

Synthesis of Ultrafine and Spherical Barium Titanate Powders Using a Titania Nano-Sol

Jai Joon Lee, Kum Jin Park,[‡] Kang Heon Hur,[‡] Sung Chul Yi, and Sang Man Koo[†]

Ceramic Processing Research Center and Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

A novel synthetic method for the preparation of spherical, homogeneous, and ultrafine barium titanate (BaTiO₃) powders is described. An aqueous titania nano-sol was prepared by peptizing coarse aggregate of hydrous titania with nitric acid. BaTiO₃ powders could be synthesized through a simple reflux method using the titania nano-sol and barium hydroxide. As decreasing the titanium concentration, the particle size of the resulting spherical BaTiO₃ powder was increased from 40 to 130 nm and the porosity also increased. It was revealed that the smaller as-prepared BaTiO₃ powder was less porous and became more tetragonal with less intragranular pores after annealing. With this method, a highly tetragonal BaTiO₃ powder (*c/a* ~ 1.008) with a particle size of 120.0 nm was successfully prepared and would be very suitable for the thinner dielectrics in higher capacitance multilayer ceramic capacitors.

I. Introduction

THE recent development of multilayer ceramic capacitors (MLCCs) that contain thinner dielectric layers has increased the demand for smaller and more uniform barium titanate (BaTiO₃) powders. Wet chemical methods such as hydrothermal methods^{1–4} and sol–gel syntheses^{5,6} have been intensively studied for the preparation of BaTiO₃ powders that will meet the new requirements. Although the conventional hydrothermal method makes it possible to directly synthesize spherical BaTiO₃ powders, it requires relatively harsh reaction conditions and therefore special and expensive reactors capable of withstanding high pH and temperature. The sol–gel processes with titanium alkoxide allow for milder reaction conditions of <100°C and provide adequate size-control for monodisperse BaTiO₃. However, some organic solvents and inert gas atmosphere are generally required for this preparation method, which make adapting it to mass production difficult. In addition, there have been many reports^{2,3} that intragranular pores were detected in BaTiO₃ powders prepared by wet chemical methods during the annealing process. Hennings *et al.*² claimed that metal and oxygen vacancies due to the lattice hydroxyl ions might combine to form intragranular pores and negatively affect the dielectric and mechanical properties of the MLCCs. However the mechanism of the intragranular pore formation is not fully understood.

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[‡]Present address: Samsung ElectroMechanics Co. Ltd., Suwon 442-743, Korea.

[†]Author to whom all correspondence should be addressed. e-mail: sangman@hanyang.ac.kr

On the other hand, a lot of researchers have reported that stable nano-structured metal oxide particles such as titania and boehmite could be prepared by a peptization method⁷ where the coagulated precipitate was dissolved and recrystallized into the stable sol of nanoparticle with a peptizing agent such as organic acid (polycarboxylic acid),⁸ non-complexing inorganic acid (HNO₃, HCl),^{9,10} or inorganic base (tetraethylammonium hydroxide).¹¹ These peptized nano-sol of metal oxides have great potential as precursors of sol–gel reactions and various applications. However, there has been no report about the direct synthesis of BaTiO₃ powder using the peptized metal oxide nanoparticle as a precursor.

In this study, we prepared an aqueous titania (TiO₂) nano-sol obtained by the peptization method with nitric acid and used as a precursor for the synthesis of BaTiO₃ in order to overcome the problems that occur in the hydrothermal and sol–gel methods. The effect of titanium concentration on the size and porosity of BaTiO₃ powders prepared from the TiO₂ nano-sol was described. Also, the reason of the intragranular pore formation in the annealed BaTiO₃ powders was discussed with respect to the as-prepared BaTiO₃ powder's porosity.

II. Experimental Procedure

Titanium isopropoxide (Aldrich Chemical Co., Milwaukee, WI, 97%) was rapidly hydrolyzed with an excess amount of H₂O to form a highly aggregated amorphous hydrous titania. After being filtered and washed, it was redispersed in a calculated amount of deionized water ([Ti] of 0.125, 0.25, 0.5, and 1.0M). The suspension was peptized with nitric acid (Samchun Pure Chemical Co. Ltd., Pyeongtaek, Korea, 60%) at 60°C for 6 h ([H⁺]/[Ti] = 0.5) to induce transformation to the highly stable TiO₂ nano-sol. The pH of the sol was controlled to above 13 with KOH (Samchun Pure Chemical Co. Ltd., 85%). Ba(OH)₂ · 8H₂O (Acros Organics, Morris Plains, NJ, >98%) was added to the TiO₂ sol with a Ba/Ti ratio of 1.05. After 8 h of reaction at 90°C in air, the suspension was filtered and washed repeatedly with 0.5% aqueous acetic acid and deionized water. The resulting cubic BaTiO₃ powders were dried in a vacuum oven at 80°C for 24 h and annealed at 800–1000°C for 2 h for tetragonal conversion.

III. Results and Discussion

A crystalline, nanometer-ordered TiO₂ nano-sol was prepared in an aqueous medium by peptizing coarse aggregates of an amorphous hydrous titania. Figure 1 shows the XRD pattern and TEM image of the TiO₂ nano-sol dried at 70°C. It consisted of mainly anatase with minor brookite phases and its size was less than 10 nm. There have been several reports⁴ that amorphous titania is more reactive than the anatase or rutile form for the synthesis of BaTiO₃ at lower temperature. However, the anatase TiO₂ sol prepared in this study could be readily transformed to BaTiO₃ in a few hours at 90°C, which may be a result of its nanometer-ordered size. Furthermore, it did not require any

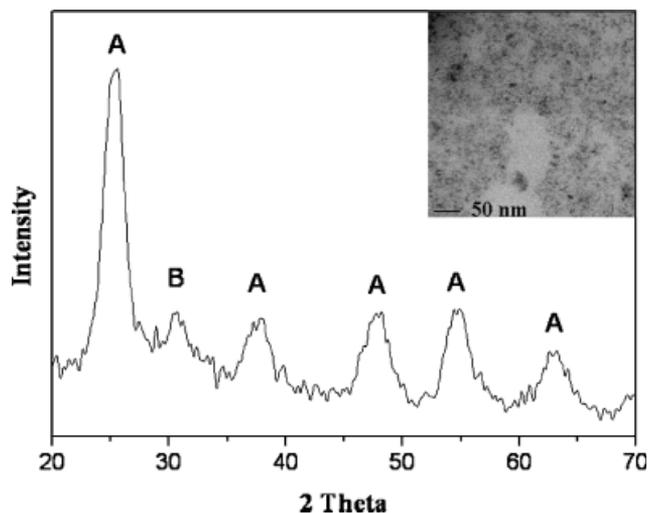


Fig. 1. XRD pattern of the TiO_2 sol prepared by the peptization method (A: anatase and B: brookite). Inset represents a TEM image of the TiO_2 sol.

organic solvents or an inert gas atmosphere for the preparation. Therefore it was concluded to be an excellent precursor for the preparation of BaTiO_3 .

Highly spherical and monodisperse BaTiO_3 powders could be obtained from the refluxing reaction between the aqueous TiO_2 nano-sol solution and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ as shown in Fig. 2. The size of the BaTiO_3 powders synthesized in this study could be easily controlled by changing the concentration of the TiO_2 nano-sol (Figs. 2(a)–2(c)). By lowering the titanium concentration from 1.00 to 0.50, and 0.25M, the mean diameter (D_{SEM}) of the resulting BaTiO_3 increased from 42.3 to 74.8 and 132.2 nm, respectively. Their specific surface areas analyzed by the BET method were 38.3, 27.1, and 17.5 m^2/g , and the diameters (D_{BET})

Table I. Variations in the Diameters of The As-Prepared BaTiO_3 Powders As Dependent on The Concentration of The TiO_2 Nano-Sol

Sample	Concentration [†] (M)	D_{SEM} [‡] (nm)	D_{BET} [§] (nm)	$D_{\text{SEM}}-D_{\text{BET}}$ (nm)
S-1000	1.000	42.3	26.1	16.2
S-500	0.500	74.8	36.8	38.0
S-250	0.250	132.2	56.9	75.3
S-125	0.125	—	30.7	—

[†]Titanium concentration in the synthetic solution. [‡]Mean diameter of particles measured from the SEM image. [§]Diameter of particles calculated from the BET-specific surface area data and theoretical density of BaTiO_3 (6.01 g/cm^3).

calculated from the surface area data and theoretical density for BaTiO_3 were 26.1, 36.8, and 56.9 nm, respectively. The discrepancy between D_{SEM} and D_{BET} increased with respect to decreasing titanium concentrations from 16.2 to 75.3 nm and these results are summarized in Table I. In particular, the BaTiO_3 powder prepared at a titanium concentration of 0.125M (S-125) was non-homogeneous and highly porous as shown in Fig. 2(d) and Table I. This result indicated that a more porous BaTiO_3 powder was synthesized as the titanium concentration decreased.

The BaTiO_3 powders were annealed at 800°–1000°C for 2 h and their morphologies were observed by SEM and TEM as shown in Fig. 3. The spherical morphology of the as-prepared powder was maintained after the annealing process. As can be seen in Fig. 3(a), particle growth and necking had already started even at 800°C for S-1000 and the TEM analysis indicated that a highly dense particle without intragranular pores was formed. On the other hand, for sample S-250, which showed a substantial discrepancy between D_{SEM} and D_{BET} (Table I), growth or necking during the annealing could not be observed even at 1000°C and a powder with substantial intragranular pores was formed, as shown in Fig. 3(b). These intragranular pores in the BaTiO_3

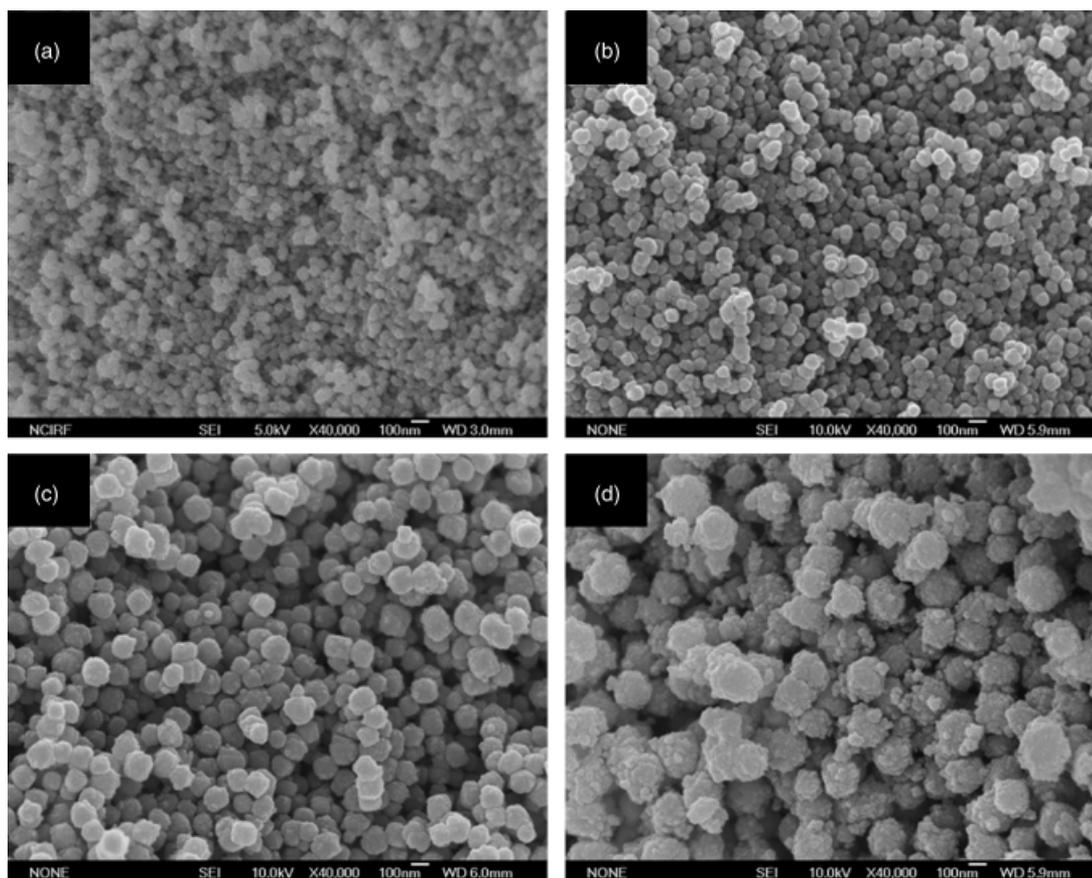


Fig. 2. SEM images of the BaTiO_3 powders synthesized at a titanium concentration of (a) 1.00M, (b) 0.50M, (c) 0.25M, and (d) 0.125M.

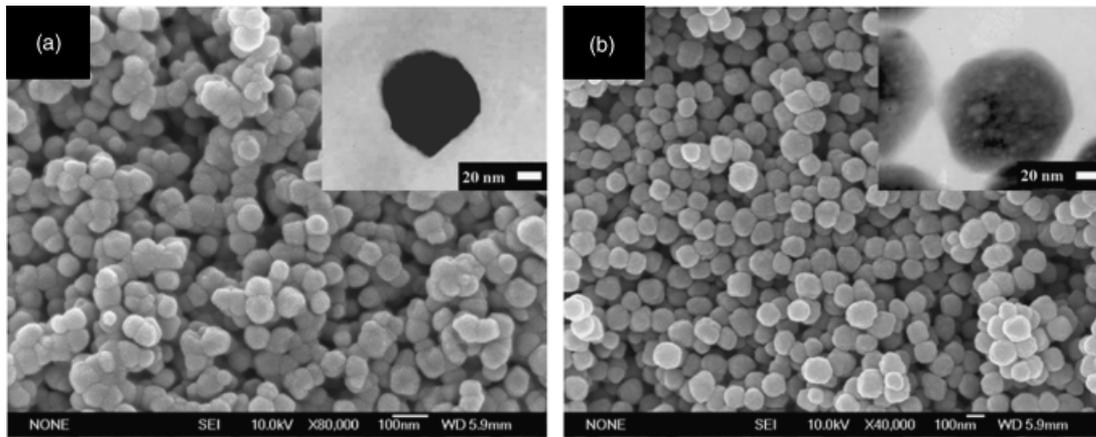


Fig. 3. SEM images of (a) the S-1000 after annealing at 800°C and (b) the S-250 after annealing at 1000°C. Insets show TEM images of each powder.

particles synthesized by wet chemical methods is known to originate from defects such as lattice hydroxyl ions and barium vacancies.^{3,6} In this study, however, it was revealed that the larger, as-prepared BaTiO₃ particles with the higher porosity exhibited more intragranular pores after annealing. This result indicated that the as-prepared BaTiO₃ powder's porosity may be one of the main factors affecting the amount of intragranular pores.

As presented in Fig. 4, the as-prepared BaTiO₃ powder had a cubic structure and was transformed to a tetragonal structure during annealing at 1000°C, which was confirmed by the peak splitting around 2θ of 45° in the XRD analysis. Furthermore, the annealed S-1000 powder had a high tetragonality (*c/a*) value of 1.0081 despite its size of 120.0 nm. Begg *et al.*¹² reported that room-temperature stabilization of the cubic structure was a result of the stress due to the large surface area and the defects that existed in the fine-grained BaTiO₃ powder. They also observed that tetragonality decreased with decreasing BaTiO₃ particle size, and reported a tetragonality value (*c/a*) of 1.0048 for hydrothermally grown BaTiO₃ with a particle size of 280 nm obtained from autoclave reaction at 300°C for 5 days, which was similar to results by other researchers.¹³

IV. Conclusions

In this study, the spherical, homogeneous and fine BaTiO₃ powders were prepared in a simple procedure using peptized TiO₂

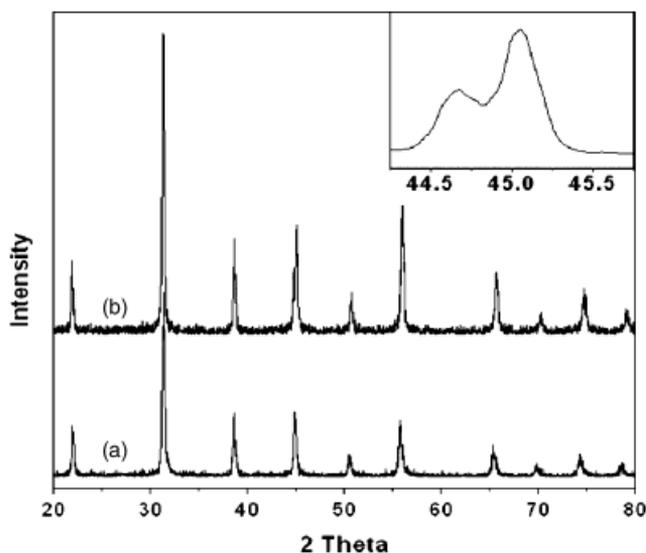


Fig. 4. XRD patterns of the S-1000 BaTiO₃ powders (a) before annealing and (b) after annealing at 1000°C. The inset represents the enlarged XRD patterns around 2θ = 45° of pattern (b).

nano-sol as a precursor at temperature as low as 90°C. The size of the as-prepared BaTiO₃ could be easily controlled from about 40 to 130 nm by lowering the solution concentration of titanium from 1.00 to 0.25M. It was also found that the porosity of the as-prepared powder was less in the smaller as-prepared powder and affected the formation of intragranular pores in each of the BaTiO₃ particle after annealing. Therefore, BaTiO₃ powders that almost did not have intragranular pores could be prepared through the annealing of the smaller as-prepared powders synthesized from solutions of higher titanium concentrations. This highly crystalline BaTiO₃ also showed high tetragonality (*c/a* ~ 1.008) with respect to its size of 120.0 nm. The BaTiO₃ powders prepared by this method could have great potential in the preparation of thinner dielectrics in higher capacitance MLCCs.

Supporting Information available: SEM image and particle size analysis data by laser light scattering of BaTiO₃ powder after annealing at 1000°C.

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