

Synthesis of Nano-sized Barium Titanate Powder by Solid-state Reaction between Barium Carbonate and Titania

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[Manuscript received June 14, 2006, in revised form April 10, 2007]

Size control of BaTiO₃ in solid-state reaction between BaCO₃ and TiO₂ was demonstrated by varying the size of TiO₂ and milling conditions of BaCO₃. The smaller TiO₂ particles had higher surface area, resulting in faster initial reaction. The mechanically milled BaCO₃ particles accelerated the diffusion process and decreased the calcinations temperature. It can be deduced from the results that the size control is possible and nano-sized BaTiO₃ particles with about 60 nm can be synthesized by using the conventional solid-state reaction between BaCO₃ and TiO₂.

KEY WORDS: Barium titanate; Mechanical milling; Solid-state reaction; Nano particles

1. Introduction

Oxide nanoparticles and nanostructures are good candidate for a variety of applications, such as high capacitance capacitors, thermistors, gas sensors and positive temperature coefficient resistors (PTCR)^[1,2]. Alkaline earth metal titanates are becoming increasingly important in the ceramic and electronic industry. Nano-sized barium titanate has been attracting interest because of their application in technical and fundamental research. It is therefore important to synthesize nano-sized BaTiO₃ powder with narrow particle size distribution. In general, BaTiO₃ nanoparticles have been synthesized by wet chemical processes^[3,4]. However, high cost and difficulty in process control in these routes forced to find other ways for the synthesis of BaTiO₃ nano particles.

BaTiO₃ powders were conventionally synthesized by solid-state reaction between BaCO₃ and TiO₂ above 1100°C^[5]. The overall reaction for the BaTiO₃ formation while heating equi-molar BaCO₂ and TiO₂ mixture is



The high calcination temperature leads to many disadvantages, such as large particle size and wide size distribution^[6]. Balaz *et al.*^[7] reported that the apparent activation energy of BaTiO₃ formation from BaCO₃ and TiO₂ decreases by pre-milling the mixture before calcinations, suggesting that calcination temperature can be decreased by using mechanically activated powders. Recently Brzozowski *et al.*^[8] suggested that the use of mechanochemical activation favors the decomposition of BaCO₃ at lower temperatures and improves the barium ion diffusion through the BaTiO₃ layer. Kong *et al.*^[9] also reported the single phase BaTiO₃ using milled powders, at temperatures as low as 800°C. Xue *et al.*^[10] reported a breakthrough by performing a room temperature BaTiO₃ synthesis by milling a mixture of barium and titanium oxides under nitrogen^[10]. How-

ever, this room temperature synthesis starting from the oxides has to overcome the problem of hydration/carbonation, barium oxide by air and moisture^[11].

In this study, size control and synthesis of nano-sized barium titanate was demonstrated by using mechanically activated BaCO₃ and nano-sized TiO₂.

2. Experimental

Barium titanate was synthesized from commercially available BaCO₃ (99%, purity) and TiO₂ (KA100, Hankook Titanium Industry Co. Ltd., Korea, *d*₅₀=200 nm). For comparison, smaller TiO₂ (P25, Degussa Co. Germany, *d*₅₀=30 nm) was used and the milling of BaCO₃ was done in pulverizer (Fritish, Oberstein, Germany) for 50 h, prior of mixing with titania.

The equi-molar, oven-dried BaCO₃ and TiO₂ powders were mixed in the centrifugal mill for 15 h in ethanol with 10 mm ZrO₂ milling media. The powder mixture was dried and kept at 60°C. The soft agglomeration was broken and 5 g batches were calcined in a tube furnace using an alumina boat. The calcination temperature was 600, 800 and 900°C, calcination time was fixed for 2 h and heating and cooling rates were 10°C/min. All the experiments were done in air. A scanning electron microscope (FESEM, XL30 SFEG, Philips, Netherlands) and a transmission electron microscope (TEM, JEM-3010, Jeol, Tokyo, Japan) were used for the characterization of morphology and size analysis, X-ray diffractometer (D/max-IIIC, Rigaku, Tokyo, Japan) for phase analysis and TG/DTA (TG92, SETARAM, Caluire, France) for weight loss. At least 100 particles were averaged for the particle size measurement by SEM.

3. Results and Discussion

The SEM micrographs in Fig.1 (supporting figure) show some of the intermediate steps during the calcination process. Rod like BaCO₃ particles are clearly visible even after 800°C and their irregular shape sug-

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Table 1 Starting mixtures and major phases at different calcination temperatures

Sample ID	Starting materials		Phase (temperature, time)		
	TiO ₂	BaCO ₃	600°C, 2 h	800°C, 2 h	900°C, 2 h
UM-200	200 nm	As received	BaCO ₃ (v) ¹⁾	BaCO ₃ (v)	BaCO ₃ (w) ³⁾
M-200	200 nm	50 h milled	BaCO ₃ (s) ²⁾	BaCO ₃ (w)	BaTi ₃
M-30	30 nm	50 h milled	BaCO ₃ (s)	BaTi ₃	BaTi ₃

Notes: 1) v—very strong intensity, 2) s—strong intensity, 3) w—weak intensity

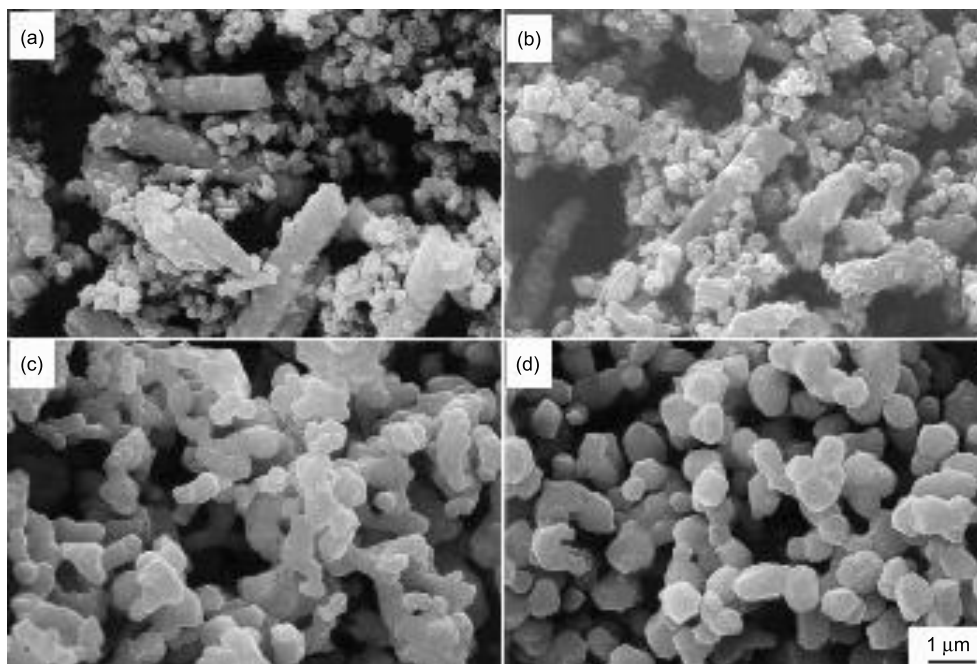


Fig.1 SEM micrographs showing intermediate stages of the reaction between as received BaCO₃ and TiO₂: (a) starting TiO₂ and BaCO₃ equi-molar mixture just after milling, (b) powder calcined at 800°C. Consumption of rod like BaCO₃ and increase in smaller TiO₂ particle size is clearly visible, (c) powder calcined at 900°C and difficult to distinguish between BaCO₃, TiO₂ and BaTiO₃ particles, (d) single phase BaTiO₃ particles calcined at 1300°C

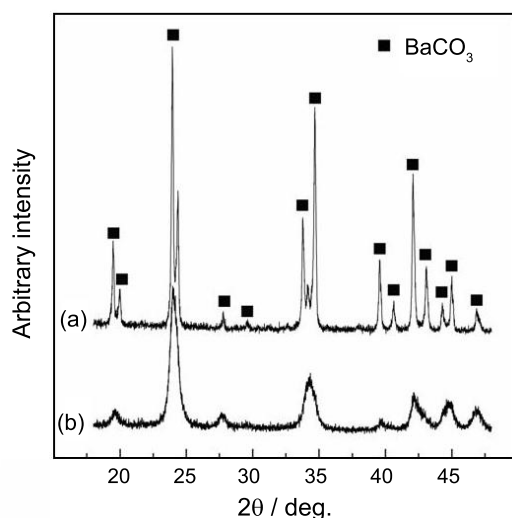


Fig.2 XRD results of (a) as-received BaCO₃ and (b) 50 h milled BaCO₃. The broadening of XRD peaks in the milled powder is an indication of lattice distortion. The inset shows SEM micrographs of unmilled and 50 h milled BaCO₃

temperature of 1300°C clearly shows that the shape is more close to the starting TiO₂ particle, with an obvious increase in the particle size^[12,13]. The results suggested that controlling the size and milling condition of the starting powders could control the size of the final BaTiO₃. Therefore two different parameters were considered to control the particle size. One was the milling of BaCO₃ and the other was particle size of TiO₂. Table 1 shows the summary of the starting materials and the major phases formed after calcination at different temperatures.

Mechanical milling of BaCO₃ powder changes the morphology from rod-like to more or less round without having a dominant effect on the particle size, ensuring a well-mixed powder mixture (inset in Fig.2). XRD results of as received and 50 h milled BaCO₃ are shown in Fig.2. The broadening and decreasing in intensity of XRD peaks in the milled powder is an indication of lattice distortion^[14].

Figure 3 shows the XRD results of three different powder mixtures (Table 1), calcined at 600, 800 and 900°C. In UM-200 (as received BaCO₃ and 200 nm TiO₂), after calcination of powder mixtures at 600°C, the XRD only shows the BaCO₃ and TiO₂ peaks with traces of BaTiO₃. With the increase in calcination temperature, the amount of BaTiO₃ phase increases. But even after calcining at 900°C, significant amount

gested diffusion of barium source in the TiO₂ particle. The final shape of the BT particles at calcination

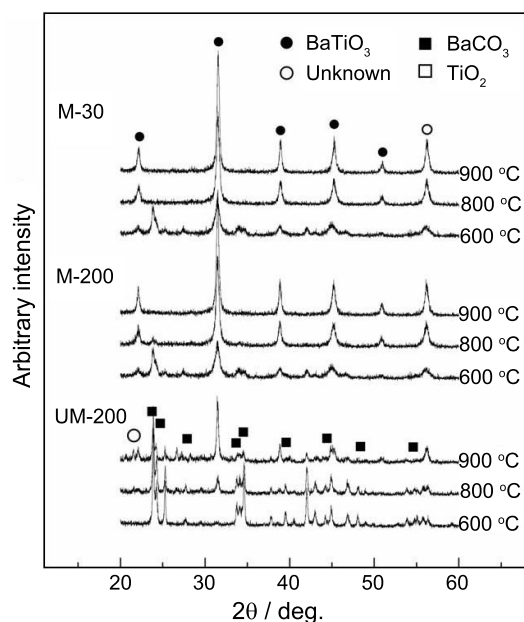


Fig.3 XRD results of powder mixtures calcined at different temperatures for 2 h. The XRD of M30 at 800°C shows single phase BaTiO₃

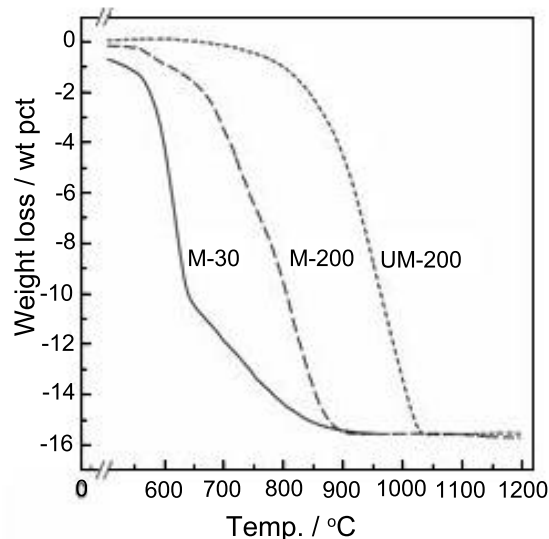


Fig.4 TGA curves of UM-200, M-200 and M-30. Weight loss is an indication of consumption of BaCO₃. Milled BaCO₃ clearly indicate faster reaction kinetics

of BaCO₃ is present suggesting that higher temperatures are needed for completion of the reaction. The small peaks may be due to the orthotitanate phases formed during the process.

In M200 (50 h milled BaCO₃ and 200 nm TiO₂), a significant amount of BaTiO₃ is formed even at 600°C. Calcination at 800°C results in only a small amount of BaCO₃ peak, which disappear at 900°C, clearly indicating single phase BaTiO₃. The sample M-30 (50 h milled BaCO₃ and 30 nm TiO₂) shows exciting results and BaTiO₃ exists as a major phase even at 600°C. At 800°C the XRD shows single phase BaTiO₃. The low temperature synthesis is at-

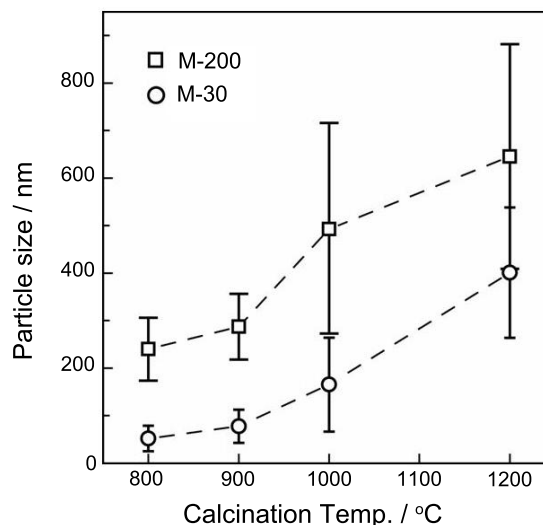


Fig.5 Particle size analysis of M-200 and M-30. BaTiO₃ formed by reacting smaller TiO₂ shows smaller size

tributed to the prior milling of the starting powders and other researchers had also shown the formation of BaTiO₃ at this low temperature. However, in the previously reported results, BaCO₃ and TiO₂ were mixed together instead of using milled BaCO₃ and then mixing^[15]. The unwanted orthotitanates in the milled samples were either absent or present in the trace amounts. The BaCO₃ decomposition is favored by the presence of more reactive TiO₂. An effective way of limiting the existence of secondary phases is to modify the reactivity of the raw materials. In this work, such goal was achieved by increasing the reactivity of BaCO₃ by milling^[16].

The weight loss during calcinations is due to the CO₂ gas formed according to Eq.(1). The weight loss curves in Fig.4 clearly indicate the decrease in reaction temperature due to the mechanical activation of BaCO₃ and faster reaction kinetics in case of smaller TiO₂ particles. In sample M-200, the slope is steeper than that of UM-200 and the reaction was completed at 930°C. Brzozowski *et al.*^[8] and Gomez-Yanez group^[14] also showed similar results, suggesting that this is due to the milling of the starting powders.

The weight change curve for M-30 indicates that the initial reaction is very fast in the beginning. It is believed that the smaller TiO₂ particles increase the contact area between TiO₂ and BaCO₃ resulting in faster initial reaction. A layer of primary BaTiO₃ is formed on the TiO₂ particle. The reaction then becomes diffusion-controlled and the outer BaTiO₃ layer on TiO₂ particle makes further diffusion increasingly difficult. Thus the curve showed slower rate in the intermediate stage^[8].

The particle size analysis of M200 and M-30 with calcination temperature is presented in Fig.5. Both curves show an increase in the particle size with temperature. This increase in particle size may be attributed to the higher diffusion rate at higher temperatures, giving rise to strong particle growth and particle aggregation^[16,17]. The general trend for both of the curves in Fig.5 is also similar. However, the BaTiO₃ formed by reacting smaller TiO₂ shows

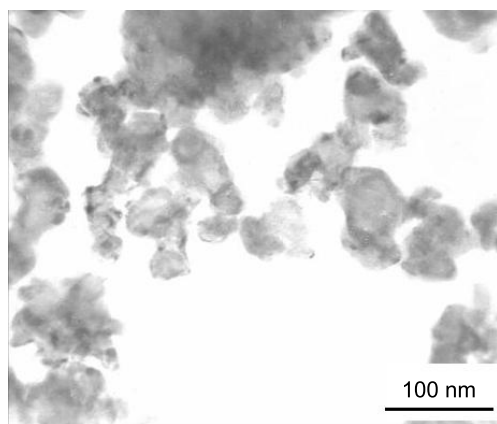


Fig.6 TEM micrograph of BaTiO₃ (M-30) calcined at 800°C for 2 h. The results suggest that the primary particle size is less than 60 nm

smaller size. It can be deduced from the experimental results that the nano-sized BaTiO₃ can be synthesized by the conventional solid-state reaction between BaCO₃ and TiO₂.

Figure 6 shows the TEM micrograph of sample M-30 calcined at 800°C for 2 h without post milling treatment. The micrograph also supported and confirmed the evidence that the primary BaTiO₃ particles were below 60 nm in size. It may be due to the fact that after milling, BaCO₃ particles become mechanically activated; sticky and round shape resulting in a decrease in calcination temperature and well mixed TiO₂ and BaCO₃ mixture. Therefore, by carefully controlling the milling and calcination conditions, the diffusion process and thus the particle size can be controlled. The unwanted secondary agglomeration is also present along with the primary individual particles. However, this unwanted agglomeration can be suppressed by using rotary furnace for the calcination or the post milling of the calcined powder.

4. Conclusions

(1) Smaller TiO₂ particles resulted in smaller BaTiO₃ powder and enhanced the initial reaction rate by increasing the contact area between BaCO₃ and TiO₂. Mechanical milling of BaCO₃ results in spherical particles ensuring better mixing and decreases the reaction temperature which suppresses BaTiO₃ particle growth and particle aggregation.

(2) The single phase nano-sized BaTiO₃ was observed at lower temperature than the conventional processing.

(3) It can be deduced from the results that size control is possible and nano-sized BaTiO₃ particles (about 60 nm) can be synthesized by the conventional solid-state reaction between BaCO₃ and TiO₂.

Acknowledgement

This work was supported by Hanchang Chemical Co. and partially by the Korea Ministry of Education through Brain Korea 21 Program.

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