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Effect of different Ba-sources on the sonochemically activated solid-state synthesis of $BaTiO_3$ powders

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We report the impact of Ba sources in the sonochemically activated solid-state synthesis of $BaTiO_3$ powders. A water-soluble $Ba(CH_3COO)_2$ and TiO_2 powders were sonochemically mixed in aqueous medium with controlled pH values and subsequently calcined following a drying process. For a comparative study, solid-state $BaCO_3$ powders were also used to synthesize $BaTiO_3$ powders under the same ultrasonication, drying, and calcination conditions. Phase conversion ratio to $BaTiO_3$ and structural properties of the resulting powders for each case were characterized and compared in detail. We expect that this study will be helpful in understanding the process for synthesizing and doping $BaTiO_3$ powders using water-soluble raw materials.

Keywords: $BaTiO_3$, Powder, Sonochemical, Solid-state reaction.

Introduction

Solid-state synthesis of $BaTiO_3$ has been carried out conventionally by using $BaCO_3$ and TiO_2 raw powders, as described in (1) [1-4].

$$BaCO_3\ (s) + TiO_2\ (s) \rightarrow BaTiO_3\ (s) + CO_2\ (g) \quad (1)$$

In this process, the reaction takes place by coupled diffusion of Ba^{2+} and O^{2-} ions into the TiO_2 lattice from the contact point between the raw materials [3-5]. Therefore, the intimate and uniform mixing of $BaCO_3$ and TiO_2 to increase the initial contact surface area have been considered critical factors for the process. Accordingly, efforts have been made to promote the solid-state reaction of $BaTiO_3$ by utilizing nanometer-sized ultrafine raw materials or by reducing the particle size through high-energy milling processes [6-17].

Recently, it has been reported that the mixing process of raw materials can be effectively performed by using ultrasonication process within only a few minutes and that the solid-state reaction in (1) can be accelerated by the sonochemical activation effect [18-21]. We reported that when the raw materials were dispersed in aqueous medium, the sonochemical mixing process was strongly affected by pH of the aqueous medium due to the pH-dependent partial solubility of $BaCO_3$ in water [18].

Therefore, it is also intriguing to study the solid-state reaction using a water-soluble source instead of the solid-state source of $BaCO_3$ with a partial solubility since the solubility of Ba source was proved to be a critical factor for the sonochemically activated solid-state reaction in our previous study [18].

In this study, the effect of Ba-sources for sonochemically activated solid-state synthesis of $BaTiO_3$ powders is presented. We ultrasonicated the mixtures of TiO_2 powder with different Ba sources of water-soluble $Ba(CH_3COO)_2$ and solid-state $BaCO_3$ in aqueous medium with adjusted pH values and compared the properties of resulting powders. The results revealed that the phase conversion ratio through the solid-state reaction was critically dependent on the type of Ba source. Detailed microstructural and crystal structural characterizations were conducted on each resulting $BaTiO_3$ powder and compared.

Experimental

Sample preparation

Barium acetate ($Ba(CH_3COO)_2$, ≥99%, Alfa Aesar, USA) and titanium dioxide (TiO_2, ≥99%, Sigma-Aldrich, USA) were used as raw materials, with the pH of distilled water controlled using potassium hydroxide (KOH) and hydrochloric acid (HCl) solutions. 150 ml of distilled water with controlled pH values (3, 5, 7, 9 and 11) was placed in a 250 ml beaker, and $Ba(CH_3COO)_2$ and TiO_2 were introduced stoichiometrically into the solvent as shown in Fig. 1. Sonochemical mixing process

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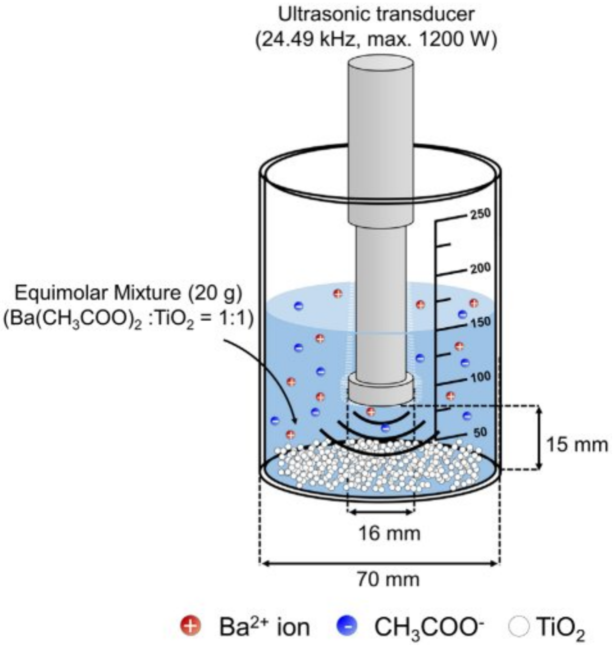

Fig. 1. A schematic of sonochemical mixing process.

was carried out for 5 min at an ultrasonic power of 900 W using an ultrasonic homogenizer (Boshi Electronic Instrument, Hangzhou, China). The ultrasonicated mixtures were oven-dried at 120 °C for 12 hours, and the resulting dried powder was ground using a mortar and pestle. The powder was calcined in air at 900 °C (heating rate=5 °C/min) for 3 h for the solid-state synthesis of $BaTiO_3$. The synthesized powder with the water-soluble Ba-source was referred to as W-BT. In addition, for a comparative study with the conventional solid-state synthesis of $BaTiO_3$, the same experimental procedure was carried out using barium carbonate ($BaCO_3$, 99%; Sigma-Aldrich, USA) and TiO_2 as raw materials. The synthesized powder was referred to as solid-state source $BaTiO_3$ (S-BT).

Characterizations

Crystal structures of calcined powders were investigated using an X-ray diffractometer (XRD, Ultima IV, Rigaku Corp, Tokyo, Japan) and Rietveld refinements were performed using Profex software (ver. 3.14.3). microstructural characterization was carried out using a field emission scanning electron microscope (FESEM, Mira 3, Tescan, Brno, Czech) and a transmission electron microscope (TEM, Titan Themis Z, FEI Company, USA). In addition, particle size analysis of the powder was conducted using a particle size analyzer (PSA, LA-950, Horiba Ltd., Japan).

Results and Discussion

Effect of pH on the particle size of ultrasonicated raw materials

Fig. 2(a) shows a SEM micrograph of water-soluble $Ba(CH_3COO)_2$ raw powder before ultrasonication, and (b)-(d) represent their microstructures after ultrasonication in aqueous medium at various pH levels and the subsequent drying process. All dried powders after ultrasonication exhibited a smaller particle size than untreated powder and showed a tendency that the particle size increased with the increase in pH of solvent. It has been reported that the solubility of the barium compounds decreases with an increase in the pH [22]. Therefore, $Ba(CH_3COO)_2$ dissolved in high pH aqueous medium recrystallizes rapidly during drying, and the particles formed through this process will grow in size. This can be considered the factor influencing the pH-dependent particle size after dissolution with ultrasonication and subsequent recrystallization.

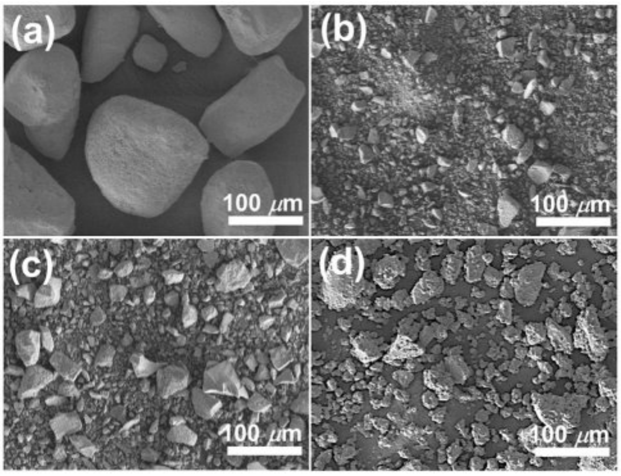

Fig. 2. SEM micrographs of (a) as-is and (b)-(d) ultrasonicated and subsequently dried $Ba(CH_3COO)_2$ powders at pH=3, 7 and 11, respectively.

Fig. 3(a) shows a SEM micrograph of solid-state $BaCO_3$ raw powder before ultrasonication, and (b)-(d) represent their microstructures after ultrasonication in

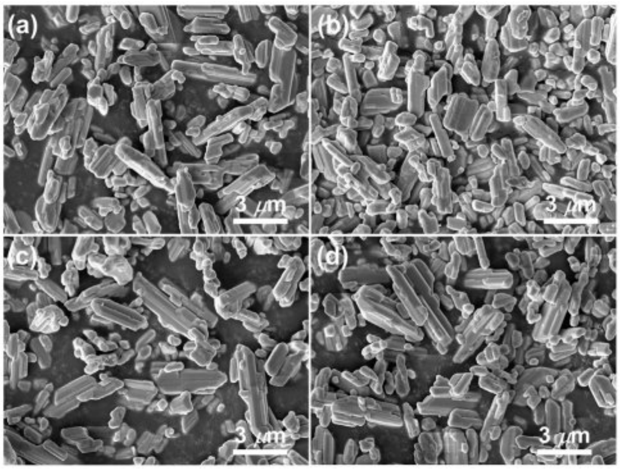

Fig. 3. SEM micrographs of (a) as-is and (b)-(d) ultrasonicated and subsequently dried $BaCO_3$ powders at pH=3, 7 and 11, respectively.

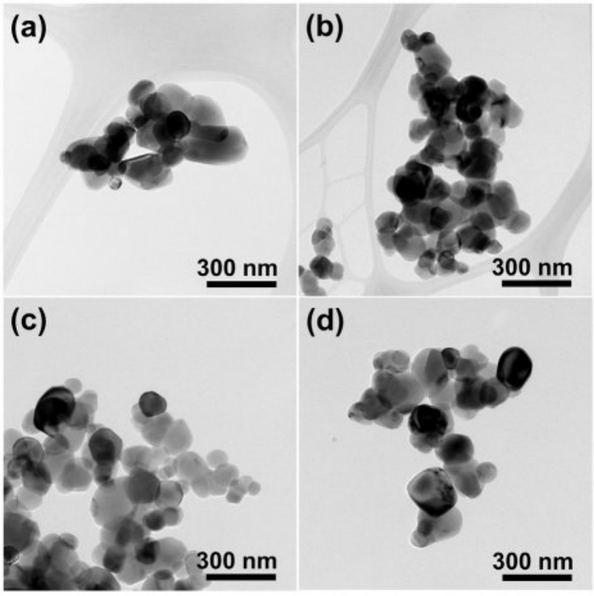

Fig. 4. TEM micrographs of (a) as-is and (b)-(d) ultrasonicated and subsequently dried TiO_2 powders at pH=3, 7 and 11, respectively.

aqueous medium at various pH levels and the subsequent drying process. It has been reported that $BaCO_3$ is partially soluble in water and its partial solubility is dependent on the pH [18, 23, 27]. However, although the degree of the fragmentation in $BaCO_3$ powder decreased with increasing pH [18], the changes in size with respect to pH were not significant and all resulting powders exhibited a smaller particle size and a narrower size distribution compared to the $Ba(CH_3COO)_2$ powders in Fig. 2.

Fig. 4(a) shows a TEM micrograph of TiO_2 raw powder before ultrasonication, and (b)-(d) represent their microstructures after ultrasonication in aqueous medium at various pH levels and the subsequent drying process. Regardless of the pH, no significant change was observed in the particle size of TiO_2 before and after the sonochemical process and the particle size was ~80 nm for all samples. It has been reported that TiO_2 is chemically stable and does not dissolve in water [24], and the influence of pH on the TiO_2 particle size was negligible also in this experiment.

Effect of pH on the solid-state reaction for $BaTiO_3$

Fig. 5(a) shows XRD patterns of W-BT powders synthesized by the calcination of sonochemical mixtures of water-soluble $Ba(CH_3COO)_2$ and TiO_2 at 900 ºC for 3 h. For pH=3, the powder was composed of major $BaTiO_3$ phase and a secondary Ba_2TiO_4 phase. $BaCO_3$ phase started to appear from pH=5, and multiphase of $BaTiO_3$, Ba_2TiO_4 and $BaCO_3$ were observed in W-BT powders up to pH=11.

Rietveld refinements on the XRD patterns were performed to investigate the phase conversion ratio to $BaTiO_3$ in the powders depending on the starting materials and pH. As shown in Fig. 6, a high conversion

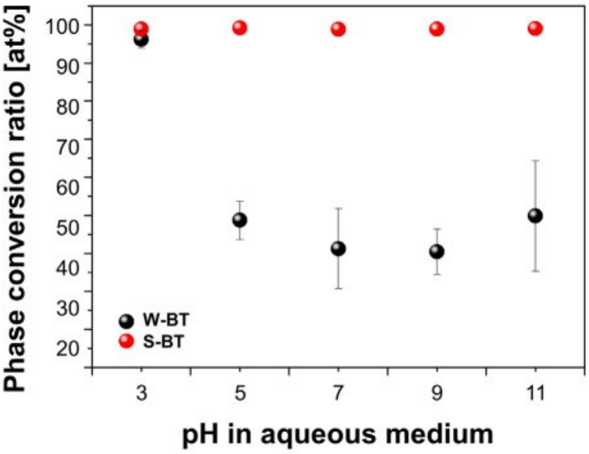

Fig. 6. Phase conversion ratio to $BaTiO_3$ as a function of pH in aqueous medium with different barium sources.

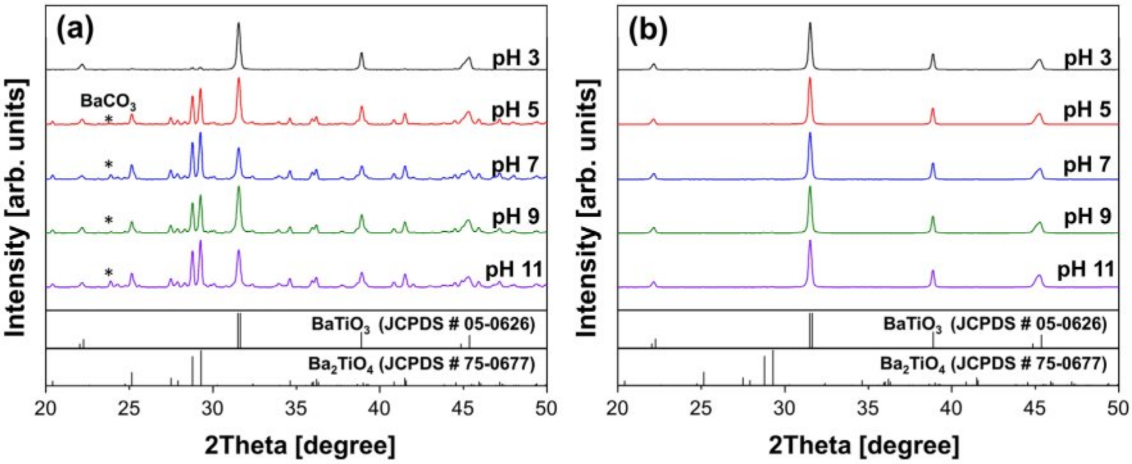

Fig. 5. XRD patterns of solid-state synthesized $BaTiO_3$ powder using (a) water-soluble $Ba(CH_3COO)_2$ and (b) solid-state $BaCO_3$ for Ba source.

ratio of ~95% was obtained in the solid-state synthesized W-BT only for pH=3. For higher pH values (pH=5-11), a relatively low $BaTiO_3$ phase conversion ratio of 40-50% was obtained in W-BT powders. On the other hand, S-BT, which uses conventional solid-state source of $BaCO_3$ and TiO_2, exhibited almost single perovskite phase regardless of pH as shown in Fig. 5(b) and Fig. 6.

Because the solid-state reaction takes place through the coupled diffusion of Ba^{2+} and O^{2-} ions into the TiO_2 lattice at the contact point between the starting materials [3-5], phase conversion ratio is determined by the properties of starting powders such as particle size, distribution, and surface area. Therefore, there have been reports on the enhancement of the solid-state reaction for $BaTiO_3$ by using nanosized raw materials to maximize the contacting area [6-17]. In Figs. 2 and 3, we observed the particle size of ultrasonicated Ba sources under different pH values. Regardless of pH values, the particle size of $BaCO_3$ source was much smaller than that of $Ba(CH_3COO)_2$ source and that is the reason for that the conversion ratio in S-BT was much higher than that in W-BT. Among the W-BT powders, the conversion ratio was much higher at pH=3 than at pH≥5 and this can be attributed to the fact that the particle size of $Ba(CH_3COO)_2$ was much smaller than the others, as shown in Fig. 2.

On the other hand, the conversion ratio was higher than 98% for all S-BT powders regardless of the pH in the aqueous medium. In this experiment, the calcination of the ultrasonicated mixtures for S-BT was carried out only at 900 °C for 3 h and this is relatively low temperature for the solid-state reaction for $BaTiO_3$ as compared to the conventional calcination temperatures in literature [1, 18, 19]. Therefore, the high conversion ratio of S-BT in this experiment shows the effect of the sonochemical activation on the enhancement of the solid-state reaction and this result is quite consistent with our previous reports [18, 19].

Structural characterizations of W-BT and S-BT

For microstructural characterizations, we selected W-BT and S-BT powders synthesized at pH=3 as they both exhibited a sufficiently high conversion ratio for comparative analysis. Fig. 7(a) shows SEM micrographs of the W-BT powder and the enlarged micrograph is shown in the inset. Strongly agglomerated particles (>10 μm) were easily observed in W-BT even though its primary particle size was ~160 nm as shown in the inset. On the other hand, Fig. 7(b) shows that the agglomeration in S-BT was much weaker than that in W-BT. Even in this case, the primary particle size was measured to be ~160 nm. It has been reported that the crystallite size of solid-state synthesized $BaTiO_3$ powder is predominantly affected by the initial TiO_2 particle size [25, 26]. Because the particle size of TiO_2 was not changed by the sonochemical process in aqueous medium as shown in Fig. 4, this result is consistent with the reported results. With this result, it was found that different barium sources only affect the degree of agglomeration of primary particles, not the primary particle size, in this set of $BaTiO_3$ powders. To investigate the degree of the agglomeration quantitatively, we also carried out the particle size analysis (PSA) for the powders and the results are shown in Fig. 8. The D50 of W-BT was measured to be 16.7 μm, while for S-BT, it was 2.2 μm. These quantitative results are quite consistent with the qualitative observations in Fig. 7.

The structural characterizations of W-BT and S-BT

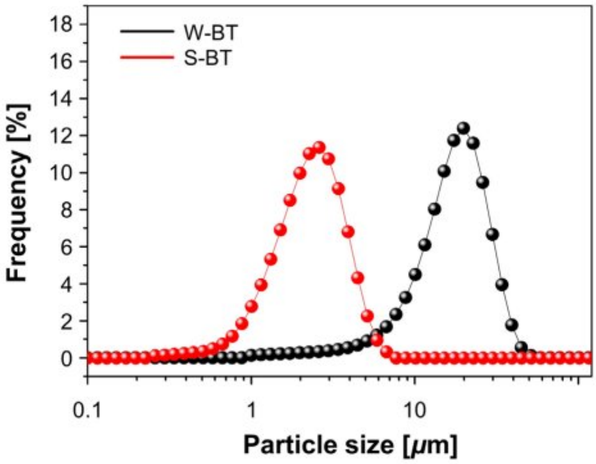

Fig. 8. PSA results of W-BT and S-BT powders.

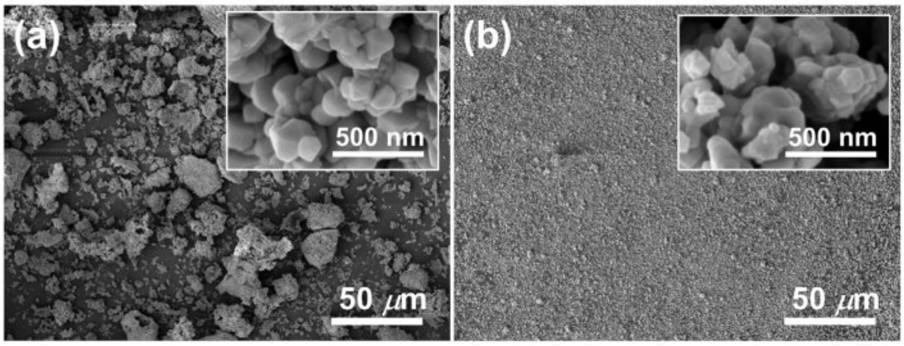

Fig. 7. SEM micrographs of (a) W-BT and (b) S-BT powders.

Table 1. Refined structural parameters for W-BT and S-BT powders at room temperature.

Powder	a (Å)	c (Å)	V (Å^3)	Tetragonality (%)	GOF	R_{wp} (%)
W-BT	3.9993	4.0200	64.2975	0.516	2.32	7.71
S-BT	4.0015	4.0222	64.4035	0.517	1.51	3.36

powders were conducted through Rietveld refinements using the XRD patterns shown in Fig. 5, and the summarized results are presented in Table 1. The lattice parameters, volume and tetragonality were almost similar in both powders. Therefore, it was found that Ba sources do not affect the crystallographic properties of the resulting primary $BaTiO_3$ particles, but rather only influence the degree of agglomeration.

Conclusions

In summary, we reported the effect of Ba-sources on the sonochemically activated solid-state synthesis of $BaTiO_3$ powders. We ultrasonicated the mixtures of TiO_2 powder with different Ba sources of water-soluble $Ba(CH_3COO)_2$ and solid-state $BaCO_3$, and we compared the properties of resulting powders. When we used water-soluble source of $Ba(CH_3COO)_2$, the phase conversion to $BaTiO_3$ showed a strong pH dependence. Except for pH=3, the conversion ratio of W-BT powders was quite low (40-50%) and this was mainly attributed to the change in the particle size of Ba source during the ultrasonication and drying process depending on pH in the aqueous medium. On the other hand, when using the solid-state $BaCO_3$ powder, the conversion ratio surpassed 98% for all S-BT powders under the same calcination condition (900 ºC for 3 h in air). Considering that the $BaCO_3$ was micron-sized, this high conversion ratio indicates that the solid-state reaction to $BaTiO_3$ was significantly accelerated by the sonochemical mixing process compared with the conventional solid-state reaction employing a ball-mill process. Detailed microstructural and crystal-structural characterizations of W-BT and S-BT powders revealed that the properties of primary $BaTiO_3$ particles were not significantly affected by the Ba sources. However, the degree of agglomeration of primary particles was strongly associated with the type of Ba source. We expect that this study will be helpful in understanding the process for synthesizing and doping $BaTiO_3$ powders using water-soluble raw materials.

Acknowledgement

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