

## Hydrothermal synthesis of barium titanate powders from a co-precipitated precursor

Byeong Woo Lee\* and Gyoung Sik Choi

Department of Materials Engineering, Korea Maritime University, Busan 606-791, Korea

BaTiO<sub>3</sub> powders were synthesized by a hydrothermal process via a co-precipitation route. BaTi-peroxo-hydroxide co-precipitate was formed when a BaCl<sub>2</sub>, TiOCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> aqueous solution was added to an ammonium solution and the co-precipitate was used as the precursor for a hydrothermal synthesis process. It was found that phase-pure BaTiO<sub>3</sub> powders were formed under mild hydrothermal conditions; over a temperature range of 110-130°C, in the pH range of 10-12 and under a pressure below 1.8 MPa. The crystalline (perovskite) BaTiO<sub>3</sub> powders were synthesized from the amorphous precipitate almost immediately without a dissolution process. An ultrafine powder of around 15 nm size was obtained and its BET surface area was as high as 70 m<sup>2</sup>/g. Using these reactive fine powders, a fairly high density of 97% of theoretical and a high dielectric constant ( $\epsilon_r$ ) of 4000 were achieved for the ceramics sintered at a temperature as low as 1200°C.

**Key words:** hydrothermal synthesis, co-precipitation, barium titanate, perovskite, powder preparation.

### Introduction

Barium titanate (BaTiO<sub>3</sub>) has superior dielectric properties and is used extensively in electronic components, especially for multilayer ceramic capacitors (MLCC). To achieve desirable features for electronic applications, raw materials of ultra fine, high purity and homogeneous powders are needed. A wet chemical (solution) process has been extensively studied for the synthesis of various ceramic powders due to the merits of fine size, easy composition control, better homogeneity and low processing temperature in comparison to the conventional solid-state reaction process. For these reasons, various wet chemical techniques including the oxalate process [1-3], citrate modification [4, 5], sol-gel [6, 7], and hydrothermal synthesis [8-11] have been investigated to prepare BaTiO<sub>3</sub> powders for electronic applications.

To achieve complete solid solution and phase-pure BaTiO<sub>3</sub> powders, a conventional solid-state reaction process needs high temperature calcination, which results in the formation of coarse hard aggregates, and a subsequent milling process is required. Furthermore, some wet chemical processes also need a calcination step at relatively high temperatures ( $T > 500^\circ\text{C}$ ) and a subsequent milling process. For example, the oxalate process which is known as an applicable wet chemical process to produce commercial BaTiO<sub>3</sub> powders requires the time and energy-consuming milling process, because the synthesis temperature is considerably higher at around

600°C. By contrast, the hydrothermal process has been proposed to be an effective method for the preparation of commercially-viable powders at low synthesis temperatures, which eliminates the need for high temperature calcination and milling processes required in the solid-state reaction process as well as other chemical processes.

In the conventional hydrothermal process, it is generally known that crystalline BaTiO<sub>3</sub> powders can only be synthesized above pH 13 and the process requires strong basic conditions using KOH or NaOH [8-11]. It is well known that hydrothermal BaTiO<sub>3</sub> powders may be prepared by a dissolution-precipitation process, which is based on the dissolution of precursors and precipitation (nucleation-growth) of supersaturated cations under hydrothermal conditions. Since the dissolution-precipitation process is governed by the dissolution rate as well as the nucleation-growth rate, hydrothermal synthesis needs considerably higher temperature and long reaction times under strong basic conditions. Furthermore, the alkaline cations (K or Na), which are known to be difficult to remove, influence the performance of the prepared powders and resulting sintered ceramics [12], and deteriorate the electronic properties of the ceramics [13], if they remain in the prepared powders.

To overcome the problems described, a modified hydrothermal synthesis of BaTiO<sub>3</sub> powders via a co-precipitation route is adopted. The present hydrothermal process implies that the powders were prepared by a direct (in-situ) transformation mechanism from amorphous co-precipitates (BaTi-peroxo-hydroxide) to crystalline BaTiO<sub>3</sub> powders not by the ordinary dissolution-precipitation process under the highly alkaline condition made by KOH or NaOH. The present process offers the advantageous synthesis conditions of considerably

\*Corresponding author:  
Tel : +82-51-410-4356  
Fax: +82-51-404-3986  
E-mail: bwlee@hhu.ac.kr

lower reaction pH (<pH 12) using ammonium solution and lower temperatures (<130°C) with shorter reaction times (<2 h).

### Experimental Procedure

BaTiO<sub>3</sub> powders were synthesized by a modified hydrothermal process from the precursor made by co-precipitation. In co-precipitation, the BaTi-peroxo-hydroxide precursor was prepared by the following process. Concentration-determined BaCl<sub>2</sub> and TiOCl<sub>2</sub> aqueous solution were mixed and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added to form a peroxo-complex solution of BaTi. The Ba/Ti and H<sub>2</sub>O<sub>2</sub>/Ti molar ratios were fixed at 1.65 and 3, respectively. The clear mixed solution turned red on adding the hydrogen peroxide. BaTi-peroxo-hydroxide precipitate was formed when the mixed solution was added to an ammonium solution by maintaining the final pH value of 11. The co-precipitate and resulting solution were used as the precursor and reaction medium for hydrothermal synthesis.

In hydrothermal synthesis, the co-precipitate and resulting solution were charged into a teflon-lined autoclave of 300 ml capacity and heated to 90–130°C for various reaction times and pressures to a maximum of 1.8 MPa at 130°C. The reaction products were filtered and washed with distilled water to remove all the soluble components, including excess Ba<sup>2+</sup> and Cl<sup>−</sup> and then dried at 80°C for 12 h.

The crystal structure of the powders was characterized by X-ray powder diffractometry (XRD, Cu-Kα) and the morphology of powders was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The surface area of the powders was measured by the BET technique.

The hydrothermally-synthesized powders were pressed in the form of discs under a pressure of 80 MPa and sintered at 1200°C for 2 h. The dielectric constant was measured by an inductance, capacitance, and resistance (LCR) meter at 1 kHz.

### Results and Discussion

#### Preparation of co-precipitate precursor

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added to the mixed BaCl<sub>2</sub> and TiOCl<sub>2</sub> aqueous solution to improve the co-precipitation at lower pH conditions. The basic principle of the co-precipitation method is a solubility change depending on pH. In the case of TiO-hydroxide, precipitation is completed at low pH <8, but Ba-hydroxide is precipitated at high pH >13 [14]. Therefore co-precipitation takes place only above pH 13, i.e. highly basic conditions with use of NaOH or KOH. While, in the co-precipitation process, it is well known that the peroxide route via peroxo-precurors can produce homogeneous precipitates in a lower pH range from 10 to 12 [15, 16]. With the help of hydrogen peroxide, the

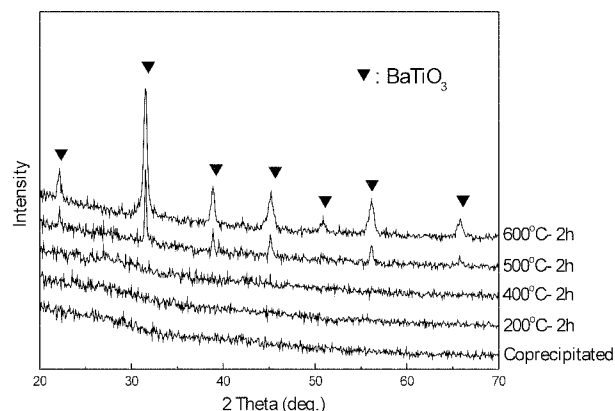
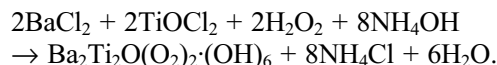


Fig. 1. XRD patterns of coprecipitates heat-treated at various temperatures.

co-precipitation method employed in the present study led to BaTi-peroxo-hydroxide precipitation below pH 12. The formation of these precipitates can be described by the following reaction:



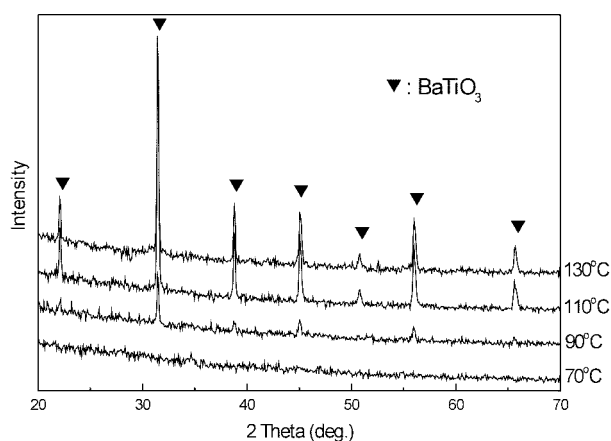
The XRD results from the co-precipitates heat-treated at various temperatures are given in Fig. 1 and show that the as-co-precipitated powder was amorphous and the desired perovskite phase was formed at temperatures above 500°C.

The amorphous powder as-prepared was used as the precursor in the present hydrothermal study.

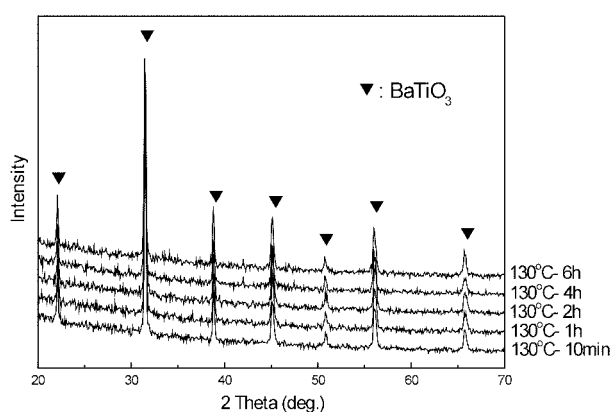
#### Hydrothermal synthesis

The hydrothermal conditions employed in the present study led to a phase-pure crystalline BaTiO<sub>3</sub> powder by direct transformation from the co-precipitated amorphous precursor. The reaction, from the Ba<sub>2</sub>Ti<sub>2</sub>O(O<sub>2</sub>)<sub>2</sub>(OH)<sub>6</sub> precursor to the BaTiO<sub>3</sub> powder, does not involve the time-consuming dissolution-precipitation process, which means the process takes place almost instantaneously when the reaction conditions reach certain synthesis conditions.

Crystalline (perovskite) BaTiO<sub>3</sub> powders were obtained after hydrothermal processing conducted at temperatures above 110°C, as shown in Fig. 2. The synthesis temperatures were considerably lower than those used in conventional hydrothermal synthesis studies conducted under strong basic conditions [8–11]. Figure 3 shows the XRD results of the products hydrothermally synthesized at 130°C for different reaction times. Regardless of the reaction times, the same diffraction patterns were obtained. Thus, it seems clear that a direct (in-situ) transformation from the amorphous precipitates occurred. The thermal decomposition of the peroxo-precurors takes place at temperature above 500°C in an air atmosphere as shown in Fig. 1, but, with these hydrothermal conditions, the decomposition happens at as low a temperature as 110°C, in an instantaneous manner.



**Fig. 2.** XRD patterns of  $\text{BaTiO}_3$  powders obtained by hydrothermal processing conducted at different temperatures for 2 h.

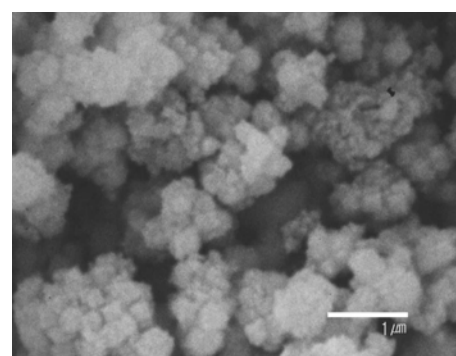


**Fig. 3.** XRD patterns of  $\text{BaTiO}_3$  powders obtained by hydrothermal processing conducted at  $130^\circ\text{C}$ , for different reaction times.

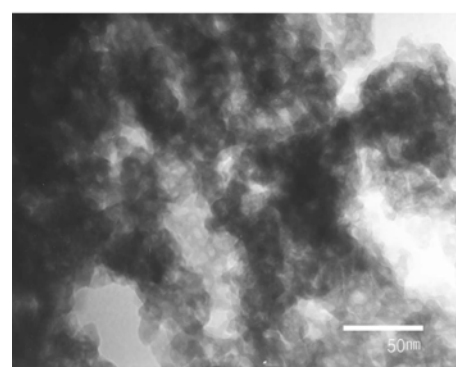
No evidence of dissolution of the precursor components was found.

Figure 4(a) shows the SEM morphology of the synthesized powders prepared at  $130^\circ\text{C}$  for 2 h. The powders obtained contain a large portion of agglomerates with a small particulate size. Since the agglomeration was sufficiently small and soft, there was no need for a milling process. During compaction, the powders are easily formed into homogeneous green compacts. The value of specific surface area of the synthesized powders determined by BET analysis was as high as  $70 \text{ m}^2/\text{g}$ , which reflected well the SEM and TEM (Fig. 4(b)) results. The particle size ( $D_{\text{BET}}$ ) calculated [17] from the value of the specific surface area was 14 nm. The TEM result shows the average particle size of the primary particles (particulates) is about 15 nm, in good agreement with the value deduced from the BET surface area. The BET surface area is considerably larger than the values of around  $20 \text{ m}^2/\text{g}$  for the conventional hydrothermal reaction products [8-11].

XRD patterns of  $\text{BaTiO}_3$  derived from hydrothermal synthesis at  $130^\circ\text{C}$  for 2 h and heat-treated at three different temperatures are shown in Fig. 5. Powders as-prepared and heat-treated at  $600^\circ\text{C}$  show cubic sym-



(a)



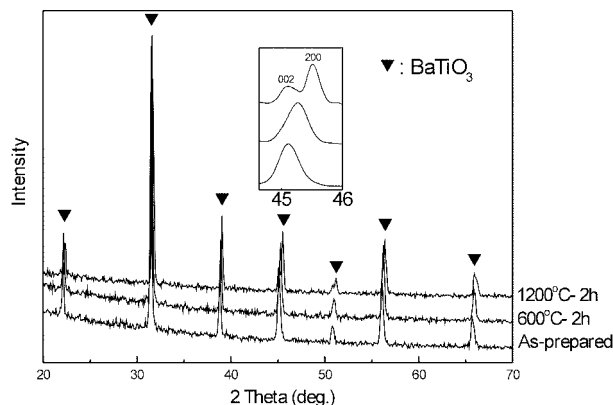
(b)

**Fig. 4.** Microstructures of powders hydrothermally prepared at  $130^\circ\text{C}$  for 2 h: (a) SEM and (b) TEM photograph.

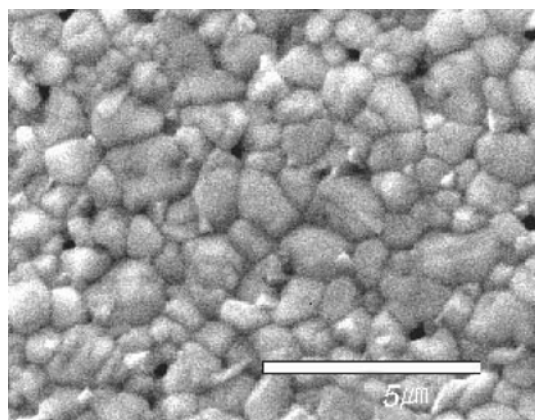
metry without splitting of the (00h)/(h00) peaks. The crystallinity measured by relative peak intensities between the as-prepared and the heat-treated at low ( $600^\circ\text{C}$ ) and high ( $1200^\circ\text{C}$ ) samples was almost same except for the improved tetragonality (c/a ratio) in the powders obtained at the high temperature. A particle size dependence of crystal structures in  $\text{BaTiO}_3$  powders has been reported [18]. Between 1.5 and  $0.5 \mu\text{m}$ , the tetragonality decreases from 1.01 to 1.005 with decreasing particle size. Below  $0.5 \mu\text{m}$ , the powders exhibit a cubic phase at room temperature instead of one that is tetragonal. This is also in good agreement with the results in this study. By contrast, a different explanation for the lack of tetragonality has been reported [10] in that the cubic structure shown in hydrothermally-prepared powders can be explained by lattice defects (distortions) due to the  $\text{OH}^-$  incorporated in the perovskite lattice. In the present study, however, the cubic phase shown in the  $\text{OH}^-$ -free powders heat treated at  $600^\circ\text{C}$  (Fig. 5) shows that the results agree with the crystallite size effect rather than the lattice defect model.

### Sintered ceramics

It has been proposed that, to obtain a high density with a small grain size, the sintering temperature should be reduced below  $1230^\circ\text{C}$ , which also leads to a homogeneous grain size without the abnormal grain growth normally shown in ceramics sintered at higher temperatures [5]. An optimum grain size, which was proposed



**Fig. 5.** XRD patterns of BaTiO<sub>3</sub> powders obtained by hydrothermal synthesis at 130°C for 2 h, and heat-treated at different temperatures for 2 h.



**Fig. 6.** Microstructures of BaTiO<sub>3</sub> ceramic sintered at 1200°C for 2 h from the powder hydrothermally prepared at 130°C for 2 h.

to achieve high dielectric constant and volume efficiency, was 0.5 to 2  $\mu\text{m}$ . The sinterability of synthesized powders was in proportion with their specific surface areas. The higher surface area leads to a higher sintered density. With use of the reactive fine powders in this study, a fairly high density of 97% of theoretical was obtained for the ceramics sintered at a temperature as low as 1200°C. A homogeneous microstructure and grain sizes of the optimum values in the range of 1 to 2  $\mu\text{m}$  were obtained (Fig. 6). The dielectric constant ( $\epsilon_r$ ) measured in the ceramic was as high as 4000 as expected and the value was considerably higher compared to that,  $\sim 1000$ , of conventional ceramics sintered at higher temperatures.

## Conclusions

It has been shown that the BaTiO<sub>3</sub> powders can be prepared by a modified hydrothermal synthesis via a co-precipitation route. A co-precipitate, BaTi-peroxo-hydroxide, was used as a precursor for the hydrothermal synthesis. The modified hydrothermal approach adopted in this study was found to be quite suitable for the

synthesis of BaTiO<sub>3</sub> powder and had been shown to have several advantages, such as low reaction pH and low temperatures with short reaction times, over the conventional hydrothermal process. It has been proposed that the BaTiO<sub>3</sub> powders were synthesized by a direct (in-situ) transformation mechanism from amorphous co-precipitates to crystalline powders and not by the ordinary dissolution and precipitation route.

The powders prepared were constituted by nano-sized crystallites with a cubic structure. A BET surface area as high as 70 m<sup>2</sup>/g was obtained. The resulting powders offered low ceramic processing temperatures and high-density ceramic products. A very high dielectric constant was also achieved in the sintered ceramic.

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