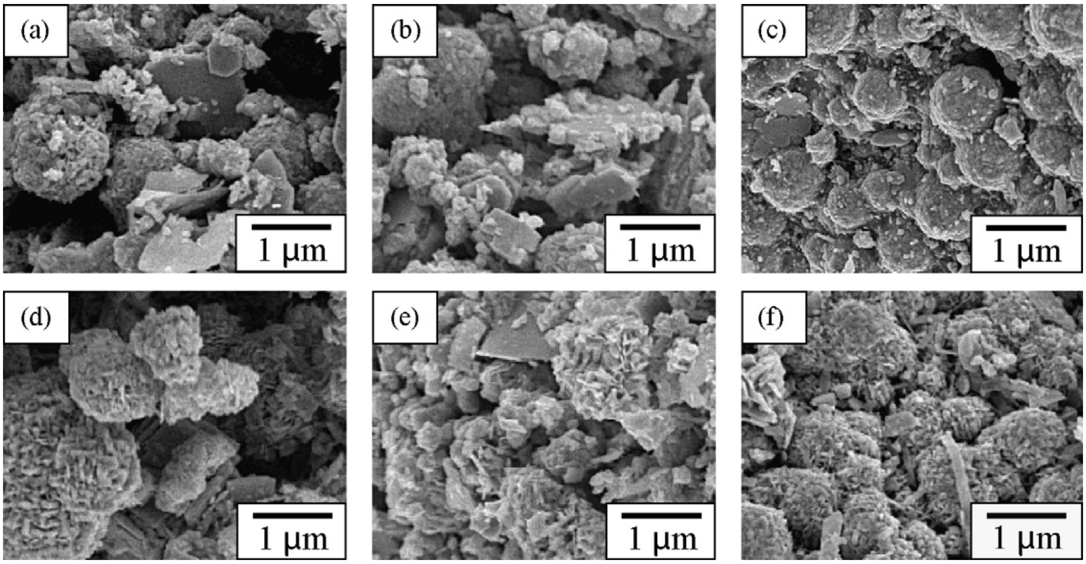

Fig. 9. SEM images of the hydrothermally prepared samples with various hydrothermal treatment times (hydrothermally treated at 180 °C): (a) 1 h, (b) 2 h, (c) 4 h, (d) 12 h, (e) 24 h, and (f) 72 h.

must proceed via dissolution of the precursors and recrystallization from a supersaturated solution.[34,35] Fig. 10 shows an SEM image of a large particle with spherical holes. Large particles of this kind with regularly arranged spherical holes were sometimes observed when the hydrothermal treatment temperatures were low (140–160 °C) and were not observed when samples were treated at higher temperatures. In addition, the quantities of these large agglomerates with holes increased concomitantly with an increase in the starting ratio of Ti to Bi. The holes' size nearly corresponded to the size of hydrous titania used as the titanium source. Consequently, these holes must be empty shells of the hydrous titania, which was eluted after formation of Bi–Ti–O system compounds around the aggregated hydrous titania particles. At the stage of hydrous titania particle dispersion, aggregations of the particles were deflocculated carefully using ultrasonic irradiation. However, some of the particles might aggregate at the stage of hydrothermal treatment because the hydrothermal treatment was conducted without stirring. For the area in which hydrous titania particles were aggregated, the titanium species concentration in the solution must be high even at low temperatures; BIT crystals might nucleate before the complete dissolution of hydrous titania particles. Using the results described above, the formation mechanism of the spherical BIT particles with spherulite-like structure in this system is considered to be the following. First, titanium source particles start to dissolve into the reaction solution. With dissolution of the titanium source, the concentration of titanium ions or complex ions around the titanium source particles increases steeply. At that point, with the high concentration of titanium species, nucleation of BIT crystals might occur. Generally, plate-shaped BIT crystals can be grown easily because of the layered structure of BIT.[4–9] From SEM images of spherical BIT particles with large primary crystals (Figs. 5(d) and 9(d)–(f)), it appears that the primary crystals of spherical BIT particles were also plate-like in this study. Those plate-like nanocrystals were aligned radially in each spherical BIT particle, which is a typical structure of spherulite.[30–33] Therefore, this structure must be constructed through rapid growth of the plate-like crystals with branching by secondary nucleation of BIT on the growing crystals. Spherulite is known to be easy to form when the system is highly non-equilibrium conditions that increase the driving force for crystallization.[30–33] The results shown in Figs. 6 and 7 indicate that high concentrations of titanium sources are suitable to obtain spherical BIT particles. The high concentration of the titanium source must result in increased driving force for crystallization; it also depresses formation of $Bi_{12}TiO_{20}$. Therefore, the local high concentration region of titanium species, which occurred by dissolution of hydrous titania, is suitable for formation of spherical BIT particles. Moreover, plate-like particles were formed at the higher treatment temperature range. The high-temperature might accelerate the diffusion of titanium species and disturb spherulite formation. The dissolution of anatase might be too slow and dis-

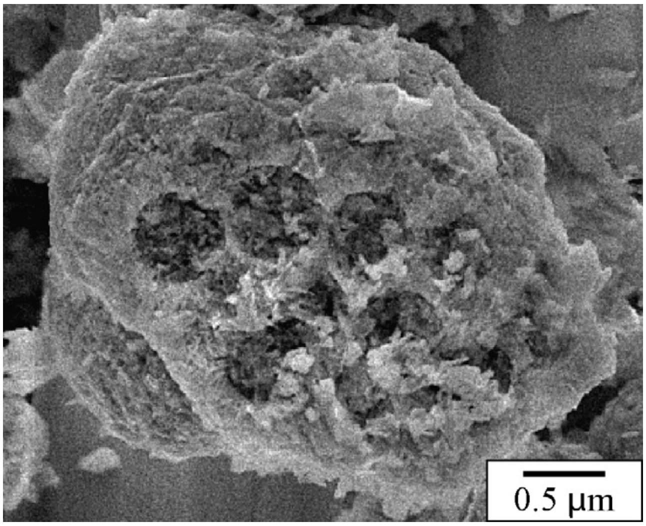

Fig. 10. Microstructure of a large particle with spherical holes (Bi:Ti = 4:3, hydrothermally treated at 160 °C for 24 h).

solution and diffusion of titanium hydroxide might be too rapid to maintain the high concentration of titanium species that is suitable for BIT formation when anatase or titanium hydroxide is used as the titanium source.

4. Conclusions

Effects of treatment conditions and titanium sources on hydrothermal synthesis of BIT particles were investigated. Hydrothermal treatment of a mixture of bismuth nitrate and various titanium sources was conducted under coexistence of a mineralizer. Results proved that hydrous titania is suitable to obtain BIT phase. Plate-like BIT particles were obtained when hydrothermal conditions were set at a high temperature. Spherical BIT particles were obtained at low temperature and long treatment time. These BIT particles are suitable for use as a raw material for the BIT sintered body.

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