

## Synthesis of Monodispersed Barium Titanate Nanopowders by Alkoxide-Hydroxide Sol-Precipitation Method

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### ABSTRACT

Barium titanate nanoparticles were synthesized under  $N_2$  atmosphere by the hydrolysis and condensation of barium hydroxide octahydrate and titanium (IV) isopropoxide. The synthesized particles were aggregates of nanosized primary particles. The primary particles of about 20–50 nm in diameter became building blocks of larger secondary particles, which are in most cases spherical in shape. The size and morphological evolution of secondary particles are strongly related to the precursor concentration. The observations suggest that formation and control of secondary particles is an essential step in the alkoxide-hydroxide sol-precipitation process to obtain monodispersed barium titanate nanopowders.

**Key words:** Barium titanate, Nanoparticles, Alkoxide-hydroxide sol-precipitation, Aggregation

### 1. Introduction

Barium titanate ( $BaTiO_3$ ) has been one of the most extensively studied ferroelectric perovskite due to its excellent dielectric, piezoelectric and ferroelectric properties.<sup>1)</sup>  $BaTiO_3$  has been widely used in various electronic components including thermistors, sensors, electro-optical devices and Multi-Layer Ceramic Capacitors (MLCCs).<sup>2,3)</sup> Recently, MLCC industries, in particular, have been investigating urgently to produce extremely thin dielectric layers thinner than 0.1  $\mu m$  with reliable synthesis methods. To manufacture reliable future MLCCs, the main challenge lies in the synthesis of barium titanate nanopowders of about 100 nm or less in diameter with a high dielectric constant for further down sizing of the dielectric layers.<sup>4)</sup>

Nano-sized  $BaTiO_3$  powders have been prepared conventionally by various methods including solid state reaction,<sup>5)</sup> hydrothermal<sup>6)</sup> and solvothermal<sup>7)</sup> methods, microemulsion technique,<sup>8)</sup> controlled precipitation method,<sup>9)</sup> and sol-gel method.<sup>10)</sup> In most cases, particle agglomeration could not be avoided and/or most of the methods have been found inadequate to produce mono-dispersed  $BaTiO_3$  powders smaller than 100 nm in average sizes.

Since Flaschen<sup>11)</sup> first proposed the synthesis of crystalline barium titanate by an alkoxide-hydroxide sol-precipitation process, a number of relevant publications and patents have appeared in the literature.<sup>12-14)</sup> Since the conventional

alkoxide-hydroxide sol-precipitation method adopted aqueous solution of barium hydroxide, the hydrolysis and condensation reaction occurred immediately when titanium alkoxide react rapidly with aqueous solution of barium hydroxide. It often produces highly agglomerated, irregular shaped powders of cubic phase. In our recent study, we could synthesize  $BaTiO_3$  nanopowders via alkoxide-hydroxide sol-precipitation method using the water molecules in the  $Ba(OH)_2 \cdot 8H_2O$  precursors.<sup>15)</sup> Subsequently, we studied the effects of water addition on the preparation of  $BaTiO_3$  nanoparticles with controlled particle size and crystal structure.<sup>16)</sup>

In this study, we report the effects of precursor concentrations on the preparation of  $BaTiO_3$  powders with controlled morphology using the alkoxide-hydroxide sol-precipitation method. It is expected that differentiated chemical conditions of reaction in the alcoholic solution due to varied concentrations of precursor would affect drastically the kinetics of crystal growth and aggregation behavior of  $BaTiO_3$  nanoparticles.

### 2. Experimental Procedures

$BaTiO_3$  nanoparticles are synthesized via the hydrolysis and condensation of barium hydroxide octahydrate ( $Ba(OH)_2 \cdot 8H_2O$ ; 99.995%, Aldrich, Milwaukee, WI) and titanium (IV) isopropoxide ( $Ti[OCH(CH_3)_2]_4$ , 99.999%, Aldrich). Because both alkoxides and hydroxides are extremely sensitive to  $CO_2$ , the reaction requires  $CO_2$ -free environment and all reaction was performed in a glove box filled with nitrogen gas. Titanium (IV) isopropoxide was diluted

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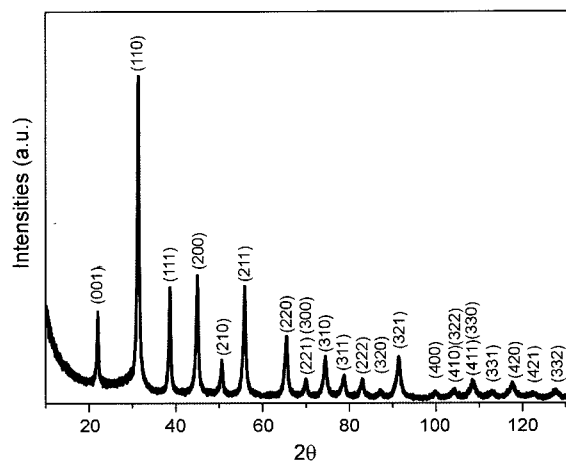
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in isopropanol (1 mol;  $C_3H_7OH$ , 99.9%, Mallinckrodt Baker Inc., Phillipsburg, NJ) at room temperature. Subsequently, barium hydroxide octahydrate was added to the isopropanol solution in a 3-neck flask fitted with a condenser while stirring vigorously. Three different samples were prepared with different amounts of precursors: 0.01, 0.0025, and 0.000625 mol. Then the mixture solution was heated to  $80^\circ C$  at the rate of  $2^\circ C/min$ . As soon as the solution temperature reached at  $80^\circ C$ , we slowly added the deionized distilled water (0.25 mol) to the solution as droplets. Even though 8 mol of water was supplied for each mole of the barium hydroxide precursor, sufficient amount of additional water was slowly added to the solution in order to enhance the reaction kinetics. After 60 min of refluxing at  $80^\circ C$ , the solutions were centrifuged at 10,000 rpm for 10 min and then dried at  $60^\circ C$  for 12 h in an oven.

With the synthesized nanoparticles, powder diffraction experiments were carried out at 8C2 HRPD beamline at Pohang Light Source (PLS). The incident X-rays were monochromatized to the wavelength of  $1.5452 \text{ \AA}$  by a double bounce Si (111) monochromator. The diffraction pattern was scanned from  $10$  to  $132^\circ$  ( $2\theta$ ) with a step length of  $0.02^\circ$ . A small amount of the mixture solution was also extracted from the 3-neck flask, applied immediately to 400-mesh carbon-coated copper grids, and dried in air. The morphology and size of synthesized  $BaTiO_3$  nanoparticles were examined directly by a high resolution transmission electron microscopy (Model JEM-2010F, JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 200 kV. The samples for the field emission scanning electron microscopy (Model 6330F, JEOL Ltd., Tokyo, Japan) were prepared from the solution mixture by dropping the solutions on silicon substrate and drying in air.

### 3. Results

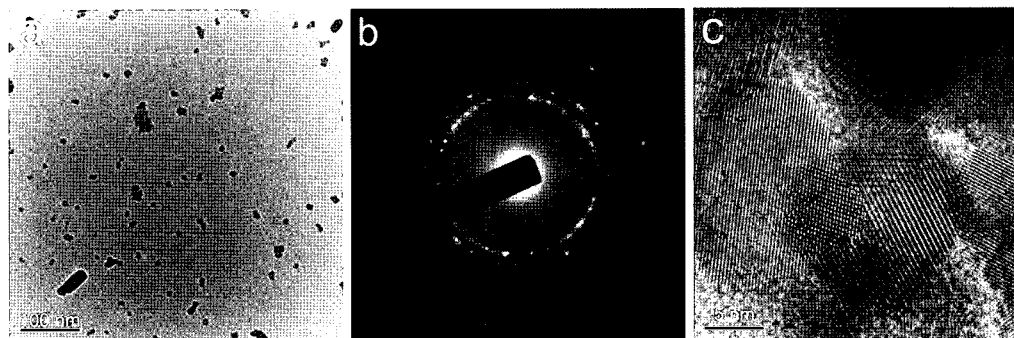
Fig. 1 shows synchrotron X-ray diffraction spectrum of barium titanate nanoparticles synthesized with 0.01 mol of precursor concentration. It shows well-defined  $BaTiO_3$  peaks without any detectable impurities or secondary



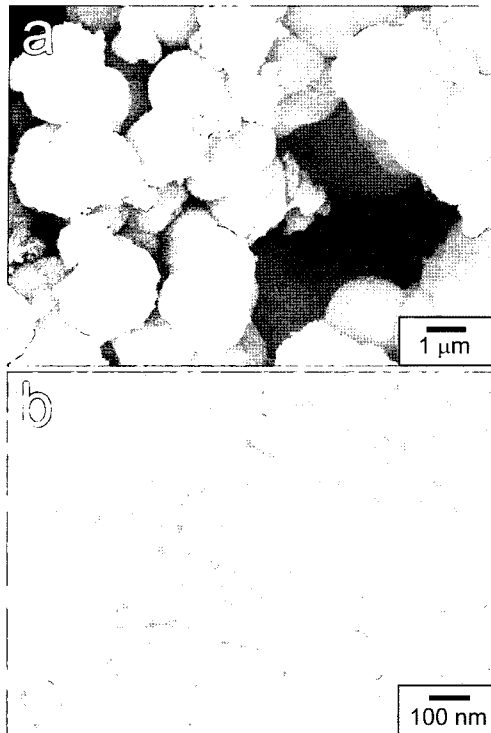
**Fig. 1.** Synchrotron X-ray diffraction spectrum of  $BaTiO_3$  powders taken with the wavelength of  $1.5452 \text{ \AA}$  monochromatic beam in  $2\theta$  range of  $10$  to  $132^\circ$ .  $BaTiO_3$  powders are synthesized with 0.01 mol precursor concentration and 1 h reflux after water addition.

phases. The detail information on crystal structure has been reported in the previous paper.<sup>16)</sup>

Fig. 2 presents the TEM images of barium titanate nanoparticles synthesized with 0.01 mol of precursor concentration. The particle size varies from about 10 nm to 50 nm. However, closer observation on the individual particles reveals that, as shown in Fig. 2(c), they are in fact aggregates of crystalline nuclei of less than 8 nm in diameter. Selected Area Electron Diffraction (SAED) pattern for an aggregate, Fig. 2(b), shows the typical ring patterns representing the polycrystalline barium titanate, which indicates that the products are randomly oriented aggregates of many crystalline nuclei. It can be thus inferred that  $BaTiO_3$  crystalline nuclei are formulated starting at  $50$ – $60^\circ C$  in the course of heating up the precursor solution<sup>15)</sup> and grow to the primary particles by random aggregation of such nuclei at the reaction temperature. The primary particles observed by Transmission Electron Microscope (TEM) images are generally



**Fig. 2.** TEM micrographs of as-synthesized  $BaTiO_3$  nanoparticles synthesized with 0.01 mol of precursor concentration after water addition: (a) primary nanoparticles, (b) Selected Area Electron Diffraction (SAED) pattern of primary nanoparticles showing that they in fact consist of randomly oriented smaller particles, and (c) high resolution TEM images exhibiting individual  $BaTiO_3$  nanocrystalline nuclei.

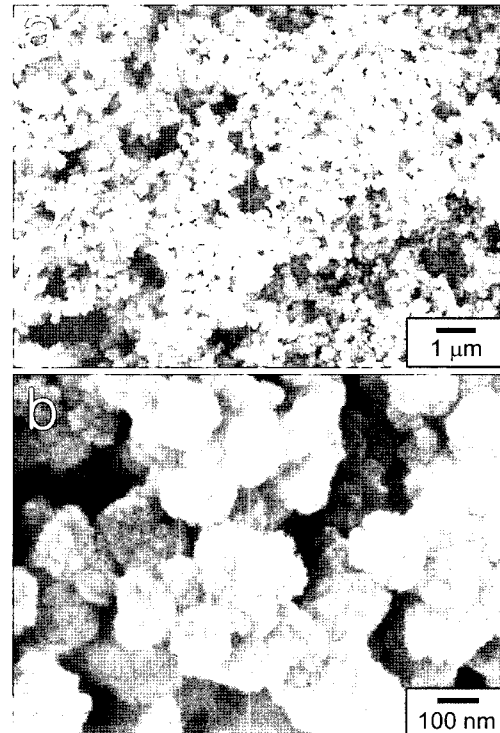


**Fig. 3.** SEM micrographs of the synthesized  $\text{BaTiO}_3$  powders with 0.01 mol precursor concentration after one hour reflux with added water: (a) secondary particles are formed by the aggregation of primary nanoparticles, (b) enlarged image of (a), which reveals the presence of primary nanoparticles (20–50 nm).

spherical in shape and approximately 50 nm or less in diameters. In other words, the primary particles are formed by random aggregation of tiny crystalline nuclei of less than 8 nm in diameters.

The SEM micrographs of  $\text{BaTiO}_3$  powders which were synthesized with the use of 0.01 mol of precursor concentration are shown in Fig. 3. The particles are fairly spherical, from about 0.5 to a few  $\mu\text{m}$  in diameters, and also highly agglomerated. However, as shown by the magnified view in Fig. 3(b), which is the surface of one of the spherical particles, they are in fact secondary particles formed by aggregation of the primary particles having approximate sizes of 20–50 nm. The observation is consistent with so called “aggregation-of-subunits mechanism” that has been reported as one of the dominant mechanisms in later stage of crystal growth and subsequent microstructural development of nanoparticles.<sup>17–19)</sup>

Fig. 4 shows  $\text{BaTiO}_3$  powder synthesized under the identical experimental conditions except that the concentration of precursor solution was reduced to 0.0025 mol. The particle sizes are fairly uniform and approximately 200–300 nm in diameter. As the individual particles are magnified in Fig. 4(b), they are also revealed to be aggregates of much smaller subunits, which are again 20–50 nm in diameters. Therefore, only difference due to the change in precursor concentration is the size of secondary particles.

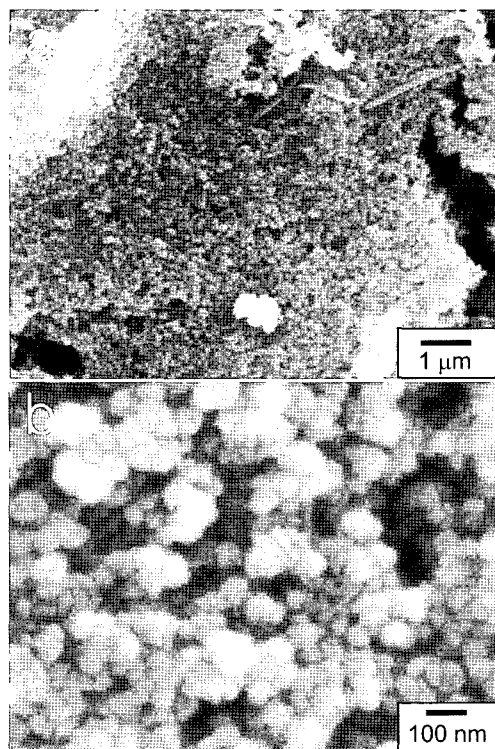


**Fig. 4.** SEM micrographs of the synthesized  $\text{BaTiO}_3$  powders with molar concentrations of precursor solutions reduced to 0.0025 mol: (a) monodispersed and smaller secondary particles, (b) enlarged image of (a) showing that they are also made up of smaller primary particles of 20–50 nm.

The morphological characteristics of primary particle formation remain unchanged. Such a behavior is manifested more clearly as the molar concentrations of precursor solutions reduced to 0.000625 mol. The final product is shown in Fig. 5, which shows a  $\text{BaTiO}_3$  aggregate consisted of monodispersed uniform particles. Interestingly, as the aggregate particles are viewed under a highly magnified SEM stage, each particle is in fact a secondary particle of uniform size of approximately 100 nm or less formed by aggregation of similar subunits (primary particles) formed in the initial stage of sol-precipitation process.

#### 4. Discussions

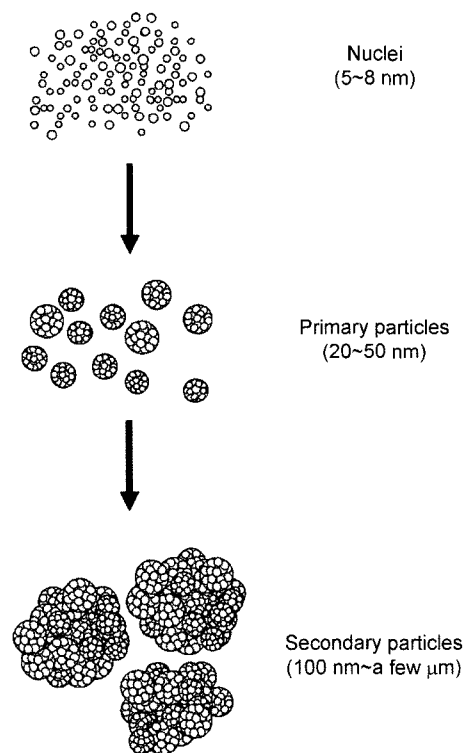
Since the alkoxide-hydroxide sol-precipitation method was first proposed to synthesize barium titanate powder in 1955,<sup>11)</sup> many researchers have attempted to produce barium titanate powders using this method with small modifications.<sup>12–14)</sup> However, with the aqueous or alcoholic solution of barium hydroxide, hydrolysis and condensation reaction with titanium (IV) isopropoxide in the presence of barium ions is too fast to be controlled. As a result, although barium titanate powders could be synthesized at relatively low temperature with reasonable characteristics, they have been often highly agglomerate and monodispersed powders could not be obtained.



**Fig. 5.** SEM micrographs of the synthesized  $\text{BaTiO}_3$  powders with molar concentrations of precursor solutions reduced to 0.000625 mol: (a) soft aggregates of monodispersed smaller particles of about 100 nm or less, (b) enlarged image of (a) depicting that each particle consists of smaller primary particles.

In order to overcome such difficulties in controlling the reaction kinetics, the key step seems to be how the water molecules are introduced in the reaction system in a controlled manner. The present study focuses on homogeneous mixing of barium hydroxide octahydrate and titanium (IV) isopropoxide at room temperature. Afterward, water was added in a pre-designed condition, where it was first supplied slowly and homogeneously as barium hydroxide octahydrate was dissolved during heating up and water molecules were released starting from 50–60°C. Later, a small amount of deionized distilled water was added at 80°C as fine droplets using a spray nozzle to enhance homogeneous introduction of water and reaction. During heating the mixing solution up to 80°C, crystalline nuclei were formed by the reaction of barium hydroxide octahydrate and titanium (IV) isopropoxide with the released water.<sup>15)</sup> The additional water introduced as fine droplets at 80°C under vigorous stirring condition played multiple roles during the early nanoparticle formation. It acted not only as the reaction enhancer which leads to homogeneous growth of primary particles of about 20–50 nm diameter but also as a binder, causing the aggregation of primary particles to formulate secondary spherical particles.

Fig. 6 illustrates graphically the reaction processes leading to well-dispersed spherical barium titanate powder. In



**Fig. 6.** Schematics illustrating sequential  $\text{BaTiO}_3$  nanoparticle growth mechanism. Initially, tiny nuclei (5–8 nm) are formed in the mixed solution during heating. Subsequently, the nuclei coagulate together to form primary nanoparticles (20–50 nm) as additional water is introduced. The primary particles aggregate to form spherical secondary particles of about 100 nm–a few  $\mu\text{m}$ . The size of secondary particles differs depending on the precursor concentrations.

the course of heating up the mixed isopropanol solution of alkoxide and hydroxide, nanocrystalline nuclei (5–8 nm) form homogeneously as barium hydroxide octahydrate is dissolved and water molecules are released starting from 50–60°C. As the solution temperature reaches 80°C, the nanocrystalline nuclei tend to grow to primary particles (20–50 nm) of spherical shape by random attachment. During subsequent heating and refluxing of the solution, the primary particles coagulate to much larger secondary particles of about 100 nm to a few  $\mu\text{m}$  to eliminate high surface energies of primary particles.

In Figs. 3–5, morphological evolution of secondary particle is shown as a function of precursor concentration. Lowering the precursor concentration reduces the available hydroxyl ions and barium concentration, which results in decreasing pH of the solutions. Lencka and Riman<sup>20)</sup> reported that calculated stability of  $\text{BaTiO}_3$  under hydrothermal conditions increases with high pH, moving the system further into the region of stable  $\text{BaTiO}_3$  formation. Therefore, it seems that reduced precursor concentration lower the pH of solution decreasing the kinetics of particle growth. In other words, different pH conditions result in the different size and morphology of secondary particles. Primary nanoparticle

size, however, have not been affected by the precursor concentration. It implies that nucleation is relatively insensitive to the change in the pH of the solution. Therefore, the morphological change of secondary particles as a result of lowering the precursor concentration seems to stem from the decrease in the growth rate, rather than the nucleation rate. However, if the concentration of barium hydroxide octahydrate is lower than a critical value, the precipitation reaction would be hindered because OH<sup>-</sup> ions provided by barium hydroxide precursor is not sufficient for providing proper pH condition for barium titanate formation.<sup>21)</sup>

## 5. Summary

BaTiO<sub>3</sub> nanoparticles were synthesized by alkoxide-hydroxide sol-precipitation method at 80°C using barium hydroxide octahydrate and titanium (IV) isopropoxide. Nanocrystalline nuclei of 5–8 nm were formed as the hydrolysis and condensation reaction was triggered homogeneously by the water molecules, which was released from barium hydroxide octahydrate in the course of heating up the mixed solution. As a small amount of additional water was introduced in the solution at 80°C, primary nanoparticles of 20–50 nm were formulated from the tiny crystalline nuclei, which then aggregated to form spherical secondary particles of about 100 nm to a few μm. The size and morphological evolution of secondary particles were largely dependent on the precursor concentration of barium hydroxide octahydrate and titanium (IV) isopropoxide. However, the size and morphology of primary particles was insensitive to the precursor concentration. It was thus possible to synthesize monodispersed spherical barium titanate nanoparticles by selecting proper concentration of precursors using alkoxide-hydroxide sol-precipitation method.

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