

Low Temperature One Step Synthesis of Barium Titanate: Particle Formation Mechanism and Large-scale Synthesis*

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Abstract The formation of BaTiO₃ nanoparticles *via* the reaction of BaCl₂, TiCl₄ and NaOH in aqueous solution has been systematically studied. The formation of BaTiO₃ from the ionic precursors has been elucidated to be a very rapid process, occurring at temperature higher than 60°C. Furthermore, the particle size could be controlled by the proper selection of the synthesis conditions (*e.g.* reactant concentration of 0.5—1.0 mol·L⁻¹, temperature of 80—95°C and pH ≥ 13). A two-step precipitation mechanism was proposed. The first stage of the synthesis involved the formation of amorphous Ti-rich gel phase. The second stage of the synthesis was the reaction between the amorphous phase and the solution-based Ba²⁺ ions, which led to the crystallization of BaTiO₃. Based on the particle formation mechanism, a novel method, high gravity reactive precipitation, was proposed and used to mass production of BaTiO₃ of average particle size of about 60 nm and with narrow particle size distribution. Because it could break up the amorphous Ti-rich gel into small pieces, intensify mass transfer, promote the reaction rate of amorphous Ti-rich gel with Ba²⁺ ions.

Keywords nanoparticles synthesis, particle formation mechanism, barium titanate, perovskite phase, high gravity reactive precipitation

1 INTRODUCTION

Barium titanate (BaTiO₃) is one of the most widely used ferroelectric materials in the electro-ceramics industry, especially for the manufacture of multi-layer ceramic capacitors (MLCCs)^[1—3]. Recently, there has been an emphasis towards the miniaturization of electronic devices. Hence, the trend is to make polycrystalline layers thinner, which requires fine (<1 μm) or ultrafine (<100 nm) particles with controlled, rounded morphology, narrow size distribution, and of high purity. Conventional BaTiO₃ powders obtained by solid-state reaction between TiO₂ and BaCO₃ or by the oxalate route are generally rather coarse, non-uniform and, therefore, not always suitable for preparing very thin layers. In contrast, many chemical methods^[4—19] were proposed for the synthesis of high quality BaTiO₃ powders. Among them, the so-called liquid processes, especially sol-gel technique^[9—12] and hydrothermal synthesis^[13—19], have received particular attention from the viewpoint of stoichiometry control, reproducibility, purity and smaller particle size. The hydrothermal production of barium titanate has been commercialized in both the United States and Japan, and the produced powders were used in diversified application.

In recent years an increasing amount of interest has been focused on the direct precipitation of BaTiO₃ in aqueous medium or mixed organic-aqueous media

at temperatures <100°C and ambient pressure using solutions of organometallic^[7,8] or inorganic compounds^[20—22]. This is due to their low cost and attractive processing conditions (*e.g.* single-step process and high-yield of the anhydrous product). The flurry of attention given to low temperature aqueous synthesis (LTAS)^[20,21] or low temperature direct synthesis (LTDS)^[22] justifies the great need to develop engineering principles for process development, based on thorough understanding of the mechanism and kinetics of powder formation. In the past decade, the kinetics and particle formation mechanism of hydrothermal reactions have been examined by several groups^[23—26] and two transformation mechanisms had been proposed, which were (1) *in-situ* transformation and (2) dissolution-precipitation. However, it is only more recently, Testino *et al.*^[27] had adapted the method for the particle formation mechanism of hydrothermal reactions and systematically investigated the formation kinetics of BaTiO₃ *via* LTAS. Their precipitation experiments were carried out by first premixing the reactant solutions at room temperature, where the gel were formed, and then heating the resulting gel suspension to high temperature. Moreover, Their study was conducted in dilute (≤0.1 mol·L⁻¹) aqueous metal chloride solutions. Thus the BaTiO₃ crystals were formed during heating, with the whole reaction lasting 30—1320 min. The final size of the particles varies

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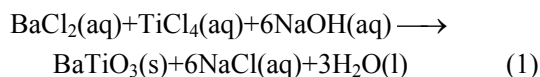
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from about 0.3 to 1.6 μm . However, for the large-scale production of fine and ultrafine BaTiO_3 powders, higher concentration of reactants and shorter reaction time should be considered. Therefore, the kinetic and particle formation mechanism of LTDS using high concentration has yet to be studied in depth.

Consequently, the research objectives of this study were: (1) to evaluate synthesis parameter effects including solution pH, reactant concentration in the initial solution, time and temperature on BaTiO_3 phase development and particle size, (2) to gain a better understanding of the formation mechanism of barium titanate particle from high aqueous metal chloride solutions *via* direct synthesis at low temperature, and (3) to choose an appropriate reactor and feasible technique [*i.e.* high gravity reactive precipitation (HGRP)] for the mass production of BaTiO_3 nanoparticles.

2 EXPERIMENTAL

Barium titanate was prepared *via* precipitation reaction in aqueous solution, according to the following reaction



The reagents used were of chemical grade without further purification. At first, pure TiCl_4 was slowly added into ice water to form $2\text{mol}\cdot\text{L}^{-1}$ Ti precursor solution. Then the Ti precursor solution was added to $2\text{mol}\cdot\text{L}^{-1}$ BaCl_2 solution at room temperature to form the mixed chloride solution with constant stirring rate. The mixed chloride solution was filtered to remove any particulate impurities. Then the above mixed chloride solution was diluted to detail concentration for given experiment. To monitor the progress of crystallization in the reactor, a 1.0L glass reaction-vessel was fitted with a condenser, thermocouple, gas inlet port, and a sampling dip-tube. In a 'standard' run, 300ml of a mixed chloride solution was introduced instantaneously into the reactor, which was previously filled with 300ml NaOH solution preheated to 80°C and with adequate stirring. More details of experimental parameters were described in Table 1. The temperature of the reactor was regulated by means of a thermostatic bath. Process samples (about 30ml) were collected *via* syringes, with the temperature and reaction time recorded for each sample. 'Time-zero' corresponded to the instant whereby the mixed chlorides were added into the reactor. Each collected sample was quickly cooled to below 5°C by liquid nitrogen. The suspensions were eventually washed thrice with 10ml of distilled water, and freeze-dried.

For the HGRP synthesis, the key part of the rotating packed bed (RPB, Hige machine) is a packed rotator, with an inner and outer diameter of 50mm and 150mm, respectively. The axial width of the rotating bed is 50mm. More details about this equipment can

be seen in our previous paper^[28]. The entire experimental setup was made of titanium. In a typical run, mixed BaCl_2 - TiCl_4 solution, and NaOH solution were simultaneously and continuously pumped from their storage tanks into different slotted pipe distributors. The two liquid streams parallel sprayed onto the inside edge of the rotator, mix and react together to yield particles. The rotated packing provided intense mixing for the reaction to yield the white precipitate of BaTiO_3 . The flow rates of the mixed chlorides and NaOH solutions were kept constant at 40 and $35\text{L}\cdot\text{h}^{-1}$ respectively. The high-gravity level, g_r [here, $g_r = (2\pi N/60)^2 \cdot \frac{d_{\text{in}} + d_{\text{out}}}{2}$, where N is the rotating

speed of the rotator in rpm, $d_{\text{in}}=50\text{mm}$ is the inner diameter and $d_{\text{out}}=150\text{mm}$ is the outer diameter] for RPB, was $1579\text{m}\cdot\text{s}^{-2}$. The entire precipitation process lasted 15min and was carried out in air at 85°C , which was maintained by a constant-temperature circulation from a thermostat. After the reaction was finished, the BaTiO_3 suspension was filtered and the solid was then washed with de-ionized water to remove the side products. The powders were then dried at 100°C . The concentration of BaCl_2 in the mixed chloride solution was $0.5\text{mol}\cdot\text{L}^{-1}$. The quantities of reactants were determined in advance such that a final concentration of $0.25\text{mol}\cdot\text{L}^{-1}$ BaTiO_3 suspension was resulted if the precursors reacted to completion. The concentration of NaOH solution was that required to achieve $\text{pH}>13$ after quantitative precipitation of BaTiO_3 according to reaction (1). In view of the fact that a small amount of barium ions was often found to remain in solution during the direct liquid precipitation of barium titanate, an additional 7% (mol) of barium chloride was added to achieve stoichiometric precipitation of barium ions.

The as-prepared powders collected under different conditions and reaction times, were characterized *via* different techniques. The relative primary particle size and morphology of selected BaTiO_3 powders were characterized *via* transmission electron microscopy (TEM, Hitachi H-800, Cambridge, UK) and scanning electron microscopy (SEM, Philips XL30 ESEM-FEG). The TEM instrument was equipped with a system performing selected area electron diffraction (SAED) to further characterize BaTiO_3 nanostructures. 100 BaTiO_3 particles were measured to determine the average particle size from TEM or SEM. Phase identification was conducted *via* an X-ray diffractometer (Shimadzu XRD-6000) with Cu K_α radiation at a scan speed of $2^\circ\cdot\text{min}^{-1}$. A S250MK-30 SEM (Cambridge, UK) equipped with a LINK AN10000 energy-dispersive spectroscopy (EDS) system with a Si(Li) detector (nominal resolution 65keV at Mn K_α) was used to semi-quantitatively analyze the chemical composition of the as-prepared powders.

3 RESULTS AND DISCUSSION

3.1 Synthesis results

To investigate the effects of reaction temperature, molar ratio of $[\text{BaCl}_2]/[\text{TiCl}_4]$, and the concentration of reactants on the properties of the resulting particles, separate experiments were carried out by varying single parameter with other parameters kept constant as in the 'standard' run. Detailed information of tested experimental conditions is listed in Table 1.

(1) Effect of temperature

The reaction temperature had a pronounced effect on the final products (Table 1, Nos. 1—5). At room temperature, although the formation of BaTiO_3 was feasible from a thermodynamical point of view^[29–31], BaTiO_3 particle formation was not experimentally observed even after a very long time (*i.e.* 12h) due to slow kinetics in good agreement with literature reports^[27,32]. Pseudo-cubic BaTiO_3 was detected at 60°C and above, with small amount of a secondary phase consisting of BaCO_3 . Possible explanations to this phenomenon were: ① higher temperature led to improved crystallinity of BaTiO_3 ; ② fast reaction, avoided the superabundant contamination of CO_2 and subsequently the formation of BaCO_3 impurities.

(2) Effect of molar ratio $[\text{BaCl}_2]/[\text{TiCl}_4]$

It is observed from Table 1 (*i.e.* samples 5 to 9) that when the molar ratio of $[\text{BaCl}_2]/[\text{TiCl}_4] < 1.0$, amorphous, irregular and aggregated substances with large particle size were formed, but when the molar ratio > 1.0 , spherical pseudo-cubic BaTiO_3 particles were formed. The size of particles decreased slightly

with further increase in Ba/Ti molar ratio, and the Ba/Ti molar ratio of the final products could be regulated close to a stoichiometric unity *via* controlling the washing procedures. However, only a few experiments were performed to study the effect of this parameter and additional data should be collected.

(3) Effect of BaCl_2 concentration

From the experimental results (*i.e.* Table 1, samples 5, 10—14), a critical BaCl_2 concentration threshold of about $0.1\text{mol}\cdot\text{L}^{-1}$ was identified. Above this value, complete conversion to BaTiO_3 could be attained within a few minutes; below this value, crystallization was much slower and the resulting precipitate had $\text{Ba/Ti} < 1$. This was because higher reactant concentrations (and, consequently, of supersaturation) lead to higher nucleation rates, producing a larger number of smaller nucleuses, which favors the precipitation of particles with much smaller size and uniform size distribution. However, excessively high concentration could effect the separation of $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ from the solution^[29], which could affect the accurate control of the Ba/Ti molar ratio.

(4) Effect of NaOH concentration

Precipitation reaction with high concentration of OH^- would maintain a high degree of supersaturation in the reaction system. This would lead to improved crystallinity of BaTiO_3 .

From Table 1 (*i.e.* samples 5, 15, 16), it was observed that at high pH (*i.e.* $C_{\text{NaOH}} \geq 6.0\text{mol}\cdot\text{L}^{-1}$), pure and well-defined cubic phase BaTiO_3 was obtained; while at low pH (*i.e.* $C_{\text{NaOH}} \leq 2.0\text{mol}\cdot\text{L}^{-1}$), the resulting

Table 1 Experimental conditions for the preparation of BaTiO_3 by the LTDS process

| No. | Temp., °C | $[\text{NaOH}]_{\text{stock}}$, $\text{mol}\cdot\text{L}^{-1}$ | $[\text{BaCl}_2]_{\text{stock}}$, $\text{mol}\cdot\text{L}^{-1}$ | $[\text{BaCl}_2]/[\text{TiCl}_4]$ | Primary phase | Minor phase | Morphology | Mean size, nm |
|----------------|--------------|--|--|-----------------------------------|------------------|----------------|------------|------------------|
| 1 | 25 | 6.0 | 0.5 | 1.07 | AM | BC, NA | I, A | |
| 2 | 60 | 6.0 | 0.5 | 1.07 | BT | BC, AM | S, A | 110 |
| 3 | 75 | 6.0 | 0.5 | 1.07 | BT | BC | S, A | 90 |
| 4 ^① | 80 | 4.0 | 0.5 | 1.07 | BT | BC | S | 80 |
| 5 | 90 | 6.0 | 0.5 | 1.07 | BT | | S | 60 |
| 6 | 90 | 6.0 | 0.5 | 0.8 | AM | BT | I, A | |
| 7 | 90 | 6.0 | 0.5 | 0.95 | BT | AM | S, I, A | 80 |
| 8 | 90 | 6.0 | 0.5 | 1.15 | BT | | S | 60 |
| 9 | 90 | 6.0 | 0.5 | 1.2 | BT | BC | S | 60 |
| 10 | 90 | 6.0 | 0.1 | 1.07 | AM, BC | BT | I, A, S | |
| 11 | 90 | 6.0 | 0.05 | 1.07 | AM, BC | | I, A | |
| 12 | 90 | 6.0 | 0.2 | 1.07 | BT | BC | I, S | 90 |
| 13 | 90 | 6.0 | 0.7 | 1.07 | BT | | S | 50 |
| 14 | 90 | 6.0 | 1.0 | 1.07 | BT | | S | 40 |
| 15 | 90 | 2.0 | 0.5 | 1.07 | AM | BC, NA | A, I | |
| 16 | 90 | 3.5 | 0.5 | 1.07 | BT | AM, BC | S, A | 100 |

① Standard conditions, reaction time 10 min.

Note: AM: amorphous phase; BC: BaCO_3 (witherite, JCPDS No. 05-0378); BT: cubic BaTiO_3 (JCPDS No. 31-0174); NA: NaCl (halite, JCPDS No. 05-0628).

S: spheres; A: aggregates; I: irregular.

particles were irregular and aggregated. However, a moderate concentration of NaOH was preferentially desired because excess NaOH would lead to a defect in the crystal lattice^[22], coupled with certain environmental repercussions.

As discussed previously, it was evident that the reaction temperature was an important factor influencing the formation of BaTiO₃ particles. When the temperature was higher than 60°C, good crystallinity for BaTiO₃ product could be achieved. Hence, moderate conditions (*i.e.* reaction temperature of 80°C) were employed in the subsequent study of the particle formation mechanism *via* LTDS.

3.2 Formation mechanism

The reaction proceeded at the standard conditions and samples were taken at various stages to monitor the growth development of the BaTiO₃ particles. Fig.1 and 2 illustrated the typical TEM micrographs with SAED pattern inset, and XRD patterns of the as-synthesized BaTiO₃ powders respectively.

As observed from Fig.1(a), sample 1 (15s) constituted mainly of amorphous gel, with some BaTiO₃ nuclei existing distinctively among gel. The XRD pattern indicated that the main peaks could be indexed to halite (JCPDS No. 05-0628) of NaCl. The SAED pattern exhibited only faint diffuse rings indicative of amorphous substances (*i.e.* typical feature of gel). The EDS analysis gave additional evidence that the gel was enriched in Ti, with traces of Ba²⁺ ions. The XRD patterns were in good agreement with the EDS results.

Crystalline particles, distinct from the nuclei, were detected in samples taken at time of 30s [in Fig.1(b)]. The progressive growth of primary BaTiO₃ nanocrystals was evident in the samples taken after 1min [Figs.1(c), (d), (e)]. It was observed that in Fig.1(e), the majority of particles were single crystals, with some double- or triple-paired crystallites. Images of some isolated nanocrystals at higher magnification revealed a thin outer-layer surrounding some BaTiO₃ crystal particles, which suggested the possibility of crystal lattice defects. The crystal lattice defects could be eliminated *via* a long time drying at 120°C [See Fig.1(f)]. Overall the SAED patterns indicated the morphological evolution of the solid phase supported nucleation and growth. The XRD analysis (Fig.2) showed process lagged behind but in accord with that of TEM. In addition, according to the EDS examination, the ratio of Ba and Ti increased with reaction progression, ultimately achieving a stoichiometric ratio close to 1:1.

Based on the above experimental results, the formation mechanism of BaTiO₃ *via* the reaction between a mixed BaCl₂-TiCl₄ solution and liquid NaOH at 80°C could be illustrated by Fig.3. Basically, it was similar with the particle formation mechanism of LTAS at lower concentration^[27], and there were two

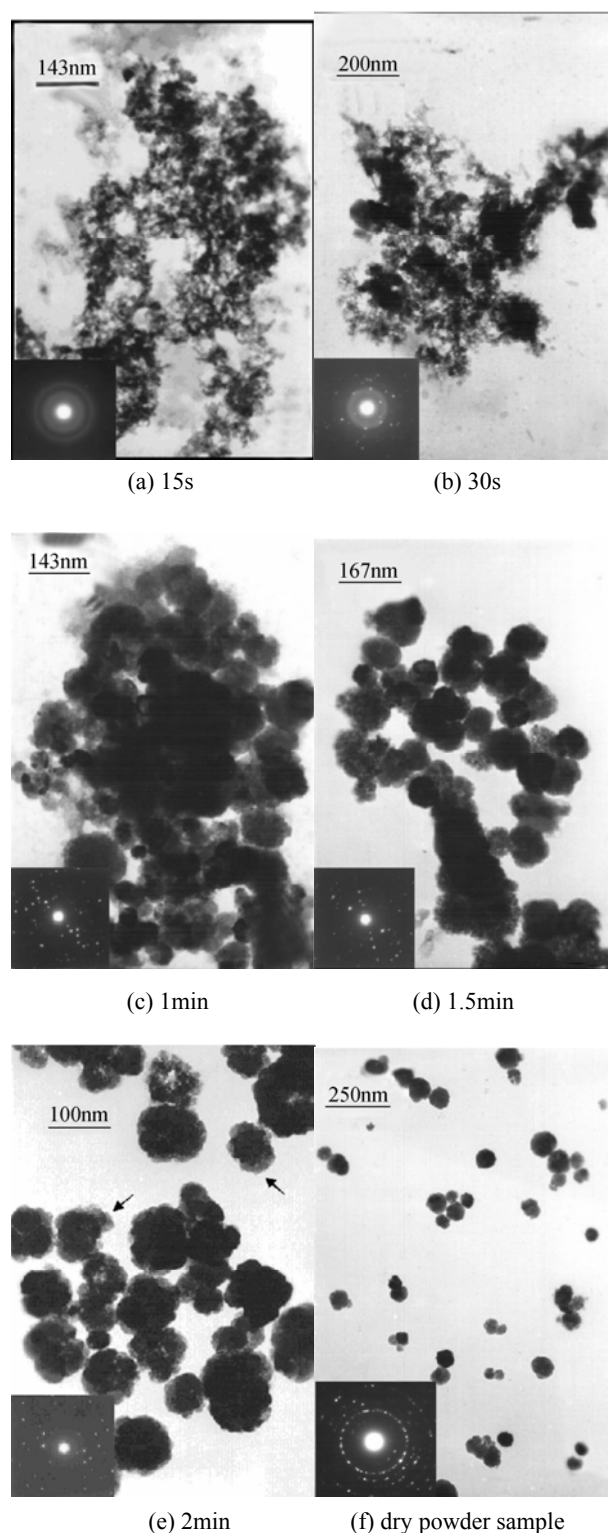


Figure 1 TEM micrographs with SAED pattern inset of the samples at different reaction time

stages involved. The first stage of the LTDS, involved with the formation of the Ti-rich amorphous phase. The second stage of the LTDS was the crystallization of BaTiO₃ *via* the reaction of the amorphous phase with Ba²⁺ or BaOH⁺ left in solution. Eventually, the nanocrystalline BaTiO₃ particles were formed following

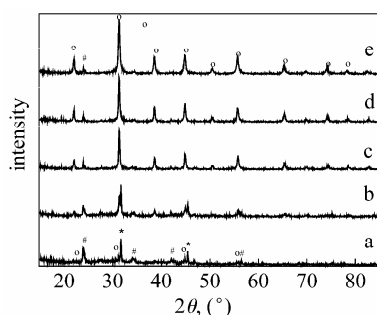


Figure 2 XRD patterns showing the influence of the reaction time on the formation of cubic BaTiO₃ particles by LTDS

a—15s; b—30s; c—1min; d—1.5min; e—2min; o BaTiO₃; # BaCO₃; * NaCl

nucleation and growth. Quite often, it was impossible to determine whether the initial nucleation was predominantly homogeneous or heterogeneous.

Although thermodynamic variables have influence on both the reaction and crystallization kinetics, the non-thermodynamic variables associated with the reactors used in ceramic powder crystallization, are also very important. As our previous study^[33] indicated, the mixing conditions were found to have a significant influence on the particle size distribution and on the formation of secondary phases. In particular, if the reactants were not efficiently mixed, composition inhomogeneities would be produced and the particle size distribution became wider. Moreover, the crystallization of BaTiO₃ is slowed down. Hence, reactor selection was of paramount importance to the final products. Moreover, if we can choose a suitable mixer and process, the batch production technique can be easily extended to a continuous precipitation process.

3.3 The HGRP route for large-scale BaTiO₃ nanopowder preparation

The relationship between the characteristic micromixing time (t_m) and the induction time (t_n) has great impact on both reaction and nucleation (*i.e.* con-

trolled by the intrinsic kinetics when $t_m < t_n$, and controlled or influenced by micromixing while $t_m > t_n$)^[34]. For a conventional stirred tank reactor, $t_m \gg t_n$, which implies that the particle size distribution cannot be easily controlled, and any subsequent scale-ups will result in poor micromixing.

HGRP platform in the form of a rotating packed bed (RPB) is effective to intensify the mass transfer and heat transfer in multiphase systems. The basic principle is to create a high-gravity environment *via* the centrifugal forces. In a RPB the gravity is of the order of several hundred to even several thousand times higher than the gravitational acceleration of the earth. Hence, the fluids in RPB could be spread out or split into micro/nano droplets, threads or thin films^[35]. In addition, micromixing and mass transfer rate in a RPB is 1–3 orders of magnitude better than that achievable in a conventional stirred tank reactor, very beneficial in establishing highly supersaturated product concentration in the precipitation process. The value of t_m in the RPB is about 10–100 μ s, which is smaller than the typical value of t_n in aqueous solution^[28,35,36]. Hence, it could meet the requirement of $t_m < t_n$ and consequently, the particle size distribution could be well-controlled. HGRP technique has been successfully employed in industry for the production of nanosized calcium carbonate. Three commercial production lines having an annual capacity of 10000 tons, have been instrumental in the production of nanosized CaCO₃ at average particle size of 15–30nm since 2001^[28]. Recently, HGRP platform has also been proven successful in the generation of uniform crystalline aluminium hydroxide, zinc sulfide and titanium oxide nanoparticles^[37–39].

As discussed previously, the network-like Ti-rich gel, which was instantaneously formed in the early stages of the reaction, was of very small size in the RPB, resulting in the nucleation and growth of BaTiO₃ crystals in a uniform environment. To date, the nanosized BaTiO₃ production *via* the HGRP platform

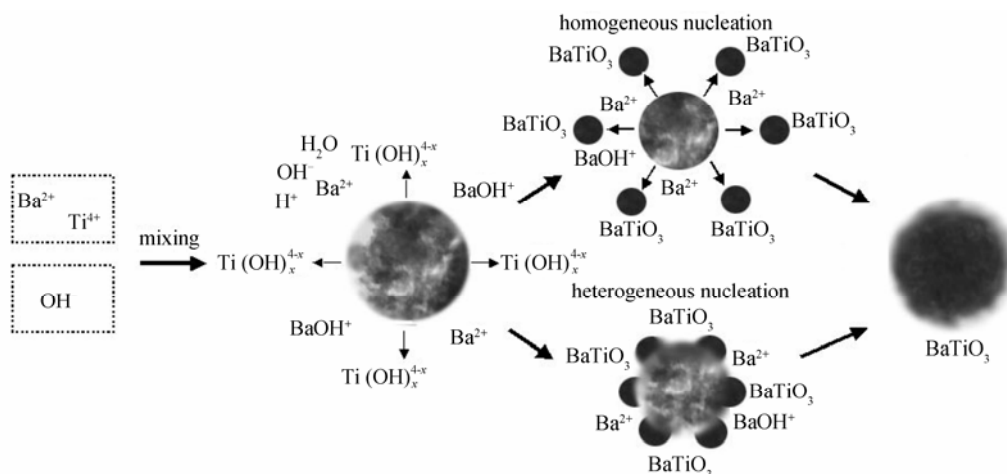
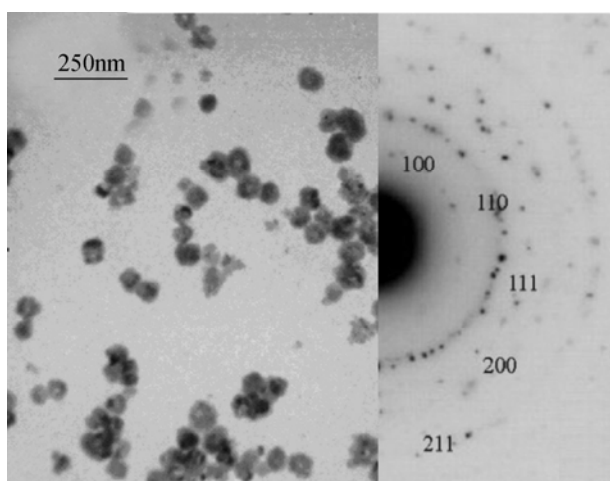
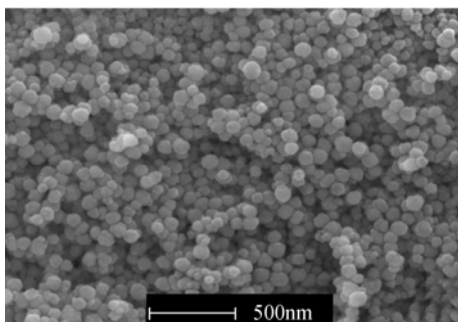


Figure 3 Proposed BaTiO₃ particle formation mechanism by LTDS using BaCl₂·2H₂O and TiCl₄ as ionic precursors and NaOH as mineralizer

was very encouraging. Preliminary results [*i.e.* Fig.4(a) and 4(c)] had demonstrated that the BaTiO₃ product by HGRP consists entirely of individual barium titanate nanoparticles with little aggregation. The particles were uniform in size and mostly spherical. Typically, The primary average particle size of HGRP powder was about 60nm, which was much finer than the controlled double-jet precipitation (CDJP)-obtained powder^[21], while crystallinity and phase are further confirmed by SAED analysis [Fig.4(b)], revealing diffraction rings typical for the barium titanate phase. Furthermore, the achieved particle size distribution was also much narrower than that of the batch stirred tank reactor (BSTR)-obtained powders^[40].



(a) An overview image of TEM (b) Selected area electron diffraction with diffraction rings corresponding to the BaTiO₃ phase



(c) SEM image of a BaTiO₃ nanosphere ensemble

Figure 4 Representative TEM and SEM micrographs of as-synthesized BaTiO₃ nanoparticles by typic HGRP ($g \cdot 1579m \cdot s^{-2}$; flow rate for mixed chlorides and NaOH solutions: 40 and 35L·h⁻¹; the concentration of BaCl₂ in mixed chloride solution: 0.5mol·L⁻¹; temperature: 85°C; Ba/Ti ratio in mixed chlorides: 1.07)

At the same time, the size of BaTiO₃ particles can be tailored by changing synthesis parameters. Increasing the high-gravity level and concentration of mixing chlorides solution introduced resulted in the formation of smaller BaTiO₃ particles (*i.e.* 30nm)^[41]. The reactant solutions of the metal salts can be used in

high concentrations and the yield is quantitative. Despite the moderate size of the experimental reactor, about 5.0kg of the well-defined crystalline barium titanate powder can be generated per hour, which can be further increased. Further investigations are underway.

4 CONCLUSIONS

In this paper, the synthesis and particle formation of BaTiO₃ nanoparticles by low temperature direct synthesis was demonstrated *via* the direct reaction of BaCl₂, TiCl₄ and NaOH solutions. It was found that the variation of the operating parameters, like temperature, pH, feedstock composition and reagent concentration, influenced the phase, morphology and particle formation rate of BaTiO₃. The reaction process involved two steps: Ti-rich gel formation and crystallization of BaTiO₃. The Ti-rich gel formation was instantaneous and after nucleation and growth, nanocrystalline BaTiO₃ particles were formed. Nucleation apparently occurred in the amorphous phase and the perovskite crystals grew at the expense of the parent phase. The driving force for nucleation and growth was affected by supersaturation.

A reactive-precipitation method, the high gravity reactive precipitation, has been used to mass production of BaTiO₃ nanoparticles. This method circumvented the restrictions posed by the existing methods, and could be used for the mass production of BaTiO₃ with tunable size and narrow particle size distribution.

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REFERENCES

- Chandler, C.D., Roger, C., Hampden-Smith, M.J., "Chemical aspects of solution routes to perovskite-phase mixed-metal oxides from metal-organic precursors", *Chem. Rev.*, **93**, 1205(1993).
- Millis, A.J., "Lattice effects in magnetoresistive perovskites", *Nature*, **392**, 147(1998).
- Pena, M.A., Fierro, J.L.G., "Chemical structures and performance of perovskite oxides", *Chem. Rev.*, **101**, 1981(2001).
- Potdar, H.S., Deshpande, S.B., Date, S.K., "Chemical coprecipitation of mixed (Ba+Ti) oxalates precursor leading to BaTiO₃ powders", *Mater. Chem. Phys.*, **58**, 121(1999).
- Hu, M.Z.C., Miller, G.A., Payzant, E.A., Rawn, C.J., "Homogeneous (co)precipitation of inorganic salts for synthesis of monodispersed barium titanate particles", *J. Mater. Sci.*, **35**, 2927(2000).
- Rumpf, H., Modrow, H., Hormes, J., Glasel, H.J., Hartmann, E., Erdem, E., Bottcher, R., Hallmeier, K.H., "Preparation of nanocrystalline BaTiO₃ characterized by *in Situ* X-ray absorption spectroscopy", *J. Phys. Chem. B*, **105**, 3415(2001).
- Kumar, V., "Solution-precipitation of fine powders of barium titanate and strontium titanate", *J. Am. Ceram. Soc.*, **82**, 2580(1999).
- Grohe, B., Mieke, G., Wegner, G., "Additive controlled

- crystallization of barium titanate powders and their application for thin-film ceramic production: (I). Powder synthesis", *J. Mater. Res.*, **16**, 1901(2001).
- 9 Frey, M.H., Payne, D.A., "Synthesis and processing of barium titanate ceramics from alkoxide solutions and monolithic gels", *Chem. Mater.*, **7**, 123(1995).
 - 10 Shimooka, H., Kohiki, S., Kobayashi, T., Kuwabara, M., "Preparation of translucent barium titanate ceramics from sol-gel-derived transparent monolithic gels", *J. Mater. Chem.*, **10**, 1511(2000).
 - 11 Hung, K.M., Yang, W.D., Huang, C.C. "Preparation of nanometer-sized barium titanate powders by a sol-precipitation process with surfactants", *J. Eur. Ceram. Soc.*, **23**, 1901(2003).
 - 12 Dixit, A., Majumder, S.B., Dobal, P.S., Katiyar, R.S., Bhalla, A.S., "Phase transition studies of sol-gel deposited barium zirconate titanate thin films", *Thin Solid Films*, **447/448**, 284(2004).
 - 13 Dutta, P.K., Gregg, J.R., "Hydrothermal synthesis of tetragonal barium titanate (BaTiO₃)", *Chem. Mater.*, **4**, 843(1992).
 - 14 Lencka, M.M., Nielsen, E., Anderko, A., Riman, R.E., "Hydrothermal synthesis of carbonate-free strontium zirconate: thermodynamic modeling and experimental verification", *Chem. Mater.*, **9**, 1116(1997).
 - 15 Clark, I.J., Takeuchi, T., Ohtori, N., Sinclair, D.C., "Hydrothermal synthesis and characterisation of BaTiO₃ fine powders: precursors, polymorphism and properties", *J. Mater. Chem.*, **9**, 83(1999).
 - 16 Ciftci, E., Rahaman, M.N., "Hydrothermal precipitation and characterization of nanocrystalline BaTiO₃ particles", *J. Mater. Sci.*, **36**, 4875(2001).
 - 17 Walton, R.I., Millange, F., Smith, R., Hansen, T.C., O'Hare, D., "Real time observation of the hydrothermal crystallization of barium titanate using *in situ* neutron powder diffraction", *J. Am. Chem. Soc.*, **123**, 12547(2001).
 - 18 Xu, H., Gao, L., Guo, J.K., "Hydrothermal synthesis of tetragonal barium titanate from barium chloride and titanium tetrachloride under moderate conditions", *J. Am. Ceram. Soc.*, **85**, 727(2002).
 - 19 Mao, Y.B., Banerjee, S., Wong, S.S., "Hydrothermal synthesis of perovskite nanotubes", *Chem. Commun.*, 408(2003).
 - 20 Nanni, P., Leoni, M., Buscaglia, V., Aliprandi, G., "Low-temperature aqueous preparation of barium metatitanate powders", *J. Eur. Ceram. Soc.*, **14**, 85(1994).
 - 21 Her, Y.S., Matijevic, E., Chon, M., "Preparation of well-defined colloidal barium titanate crystals by the controlled double-jet precipitation", *J. Mater. Res.*, **10**, 3106(1995).
 - 22 Wade, S., Tsurumi, T., Chikamori, H., Noma, T., Suzuki, T., "Preparation of nm-sized BaTiO₃ crystallites by a LTDS method using a highly concentrated aqueous solution", *J. Cryst. Growth*, **229**, 433(2001).
 - 23 Eckert, J.O.J., Hung-Houston, C.C., Gersten, B.L., Lencka, M.M., Riman, R.E., "Kinetics and mechanisms of hydrothermal synthesis of barium titanate", *J. Am. Ceram. Soc.*, **79**, 2929(1996).
 - 24 Zhao, L., Chien, A.T., Lange, F.F., Speck, J.S., "Microstructural development of BaTiO₃ powders synthesized by aqueous methods", *J. Mater. Res.*, **11**, 1325(1996).
 - 25 Wang, X., Lee, B. I., Hu, M.Z., Payzant, E.A., Blow, D.A., "Mechanism of nanocrystalline BaTiO₃ particle formation by hydrothermal refluxing synthesis", *J. Mater. Sci.*, **14**, 495(2003).
 - 26 Moon, J., Suvaci, E., Morrone, A., Costantino, S.A., Adair, J.H., "Formation mechanisms and morphological changes during the hydrothermal synthesis of BaTiO₃ particles from a chemically modified, amorphous titanium (hydrrous) oxide precursor", *J. Eur. Ceram. Soc.*, **23**, 2153(2003).
 - 27 Testino, A., Buscaglia, M.T., Buscaglia, V., Viviani, M., Bottino C., Nanni, P., "Kinetics and mechanism of aqueous chemical synthesis of BaTiO₃ particles", *Chem. Mater.*, **16**, 1536(2004).
 - 28 Chen, J.F., Wang, Y.H., Guo, F., Wang, X.M., Zheng C., "Synthesis of nanoparticles with novel technology: High-gravity reactive precipitation", *Ind. Eng. Chem. Res.*, **39**, 948(2000).
 - 29 Lencka, M.M., Riman, R.E., "Thermodynamic modeling of hydrothermal synthesis of ceramic powders", *Chem. Mater.*, **5**, 61(1993).
 - 30 Lencka, M.M., Riman, R.E., "Hydrothermal synthesis of perovskite materials: thermodynamic modeling and experimental verification", *Ferroelectrics*, **151**, 159(1994).
 - 31 Lencka, M.M., Riman, R.E., "Thermodynamics of the hydrothermal synthesis of calcium titanate with reference to other alkaline-earth titanates", *Chem. Mater.*, **7**, 18(1995).
 - 32 MacLaren, I., Ponton, C.B., "A TEM and HREM study of particle formation during barium titanate synthesis in aqueous solution", *J. Eur. Ceram. Soc.*, **20**, 1267(2000).
 - 33 Shen, Z.G., Li, S.G., Liu, C.W., Zhang, J.W., Chen, J.F., "Low temperature one step synthesis of barium titanate: Thermodynamic modeling and experimental synthesis", *Chin. J. Chem. Eng.*, **13**(2), 225(2005).
 - 34 Dirksen, J.A., Ring, T.A., "Fundamentals of crystallization: kinetic effects on particle size distributions and morphology", *Chem. Eng. Sci.*, **46**, 2389(1991).
 - 35 Guo, K., Guo, F., Feng, Y.D., Chen, J.F., Zheng, C., "Synchronous visual and RTD study on liquid flow in rotating packed-bed contactor", *Chem. Eng. Sci.*, **55**, 1699(2000).
 - 36 Chen, J.F., Zheng, C., Chen, G.T., "Interaction of macro- and micromixing on particle size distribution in reactive precipitation", *Chem. Eng. Sci.*, **51**, 1957(1996).
 - 37 Chen, J.F., Shao, L., Guo, F., Wang, X.M., "Synthesis of nano-fibers of aluminum hydroxide in novel rotating packed bed reactor", *Chem. Eng. Sci.*, **58**, 569(2003).
 - 38 Chen, J.F., Li, Y.L., Wang, Y.H., Yun, J., Cao, D.P., "Preparation and characterization of zinc sulfide nanoparticles under high-gravity environment", *Mater. Res. Bull.*, **39**, 185(2004).
 - 39 Chen, J.F., Shao, L., Zhang, C.G., Chen, J.M., Chu, G.W., "Preparation of TiO₂ nanoparticles by a rotating packed bed reactor", *J. Mater. Sci. Lett.*, **22**, 437(2003).
 - 40 Chen, J.F., Shen, Z.G., Liu, F.T., Liu, X.L., Yun, J., "Preparation and properties of barium titanate nanopowder by conventional and high-gravity reactive precipitation methods", *Scr. Mater.*, **49**, 509(2003).
 - 41 Shen, Z.G., Shao, L., Chen, J.F., Yun, J., "Mass production of Ba_{1-x}Sr_xTi_{1-y}Zr_yO₃ (0 ≤ x ≤ 1, 0 ≤ y ≤ 0.5) nanoparticles", *Mater. Lett.*, **59**, 2232 (2005).