Low temperature synthesis of nano-sized BaTiO₃ powders by the microwave-assisted process

Hiroaki KATSUKI[†] and Sridhar KOMARNENI*

Saga Ceramics Research Laboratory, 3037-7 Arita-machi, Saga 844-0022

*Materials Research Institute and Department of Crop and Soil Sciences, 205 Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, U.S.A.

Nano-sized BaTiO₃ particles were prepared at 90°C using TiO₂ and Ba(OH)₂ as precursors by microwave-assisted (M-A) heating and conventional-heating (C-H) processes. Compared to the formation of BaTiO₃ particles using the C-H process, the M-A process led to increased rate of formation by about 6 times. BaTiO₃ particles of 29 nm in average particle size were obtained after treatment for 15 min by using microwaves during the heating process at 90°C. The use of microwaves led to the formation of smaller sized particles with narrower particle size distribution compared to that of C-H process.

©2011 The Ceramic Society of Japan. All rights reserved.

Key-words : Barium titanate, Microwave-assisted heating, Nano particle, Kinetics

[Received February 9, 2011; Accepted April 7, 2011]

1. Introduction

BaTiO₃ (BT) material is widely used in multi-layer ceramic capacitors (MLCCs), piezoelectric and ferroelectric devices, positive temperature coefficient (PTC) thermistors, field-effect transistors, etc. BaTiO₃ powders should have small particle size with narrow size distribution and high purity for making compact MLCCs.^{1,2)} BaTiO₃ powder has been prepared by the traditional solid-state process, sol-gel process and many other techniques including the hydrothermal process.³⁾⁻⁵⁾

Microwave-assisted hydrothermal/solvothermal process has been developed for the synthesis of nano-sized oxide and metal materials and it has many advantages such as (a) rapid heating to temperature of reaction, (b) increased reaction kinetics, and (c) forming nano-sized powders etc.⁶⁾⁻¹³⁾

We have previously demonstrated the synthesis of nano-sized cubic BaTiO₃ powders with narrow size distribution from TiO₂ and Ba(OH)₂ at 150–200°C for 10 min using microwave-hydrothermal (M-H) process.^{14),15)} However, it is necessary to prepare BaTiO₃ powders at ambient pressure (ca. below 100°C) from the standpoint of continuous production of BaTiO₃ powders using the microwave-assisted (M-A) process. Thus, the objective of this study was to investigate the synthesis and some properties of nano-sized BaTiO₃ powders at 90°C by the M-A process. Furthermore, the formation kinetics for BT powder by M-A process was compared with that for BT powder by the conventional-heating (C-H) process.

2. Experimental

A microwave digestion system (multi-mode, model MARS 5, CEM Corp., Matthews, NC) was used to conduct the M-A syntheses. BT powders were prepared from 0.6361 g (7.9×10^{-3} mol) of TiO₂ (Anatase type, ST01, Ishihara Sangyo Ltd., Japan) and 1.3695 g (7.99×10^{-3} mol) of Ba(OH)₂ (Special grade, Wako Pure Chemical Ltd., Japan: Average particle size = 7 nm) and

15 ml of distilled water. Molar ratio of Ba/Ti was kept at 1 for all syntheses. The precursor mixtures were treated at 90°C for 1 to 15 min in a Teflon^{TM} vessel without stirring. The system operated at a frequency of 2.45 GHz and could operate at 0–100% full power with 600 W. The temperature of the system was monitored using an in-vessel temperature sensor (Model EST-300, CEM Corp., Matthews, NC). The C-H reactions were carried out in polyethylene vessels of 50 ml capacity at 90°C for 15 to 60 min without stirring in a drying oven that was preheated to 90°C. After the heat treatment of reactants, the solid samples were separated from solutions by centrifugation and were thoroughly washed with distilled water, and then dried at 70°C. Conversion ratio (IBaTiO₃/ITiO₂ + IBaTiO₃) of TiO₂ to BaTiO₃ was calculated from the ratio of the X-ray intensities of the TiO₂ peak ($hkl = 101$, $2\theta = 25.28^\circ$) and the BaTiO₃ peak ($hkl = 110$, $2\theta = 31.36^\circ$) measured by the XRD (model X'Pert-MRD, PANalytical Co., Japan) using Cu K α radiation. The morphology and particle size were determined by a transmission electron microscope (TEM; model 2010, JEOL, Tokyo, Japan). The size of the BaTiO₃ crystallites was calculated by means of the Debye-Scherrer formula from (100) and (110) XRD reflections.

3. Results and discussion

Figures 1 and 2 show the XRD patterns of powders prepared by C-H and M-A processes at 90°C. XRD results at 90°C by both C-H and M-A processes showed the crystallization of cubic BaTiO₃ with a trace amount of BaCO₃. Insoluble BaCO₃ impurity resulted by the reaction of Ba(OH)₂ with the CO₂ dissolved in solution. BaCO₃, however, could be removed by washing with dilute acetic acid if needed. No tetragonal phase of BaTiO₃ was detected for all samples. Table 1 shows the conversion ratio of TiO₂ to cubic BaTiO₃ powders. The conversion of TiO₂ to BaTiO₃ reached 100% after 60 min via the C-H process and after 10 min via the M-A process, respectively. Based on the reaction time that was necessary to attain 100% conversion of precursors to BaTiO₃, the use of microwaves during the synthesis of BaTiO₃ was found to increase the reaction kinetics by approximately 6 times.

[†] Corresponding author: H. Katsuki; E-mail: katsuki-hiroaki@pref.saga.lg.jp

Fig. 1. XRD patterns of cubic BaTiO₃ powders prepared from Ba(OH)₂ and TiO₂ by a conventional heating process at 90°C. (a) Original TiO₂ powder, (b) 20, (c) 30, (d) 60, and (e) 120 min ●: c-BaTiO₃, ■: BaCO₃, ▲: TiO₂.

Fig. 2. XRD patterns of cubic BaTiO₃ powders prepared from Ba(OH)₂ and TiO₂ by a microwave-assisted process at 90°C. (a) 1, (b) 2, (c) 5, and (d) 15 min ●: c-BaTiO₃, ■: BaCO₃, ▲: TiO₂.

Table 1. Conversion rate of TiO₂ to cubic BaTiO₃ by conventional heating and microwave-assisted processes at 90°C

Reaction time (min)	Conversion rate by C-H process (%)	Conversion rate by M-A process (%)
1	0	73.7
2	0	85.7
5	0	95.8
10	1.7	100
15	8.2	100
20	51.4	
30	95.1	
60	100	

Figures 3 and 4 show the morphology and particle size distribution of the resulting cubic BT powders prepared at 90°C for 15 min via the M-A process and for 60 min via the C-H process determined by TEM. The BT particles prepared by M-A

Fig. 3. Morphologies of c-BaTiO₃ powders prepared by a microwave-assisted reaction at 90°C for 15 min (a), and by a conventional heating reaction at 90°C for 1 h (b).

Fig. 4. Particle size distribution as determined by TEM analysis of cubic BaTiO₃ powders synthesized by microwave-assisted process at 90°C for 15 min (a) and by conventional heating process at 90°C for 60 min (b).

process show well-defined edges (somewhat faceted) compared to the particles prepared by C-H process, which have diffuse edges surrounded by amorphous material (Fig. 3). Particle size distribution of BaTiO₃ by the M-A process was in the range of 20 to 72 nm, and the average size was 29 nm. Particle size distribution of BaTiO₃ via the C-H process was in the range of 42 to 125 nm, and the average size was 69 nm. Particle size distributions were determined from TEM images by counting 100 particles prepared from both C-H and M-A reactions. The particle size distribution and the average particle size were calculated using a Gaussian distribution curve of the particles. Electron diffraction study showed that the nanoparticles obtained

via the M-A process were single crystals while the larger particles resulting from the C-H process were composed of aggregated small single crystals. Average crystallite size of BT particles by the XRD were 21 ± 3 nm by the M-A process and 34 ± 4 nm by the C-H process, respectively.

The M-A process led to better dispersed smaller crystals and a narrower particle size distribution [Figs. 3(a) and 4(a)] compared to crystals by C-H process [Figs. 3(b) and 4(b)]. The increased kinetics and narrower size distribution for the BT particles by the M-A process could be explained by an instantaneous localized superheating¹⁶⁾ in the alkaline solution by using microwaves for heating. The time periods needed to heat the solutions from 18 to 90°C were 15 s and 21 min for the M-A and C-H processes, respectively. Water has a large loss tangent ($\epsilon'' = \tan \delta \times \epsilon' = 0.157 \times 76.7 = 12.04$ at 25°C¹⁶⁾), and hence it is possible to use this property to heat the solution rapidly by microwaves and thereby to obtain the product in a faster time. It is hypothesized that the increased mobility of the chemical species led to effective coupling with the microwaves for a rapid transfer of energy to the bulk of the sample, which ensures rapid reaction. Microwaves facilitated the dissolution of TiO₂ particles by Ba(OH)₂ followed by very rapid crystallization of BaTiO₃. The microwave-assisted dissolution led to smaller size particles with a narrower particle size distribution probably due to uniform nucleation from the supersaturated solution. The present results are supported by those reported previously by Takizawa et al.,¹³⁾ who reported the formation of fine single crystal-like cubic BaTiO₃ powders from TiO₂ and Ba(OH)₂·8H₂O by a microwave-assisted liquid process at ambient pressure using a reflux apparatus. The effect of microwave irradiation on the formation of fine BaTiO₃ powders was thoroughly discussed by Takizawa et al.,¹³⁾ although temperature was not specified. The BaTiO₃ powders synthesized by microwave-assisted process were finer with an average particle size of 100 nm after 240 min, and more uniform compared to the powders synthesized by a conventional process¹³⁾ as was found in the work reported here. Takizawa et al.,¹³⁾ used a commercial p-25 TiO₂ powder (Degussa, average particle size: 21 nm) as a raw material. However, we used smaller TiO₂ powder (average particle size: 7 nm), which led to smaller BT particles in this study than those reported by Takizawa et al.¹³⁾ By comparing the results of these two studies, it appears that a smaller TiO₂ powder as raw material is expected to form finer cubic BaTiO₃ powder. Some properties evaluation (e.g., Ba/Ti molar ratios and crystal water) of nano-sized BaTiO₃ particles prepared in this study is currently in progress.

4. Conclusion

In this study, the synthesis of nano-sized cubic BaTiO₃ powder was studied using a commercial TiO₂ and Ba(OH)₂ as precursors by microwave-assisted (M-A) heating and conventional-heating (C-H) processes. Using microwaves, the conversion percent of TiO₂ to cubic BaTiO₃ reached around 100% in about 10 min. Compared to the formation of BaTiO₃ particles using the C-H process, the M-A process led to increased rate of formation by about 6 times. An average BaTiO₃ particle size of about 29 nm was obtained after treatment for 15 min by applying microwaves during the heating process.

References

- 1) H. Kishi, Y. Mizuno and H. Chozano, *Jpn. J. Appl. Phys.*, **42**, 1–15 (2003).
- 2) A. Arora, *Adv. Eng. Mater.*, **6**, 244–247 (2004).
- 3) P. P. Pule and S. H. Risbud, *J. Mater. Sci.*, **25**, 1169–1183 (1990).
- 4) J. O. Eckert, Jr., C. C. Hung-Houston, B. L. Gersten, M. M. Lencka and R. E. Riman, *J. Am. Ceram. Soc.*, **90**, 311–314 (1996).
- 5) B. Li, X. Wang and L. Li, *Mater. Chem. Phys.*, **78**, 292–298 (2002).
- 6) H. Katsuki, S. Furuta, T. Watari and S. Komarneni, *Micro-porous Mesoporous Mater.*, **86**, 145–151 (2005).
- 7) H. Katsuki, A. Shiraishi, S. Komarneni, W. J. Moon, S. Tho and K. Kaneko, *J. Ceram. Soc. Japan*, **112**, 384–387 (2004).
- 8) M. Tsuji, M. Kubokawa, R. Yano, N. Miyamae, T. Tsuji, P. Y. Hyung, S. H. Yoon and I. Mochida, *Langmuir*, **23**, 387–390 (2007).
- 9) M. Tsuji, K. Matsumoto, N. Miyake, T. Tsuji and X. Zhang, *Cryst. Growth Des.*, **7**, 311–320 (2007).
- 10) W. Sun, J. Li, W. Liu and C. Li, *J. Am. Ceram. Soc.*, **89**, 118–123 (2006).
- 11) X. Zhu, J. Wang, Z. Zhang, J. Zhu, S. Zhou, Z. Liu and N. Ming, *J. Am. Ceram. Soc.*, **91**, 2683–2689 (2008).
- 12) S. Komarneni, Y. D. Noh, J. Y. Kim, S. H. Kim and H. Katsuki, *Z. Naturforsch.*, **65b**, 1033–1037 (2010).
- 13) R. Motoba, Y. Hayashi and H. Takizawa, *J. Ceram. Soc. Japan*, **117**, 388–391 (2009).
- 14) S. Komarneni and H. Katsuki, *Ceram. Int.*, **36**, 1165–1169 (2010).
- 15) S. Komarneni, R. Roy and Q. H. Li, *Mater. Res. Bull.*, **27**, 1393–1405 (1992).
- 16) A. Zlotorzynski, *Crit. Rev. Anal. Chem.*, **25**, 43–76 (1995).