



Hydrothermal Preparation and Characterization of Ultra-Fine BaTiO₃ Powders from Amorphous Peroxo-Hydroxide Precursor

BYEONG WOO LEE¹ & SEUNG-BEOM CHO²

¹Department of Materials Engineering, Korea Maritime University, Busan 606-791, Korea

²Corporate R&D, LG Chem. Ltd, Daejeon 305-380, Korea

Submitted February 13, 2003; Revised November 8, 2003; Accepted December 16, 2003

Abstract. Ultra-fine BaTiO₃ powders were hydrothermally prepared by using Ba·Ti-peroxo-hydroxide precursor. Amorphous Ba·Ti-peroxo-hydroxide precursor were prepared by coprecipitation of Ba(NO₃)₂ and TiCl₄ aqueous solution adding in NH₄OH aqueous solution. The phase-pure BaTiO₃ powders with a cubic perovskite structure were synthesized at temperature as low as 110°C and in the pH range of 10–12. This processing method provides a simple low temperature route for producing BaTiO₃ nanoparticles. Under a TEM image and a SAD pattern analysis, it is evident that BaTiO₃ powders had spherical shape and single crystal nature. The BaTiO₃ ceramic sintered at 1200°C for 1 h had 97% of theoretical density and a relatively high dielectric constant ($\epsilon_r = 3500$).

Keywords: barium titanate, BaTiO₃, hydrothermal synthesis, coprecipitation, peroxo-hydroxide

1. Introduction

Due to the excellent and tunable dielectric properties, barium titanate (BaTiO₃), especially in the form of multilayer ceramic capacitors (MLCC), has received much attention and widely utilized in electronic devices. Advanced miniaturization of electronic devices implies the reduced MLCC dimension with high capacitance, which is obtained by the decrease of the dielectric layer thickness accompanied with the increase of the number of the layers and by the increase of relative dielectric constant (ϵ_r) with use of ceramics having optimal grain sizes below 5 μm . Sintered barium titanate having near the theoretical density and fine grain sizes of 1–5 μm shows superior dielectric properties with the high ϵ_r over 3500 [1, 2]. Thus, the manufacture of the fine-grained ceramics needs the use of the fine reactive powders (<0.1 μm). Decreasing the dielectric layer thickness in the MLCC preferably down to several microns also needs an ultra-fine and uniform particle size of raw materials. Conventionally, barium titanate powders have been prepared by the solid-state reaction of mechanically mixed BaCO₃ and TiO₂ at high calcination temperatures above 900°C. This process causes

a lack of compositional uniformity and produces large and hard agglomerated powders. Therefore, for the synthesis of high quality powders of ultra-fine, uniform and homogeneous toward the MLCC having higher level of volumetric efficiency, many wet chemical methods for the synthesis of BaTiO₃ powders have been developed. These methods include the thermal decomposition of double salts, such as oxalates [2, 3], citrates [4], or catecholates [5], sol-gel [6] and hydrothermal [7–10] processes. To achieve complete solid solution, most of wet chemical methods need the calcination at relatively high temperatures (>500°C) and a consecutive milling process as same as the solid-state reaction process. Among the various chemical processes, therefore, the hydrothermal process has been proposed to be an effective method for the industrial requirements of BaTiO₃ powders due to its attractive processing feature of low temperature processing without calcination and milling step.

Although the hydrothermal process offers a promising approach to prepare ultra-fine, crystalline ceramics by using an aqueous medium, the process has been conducted under strong alkaline conditions (>pH 13) with use of NaOH and/or KOH [7–10], thus leaving the

contaminants, Na⁺ and K⁺ cations [11]. In the present study, to prepare reactive BaTiO₃ powders under mild pH condition (≤ 12) by ammonia solution, a coprecipitated peroxy-hydroxide precursor was used as a starting material. Comparing to the conventional barium-titanium precursor for the BaTiO₃ powder preparation, the coprecipitated peroxy-hydroxide precursor offers fast and low-temperature synthesis conditions under considerably low alkaline condition.

2. Experimental Procedure

A chemically modified, amorphous peroxy-hydroxide precursor via coprecipitation was used to synthesize BaTiO₃ powders in hydrothermal conditions. Ba(NO₃)₂ and TiCl₄ were used as raw materials for the coprecipitation. A peroxy-complex solution of Ba·Ti was prepared by adding hydrogen peroxide (H₂O₂) in Ba(NO₃)₂ and TiCl₄ mixed aqueous solution. The molar ratios of Ba/Ti and H₂O₂/Ti were fixed at 2 and 3, respectively. Amorphous Ba·Ti-peroxy-hydroxide precipitate was formed by adding the peroxy-complex solution of Ba·Ti in an ammonium solution. The final pH of the solution was maintained between 10 and 12. The coprecipitated precursor was used as the starting material for the hydrothermal synthesis.

In hydrothermal synthesis, the suspension containing the coprecipitated precursors were charged into teflon-lined autoclave of 300 ml capacity with a fill factor of 80 vol% and heated to 90–150°C with autogeneous pressure for various reaction times. Maximum autogeneous pressure was 4.3 MPa at 150°C. The reaction products were filtered and washed with distilled water to remove soluble components, including excess Ba²⁺ and Cl⁻ and then dried at 90°C for 12 h. The hydrothermally synthesized powders were pressed in the form of discs under a pressure of 80 MPa and sintered at 1200°C for 1 h.

Thermo-gravimetric analysis (TGA) was carried out for the prepared powders. The crystalline structure and phase of the prepared and heat-treated powders were identified by X-ray powder diffractometry (XRD, Cu-K α) and the morphologies of powders and sintered ceramics were examined by using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The surface area of the powders was measured by the BET technique. The dielectric properties were measured at 1 kHz with a LCR meter.

3. Results and Discussion

3.1. Coprecipitation of Peroxy-Hydroxide Precursor

In an aqueous solution, the basic principle of coprecipitation is a solubility change of metal-hydroxides depending on pH. In the case of barium titanate, it is well known that coprecipitation takes place only at the pH value above 13. However, the strong basic condition by use of NaOH and/or KOH accompanies the undesirable metal impurities. In comparison, with the help of hydrogen peroxide, it has been known that the peroxy-hydroxide coprecipitation could be formed at a relatively lower pH range from 10 to 12 with NH₄OH [12], which has no metal impurities. Therefore, the pH range in this study including hydrothermal synthesis was fixed from 10 to 12. While the mechanism of the peroxy-compound formation is complicated and not fully understood, it was suggested that the coprecipitation condition employed in this study led to Ba·Ti-peroxy-hydroxide [Ba₂Ti₂O₅(OH)₆] precipitate above pH 10 [12]. An as-coprecipitated powder was amorphous and the desired perovskite phase was formed at temperatures above 500°C. The resulting coprecipitated Ba·Ti-peroxy-hydroxide was used as the precursor for the hydrothermal process.

3.2. Hydrothermal Synthesis

The processing conditions used in this hydrothermal study and some physical properties of the prepared BaTiO₃ powders are shown in Table 1. Regardless of reaction conditions as temperature, pressure, pH and

Table 1. Hydrothermal processing conditions and some physical properties of as-prepared BaTiO₃ powders.

Sample no.	Reaction conditions			S _{BET} ^a (m ² /g)	Phase	V ^c (10 ³ × nm ³)
	Temp., Time	pH, Press. (MPa)				
1	110°C, 1 hr	11, 2.9		42		
2	130°C, 0 hr	11, 3.1		39		
3	130°C, 1 hr	11, 3.1		38		
4	130°C, 5 hr	11, 3.1		41	BT (C) ^b	65.072
5	150°C, 1 hr	11, 4.4		40		
6	130°C, 1 hr	10, 3.1		36		
7	130°C, 1 hr	12, 4.0		37		

^aS = BET surface area, ^bBT (C): Cubic BaTiO₃, and ^cV: Unit cell volume.

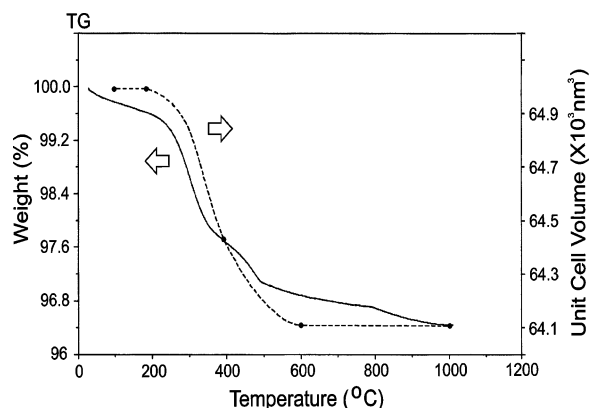
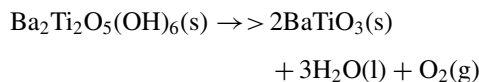


Fig. 1. TG curve of BaTiO₃ powder hydrothermally prepared at 130°C and pH 11 for 1 h, and unit cell volume changes of the heat-treated powders at different temperatures for 1 h.

time, the physical properties of prepared BaTiO₃ powders were almost identical. This observation implies that the hydrothermal synthesis of BaTiO₃ powder using coprecipitated Ba-Ti-peroxo-hydroxide precursor led to a phase-pure crystalline BaTiO₃ powders almost instantaneously when the reaction conditions reach certain synthesis conditions.

The thermal decomposition of the peroxo-hydroxide precursor takes place at temperature above 500°C in an air atmosphere, but, in the hydrothermal conditions, the decomposition happens at as low as

110°C. The transition from the Ba₂Ti₂O₅(OH)₆ precursor to the BaTiO₃ powder takes place via the following reaction:



The released O₂ as well as ammonia (NH₃) gas used in the pH adjustment led to the much higher reaction pressure (4.4 Mpa at 150°), compared to the saturated gas pressure of pure water (0.5 MPa at 150°C [13]). The increased pressure by released gases and compositional homogeneity of coprecipitated Ba₂Ti₂O₅(OH)₆ precursor were supposed to provide lower phase transition barrier and caused the moderate powder synthesis conditions such as the lower pH, lower temperature and shorter reaction time.

A typical TGA result for a dried powder is presented in Fig. 1 and unit cell volumes (determined by the XRD shown in Fig. 2) of heat-treated powders at different heat-treatment temperatures are also depicted. Small amount of weight loss less than 4% was found up to 1000°C. Weight loss of about 3% was found at temperature below 600°C and this weight loss is considered to be resulting from the released OH⁻ which was defectively incorporated in the perovskite lattice [14]. The unit cell volume decreases with heat-treatment temperature and the weight decreases with increasing

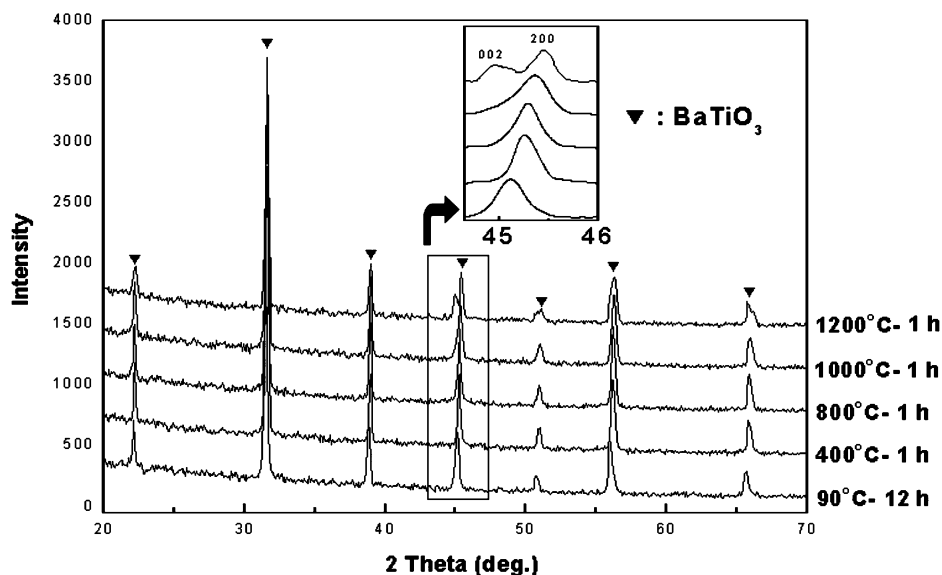


Fig. 2. XRD patterns of BaTiO₃ powders hydrothermally prepared at 130°C and pH 11 for 1 h, and heat-treated at different temperatures.

temperature in an identical manner, which confirmed the OH defect theory. Another slight weight loss shown at the temperatures above 700°C results from decomposition of small BaCO₃ impurity [10].

Figure 2 shows the XRD patterns of BaTiO₃ derived from hydrothermal synthesis at 130°C for 1 h and followed by heat-treated at different temperatures. Well-developed perovskite BaTiO₃ without impurity phase was formed during heat treatment. The crystallinity measured by relative peak intensities between the as-prepared and the heat-treated powders was almost same. On heat treatment the unit cell volume of as-prepared BaTiO₃ powder shrank from 65.072 (as-prepared) to 64.096 × 10³ nm³ (1000°C) by about 1.5%. Increased unit cell volume in the as-prepared powders is known as due to the OH⁻ ions incorporated in the lattice as mentioned above. The presence of OH defect is also known as the reason of cubic phase at room temperature [14]. As shown in Fig. 2, however, the cubic phase without the splitting of the (00h)/(h00) peaks was observed in the OH⁻-free powders heat treated at 600–1000°C. A particle size dependence of the crystal structures in BaTiO₃ powders has been reported [15]. Between 1.5 and 0.5 μm, the tetragonality decreases from 1.01 to 1.005 with decreasing particle size. Below 0.5 μm, the powders exhibit a (pseudo-) cubic phase at room temperature instead of a tetragonal phase. This is also in good agreement

with the results in this study because the particle size of BaTiO₃ powder heat-treated at 1000°C was still below 0.5 μm (Fig. 3). The uniform microstructure shown in the heat-treated powders indicates that the hydrothermal powders were fine and homogeneous. From these results, it is proposed that both the OH defect and fine powder size result in cubic phase in low temperatures (<600°C) and the crystallite size is a main factor to determine the crystal structure in higher temperatures (>600°C). The complete transformation of the cubic phase into tetragonal has been achieved at 1200°C for 1 hr and the tetragonality (*c/a* ratio) was 1.01, typical value of normal BaTiO₃ ceramics.

Figure 4 shows the TEM micrograph of the as-prepared BaTiO₃ powders synthesized at 130°C for 1 h. The ultra-fine (<30 nm) powders were obtained. Each powder has very clear boundary without any internal or surface defects and has spherical shapes. Selected area diffraction (SAD) patterns shown in Fig. 4 indicate the BaTiO₃ powder is single crystal in nature. The (pseudo-) cubic structure of the 3-fold symmetry is clearly shown in the pattern. The value of specific surface area of the as-prepared powders determined by BET analysis was an average value of 40 m²/g. The particle size (*D*_{BET}) calculated [16] from the value of specific surface area was 25 nm, which was close to the size determined by TEM.

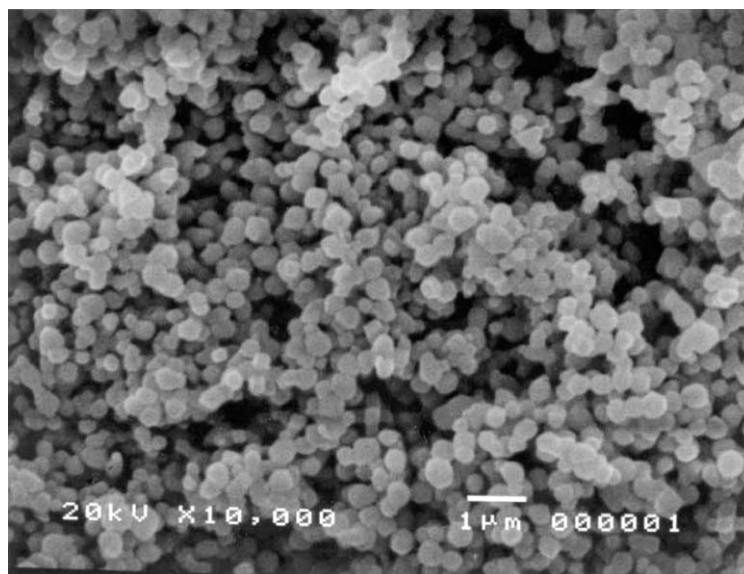


Fig. 3. SEM micrograph of BaTiO₃ powder heat-treated at 1000°C for 1 h using BaTiO₃ powder hydrothermally prepared at 130°C and pH 11 for 1 h.

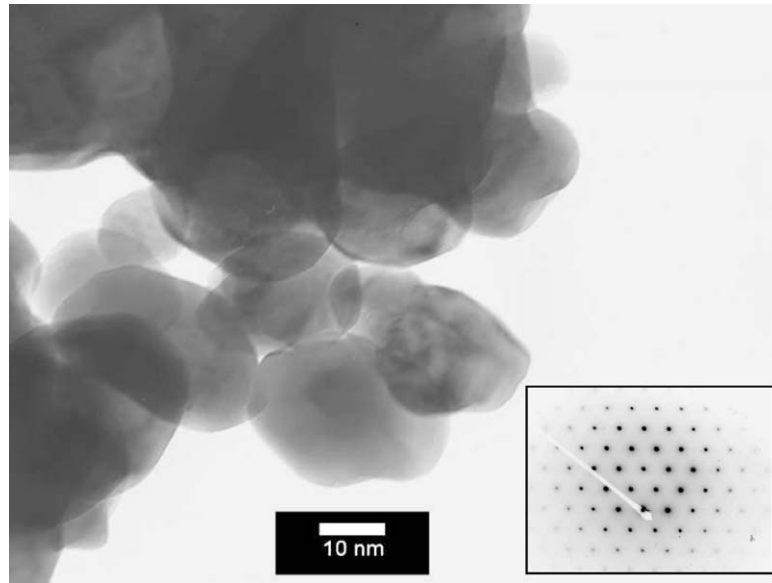


Fig. 4. TEM micrograph and SAD pattern of BaTiO₃ powder hydrothermally prepared at 130°C and pH 11 for 1 h.

The sinterability of synthesized powders was in proportion with their specific surface areas. The higher surface area leads to a higher sintered density. Using the reactive fine powders prepared at 130°C for 1 h, the BaTiO₃ ceramics sintered at 1200°C for 1 h had 97% of theoretical density. Fine grain sizes of the op-

timum values in the range of 1 to 7 μm were obtained (Fig. 5). The dielectric constant (ϵ_r) measured in the fine-grained ceramic was as high as 3500, with a dielectric loss ($\tan\delta$) of 0.034, which was considerably high compared to that ($\epsilon_r \sim 1500$) of conventional coarser-grained ceramics sintered at higher temperatures. It has

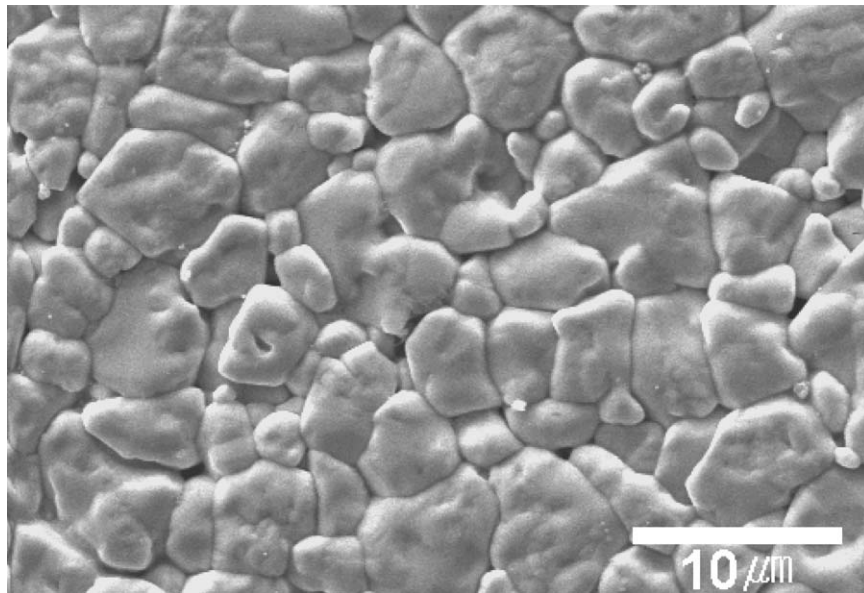


Fig. 5. SEM micrograph of the BaTiO₃ ceramic sintered at 1200°C for 1 h using BaTiO₃ powder prepared at 130°C and pH 11 for 1 h. The specimen was polished and thermally etched at 1100°C for 30 min.

been suggested that the high dielectric constant in the fine-grained material corresponds to the induced internal stress resulting from the high surface energy of finer grains [17].

4. Conclusions

The hydrothermal reaction using chemically modified Ba-Ti-peroxo-hydroxide precursor provides a simple low temperature route for producing BaTiO₃ nanoparticles. The modified hydrothermal approach offered several advantages, such as low reaction pH and low reaction temperatures with short reaction times, over the conventional hydrothermal process. The reaction pressure by released gases and compositional homogeneity of coprecipitated Ba₂Ti₂O₅(OH)₆ precursor provided lower phase transition barrier and caused the moderate powder synthesis conditions.

The weight and unit cell volume of prepared powders decreased with temperature in an identical manner, which was considered as due to the released OH incorporated in the lattice. From the TGA and XRD results, it is proposed that both the OH defect and fine crystallite (powder) size resulted in cubic phase at low temperatures (<600°) and the crystal structure was only affected by the crystallite size at higher temperatures (>600°). TEM investigation showed that the size of the BaTiO₃ powder prepared at 130°C for 1 h was below 30 nm and the BET surface area was as high as about 40 m²/g. The reactive BaTiO₃ nanoparticles offered low ceramic processing temperatures and high-density ceramic products with high dielectric constant.

Acknowledgments

This work was supported by EEC (Electronic Ceramics Center) at Dong-eui University as RRC•TIC

program which is financially supported by Korea Science and Engineering Foundation (KOSEF) under Ministry of Science and Technology (MOST), and Korea Institute of Industrial Technology Evaluation and Planning (ITEP) under Ministry of Commerce, Industry and Energy (MOCIE), and Busan Metropolitan City.

References

1. J.F. Bocquet, K. Chhor, and C. Pommier, *Mater. Chem. Phys.*, **57**, 273 (1999).
2. Y. Enomoto and A. Yamaji, *Am. Ceram. Soc. Bull.*, **60**, 566 (1981).
3. S. Suasmoro, S. Pratapa, D. Hartanto, D. Setyoko, and U.M. Dani, *J. Euro. Ceram. Soc.*, **20**, 309 (2000).
4. J.P. Coutures, P. Odier, and C. Proust, *J. Mater. Sci.*, **27**, 1949 (1992).
5. W. Maison, R. Kleeberg, R.B. Heimann, and S. Phanichphant, *J. Euro. Ceram. Soc.*, **23**, 127 (2003).
6. B. Jiang, J.L. Peng, L.A. Bursill, T.L. Ren, P.L. Zhang, and W.L. Zhong, *Physica B*, **291**, 203 (2000).
7. S. Urek and M. Drofenik, *J. Euro. Ceram. Soc.*, **18**, 279 (1998).
8. S.W. Lu, B.I. Lee, Z.L. Wang, and W.D. Samuels, *J. Crystal Growth*, **219**, 269 (2000).
9. J.H. Moon, E. Suvaci, T. Li, S.A. Costantino, and J.H. Adair, *J. Euro. Ceram. Soc.*, **22**, 809 (2002).
10. B.L. Newalkar, S. Komarneni, and H. Katsuki, *Mater. Res. Bull.*, **36**, 2347 (2001).
11. Y.S. Her, E. Matijevic, and M.C. Chon, *J. Mater. Res.*, **10**, 3106 (1995).
12. Y.P. Ahn, B.H. Kim, and T.S. Lee, *J. Kor. Ceram. Soc.*, **25**, 315 (1988).
13. R.C. Weast (Ed.), *Handbook of Chemistry and Physics*, 70th edn. (CRC Press, 1989), p. D-192.
14. C. Xia, E. Shi, W. Zhong, and J. Guo, *J. Euro. Ceram. Soc.*, **15**, 1171 (1995).
15. G. Arlt, D. Hennings, and G. de With, *J Appl. Phys.*, **58**, 1619 (1985).
16. M.D. Shaji Kumar, T.M. Srinivasan, P. Ramasamy, and C. Subramanian, *Mater. Lett.*, **25**, 171 (1995).
17. B.W. Lee and K.H. Auh, *J. Mater. Res.*, **10**, 1418 (1995).