Sonochemical activation in aqueous medium for solid-state synthesis of BaTiO\(_3\) powders

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**Abstract**

Ba\(_3\)Ti\(_3\)O\(_9\)-based oxide compounds are important ceramic materials for multilayer ceramic capacitors. In this paper, we report a sonochemical activation process of Ba\(_2\)CO\(_3\) and TiO\(_2\) in an aqueous medium for the synthesis of BaTiO\(_3\) powders through a solid-state process. Owing to the physical and chemical effects of the ultrasonication in aqueous medium on the raw materials, BaTiO\(_3\) powders could be successfully synthesized at relatively low temperatures through a solid-state reaction, which was significantly enhanced as compared to the case in ethanol medium. Detailed investigations on the resulting BaTiO\(_3\) powders and ceramics were performed, and a model to understand the role of aqueous medium on the enhancement of the solid-state reaction was proposed in terms of Ba\(^2+\) ion leaching and zeta potential of TiO\(_2\), which are strongly affected by the pH of the aqueous medium. Our results are not only helpful for cost-effective synthesis of BaTiO\(_3\) through the highly reliable solid-state reaction process, but they also provide an understanding of the role of aqueous medium for the sonochemical process using raw materials with partial solubility in water.

**1. Introduction**

Since the discovery of ferroelectricity in BaTiO\(_3\), BaTiO\(_3\)-based oxide compounds have been extensively researched for numerous applications, from electrical devices to energy utilizations [1–11]. Presently, BaTiO\(_3\) is the most important ceramic material for multilayer ceramic capacitors (MLCCs) [12–15]. With the miniaturization of MLCCs and their increased use, the volume efficiency and reliability of the dielectric layer has become increasingly important. To meet the tight limitation of layer thickness (<1 \(\mu\)m) as well as to guarantee reliability, the use of well-dispersed, fine, and uniform BaTiO\(_3\) powders is essential to fabricate the dielectric layer for MLCCs [13–17]. These powders have been prepared via a hydrothermal process [18–23]; however, the intergranular pores induced by inevitable hydroxyl groups in the hydrothermal process can deteriorate the breakdown strength of the dielectric layers, resulting in low reliability [20–23]. Furthermore, the high process cost, owing to the use of expensive precursors, and the difficulty of eliminating impurities in the hydrothermal process have been regarded as some of its other major drawbacks [1,24].

Meanwhile, the solid-state reaction in (1), using inexpensive raw materials of BaCO\(_3\) and TiO\(_2\), is a traditional process for synthesizing relatively coarse BaTiO\(_3\) powders [13,16,17,24–28].

\[
\text{BaCO}_3(s) + \text{TiO}_2(s) \rightarrow \text{BaTiO}_3(s) + \text{CO}_2(g) \tag{1}
\]

Because of its high calcination temperature (~1200 °C), solid-state reaction can provide highly dense BaTiO\(_3\) powders, which is desirable in terms of reliability. Furthermore, it has been reported that submicron-sized BaTiO\(_3\) powders can be successfully prepared via the solid-state reaction through appropriate pre-treatments of the raw materials, such as high-energy ball-milling and mechanochemical [29–32] and sonochemical activation [33–35]. These pre-treatments result in downsizing and uniform mixing of the raw materials, thereby facilitating the synthesis of BaTiO\(_3\) powders through reaction (1). Among these pre-treatment methods, sonochemical activation, which uses ultrasonication for the downsizing and mixing of raw materials, is a contamination-free, time-saving, and cost-effective process. Recently, we reported that sonochemical activation of BaCO\(_3\) and TiO\(_2\) in ethanol could significantly enhance the solid-state process for the synthesis of BaTiO\(_3\) powders (~200 nm) at a relatively low temperature (~1000 °C) [35]. This was mainly attributed to the physical effect of the ultrasonic irradiation, i.e., the preferential fragmentation of BaCO\(_3\).
Although water is a more desirable mixing medium than ethanol for sonochemical activation in terms of the process cost, BaCO$_3$ dissolves partially in water and it leads to the leaching of Ba$^{2+}$ ions. Li et al. reported that the amount of leached Ba$^{2+}$ ions from BaCO$_3$ in aqueous medium decreases with increasing pH, and the dissolution stops when the available concentration of H$_2$O$^+$ is completely consumed [36]. Therefore, understanding the chemical effect, i.e., the pH-dependent Ba$^{2+}$ leaching, is of great interest for the synthesis of BaTiO$_3$ via sonochemical activation in an aqueous medium.

Herein, we report the effect of pH on the sonochemical activation in an aqueous medium for the powder synthesis of BaTiO$_3$ through the solid-state reaction. The sonochemical activation of raw materials (BaCO$_3$ and TiO$_2$ powders) was performed under various pH conditions in an aqueous medium with controlled ultrasonic powers and then calcined at 900–1200 °C. For comparison, the raw materials were also sonochemically activated under the same experimental conditions, except that the mixing medium was ethanol. Compared with the case of ethanol, a significantly enhanced solid-state reaction for the synthesis of BaTiO$_3$ powders was achieved with the activation process in aqueous medium due to physical and chemical effects. Subsequently, a model defining the role of aqueous medium for the enhanced solid-state reaction was proposed with respect to pH. Through detailed investigations on the resulting BaTiO$_3$ powders and ceramics, we propose that sonochemical activation in aqueous medium is a cost-effective process for the synthesis of BaTiO$_3$ powders with compatible properties as compared to the process in ethanol.

2. Experimental

2.1. Materials

BaCO$_3$ (>99%, Sigma-Aldrich) and TiO$_2$ (>99%, Sigma-Aldrich) powders were used as raw materials. Deionized water under various pH conditions (controlled by titrating 0.5 M HCl and KOH solutions) and ethyl alcohol were used as dispersion media for the sonochemical activation process. A schematic of the sonochemical activation process for the synthesis of BaTiO$_3$ powder through the solid-state reaction is drawn in Fig. 1. Equimolar mixtures of raw materials were dispersed in 150 mL deionized water under various pH conditions in 250 mL beaker. The sonochemical activation of the mixtures was carried out using an ultrasonic homogenizer (Boshi Electronic Instrument) for 5 min and the ultrasonic power was controlled to be 300, 600, and 900 W. For comparison, the sonochemical activation of the same mixtures was also performed in ethanol. The ultrasonicated mixtures were oven-dried at 120 °C overnight. Calcination of the dried mixtures was performed at 900, 1000, 1100, and 1200 °C for 3 h, and green pallets were prepared by pressing under a uniaxial pressure of 100 MPa after mixing with a polyvinyl alcohol binder (Sigma-Aldrich). They were first heated at 500 °C (heating rate = 3 °C/min) for 1 h for binder burnout, and sintered in air at 1300 °C for 4 h (heating rate = 5 °C/min). The density of the sintered pellets was estimated using Archimedes’ method, and the relative density was higher than 97% for all sintered ceramics. For electric measurements, silver paste was printed on the polished pellets (thickness = 1.0 mm) using screen printing and fired at 600 °C for 1 h in air.

2.2. Characterizations

For crystal structure characterization, X-ray diffraction (XRD) was carried out using Ultima IV (Rigaku) with Cu K$_\alpha$ radiation. Scans were taken with a scan speed of 0.02°/s at an operating condition of 40 kV and 30 mA. Rietveld refinements were performed for all 72 powder XRD patterns using Profex ver. 3.14.3 with reliable refinement factors (weighted residual of least-squares refinement, $R_{wp}$ = 4.60 ± 0.72; goodness of fit, GOF = 2.03 ± 0.28). For microstructural
characterization, scanning electron microscopy (SEM) was performed using MIRA3 (Tescan) and transmission electron microscopy (TEM) was carried out using Titan Themis Z (FEI). In addition, the stoichiometric ratio between Ba and Ti in the BaTiO$_3$ ceramics was analyzed using electron probe microbeam analysis (EMPA, JXA-8530F, JEOL). A particle size analyzer (LA950, Horiba) was used for characterizing the particle size distribution of the ultrasonicated BaCO$_3$ powders. An inductively coupled plasma spectrometer (ICP, Optima 7300DV, PerkinElmer) was used for the supernatant of the centrifuged suspensions (1500 rpm for 15 min) to characterize the amount of leached Ba$^{2+}$ ions from BaCO$_3$ in aqueous medium after the sonochemical activation. The zeta potential of TiO$_2$ in aqueous medium under various pH conditions was analyzed using a zeta potential analyzer (Nano ZS90, Malvern Panalytical). The ferroelectric properties were examined using TF Analyzer 2000 (AixAcct) at a frequency of 0.5 Hz. The dielectric properties were characterized using an impedance analyzer (HP 4194A, Hewlett-Packard) with a measurement frequency of 10 kHz from -100 to 180 °C.

3. Results and discussion

3.1. pH-dependent particle size reduction of ultrasonicated raw materials in aqueous medium

Since the solid-state reaction in (1) is governed by the inward diffusion of ion species (Ba$^{2+}$ and O$^{2-}$) into the TiO$_2$ particle, the particle size of raw materials is critically important for the synthesis of BaTiO$_3$ powders [16,26,27]. To find the effect of pH on the particle size reduction via sonochemical activation, we first performed ultrasonication of BaCO$_3$ powders in an aqueous medium under various pH conditions. The ultrasonicated BaCO$_3$ particle sizes were measured using a particle size analyzer, and the results are presented in Fig. 2(a) and S1. The particle size monotonously decreased as the pH decreased. The particle size of pristine BaCO$_3$ was ~3.4 μm and it decreased to ~2.2 μm after 600 W ultrasonication at pH = 3. Furthermore, all ultrasonicated BaCO$_3$ in the aqueous medium exhibited a smaller particle size than that in ethanol (~2.9 μm). In our previous study, we performed the sonochemical activation of BaCO$_3$ in ethanol [35]. In that case, only mechanical fragmentation was attributed to the particle size reduction of the BaCO$_3$. However, the results of this study suggest that there should be an additional chemical effect on the particle size reduction in aqueous medium depending on the pH condition.

It is known that the size reduction owing to the ultrasonication can be attributed to mechanical fragmentation and chemical dissolution [24,33–35,37]. To verify the effect of pH on the dissolution of BaCO$_3$, ICP measurements for the supernatant of 600 W ultrasonicated medium were performed. As seen in Fig. 2(b), the amount of leached Ba$^{2+}$ ions decreased with increase in pH because the dissolution of BaCO$_3$ in the aqueous medium decreased under alkaline conditions. Therefore, it was confirmed that the ultrasonication of BaCO$_3$ in aqueous medium accelerates the particle size reduction due to the additional chemical effect, i.e., the dissolution of BaCO$_3$. In contrast, the ultrasonication did not affect the particle size of TiO$_2$. Fig. 3 represents TEM micrographs of TiO$_2$ particles after 600 W ultrasonication under different pH conditions. The average particle size was ~130 nm regardless of the pH condition. Because the size of the resulting BaTiO$_3$ particle is determined by the TiO$_2$ particle size [38,39], this result suggests that the resulting BaTiO$_3$ powders made from the sonochemically activated mixtures in aqueous medium do not exhibit a pH dependence in their particle size.

3.2. Effect of pH on the solid-state reaction of sonochemically activated raw materials in aqueous medium (600 W ultrasonicated mixtures)

We performed sonochemical activation of equimolar mixtures of BaCO$_3$ and TiO$_2$ at 600 W for 5 min in an aqueous medium (Fig. 1) for...
the synthesis of BaTiO$_3$ through reaction (1). The sonochemically activated mixtures were then calcined at 900, 1000, 1100, and 1200 °C for 3 h in air, and the calcined powders were characterized by XRD (Fig. S2). The majority phase was identified as tetragonal BaTiO$_3$ (JCPDS #05-0626) in all the calcined powders, and a secondary phase of Ba$_2$TiO$_4$ (JCPDS #75-0677) was also detected depending on the sonochemical activation conditions and calcination temperatures. The conversion ratio to the BaTiO$_3$ phase under each condition was calculated using Rietveld refinements.

Fig. 4 (a) represents the calculated phase conversion ratio as a function of pH at each calcination temperature. For comparison, the ratios in the calcined powders made from the ultrasonicated mixtures in ethanol are also shown using dashed lines for each calcination temperature. In this figure, it is clearly seen that the phase conversion ratio was significantly enhanced by the sonochemical activation in aqueous medium compared with the case using ethanol. The phase conversion ratios of the powders that were sonochemically prepared in aqueous medium were higher than 97% even at a calcination temperature of 900 °C regardless of the pH value, and they exhibited almost complete conversion to the BaTiO$_3$ phase at relatively higher calcination temperatures.

In our previous study, we showed that sonochemical activation, even in ethanol, could accelerate the solid-state reaction by the effect of particle size reduction through the preferential fragmentation of BaCO$_3$ [35]. In this experiment, the phase conversion (95.7–98.2% using ethanol) could be further enhanced by using aqueous medium (97.2–99.8%) for the sonochemical activation, implying that there is an additional chemical effect of the aqueous medium on the solid-state reaction, as marked by the colored arrows in Fig. 4(a). Since the solid-state reaction is significantly affected by the size of raw materials, the highest conversion ratio should be observed for the powders prepared at pH = 3 in terms of the BaCO$_3$ particle size; however, in this study, this was obtained at pH = 5. Furthermore, although the particle size of the ultrasonicated BaCO$_3$ in aqueous medium with pH = 11 (∼2.8 μm) was not very different from that in ethanol (∼2.9 μm), as shown in Fig. 2(a), the ratio increased remarkably at all calcination temperatures. These results demonstrate that the particle size is not the deterministic factor for the solid-state reaction of ultrasonicated mixtures in an aqueous medium.

As seen in Fig. 2(b), the amount of leached Ba$^{2+}$ ions increased with decreasing pH, and the particle size reduction of BaCO$_3$ was assisted by dissolution in the aqueous medium. The leached Ba$^{2+}$ ions can be reprecipitated in the form of Ba(OH)$_2$ and/or BaCO$_3$ during the drying process following the sonochemical activation [40]. Furthermore, the reprecipitation of Ba$^{2+}$ ions can occur preferentially on the surface of TiO$_2$ and form a core–shell-like surface structure when the zeta potential of TiO$_2$ is negative [41]. This core–shell structure can provide the maximum contacting surface between the reacting species; this

![Fig. 5. (a-c) Model for the rearrangement of leached Ba$^{2+}$ ions on the surface of TiO$_2$ particles in aqueous medium under pH = 3, pH = 5, and pH ≥ 7, respectively. (d) No leached Ba$^{2+}$ ions exist in ethanol.](image-url)
enhanced solid-state reaction in the TiO$_2$-BaCO$_3$ core–shell has also been previously reported [28]. Therefore, we characterized the zeta potential of TiO$_2$ in aqueous media under different pH conditions (Fig. 4(b)). TiO$_2$ exhibited a positive zeta potential only at pH $= 3$, which can lead to electrostatic repulsion with the positive Ba$^{2+}$ ions, thereby hindering the reprecipitation of Ba$^{2+}$ ions on the TiO$_2$ surface. In contrast, TiO$_2$ exhibited negative values at pH $\geq 5$. Therefore, the isoelectric point (IEP) of TiO$_2$ was located in the range of pH $= 3$–5 in this experiment. It has been reported that the zeta potential of TiO$_2$ depends on the pH of dispersion medium and TiO$_2$ particle size [42]. It has also been reported that when the size of TiO$_2$ particle is $\sim 100$ nm, the IEP is located at pH $\sim 4$, regardless of the crystal structure of TiO$_2$. Therefore, our results are consistent with the reported values in the literature.

With these results, we propose a model for the chemical effect of the sonochemical activation in aqueous medium on the solid-state reaction for BaTiO$_3$ powder synthesis. As schematically shown in Fig. 5(a), the uniform reprecipitation of the leached Ba$^{2+}$ ions on the TiO$_2$ surface is hindered by the positive zeta potential of TiO$_2$ at pH $= 3$, even though this condition offers the smallest particle size of BaCO$_3$ and the largest amount of leached Ba$^{2+}$ ions. However, although the particle size slightly increased at pH $= 5$ in Fig. 5(b), the zeta potential of TiO$_2$ becomes negative and attracts the leached Ba$^{2+}$ ions on the surface, leading to the formation of a core–shell-like surface structure on TiO$_2$ particles. Therefore, the highest phase conversion ratio was observed under these conditions. A further increase in pH value, as shown in Fig. 5(c), leads to an increase in the BaCO$_3$ particle size and a simultaneous decrease in the leaching of Ba$^{2+}$ ions. Therefore, the chemical effect of the aqueous medium at pH $= 7$–11 was smaller than that observed at pH $= 5$; however, their negative zeta potentials kept the conversion ratio higher than that observed at pH $= 3$. Therefore, it can be concluded that the observed enhancement in the BaTiO$_3$ powder synthesis in aqueous medium can be attributed not only to the accelerated size reduction of BaCO$_3$ powder but also to the reprecipitation of the leached Ba$^{2+}$ ions on TiO$_2$ particles in aqueous medium, which does not exist in ethanol (Fig. 5(d)).

3.3. Effect of sonication power on the solid-state reaction of sonochemically activated raw materials in aqueous medium (300 and 900 W ultrasonicated mixtures)

To understand the effect of sonication power on the solid-state reaction in detail, we also performed the sonochemical activation of equimolar mixtures of BaCO$_3$ and TiO$_2$ in aqueous media with different pH conditions under 300 and 900 W ultrasonic power for 5 min. After calcination, we characterized the phase conversion ratio of the resulting powders using XRD patterns (Fig. S2). For the powders prepared with 300 W ultrasonicated mixtures in Fig. 6(a), the highest conversion ratio was observed at pH $= 5$, and the chemical effect of the sonochemical activation, i.e., the pH dependence, on the solid-state reaction became more significant as compared with the powders prepared with 600 W ultrasonication.

For the powders prepared with 900 W ultrasonicated mixtures in Fig. 6(b), the phase conversion ratio was nearly pH-independent, indicating that the physical effect, i.e., the particle size reduction effect, was dominant for the solid-state reaction. It is noteworthy that, in the case of
900 W ultrasonication, all the powders prepared by sonochemical activation in aqueous medium exhibited almost complete phase conversion (≥99%) even at a calcination temperature of 900 °C. These conversion ratios were slightly higher than those prepared in ethanol, indicating that the solid-state reaction was also enhanced by the dissolution of BaCO₃ in aqueous medium, even when the physical effect was dominant at a relatively high ultrasonic power. Therefore, it was found that sonochemical activation in an aqueous medium enhances the solid-state reaction for the BaTiO₃ powder synthesis through both chemical and physical effects, and that the contribution of each effect is dependent on the ultrasonic power.

3.4. Structural characterizations of BaTiO₃ powders

We characterized the lattice constants and tetragonality of the resulting BaTiO₃ powders using Rietveld refinements. The results are shown in Figs. 7 and S3. Although the phase conversion ratio was considerably affected by the type of dispersion medium and ultrasonic power, as shown in Fig. 4(a) and 6, the structural properties were mostly influenced by the calcination temperature rather than other conditions. Because only 900 W ultrasonicated powders exhibited sufficiently high phase conversion ratios (≥99%) at all calcination temperatures (900–1200 °C), we represented the properties of the 900 W ultrasonicated powders in Fig. 7 as a function of calcination temperature. In addition, these 900 W ultrasonicated powders were chosen for the dielectric and ferroelectric measurements after sintering, as discussed in Section 3.5. Regardless of the dispersion medium, the lattice constants along the c-axis increased and those along the a-axis decreased with increasing calcination temperature, as shown in Fig. 7(a). Consequently, it led to an increase in the tetragonality (\(\sim 0.49\)).

Fig. 8. SEM micrographs of 900 °C-calcined powders for 900 W ultrasonicated mixtures (a)–(e) in aqueous medium under pH = 3, 5, 7, 9 and 11, respectively, and (f) in ethanol.

Fig. 9. SEM micrographs of (a–f) BT-3, BT-5, BT-7, BT-9, BT-11, and BT-E, respectively.
The particle size of the 900 W ultrasonicated powder was determined by SEM at each calcination temperature (Fig. S4). The average particle size and shape at each calcination temperature was not affected by the type of dispersion medium for the sonochemical activation. As an example, Fig. S4 shows the SEM micrographs of 900 W ultrasonicated mixtures in different dispersion media.

Furthermore, as shown in Fig. 10(b), all the ceramics exhibited almost identical hysteresis loops of polarization–electric field (P-E) at room temperature. Regardless of the dispersion medium, the polarizations were saturated at 30 kV/cm and their saturation polarization ($P_s$) was analyzed to be $\sim 24.1 \mu C/cm^2$ (standard deviation $= -0.5\%$). In addition, their coercive field ($E_c = 3.24 \text{ kV/cm on average}$) and remnant polarization ($P_r = \sim 10.4 \mu C/cm^2$ on average) exhibited relatively small standard deviations of less than 10%, as summarized in Table S1. Because these properties are influenced by many factors (relative density, defect density, grain size, tetragonality, nonstoichiometry, etc.), our results show that the quality of BaTiO$_3$ prepared through the solid-state reaction of ultrasonicated mixtures is not significantly affected by the dispersion medium for the sonochemical activation process. Therefore, it can be concluded that the sonochemical activation in aqueous medium not only enhances the synthesis of BaTiO$_3$ powders as compared with that in ethanol but also provides cost-effectiveness and competitive properties in the resulting BaTiO$_3$ ceramics.

4. Conclusions

In this paper, a study on the sonochemical activation of raw materials in aqueous medium for the BaTiO$_3$ powder synthesis was reported, and a model for the enhancement of the solid-state reaction via sonochemical activation was proposed. Unlike sonochemical activation in ethanol, which contributes only to the physical effect of preferential particle size reduction of BaCO$_3$ by ultrasonic irradiation, the sonochemical activation in aqueous medium accelerated the particle size reduction through both physical and chemical effects. The chemical effect not only accelerated the particle size reduction through the dissolution of BaCO$_3$, which is particularly important in acidic conditions, but also affected the rearrangement of leached Ba$^{2+}$ ions on the TiO$_2$ surface. The electrostatic attraction between Ba$^{2+}$ ions and TiO$_2$ particles with negative zeta potentials gave rise to the maximum contact surface between the reacting species for the solid-state reaction, thereby leading to a considerable enhancement in the solid-state reaction of BaTiO$_3$ particles. Our results offer an alternative to conventional ball milling for BaTiO$_3$ production in the highly competitive MLCC industry and the reported sonochemical activation process can also be applied to a variety of ceramic industries.

CRediT authorship contribution statement

Hae Won Lee: Investigation, Writing – original draft. Na Won Kim: Investigation. Wooyun Nam: Investigation. Young Soo Lim: Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial...
interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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