

## Hydrothermal Synthesis for Large Barium Titanate Powders at a Low Temperature: Effect of Titania Aging in an Alkaline Solution

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**Monodisperse and spherical barium titanate (BaTiO<sub>3</sub>) powders with diameters of 200–470 nm were directly prepared by a low-temperature hydrothermal method at 90°C. Spherical titania (TiO<sub>2</sub>) powders, ranging in size from 150 to 420 nm, were initially prepared by a controlled hydrolysis and condensation reaction, aged in a highly alkaline solution for 12 h, and then hydrothermally reacted with barium hydroxide to be converted to BaTiO<sub>3</sub> without a morphological change. The aging step of the TiO<sub>2</sub>, where the surface of TiO<sub>2</sub> was highly densified through elimination of the pores, was indispensable to retain the sizes and shapes of TiO<sub>2</sub> in the resulting BaTiO<sub>3</sub>. This was due to the fact that the formation of BaTiO<sub>3</sub> proceeded by an *in situ* reaction mechanism. The resulting BaTiO<sub>3</sub> powders exhibited dense and nonporous structures even after calcination at 1000°C.**

### I. Introduction

BARIUM titanate (BaTiO<sub>3</sub>) is a representative perovskite-structured material and is widely used as a dielectric materials in multilayered ceramic capacitors (MLCCs) because of its high dielectric constant.<sup>1</sup> Most of the hydrothermal methods for BaTiO<sub>3</sub> have usually dealt with preparations of BaTiO<sub>3</sub> smaller than about 150 nm in size. However, the hydrothermally prepared powders had to be annealed at an elevated temperature to grow it to a desirable size because the larger BaTiO<sub>3</sub> powders with a size range of 150–500 nm have mainly been used in real MLCC production due to their size dependency on the dielectric constant.<sup>2–4</sup>

On the other hand, there have been a few reports on the preparation of BaTiO<sub>3</sub> powders larger than 150 nm directly from the hydrothermal method.<sup>5–7</sup> However, they required more harsh reaction conditions, such as a higher temperature (>200°C), higher pressure (over a few tenth of atm), and extended reaction times, than that in the conventional hydrothermal methods. Michael *et al.*<sup>8</sup> and Park *et al.*<sup>9</sup> prepared large BaTiO<sub>3</sub> powders over 1 μm directly from a mild hydrothermal reaction under 100°C. They prepared large TiO<sub>2</sub> powders using a polymeric surfactant of hydroxypropylcellulose (HPC) and used them as precursors for the preparation of BaTiO<sub>3</sub>. Although the resulting BaTiO<sub>3</sub> powders were spherical and monodisperse, each particle was composed of nanometer-sized sub-particles with a substantial amount of macropores largely due to the polymeric surfactant,<sup>10</sup> which prevented them from use in MLCC application.

In this study, we prepared relatively large BaTiO<sub>3</sub> powders with diameters of 200–470 nm by a low-temperature hydrothermal synthesis at 90°C. The size of the BaTiO<sub>3</sub> powders could be varied by adjusting the size of the titania (TiO<sub>2</sub>) precursors, which were prepared by a hydrolysis–condensation reaction of titanium tetrabutoxide (Ti(O-Bu)<sub>4</sub>) without any surfactant or polymer. However, aging of the TiO<sub>2</sub> precursors in a strong alkaline solution before the hydrothermal reaction was indispensable to convert the TiO<sub>2</sub> precursors into BaTiO<sub>3</sub> to retain their morphology and, therefore, changes in the TiO<sub>2</sub> during the aging step were investigated.

### II. Experimental Procedure

A 0.125M Ti(O-Bu)<sub>4</sub> (>97%, Aldrich, Milwaukee, WI) solution was prepared by dissolving 4.255 g of Ti(O-Bu)<sub>4</sub> in 100 mL of ethyl alcohol (EtOH, >99.9%, J. T. Baker, Phillipsburg, NJ). A calculated amount of distilled-deionized water was added to another 100 mL of EtOH, where the *R* ratio ([H<sub>2</sub>O]/[Ti]) was varied from 10 to 25. Each solution was stirred for 1 h and mixed together. The solution became turbid in a few seconds, indicating that TiO<sub>2</sub> powders formed. After the solution was stirred for 2 h, 50 mL of 0.24M aqueous potassium hydroxide (KOH, >85%, Shinyo, Osaka, Japan) solution was added to the TiO<sub>2</sub> suspension and aged at 60°C for 0–12 h, respectively. Lithium hydroxide (LiOH · H<sub>2</sub>O, >95%, Junsei, Tokyo, Japan) and ammonium hydroxide (NH<sub>4</sub>OH, >28%, Acros, Morris Plains, NJ) were also used for the aging process. After repeated washings and filterings, spherical and amorphous TiO<sub>2</sub> powders were obtained.

BaTiO<sub>3</sub> powders were synthesized by a low-temperature hydrothermal reaction between the aged TiO<sub>2</sub> suspension and barium hydroxide (Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O, >98%, Acros, Morris Plains, NJ) at 90°C for 24 h. The amount of Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O was fixed to the [Ba]/[Ti] ratio of 1.05. After being cooled to room temperature, the solution was filtered through a membrane filter (nylon, 0.45 μm) and rinsed several times with distilled-deionized water. The resulting BaTiO<sub>3</sub> powders were dried in a vacuum oven at 70°C for 24 h and calcined at 1000°C for 10 h in a furnace under air.

The crystalline phase of the TiO<sub>2</sub> and BaTiO<sub>3</sub> was determined by an X-ray diffractometer (XRD, Rint-2000, Rigaku, Tokyo, Japan) using CuKα radiation at 40 kV and 100 mA. Morphologies were observed with scanning electron microscopy (SEM, JSM-2010, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2000EXII, JEOL). Surface areas and adsorption–desorption isotherms for TiO<sub>2</sub> powders were obtained at a liquid-nitrogen temperature (ASAP-2010, Micromeritics Instrument Corp., Norcross, GA).

### III. Results and Discussion

Spherical TiO<sub>2</sub> powders with diameters of 150–420 nm were successfully prepared by a controlled hydrolysis and condensation

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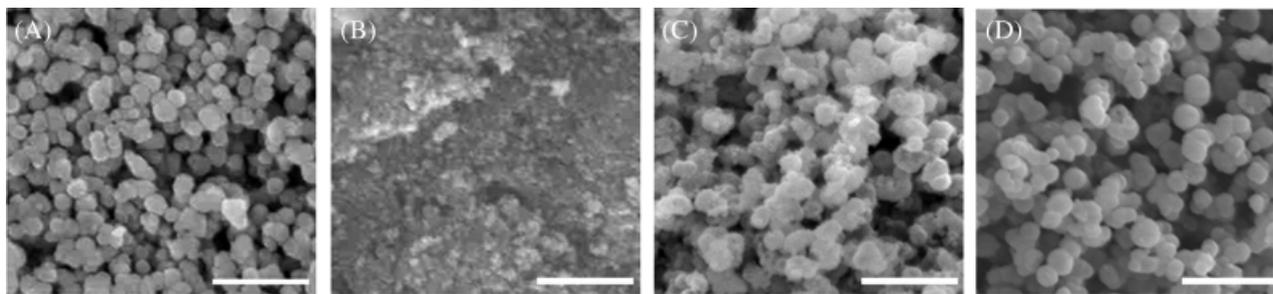


Fig. 1. Scanning electron microscopy images of (A) a titania ( $\text{TiO}_2$ ) precursor with an  $R$  ratio of 20 and barium titanate powders prepared from the aged  $\text{TiO}_2$  precursor in a potassium hydroxide solution for (B) 0, (C) 4, and (D) 12 h (scale bars = 1  $\mu\text{m}$ ).

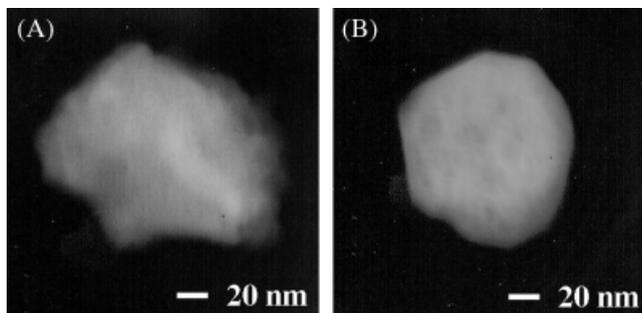


Fig. 2. Transmission electron microscopy images of titania precursors: (A) before aging and (B) after aging in a potassium hydroxide solution for 2 h at  $60^\circ\text{C}$  (scale bars = 20 nm).

reaction of  $\text{Ti}(\text{O-Bu})_4$  at an  $R$  ratio ( $[\text{H}_2\text{O}]/[\text{Ti}]$ ) from 10 to 25. When the  $\text{TiO}_2$  powders were used as precursors in a hydrothermal reaction for preparing  $\text{BaTiO}_3$  powders, their size and morphology could not be maintained unless they were aged in a KOH solution for more than 12 h before the hydrothermal reaction as shown in Fig. 1.

Although the crystallographic structure of the  $\text{TiO}_2$  precursor did not change during the aging process, showing amorphous characteristics in the XRD analysis, the surface of the  $\text{TiO}_2$  was highly densified after the aging as shown in the TEM images of Fig. 2. The fluffy surface of  $\text{TiO}_2$  before the aging turned to a well-defined surface after aging. The densification of the surface on aging of the  $\text{TiO}_2$  precursor was also confirmed by the  $\text{N}_2$  gas adsorption–desorption experiments. The specific surface area of the  $\text{TiO}_2$  was significantly reduced from 325.8 to 27.3  $\text{m}^2/\text{g}$  after aging for 12 h in a KOH solution. Also, the isotherm corresponding to the  $\text{TiO}_2$  precursor before the aging (Fig. 3(A)) exhibited abrupt adsorption of the gas at a relative pressure close to zero and the isotherm was close to type I, which is a typical characteristic of microporous materials.<sup>11</sup> However, the  $\text{TiO}_2$  precursor aged for 12 h in a KOH solution exhibited an isotherm similar to type III, which represents nonporous materials (Fig. 3(D)). The densification effect was also affected by the kind of base used. Isotherms exhibited more microporous features when weaker bases such as LiOH and  $\text{NH}_4\text{OH}$  than KOH were

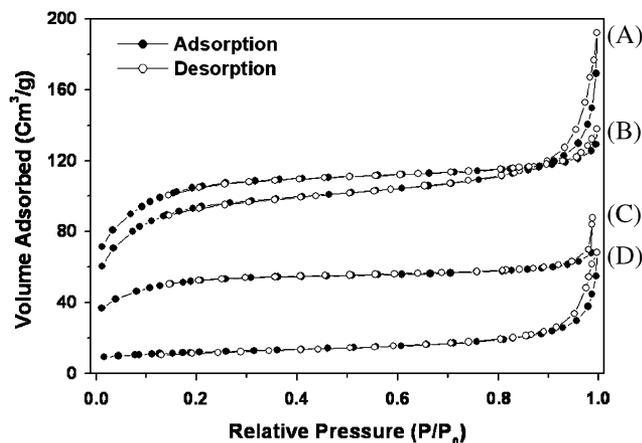


Fig. 3.  $\text{N}_2$ -gas adsorption–desorption isotherms of titania precursors (A) before aging and after aging in (B) an ammonium hydroxide, (C) lithium hydroxide, and (D) potassium hydroxide solutions for 12 h at  $60^\circ\text{C}$ .

used for aging (Figs. 3(B) and (C)). From these results, it was confirmed that the surface of the  $\text{TiO}_2$  precursor was highly densified through elimination of its pores during the aging process, where the densification effect was favored by a longer aging time or using stronger bases.

When the aged  $\text{TiO}_2$  precursor with a dense surface was used in the hydrothermal reaction with barium hydroxide,  $\text{BaTiO}_3$  nuclei formed only at the outer surface of the  $\text{TiO}_2$  and the  $\text{BaTiO}_3$  layers formed diffused into the core of the  $\text{TiO}_2$  by an *in situ* reaction mechanism. Therefore, the morphology of the original  $\text{TiO}_2$  precursor was successfully retained in the resulting  $\text{BaTiO}_3$ . In case where the  $\text{TiO}_2$  precursor was used without aging,  $\text{Ba}^{2+}$  ions could easily diffuse into the  $\text{TiO}_2$  cores through the open pores and  $\text{BaTiO}_3$  much smaller than the  $\text{TiO}_2$  precursor would form due to formation of more  $\text{BaTiO}_3$  nuclei. Then, the original  $\text{TiO}_2$  morphology is destroyed in the resulting  $\text{BaTiO}_3$  powders.

In this study, spherical and uniform  $\text{BaTiO}_3$  powders with sizes of 470, 260, and 200 nm were directly synthesized from a

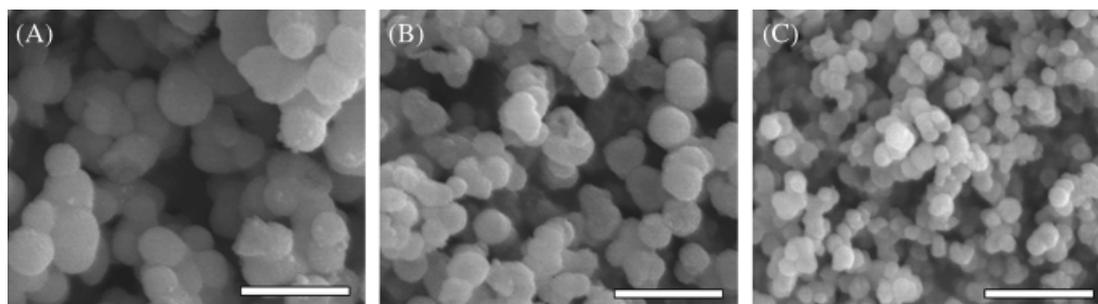


Fig. 4. Scanning electron microscopy images of barium titanate powders prepared from the size-controlled titania precursors with different diameters of (A) 420, (B) 200, and (C) 150 nm (scale bars = 1  $\mu\text{m}$ ).

low-temperature hydrothermal reaction using aged  $\text{TiO}_2$  precursors with sizes of 420, 200, and 150 nm, respectively (Fig. 4). The size and morphology of the  $\text{TiO}_2$  precursors were well conserved in the resulting  $\text{BaTiO}_3$  powders. The  $\text{BaTiO}_3$  powders had cubic structures with minor barium carbonate impurities from the XRD analysis; however, the impurities were eliminated during annealing at  $950^\circ\text{C}$ . Generally, harsh reaction conditions, such as a high temperature, high pressure, and extended reaction times, are required to synthesize spherical  $\text{BaTiO}_3$  powders larger than 150 nm from the hydrothermal reaction.<sup>5–7</sup> However, spherical  $\text{BaTiO}_3$  powders with sizes of 200–470 nm were simply prepared at  $90^\circ\text{C}$  within 24 h in this study. Also, the  $\text{BaTiO}_3$  powders had dense morphologies even after annealing at  $1000^\circ\text{C}$ , while  $\text{BaTiO}_3$  powders, prepared with a polymeric surfactant such as HPC, did not.<sup>10</sup>

*Supporting Information Available:* SEM images for spherical  $\text{TiO}_2$  precursors with various sizes and XRD patterns for  $\text{TiO}_2$  precursors and  $\text{BaTiO}_3$  powders.

#### IV. Conclusions

Spherical and monodisperse  $\text{TiO}_2$  powders with various sizes from 150 to 420 nm were aged in aqueous KOH solutions for 12 h, hydrothermally reacted with BaOH at a relatively low temperature of  $90^\circ\text{C}$ , and converted to  $\text{BaTiO}_3$  powders without morphological changes. The size and morphology of the  $\text{TiO}_2$  precursor can be retained in the resulting  $\text{BaTiO}_3$  only when the surface of the  $\text{TiO}_2$  is densified by the aging process, which was related to the fact that  $\text{BaTiO}_3$  is synthesized through an *in situ* reaction mechanism in hydrothermal synthesis. Therefore, the size of the resulting  $\text{BaTiO}_3$  powders could be controlled from 200 to 470 nm using a  $\text{TiO}_2$  precursor with various sizes in this

study. Also, the  $\text{BaTiO}_3$  powders were uniform, spherical, and dense even after annealing at  $1000^\circ\text{C}$ .

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