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Journal of the European Ceramic Society 24 (2004) 3553–3557

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Short-range dissolution–precipitation crystallization of hydrothermal barium titanate

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Received 3 September 2003; received in revised form 25 November 2003; accepted 13 December 2003

Abstract

A modified autoclave was used to investigate the crystallization mechanism of $BaTiO_3$ during the hydrothermal reaction of $Ba(OH)_2$ and TiO_2 anatase. An uneven distribution of the crystallized $BaTiO_3$ particles was observed: more than 99 wt.% of total $BaTiO_3$ particles remained where the precursor TiO_2 was put; less than 1 wt.% was collected from the areas away from the TiO_2. According to the experimental observations in this work and proofs reported in the literature, we propose that the crystallization mechanism is dissolution–precipitation in nature, but the soluble Ti^{4+} species can only redisperse in a short distance away from TiO_2 particles before precipitation. In other words, the nucleation of hydrothermal $BaTiO_3$ starts at a low concentration of Ti^{4+}. The mechanism of the $Ba(OH)_2$–$Ti(OH)_4$ reaction is a fast dehydration process.

Keywords: $BaTiO_3$ and titanates; Perovskites; Hydrothermal methods; Crystallisation

1. Introduction

$BaTiO_3$ is, perhaps, the best-known perovskite material and has been broadly used as a dielectric material in multi-layer ceramic capacitors (MLCCs). Hydrothermal technique is one of the most widely used methods for synthesis of well-defined submicron $BaTiO_3$ particles, which are characterized by small particle size with narrow size distribution and high purity. The hydrothermal synthesis of $BaTiO_3$ could be carried out with a variety of precursors, such as $Ba(OH)_2$–$TiCl_4$,[1] $Ba(OH)_2$–TiO_2 powder,[2] barium compounds–titanium alkoxides,[3] $BaCl_2$–$TiCl_4$,[4] or some combinations of the above barium and titanium sources.[5–7]

Since the $Ba(OH)_2$ and TiO_2 reaction pair is the least expensive but the easiest to handle, much research has been done to study the reaction. Two crystallization mechanisms have been proposed so far. One is the dissolution–precipitation mechanism[1,6,8] that involves a process of dissolution first, then followed by homogeneous nucleation and growth of $BaTiO_3$ throughout the bulk solution. The other one is the in situ diffusion–transformation mechanism[9,10] that involves a process of diffusion-controlled in situ transformation from the TiO_2 phase to $BaTiO_3$ phase. Both mechanisms are supported by some experimental evidences. However, none of those evidences can definitely rule out the possibility of the mechanism that it does not support. Thus, some researchers[11,12] proposed the possibility of competitive co-existence of the two mechanisms or a sequential domination in a proposed multistage mode.

However, it is difficult to use the in situ diffusion transformation mechanism to explain some of the experimental observations reported in the literature. Questions, such as why higher basicity facilitates the formation of $BaTiO_3$,[13] and why solvothermal of $BaTiO_3$ in non-aqueous media is difficult,[3] since the OH^- group was not necessary for the diffusion of Ba^{2+} in TiO_2 are relevant. What caused the formation of the rounding of $BaTiO_3$ particle surface[11] and the formation of necks between $BaTiO_3$ particles,[6] since Ti^{4+} did not move? Why increasing the Ba/Ti ratio decreased the $BaTiO_3$ particle size, but the ratio of 20 or higher gave a constant particle size?[14] Among these observations, the report by Pinceloup et al.[6] about the relation between solubility and $BaTiO_3$ particle size is a strong proof of a dissolution–precipitation mechanism.

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0955-2219/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2003.12.007

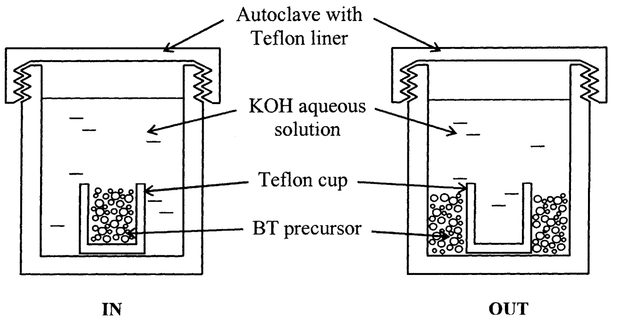

Fig. 1. Specially configured device for hydrothermal synthesis of $BaTiO_3$: IN type and OUT type.

In this work, the hydrothermal reaction of $BaTiO_3$ with different precursors was carried out in a specially configured device as shown in Fig. 1. Basically, it is a normal hydrothermal reaction, but the difference is that the starting solid precursors are confined to certain area within the autoclave. A dissolution-then-precipitation process, if it happens, will cause the presence of $BaTiO_3$ particles in other areas. Thus, the distribution of the final $BaTiO_3$ particles might cast a light on their crystallization history.

2. Experimental procedure

2.1. Hydrothermal reaction of $Ba(OH)_2$ and TiO_2

We mixed 12 g of $Ba(OH)_2$ (98.1%, Fisher) and 2 g of TiO_2 anhydrous (anatase, 99%, Fisher) by a spatula with a Ba/Ti molar ratio of 1.5:1. This Ba–Ti mixture was put into an autoclave, and an aqueous solution of KOH was added to bring up the total volume to 80 ml and to adjust the pH to 14.

2.2. Hydrothermal reaction of $Ba(OH)_2$ and $TiCl_4$

We dissolved 14.2 g of $Ba(OH)_2$ powder in 50 ml distilled water by heating to 90 °C. This solution was then cooled to room temperature before 5.7 g of $TiCl_4$ (99.9%, Aldrich) was added dropwise, giving Ba/Ti ratio of 1.5:1. The resultant white suspension was centrifuged at a speed of 3000 rpm for 2 min. The precipitate was separated from the supernatant liquid and put into an autoclave first. Then the supernatant liquid was slowly added in. Distilled water and a 10 M KOH aqueous solution were used to adjust the total volume to 80 ml and the pH to 14.

2.3. Configuration of hydrothermal autoclave

The autoclave device is schematically shown in Fig. 1. A Teflon cup (capacity of 16.7 ml) was put inside the Teflon liner (capacity of 97 ml) of the autoclave. The space inside the autoclave was defined as two connected chambers, i.e. the inside-cup chamber and the outside-cup chamber.

The reactions were carried out with two different configurations. One is that the starting solid precursors were put completely in the Teflon cup (IN type). The other one is placing all the starting precursors outside of the cup (OUT type). So, one chamber was used as the reaction chamber and the other was used as the collection chamber. Addition of liquid after loading the starting precursors was carried out carefully without causing any agitation that will transport the precursor powders from one chamber to the other.

For each Ti precursor (TiO_2 and $TiCl_4$), two samples were prepared with IN and OUT configuration, respectively. All the four samples were prepared at 200 °C for 5 h.

3. Results and discussion

The purpose of the above device configuration was to examine the distribution of crystallized $BaTiO_3$ particles, assuming that at least one of the two crystallization mechanisms happens. In a homogeneous dissolution–precipitation process, the final $BaTiO_3$ particles will appear in the other chamber that is empty at beginning, provided that they can drift that far. If the in situ diffusion transformation is the case, the final $BaTiO_3$ particles will stay in the chamber where TiO_2 is placed.

One possible confusing factor is the convection of liquid during reactions, which might physically transport either the reactants or the products from one chamber to the other. Thus, any agitation during reaction was avoided. The observed distributions of the final powders and the X-ray diffraction (XRD) analysis of all the particles collected at different chambers are listed in Table 1.

For all the four experiments, more than 99 wt.% of the total final solid particle remained where they had been placed (the reaction chamber). In the two IN cases, less than 0.1 wt.% of the total final particles was collected from outside of the cup; in the two OUT cases, about 0.5 wt.% of the total final particles was collected from inside the cup.

Obviously, such an uneven distribution rules out the possibility of a long-range dissolution–precipitation process. Although the presence of $BaTiO_3$ could be identified in those traces collected from the collection chambers, the quantity could be better explained by the convection rather than a process of dissolution and then homogeneous precipitation process. Also, we found most of the precipitates from the solution are $BaCO_3$, as shown in Figs. 2 and 3. This indicates that soluble Ti^{4+} species, if exist, are not capable of long-distance drifting, because they could not even across the edge of the teflon cup from the top portion of TiO_2 particles in the IN type (the distance is less than 1 cm). Figs. 4 and 5 are the SEM micrographs of the product particles of $Ba(OH)_2$–TiO_2 reaction collected in the reaction chamber and collection chamber, respectively. The anisomorphic morphology of those particles grown in the solution (Fig. 5) shows clear characteristics of a slow crystallization process, possibly due to the low concentration of Ti^{4+} species.

Table 1
Powder distribution and XRD analysis of hydrothermal $BaTiO_3$ in specially configured device

Ti source	Device configuration	Powder collection	Total product (wt.%)	XRD analysis
TiO_2 anatase	IN	In the cup	99.5	$BaTiO_3$ + trace $BaCO_3$
		Out	0.5	$BaCO_3$ + some $BaTiO_3$
	OUT	In the cup	0.4	$BaCO_3$ + some $BaTiO_3$
		Out	99.6	$BaTiO_3$ + some $BaCO_3$ + trace TiO_2
$TiCl_4$-gel	IN	In the cup	>99.9	$BaTiO_3$ + trace $BaCO_3$
		Out	<0.1	Not enough to analysis
	OUT	In the cup	0.1	$BaCO_3$ + some $BaTiO_3$
		Out	99.9	Pure $BaTiO_3$

TiO_2 anatase and $TiCl_4$ were used as Ti sources to react with $Ba(OH)_2$. "IN" and "OUT" indicate where the precursor gel was put before reaction. "In the cup" and "Out" indicate where the final products were collected.

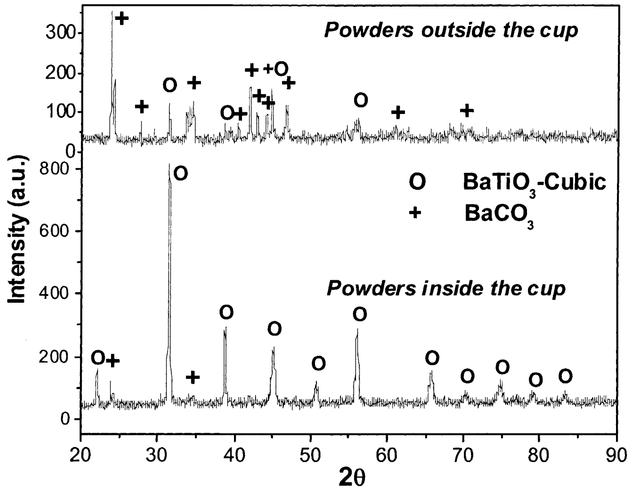

Fig. 2. Powder XRD pattern of hydrothennal $BaTiO_3$ using TiO_2 anatase as precursor with an IN type setting.

According to our observations, we propose a modified dissolution–precipitation mechanism. A similar speculation has been discussed as one of the three possible mechanisms by Eckert et al.[12] and Riman[15] in their extensive studies of hydrothermal $BaTiO_3$ as shown in Eq. (1):

$$Ba^{2+} + [Ti(OH)_6]^{2-} \rightarrow BaTiO_3 + 3H_2O \qquad (1)$$

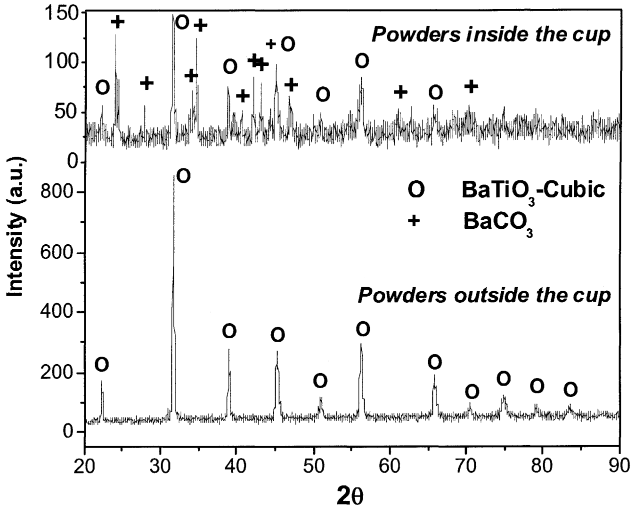

Fig. 3. Powder XRD pattern of hydrothermal $BaTiO_3$ using $TiCl_4$ as precursor with an OUT type setting.

The part that our results disagree with the in situ transformation mechanism is the ease for $BaTiO_3$ formation under a moderate hydrothermal condition (50–200 °C). It is hard to believe that the diffusion of Ba^{2+} in TiO_2 could happen so fast (within a couple of hours) at such a low temperature, since Ba^{2+} is almost as twice big as Ti^{4+}. Considering the hydrothermal synthesis of pure TiO_2,[16] there is an chemical equilibrium between TiO_2 and $[Ti(OH)_x]^{4-x}$ species. So, a high pH is definitely beneficial for dissolving Ti^{4+} and the formation of $BaTiO_3$, as observed by Xia et al.[13] It can also explain why solvothermal reaction could not proceed very well at a low pH, as observed by Chen and Jiao.[3] $[Ti(OH)_x]^{4-x}$ species are supposed to be highly active. They can either combine with the nuclei and become a part of them, or react with Ba^{2+} quickly and form new nucleus. The Ba^{2+} concentration might also be an influencing factor on the particle size, because the reaction equilibrium constant might be increased by increasing of total concentration of Ba^{2+} and Ti^{4+}. As the Ba/Ti ratio increases, the chance for each $[Ti(OH)_x]^{4-x}$ group to become a new nucleus increases, so the final particle size decreases. As the Ba/Ti ratio reaches to a certain point, the nucleation rate is high enough that a significant amount of the $[Ti(OH)_x]^{4-x}$ has been already consumed to nucleate. Thus, the particle size will not be affected by further Ba^{2+} addition as observed by Wada et al.[14]

Based on the observations in this work, we believe that this dissolution and crystallization process happens mainly in the vicinity of TiO_2 particle surfaces, because of the absence of free $[Ti(OH)_x]^{4-x}$ outside of the vicinity. This affinity between TiO_2 and $BaTiO_3$ nuclei gives the TiO_2 core–$BaTiO_3$ shell structure. Although $BaTiO_3$ nucleates in the vicinity of TiO_2 particle surface, those nuclei do not necessarily absorb on the TiO_2 surface. They may drift away by Brownian movement. So, the $BaTiO_3$ shell should be a loosely packed or porous layer, which does not totally block the transport of free Ba^{2+} and OH. Possibly, a significant amount of TiO_2 has been consumed before the formation of fully condensed $BaTiO_3$ layer, which seriously retards the reaction rate and

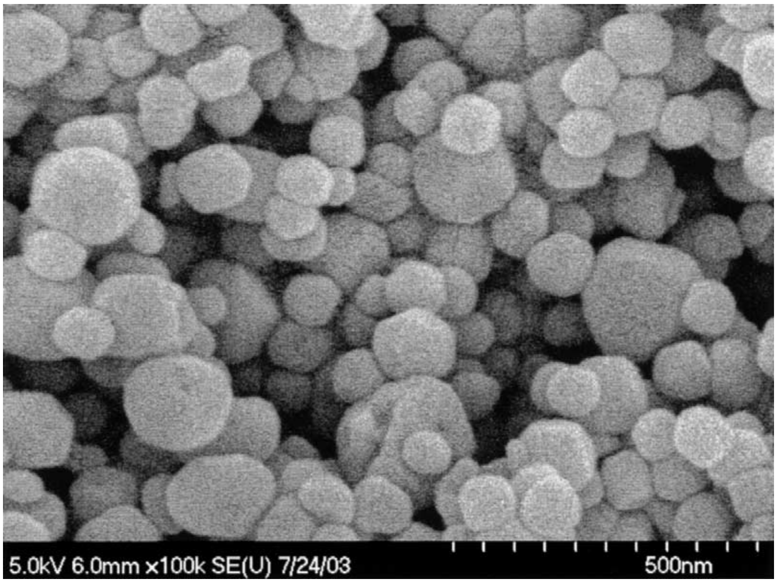

Fig. 4. SEM micrograph of hydrothermal $BaTiO_3$ using TiO_2 anatase as source with an OUT type setting. The powders were collected from the outside of the cup.

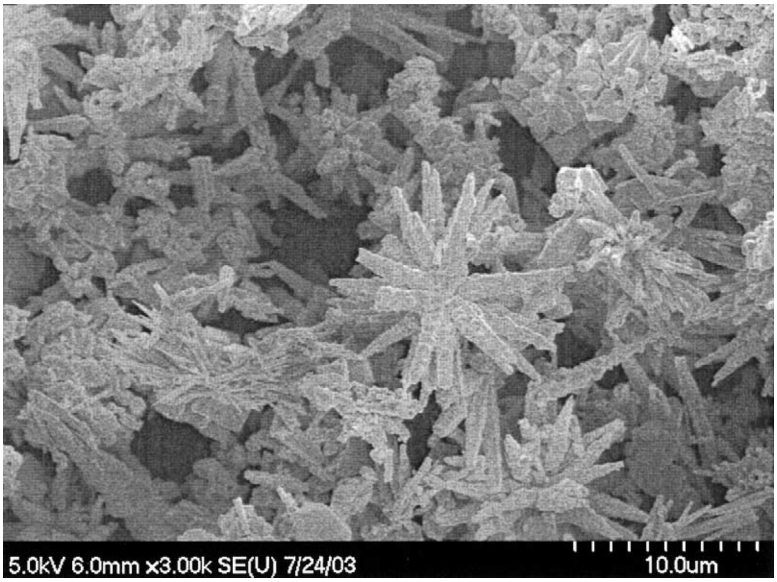

Fig. 5. SEM micrograph of the precipitate inside the cup during the hydrothermal reaction of $Ba(OH)_2$ and TiO_2 anatase with an OUT type setting. XRD shows that most of the precipitates are $BaCO_3$.

gives the appearance of a diffusion-controlled in situ transformation process. The necks between particles[6] might be caused by the higher concentration of $[Ti(OH)_x]^{4-x}$ between two TiO_2 particles, leading to a faster growth rate than average.

The mechanism of the reaction between $Ba(OH)_2$ and $TiCl_4$ is similar to the above discussion, just without the dissolution step. Thus, this reaction is supposed to have a higher reaction rate than the $Ba(OH)_2$–TiO_2 pair, which has been demonstrated by Kutty et al.[17]

4. Conclusions

The experimental observations in this work indicate a short-range dissolution–precipitation mechanism of the hydrothermal synthesis of $BaTiO_3$ from $Ba(OH)_2$ and TiO_2 powder, which explains the experimental observations in this work and the literature. Based on the above discussion, we believe that a Ba/Ti ratio larger than 1 is necessary to facilitate the reaction and produce pure $BaTiO_3$ phase.

Acknowledgements

This work is supported by the Office of Basic Energy Sciences, Division of Materials Sciences, of Department of Energy. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-ACO6-76RL01 830.

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