Mechanism of nanocrystalline BaTiO$_3$ particle formation by hydrothermal refluxing synthesis

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The nanocrystal-formation mechanisms of barium titanate (BaTiO$_3$) particles in a hydrothermal refluxing process have been studied. The refluxing method allows in situ sampling and requires ambient conditions (i.e., temperature below the boiling point of solvent and atmospheric pressure). It was found that the formation of BaTiO$_3$ from the amorphous precursor was a very rapid process. BaTiO$_3$ nuclei were formed at around 75°C, 15 min after the beginning of the hydrothermal reaction. Individual BaTiO$_3$ particles with dimensions in the range of 70–130 nm were formed 5 min after the nucleation of nanocrystals. Further reaction for crystal growth proceeded by consumption of the remaining precursors and possible aggregation of BaTiO$_3$ particles via Ostwald ripening. It is proposed on the basis of the microscopic observations that the in situ transformation mechanism, rather than dissolution–precipitation mechanism, is dominant in the early stage of BaTiO$_3$ formation.

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1. Introduction
Barium titanate (BaTiO$_3$)-based ceramics have been widely used in multilayer ceramic capacitors (MLCC), transducers, positive temperature coefficient of resistance (PTC) thermistors, etc., due to their dielectric and ferroelectric properties [1]. Conventionally, BaTiO$_3$ is prepared by solid-state reaction of barium carbonate (BaCO$_3$) and titanium dioxide (TiO$_2$) at high temperatures around 1000°C, followed by milling [2]. This method, however, leads to large BaTiO$_3$ particles (usually above 1 μm in diameter) with wide grain-size distribution and uncontrollable, irregular morphologies, which may result in poor electrical properties and reproducibility of sintered ceramics. Moreover, besides the impurities such as Si, Al, S, and P that are introduced from the ball-milling process [3], the incomplete reaction of BaCO$_3$ or the excess of BaCO$_3$ may exist in BaTiO$_3$ powders. Recent studies show that the presence of BaCO$_3$ in BaTiO$_3$ powders can affect the aqueous processing of the powder, especially the rheology of the aqueous suspension [4,5].

The MLCC industry is continuing intensive efforts to reduce component size by decreasing layer thickness [6]. Thus BaTiO$_3$ nanocrystals have great advantages over micrometer-sized ones when a single ceramic layer is less than 2 μm. In recent decades, extensive studies have been conducted to produce nanosized BaTiO$_3$ powders with narrow particle-size distribution, controlled morphology, and high purity. BaTiO$_3$ nanocrystals have been synthesized by the hydrothermal method [7–22], a sol–gel process [23–30], low-temperature aqueous synthesis (LTAS) [31–34], low-temperature direct synthesis (LTDS) [35,36], combustion synthesis [37], the oxalate coprecipitation route [38], microwave heating [39], micro-emulsion process [40], and the polymeric precursor method [41,42]. Among these methods, wet-chemical synthesis, such as hydrothermal and LTAS, which involve reactions in aqueous media under strong alkaline conditions, provides a promising way to produce nanocrystalline BaTiO$_3$ with narrow particle-size distribution, high purity, high homogeneity, and controlled morphology of the resulting particles at low temperature and under mild pressures. Recent studies of wet-chemical synthesis of BaTiO$_3$ are mainly focused on the following fields: (1) Optimization of preparation conditions, such as type of precursor, Ba/Ti ratio, reaction time and temperature, pH, and so on. The ultimate goals are to shorten the reaction time, lower the synthesis pressure/temperature, and utilize cheaper starting materials; (2) Understanding kinetics and mechanisms of BaTiO$_3$ synthesis; (3) Impurity and morphology control of BaTiO$_3$ powders.

Eckert et al. [12] studied the kinetics and mechanisms of hydrothermal synthesis of BaTiO$_3$ by means of transmission electron microscopy (TEM), X-ray diffraction (XRD), and inductively coupled plasma (ICP) spectroscopy. Two reaction-rate regimes were identified. In the first regime, at the early stage of BaTiO$_3$
formation, a dissolution-precipitation mechanism dominated. On the other hand, at longer reaction times, an *in situ* transformation may be dominant in the second regime. However, they also claimed that multiple-reaction mechanisms may be competing for rate control. MacLaren and Ponton [21] investigated the BaTiO$_3$ formation in an aqueous media at temperatures between 20 and 80°C by TEM and high-resolution TEM (HREM). They found that BaTiO$_3$ nanocrystals began to form after heating at only 40°C, and continued growing to around 100 nm at 80°C. It was proposed that the BaTiO$_3$ particles were formed by an *in situ* transformation of the amorphous TiO$_2$ gel (i.e., BaTiO$_3$ formation by Ba ions diffusion into the titania gel), while dissolution–precipitation might be the mechanism for particle rounding. Although the experiment was carried out in an open reaction vessel, the authors claimed that there is unlikely to be a significant difference from the closed system under 80°C.

Using the recently developed Oxford/ISIS hydrothermal cell Walton et al. [43] studied the BaTiO$_3$ formation by time-resolved powder neutron diffraction methods. They observed the rapid dissolution of the Ba source, followed by dissolution of titanium source before the onset of crystallization of BaTiO$_3$. Thus, they proposed the predominance of the homogeneous dissolution-precipitation mechanism for hydrothermal formation of BaTiO$_3$.

In a recently prepared paper of ours [44], we synthesized BaTiO$_3$ nanoparticles in various solvents by a refluxing method in which evaporated solvent is condensed by a water-cooled condenser and flows back into the reaction medium. Compared to the conventional hydrothermal method, the refluxing method is carried out under ambient condition, using a three-neck glass flask instead of a pressure vessel such as autoclave bomb, typically used for hydrothermal studies. Thus, samples can be taken out easily without interrupting the reaction and one can get relatively real-time results. In this paper, we studied the mechanisms of BaTiO$_3$ formation in aqueous media by the refluxing method.

### 2. Experimental

The raw materials used in this study were barium chloride (99.6% BaCl$_2$·2H$_2$O, Fisher Scientific), titanium tetrachloride (99.6% TiCl$_4$ Alfa Aesar). An aqueous solution of barium and titanium was obtained by mixing 21.99 g BaCl$_2$·2H$_2$O in 90 ml deionized water and 11.38 g TiCl$_4$ in 15 ml concentrated HCl. The Ba/Ti ratio in the solution was 1.5:1. The solution pH was then adjusted by dropwise addition of 25 ml 10 M KOH with stirring. After dilution with deionized water, a white chalky precursor slurry with 0.2 M Ti equivalent in 300 ml at pH = 14.0 was obtained. The precursor slurry was then transferred into a 500-ml three-neck glass flask, heated in an oil bath under magnetic stirring and maintained under refluxing condition. Small amounts of samples (20 ml each) were taken from the flask at 0, 5, 10, 15, 20, 25, 30, 60, 180, 360 min after the start of heating and the temperature of the aqueous slurry was also recorded. Each sample was cooled down in an ice-water bath, then 5 drops were taken for particle-size measurement and the remainder was centrifuged and washed with dilute 0.2 M acetic acid and water, followed by drying in an oven at 80°C overnight.

Room-temperature XRD (RTXRD, Scintag PAD V using CuK$_{α}$ with λ = 0.15406 nm) was used for crystalline phase identification of the particle samples and determination of crystallite size from 20 = 20–80° with a scan step of 1°. The crystallite size of BaTiO$_3$ powders was calculated by the Scherrer equation

$$d_c = \frac{0.94\lambda}{\beta\cos \theta}$$

(1)

where $d_c$ is the crystallite size, $λ$ is the wavelength, $β$ is the full-width at half-maximum (FWHM), and $θ$ is the diffraction angle. The (2 0 0) peak was used to calculate the crystallite size.

Dynamic light scattering (DLS) was applied to estimate the particle size and particle-size distribution of the resulting BaTiO$_3$ nanoparticle samples. The samples were diluted with deionized water and ultrasonicated for 15 min before analysis. A low-power (10 mW) He–Ne laser tube generates an incidental beam (wavelength 632.8 nm) going through the sample solution. The light that was scattered from the sample was monitored by a photomultiplier tube that was placed at a 90° angle to the incident beam. The data processing was performed using a digital correlator (Model BI-9000AT, Brookhaven Instruments Corp., Holtsville, NY), which collected pulsed signals from the photomultiplier and generated an autocorrelation function. The results are listed in Table I.

The particle size and morphology of the resulting powders were analyzed by TEM (Hitachi HF-2000). A tiny amount of BaTiO$_3$ particles was dispersed into isopropanol by grinding in an agate mortar. A copper grid with a supported thin carbon film was dipped into the suspension, removed, and dried on a filter paper.

### 3. Results and discussion

With the refluxing technique, samples were taken at various stages of the hydrothermal reaction; the temperature and time at each sampling point are recorded and presented in Table I. It can be seen that the temperature reached a stable boiling-point value after 20 min.