Low Temperature Synthesis of BaTiO₃ from Layered Titanate Nanosheet

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A H⁺-form lepidocrocite-like layered titanate H₃.₅Ti₁.₇3O₂ was exfoliated in a n-propyamine solution to prepare a colloidal solution of the titanate nanosheet. The nanosheet colloidal solution shows a very high reactivity with Ba(OH)₂ in the formation reaction of BaTiO₃. The sub-micrometer BaTiO₃ sheet-like and spherical particles can be obtained by reacting the nanosheet colloidal solution with Ba(OH)₂ at 80°C. This reaction provides a novel low temperature process for the preparation of BaTiO₃.

[Received November 6, 2006; Accepted December 18, 2006]

Key-words: Low temperature synthesis, Barium titanate, Layered titanate nanosheet, Particle morphology

1. Introduction

Barium titanate (BaTiO₃) is an excellent electroceramic material, and widely utilized in the manufacture of multilayer capacitors, thermistors, and electro-optic devices because of its high dielectric permittivity and ferroelectric properties.¹⁻³ Up to now a large number of studies have been carried out on the preparation of BaTiO₃ particles. Recently, most of the studies focused on preparation of high purity BaTiO₃ particles with nanometer and sub-micrometer particle sizes, which have potential application in the manufacture of high performance multilayer capacitors.⁴⁻⁵

Low temperature solution processes, such as sol-gel process and hydrothermal process, are promising for the preparation of high-purity BaTiO₃ with nanometer and sub-micrometer particle sizes. In the sol-gel process, usually BaTiO₃ is prepared by hydrolyzing Ba and Ti alkoxides solutions.⁴⁻⁵ This process ensures a homogeneous mixing of all metal cations at a molecular level, and makes crystallization at low temperature. Therefore, this process allows nano-level compositional control, lowering processing temperature, and providing the nanoparticles. However, there are several disadvantages for the sol-gel process, including expensive starting materials, difficulty for controlling the hydrolysis conditions, including amount of water and the humidity in air in the processing, and relatively lower crystalline BaTiO₃ obtained by this process. To increase the crystallinity, a further heat-treatment or hydrothermal treatment is necessary. In the hydrothermal process, usually TiO₂ fine particles or Ti(OH)₄ slurry is used as the precursor, and reacted with Ba(OH)₂ under hydrothermal conditions.⁷⁻⁹ This process can give well crystalline sub-micrometer BaTiO₃ particles, which has been employed to produce commercial BaTiO₃ powders. The disadvantage of this process is the cost to keep the high pressure for the hydrothermal reaction with a reaction autoclave.

Hydrothermal soft chemical process is an unique process for the BaTiO₃ synthesis.¹⁰⁻¹³ In this process, a layered titanate that shows ion-exchange properties is used as the precursor, and reacted with Ba(OH)₂ solution under hydrothermal conditions. BaTiO₃ with special particle morphology can be prepared by using this process. Plate-like, fibrous, and book-like BaTiO₃ particles have been prepared by hydrothermal soft chemical process with plate-like and fibrous layered titanate precursors. Another interesting fact is that the layered titanates show a high reactivity in the BaTiO₃ formation reactions because of the ion-exchange properties of layered titanates. For example, an H⁺-form lepidocrocite-like layered titanate of H₃.₅Ti₁.₇3O₂ with a particle size of amount 50 μm shows almost same reactivity as that of TiO₂ with sub-micrometer particle size in normal hydrothermal process.¹⁰⁻¹³ The Ba⁺⁺ ions can intercalated into the interlayer space of the layered titanate, and reaction with the titanate in the formation reaction of BaTiO₃.

The lepidocrocite-like layered titanate shows an interesting property. It can be exfoliated into the elementary layer of its structure in organic amine solutions.¹⁴⁻¹⁶ The elemental layer has thickness of about 1 nm, and called layered titanate nanosheet. It is expected that the nanosheet colloidal solution obtained by the exfoliation shows a high reactivity in the formation of BaTiO₃, and is a promising precursor for the low temperature synthesis. Up to now, however, without any study on the preparation BaTiO₃ particles using titanate nanosheet as precursor has been reported. In the present paper, we describe a novel process for preparation of BaTiO₃ sub-micrometer particles from the exfoliated layered titanate nanosheet precursor under low temperature conditions.

2. Experimental

A lepidocrocite-like layered titanate KₓTi₅.₇3Li₁.₇3O₂ (KTLO) was prepared by a conventional solid-state reaction.¹⁶ Stoichiometric K₂CO₃, TiO₂ (anatase), and Li₂CO₃ were mixed and ground together, and then the mixture was heated at 1000°C for 20 h. An H⁺-form layered titanate H₃.₅Ti₁.₇3O₂ (HTO) was prepared by treating KTLO (10 g) with a 1 M HNO₃ solution (1 L) for 1 day to exchange K⁺ and Li⁺ ions in KTLO with H⁺ ions. The acid-treatment was repeated twice to complete the ion-exchange reaction. A nanosheet colloidal solution of the layered titanate was prepared by treating HTO powder sample (1 g) with a 0.1 M n-propyamine solution (100 mL) at room temperature for 1 day with stirring.¹⁶ The titanium content in the resulted nanosheet colloidal solution was adjusted to 0.1 M. A desired amount of Ba(OH)₂ · 8H₂O was added into the nanosheet colloidal solution (15 mL) to adjust the concentration of Ba(OH)₂ to 0.1, 0.2, and 0.3 M, and then the Ba/Ti molar ratios in the reaction system were controlled to be 1, 2, and 3, respectively. The mixture was placed in the Teflon-lined, sealed stainless steel vessel, and then treated at a desired temperature for 1 day under stirring conditions to prepare BaTiO₃. The product was filtered, washed with hot distilled water, and then dried at 80°C for 1 day.

Powder X-ray diffraction (XRD) patterns of the samples were carried out on a SHIMADZU XRD 6100 X-ray diffraction.
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Fig. 1. X-ray diffraction patterns of (a) layered titanate K$_{0.8}$Ti$_{1.73}$Li$_{0.25}$O$_4$ (KTLO) prepared by solid state reaction and (b) H$^+$-form layered titanate H$_{1.07}$Ti$_{1.73}$O$_4$ (HTO) obtained by acid-treatment of KTLO.

In the synthesis process, first layered titanate K$_{0.8}$Ti$_{1.73}$Li$_{0.25}$O$_4$ (KTLO) was prepared, and the KTLO was treated with a 1 M HNO$_3$ solution to prepare H$^+$-form layered titanate H$_{1.07}$Ti$_{1.73}$O$_4$ (HTO). Figure 1 shows XRD patterns of KTLO and HTO. KTLO has a lepidocrocite-like layered structure with a basal spacing of 0.781 nm. After the acid-treatment, K$^+$ and Li$^+$ in the layered structure were ion-exchanged with H$_3$O$^+$, and basal spacing increased to 0.935 nm, but retained the lepidocrocite-like layered structure. A SEM study indicates that HTO has a plate-like particle morphology and particle size of about 10 μm (Fig. 2(a)), same as the particle morphology of KTLO.

When HTO was treated in the n-propylamine solution, n-propylamine molecules intercalate into the interlayer space of HTO, which causes expands the basal spacing of HTO. The increasing basal spacing results decreasing holding force of the layered structure, and intercalation of a large amount water molecules into the interlayer by wetting effect, and then the exfoliation of the layered structure into the nanosheets of elementary layer of its structure. After the exfoliation treatment, a colloidal solution of the titanate nanosheet was obtained, and the colloidal solution was used as the precursor for the synthesis of BaTiO$_3$.

When Ba(OH)$_2$ was added into the nanosheet colloidal solution, Ba$^{2+}$ ions attract the negatively charged titanate nanosheets together and form a precipitate. The precipitate was heated in the solution to prepare BaTiO$_3$. Figure 3 shows the XRD patterns of samples obtained by reacting the nanosheet colloidal solution with Ba(OH)$_2$ at 80°C. In the reaction system containing 0.1 M Ba(OH)$_2$ solution, most of the nanosheets were transformed to a BaTiO$_3$ phase, and only very small amount of unreacted layered titanate phase remained after the hydrothermal reaction. All the nanosheets were transformed completely to the BaTiO$_3$ phase in the reaction systems containing 0.2 and 0.3 M Ba(OH)$_2$. Chemical compositional analysis indicated that Ba/Ti molar ratio in the products increased with increasing Ba(OH)$_2$ concentration, and the Ba/Ti molar ratio of the product obtained at 0.3 M Ba(OH)$_2$ is close to the stoichiometry of BaTiO$_3$ (Table 1). These results suggest that the titanate nanosheets show a high reactivity, and the formation of BaTiO$_3$ increases with increasing the concentration of Ba(OH)$_2$ in the reaction system.

In the reaction system containing 0.1 M Ba(OH)$_2$, sheet-like particles and small spherical particles were observed (Fig. 2(b)). The thickness of the sheet-like particles is submicrometer, and the size of the spherical particles is about 100 nm. In the reaction system containing 0.2 M Ba(OH)$_2$, the sheet-like particles and small spherical particles aggregate together (Fig. 2(c)). In the reaction system containing 0.3 M
Table 1. Chemical Compositions of the Products

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>Ba(OH)₂ concentration in the reaction solution</th>
<th>Ba/Ti molar ratio in the product</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.1</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.98</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Ba(OH)₂, no sheet-like particle, but only the aggregated small spherical particles of about 200 nm in the size were observed (Fig. 2(d)).

When the titanate nanosheet colloidal solution was reacted with Ba(OH)₂ at 100°C, the formation of BaTiO₃ increases also with increasing the concentration of Ba(OH)₂ in the reaction system similar to the reaction at 80°C, but the unreacted layered titanate phase decreased (Fig. 4), indicating the temperature promotes the formation reaction of BaTiO₃. Chemical compositional analysis indicated that Ba/Ti molar ratio in the products prepared at 100°C is slightly larger than that prepared at 80°C at the same Ba(OH)₂ concentration (Table 1), indicating also the temperature promotes the formation reaction of BaTiO₃. The sheet-like particles and small spherical particles were formed in the reaction system containing 0.1 M Ba(OH)₂ (Fig. 2(e)), and only small spherical particles were formed in the reaction systems containing high Ba(OH)₂ concentration (Fig. 2(f)).

On the basis of the above results, we propose a reaction model for the formation BaTiO₃ from the layered titanate nanosheets. When Ba(OH)₂ is added into the nanosheet colloidal solution, the exfoliated nanosheets are restacked to the layered structure, accompanying intercalation of Ba⁺⁺ ions into the interlayer spaces, owing to attraction between negatively charged nanosheet and positively charged Ba⁺⁺ ion. This reaction causes formation of a layered titanate precipitate with the sheet-like particle morphology. Under heating conditions, the layered structure is transformed to the BaTiO₃ structure under hydrothermal conditions. Under hydrothermal conditions, the layered structure is transformed to the BaTiO₃ structure by two simultaneous reactions. One is an in situ topotactic transformation reaction, in which Ba⁺⁺ migrate into the crystal bulk of layered titanate through the interlayer space, and then react with the layered titanate to form BaTiO₃ by an in situ structural transformation reaction. Another is a dissolution–deposition reaction on the surface of the particles, similar to the normal hydrothermal reaction. BaTiO₃ formed by the topotactic transformation reaction retains the particle morphology of the precursor, which shows the plate-like particle morphology. The small spherical BaTiO₃ particles on the surface of the plate-like particles are formed by the dissolution–deposition reaction that changes the morphology of the precursor.

In the present case, we think the transformation reaction from the sheet-like layered titanate to BaTiO₃ is similar to the case of the plate-like HTO particles. BaTiO₃ formed by the topotactic transformation reaction retains the sheet-like particle morphology, in which Ba⁺⁺ in the interlayer space react with the titanate layers to form BaTiO₃ phase by the in situ structural transformation reaction. The small spherical BaTiO₃ particles are formed by the dissolution–deposition reaction on the surface of the particles, which changes the morphology of the precursor. The dissolution–deposition reaction increases with increasing the alkaline concentration and reaction temperature. Since the sheet-like particles have a much thinner particle size and larger surface area than which of the plate-like HTO particles, the fraction of the dissolution–deposition reaction in the nano-sheet and Ba(OH)₂ reaction system is larger than that in the plate-like particle and Ba(OH)₂ reaction system. This means that the sheet-like particles loss their particle morphology easily in the formation process of BaTiO₃ by the dissolution–deposition reaction. Under the high Ba(OH)₂ concentration and high temperature conditions, all the sheet-like particles loss their particle morphology, and change to the spherical particles. For the plate-like HTO particles, a high reaction temperature (200°C) is necessary to transform the layered titanate completely to BaTiO₃. The titanate nano-sheets, however, can be transformed to BaTiO₃ at much lower temperature (80°C). The much higher reactivity of the titanate nano-sheet is due to its thinness and larger surface area.

In summary, the layered titanate nano-sheet shows high reactivity in the formation reaction of BaTiO₃, and sub-micrometer sheet-like and spherical BaTiO₃ particles can be prepared by using the nanosheet as the precursor. The synthesis process using the nanosheet precursor has potential application in the preparation of sub-micrometer BaTiO₃ particles, due to the much lower reaction temperature than that of the normal hydrothermal process, and much lower cost than that of the sol–gel process.

Acknowledgement This work was supported in part by the Murata Science Foundation.

References


