

Synthesis of Crystal-Axis-Oriented BaTiO₃ and Anatase Platelike Particles by a Hydrothermal Soft Chemical Process

Qi Feng,* Manabu Hirasawa, and Kazumichi Yanagisawa

Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University,
2-5-1 Akebono-cho, Kochi-shi 780-8520, Japan

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BaTiO₃ and anatase with platelike particle morphology were prepared by using a hydrothermal soft chemical process. A layered titanate of K_{0.8}Ti_{1.73}Li_{0.27}O₄ with a lepidocrocite-like layered structure, which has a platelike particle morphology, was used as a precursor. In the first step, the layered titanate was treated with an acid solution to obtain an H⁺-form layered titanate H_{1.07}Ti_{1.73}O₄·nH₂O with a lepidocrocite-like layered structure. In the second step, the H⁺-form layered titanate was treated in a Ba(OH)₂ solution or distilled water under mild hydrothermal conditions to transform the layered titanate to BaTiO₃ or anatase. The transformation reactions were investigated by XRD and SEM analyses. There are two simultaneous mechanisms in the formation of BaTiO₃ under the hydrothermal conditions. One is an in situ topotactic transformation reaction in the crystal bulk of the layered titanate, and another is a dissolution–deposition reaction on the surface of the particles. In the formation of BaTiO₃, the in situ topotactic transformation reaction is predominant in the solution of low Ba(OH)₂ concentration, while, in the formation of anatase, most of the reaction progressed by the in situ topotactic transformation mechanism. The platelike particles of BaTiO₃ and anatase, which were prepared by this method, showed a high degree of crystal-axis orientation.

Introduction

Perovskite-type barium titanate, BaTiO₃, is an important dielectric material, because of its potential commercial applications in ceramic capacitors, chemical sensors, and nonvolatile memories.^{1–3} A large number of studies on the preparation of BaTiO₃ particles have been reported.^{4–13} The morphology of particles obtained by normal methods, such as solid-state reaction, the sol–gel method, and the hydrothermal method, is usually cubic or agglomerations of cubic particles. The dielectric materials show crystal-axis anisotropic properties, but crystal-axis-oriented ceramic materials are difficult to obtain from the particles prepared by the normal methods, because of their randomly oriented grains. Particles with special morphologies, such as

fibrous and platelike particles, can be used for oriented ceramic materials, because they are easy to orient by the mechanical method.

Soft chemical synthesis is a useful method for the preparation of particles with special morphology. Since the structural transformation reaction in the soft chemical synthesis is an in situ topotactic reaction, the morphology of the precursor can be retained after the reaction. Layered metal oxides are suitable as precursors for the soft chemical syntheses, due to their open structures and ion-exchange properties, which provide a pathway for mass transfer to the crystal bulk. Shimizu et al.¹⁴ have found that fibrous BaTiO₃ particles can be obtained by hydrothermally treating a fibrous layered hydrous potassium titanate (2K₂O·11TiO₂·3H₂O) in a Ba(OH)₂ solution. The fibrous BaTiO₃ particles show a high degree of crystal-axis orientation and special dielectric properties.^{15,16} Fibrous particles of PbTiO₃ perovskite can be prepared also by hydrothermal treatment of the fibrous layered hydrous potassium titanate with Pb₂O(OH)₂ in an alkaline solution.^{17,18}

Our previous study has indicated that fibrous particles of ATiO₃ (A = Ba, Sr, Ca) perovskites can be obtained by reacting a fibrous H⁺-form tetratitanate H₂-

- (1) Phule, P. P.; Rispu, S. H. *J. Mater. Sci.* **1990**, *25*, 1169.
- (2) Ishihara, T.; Kometani, K.; Mizuhara, Y.; Takita, Y. *J. Am. Ceram. Soc.* **1992**, *75*, 613.
- (3) Ijima, I.; Tamita, Y.; Takayama, R.; Ueda, I. *J. Appl. Phys.* **1986**, *60*, 361.
- (4) Wada, S.; Susuki, T.; Noma, T. *J. Ceram. Soc. Jpn.* **1995**, *103*, 1220.
- (5) Oledzka, M.; Brese, N. E.; Riman, R. E. *Chem. Mater.* **1999**, *11*, 1931.
- (6) Lencka, M. M.; Riman, R. E. *Chem. Mater.* **1993**, *5*, 61.
- (7) Dawson, W. *J. Ceram. Bull.* **1988**, *67*, 1673.
- (8) Vivekanandan, R.; Philip, S.; Kutty, T. R. N. *Mater. Res. Bull.* **1986**, *22*, 99.
- (9) Hennings, D.; Schreinemacher, S. *J. Eur. Ceram. Soc.* **1992**, *9*, 41.
- (10) Naka, S.; Nakakita, F.; Suwa, Y.; Inagaki, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1168.
- (11) Suyama, Y.; Nagasawa, M. *J. Am. Ceram. Soc.* **1994**, *77*, 603.
- (12) Nishizawa, H.; Katsube, M. *J. Solid State Chem.* **1997**, *131*, 43.
- (13) Kakihana, M.; Arima, M.; Nakamura, Y.; Yashima, M.; Yoshimura, M. *Chem. Mater.* **1999**, *11*, 438.

- (14) Shimizu, T.; Yanagida, H.; Hori, M.; Hashimoto, K.; Nishikawa, Y. *Yogyo Kyokaiishi* **1979**, *87*, 500.
- (15) Ohara, Y.; Koumoto, K.; Yanagida, H. *J. Am. Ceram. Soc.* **1985**, *68*, C-108.
- (16) Ohara, Y.; Koumoto, K.; Yanahida, H. *J. Am. Ceram. Soc.* **1994**, *77*, 2327.
- (17) Nishi, T.; Igarashi, K.; Shimizu, T.; Koumoto, K.; Yanagida, H. *J. Mater. Sci. Lett.* **1989**, *8*, 805.
- (18) Ohara, Y.; Koumoto, K.; Shimizu, T.; Yanagida, H. *J. Ceram. Soc. Jpn.* **1994**, *102*, 88.

Ti₄O₉ in Ba(OH)₂, Sr(OH)₂, and Ca(OH)₂ solutions under hydrothermal conditions, respectively.¹⁹ The fibrous H⁺-form tetratitanate shows a higher reactivity than that for the fibrous layered hydrous potassium titanate in the ATiO₃ formation reactions. We call the method using the hydrothermal reaction for the soft chemical synthesis a hydrothermal soft chemical process.^{20,21}

Although the platelike particles are more easily handled than the fibrous particles for the preparations of oriented ceramic materials, even they can be used for an oriented film. However, to the best of our knowledge, no challenge of the preparation of the platelike ATiO₃ particles by the soft chemical method has been reported. This may be due to the difficulty of finding a suitable precursor with a platelike morphology. Recently, Sasaki et al. have reported layered titanates with a lepidocrocite-like layered structure, which have platelike particle morphology and excellent ion-exchange properties.^{22,23} We think that these layered titanates are useful as the precursor for the preparation of platelike BaTiO₃ particles by using the hydrothermal soft chemical process.

In the present study, we describe the preparation of the platelike BaTiO₃ and anatase particles from an H⁺-form titanate of H_{1.07}Ti_{1.73}O₄·nH₂O with a lepidocrocite-like layered structure by using the hydrothermal soft chemical process, and the mechanism of the structural transformation reaction from the layered titanate to BaTiO₃ and anatase.

Experimental Section

Sample Preparation. A layered titanate of K_{0.8}Ti_{1.73}Li_{0.27}O₄ (KTLO) with a lepidocrocite-like layered structure, which was used as a precursor, was prepared by a flux method. Stoichiometric K₂CO₃ and TiO₂ (anatase) and a 10% excess of Li₂CO₃ were mixed and ground together. The mixture of the starting materials was mixed with a K₂MoO₄ flux in a mole ratio of K_{0.8}Ti_{1.73}Li_{0.27}O₄/K₂MoO₄ = 3/7 and then heated to 1100 °C at a heating rate of 150 °C/h and kept at the temperature for 5 h. After the sample cooled in the furnace naturally, it was washed with boiling water to remove the K₂MoO₄ flux and dried at room temperature. The layered H⁺-form titanate H_{1.07}Ti_{1.73}O₄·nH₂O (HTO) was prepared by treatment of KTLO (10 g) with a 1 M HNO₃ solution (1 L) for 1 day to exchange K⁺ and Li⁺ in the layered structure with H⁺. The acid treatment was repeated twice to complete the ion-exchange reaction. The ion-exchanged sample was washed with distilled water and dried at room temperature.

The HTO sample (0.147 g) and distilled water (15 mL) were placed in a Teflon-lined, sealed stainless steel vessel (30 mL of inner volume), and a desired amount of Ba(OH)₂·H₂O was added into the vessel to adjust the concentration of Ba(OH)₂ to 0, 0.1, 0.2, and 0.3 M, respectively, by assuming that all added Ba(OH)₂ can dissolve in the solution. Thus, the Ba/Ti mole ratios in the reaction system are controlled to be 0, 1, 2, and 3, respectively. The sample was stirred at room temperature for 2 h to exchange H⁺ in HTO with Ba²⁺ in the solution, and then hydrothermally treated at 150 or 200 °C for 1 day

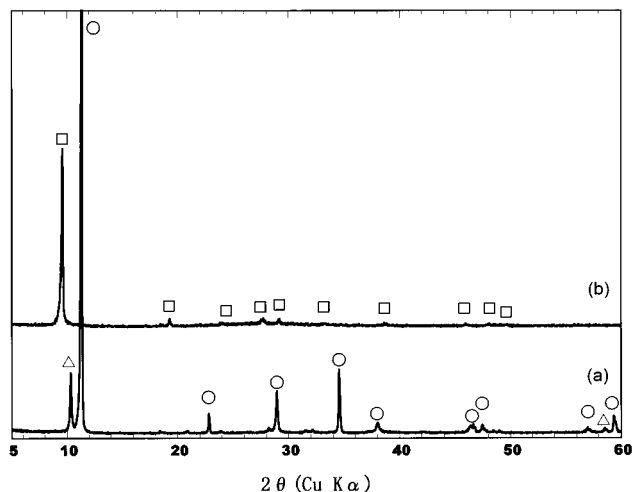


Figure 1. X-ray diffraction patterns of (a) a K_{0.8}Ti_{1.73}Li_{0.27}O₄ (KTLO) sample prepared by the flux method and (b) a H_{1.07}-Ti_{1.73}O₄·nH₂O (HTO) sample obtained by acid-treatment of the KTLO sample: ○, K_{0.8}Ti_{1.73}Li_{0.27}O₄ phase; △, hydrous K_{0.8}Ti_{1.73}-Li_{0.27} phase; □, H_{1.07}Ti_{1.73}O₄·nH₂O phase.

under autogenous pressure, then filtered, washed with hot distilled water, and dried at 80 °C for 1 day.

Characterization. The crystal structures of samples were investigated by using powder X-ray diffraction with a Rigaku Rotaflex Type X-ray diffractometer (RAD-RC). The particle size and morphology were characterized by scanning electron microscopy (SEM, Hitachi S-530).

Results and Discussion

Preparation of Layered Titanate Precursor.

Since the layered titanates, Cs_xTi_{2-x/4}O₄ and A_xTi_{2-x/3}-Li_{x/3}O₄ (A = K, Rb, Cs), having the lepidocrocite-like layered structure, show excellent ion-exchange properties,^{22–26} all these layered titanates can be used as a precursor for the BaTiO₃ preparation. These layered titanates have been prepared by solid-state reactions as longer.^{22–27} To obtain dispersed particles of the layered titanates, we used the flux method in the precursor preparation to prevent agglomeration of the particles. K_{0.8}Ti_{1.73}Li_{0.27}O₄ (KTLO) was chosen as the precursor, because a potassium-containing flux is easily available. The dispersed platelike single-crystal particles of K_{0.8}Ti_{1.73}Li_{0.27}O₄ (KTLO) were obtained by reacting K₂CO₃, Li₂CO₃, and TiO₂ in a K₂MoO₄ flux at 1100 °C. The X-ray diffraction pattern of KTLO is shown in Figure 1a. Two kinds of layered phases with basal spacings of 0.781 and 0.863 nm, respectively, were observed in the sample. The layered phase with the basal spacing of 0.781 corresponds to the KTLO phase obtained by the solid-state reaction, which has the lepidocrocite-like layered structure, as shown in Figure 2.^{23,28} The layered structure is composed of corrugated host layers of edge-shared TiO₆ octahedra and interlayer K⁺ compensating for the minus charge of the TiO₆ octahedral layers. Li⁺ occupies the Ti(IV) octahedral

(19) Feng, Q.; Yanagisawa, K.; Yamasaki, N. *High-Pressure Res.* in press.

(20) Feng, Q.; Kanoh, H.; Ooi, K. *J. Mater. Chem.* **1999**, *9*, 319.

(21) Feng, Q.; Honbu, C.; Yanagisawa, K.; Yamasaki, N. *Chem. Mater.* **1999**, *11*, 2444.

(22) Sasaki, T.; Nakano, S.; Yamauchi, S.; Watanabe, M. *Chem. Mater.* **1997**, *9*, 602.

(23) Sasaki, T.; Kooli, F.; Iida, M.; Michiue, Y.; Takenouchi, S.; Yajima, Y.; Izumi, F.; Chakoumakos, B. C.; Watanabe, M. *Chem. Mater.* **1998**, *10*, 4123.

(24) Sasaki, T.; Komatsu, Y.; Fhjiki, Y. *J. Chem. Soc., Chem Commun.* **1991**, 817.

(25) Sasaki, T.; Watanabe, M. *J. Am. Chem. Soc.* **1998**, *120*, 4682.

(26) Iida, M.; Sasaki, T.; Watanabe, M. *Chem. Mater.* **1998**, *10*, 3780.

(27) Grey, I. E.; Li, C.; Madsen, I. C.; Watts, J. A. *J. Solid State Chem.* **1987**, *66*, 7.

(28) Roth, R. S.; Parker, H. S.; Brower, W. S. *Mater. Res. Bull.* **1973**, *8*, 327.

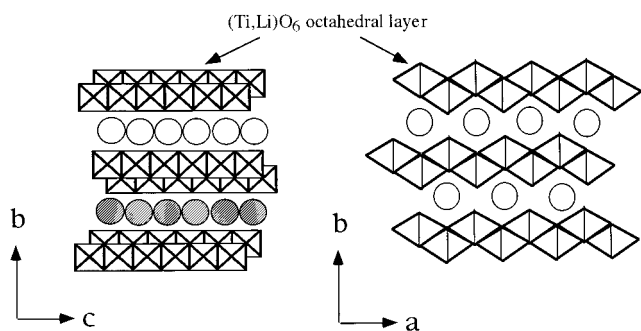


Figure 2. Layered structure of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$.

sites in the host layers. Another layered phase with the basal spacing of 0.863 nm corresponds to a hydrous KTLO phase with crystal water and K^+ in the interlayer space. The hydrous KTLO phase can return to the KTLO phase after dehydration over 400 °C.

$H_{1.07}Ti_{1.73}O_4 \cdot nH_2O$ (HTO) can be obtained by acid treatment of the $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ sample with 1 M HNO_3 . The X-ray diffraction study indicated that the HTO has a lepidocrocite-like layered structure similar to that of KTLO, but with a basal spacing of 0.922 nm (Figure 1b).²³ The crystal water and H_3O^+ occupy its interlayer space. A compositional analysis study revealed that over 98% of K^+ and Li^+ has been removed from the solid phase after the acid treatment. The results support that K^+ and Li^+ in KTLO can be exchanged with H^+ by acid treatment, and the ion-exchange is a topotactic reaction retaining the layered structure of KTLO.^{23,26}

SEM photographs of KTLO and HTO are shown in Figure 3. Well-dispersed KTLO platelike single-crystal particles were obtained. The particles have dimensions of about $50 \times 30 \times 5 \mu m^3$, which show a much higher aspect ratio than that obtained by a solid-state reaction.²⁶ HTO has the same particle morphology as KTLO, suggesting that the ion-exchange reaction progressed topotactically.

Hydrothermal Treatment of HTO. HTO was hydrothermally treated in 0, 0.1, 0.2, and 0.3 M $Ba(OH)_2$ solutions to obtain $BaTiO_3$ and anatase at 150 and 200 °C, respectively. The HTO layered phase was transformed to the anatase phase (TiO_2) after the hydrothermal treatment in distilled water, and to $BaTiO_3$ after the hydrothermal treatment in $Ba(OH)_2$ solutions at 150 °C (Figure 4). A small amount of the layered titanate phase remained after the hydrothermal treatment in the $Ba(OH)_2$ solutions, and the amount of residual layered phase decreased with increasing $Ba(OH)_2$ concentration, meaning that the formation of $BaTiO_3$ increased with increasing $Ba(OH)_2$ concentration. At 200 °C, anatase and $BaTiO_3$ were formed also with a manner similar to that at 150 °C, while the intensity of the diffraction peaks of anatase increased, and the amount of residual layered phase decrease slightly with the increase of the reaction temperature (Figure 5). Almost all of the HTO phase was transformed to the $BaTiO_3$ phase at 200 °C in a 0.3 M $Ba(OH)_2$ solution. The HTO showed somewhat lower reactivity for the formation of $BaTiO_3$ but higher reactivity for the formation of anatase than that of the fibrous $H_2Ti_4O_9$ particles.¹⁹ In the case of hydrothermal treatment of fibrous $H_2Ti_4O_9$ particles, no X-ray diffraction peaks of the

layered titanate can be observed after hydrothermal treatment in 0.3 M $Ba(OH)_2$ solution at 150 °C, and only a partial $H_2Ti_4O_9$ phase transforms to the anatase phase after hydrothermal treatment in distilled water at this temperature. The lower reactivity of HTO for the formation of $BaTiO_3$ is due to its large particle size. The different reactivities of HTO and $H_2Ti_4O_9$ in the formation reactions of anatase may be due to their different layered structures. The $BaTiO_3$ phase obtained by the hydrothermal treatment described here belongs to the cubic system with lattice constants of $a = 0.4020$ nm, which is similar to that prepared by the normal hydrothermal method.⁴

Characterization of Platelike Particles. SEM study indicated that all samples retained the platelike morphology after the hydrothermal treatments (Figure 6), meaning that the platelike particles of anatase and $BaTiO_3$ are easily obtained by using the hydrothermal soft chemical process described here. The surface of the platelike anatase particles is very smooth, similar to that of the HTO precursor (Figure 7a and b). Fine $BaTiO_3$ particles, however, were observed on the surface of the platelike $BaTiO_3$ particle, and the amount of fine particles increased with increasing concentration of $Ba(OH)_2$ solution and reaction temperature (Figure 7c and d).

The platelike $BaTiO_3$ and anatase particles prepared by this method show a high degree of crystal-axis orientation. Figure 8 shows X-ray diffraction patterns of the platelike $BaTiO_3$ and anatase particles, which were spread on a silica glass slide in such a way that the platelike particles were preferred oriented with the basal plane parallel to the plane of the glass slide. The oriented $BaTiO_3$ particles show a stronger (110) diffraction peak than that observed by using the normal method (Figure 5), meaning the (110) plane of $BaTiO_3$ parallels the basal plane of the platelike particle. In the case of the oriented anatase sample, only (101) and (103) diffraction peaks were observed. The orientation properties suggest that the formations of $BaTiO_3$ and anatase from the layered titanate are topotactic structural transformation reactions.

To analyze the crystal-axis orientation quantitatively, an orientation index was defined and calculated from the diffraction peak intensities of the X-ray diffraction patterns. An intensity factor ($IF_{(hkl)}$) is defined as the ratio of the peak intensity for the diffraction peak of interest to the sum of the intensities of the diffraction peaks and, for example, is expressed as follows:

$$IF_{(110)} = I_{(110)} / (I_{(100)} + I_{(110)} + I_{(111)}) \quad (1)$$

for the (110) diffraction peak of $BaTiO_3$ and

$$IF_{(103)} = I_{(103)} / (I_{(101)} + I_{(103)} + I_{(004)} + I_{(200)}) \quad (2)$$

for the (103) diffraction peak of anatase, where $I_{(hkl)}$ refer to the relative diffraction peak intensity in the X-ray diffraction pattern. The orientation index is defined as follows:

$$OI_{(hkl)} = IF_{(hkl)} / IFS_{(hkl)} \quad (3)$$

where $IFO_{(hkl)}$ refers to the intensity factor calculated from the X-ray diffraction pattern of the platelike

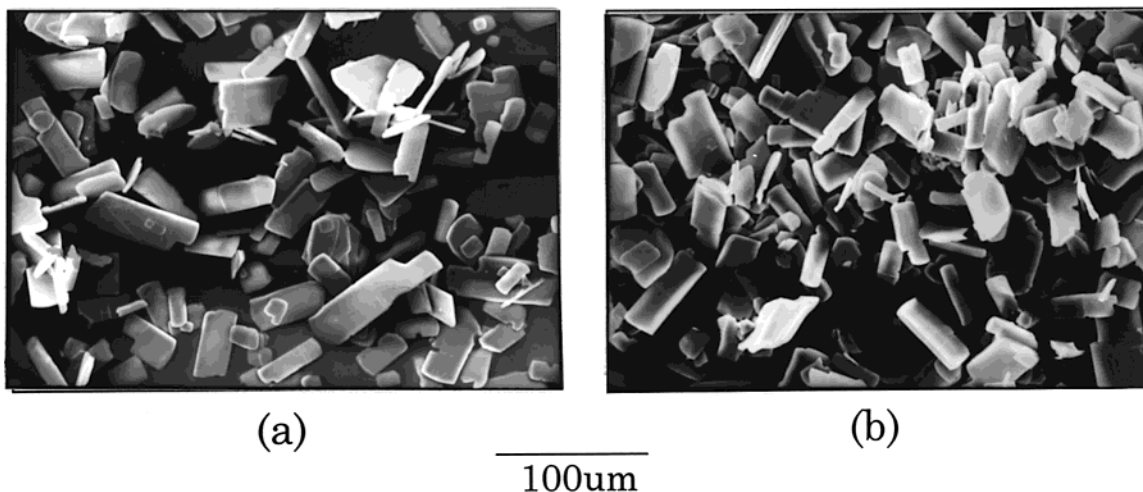


Figure 3. SEM photographs of (a) KTLO and (b) HTO samples.

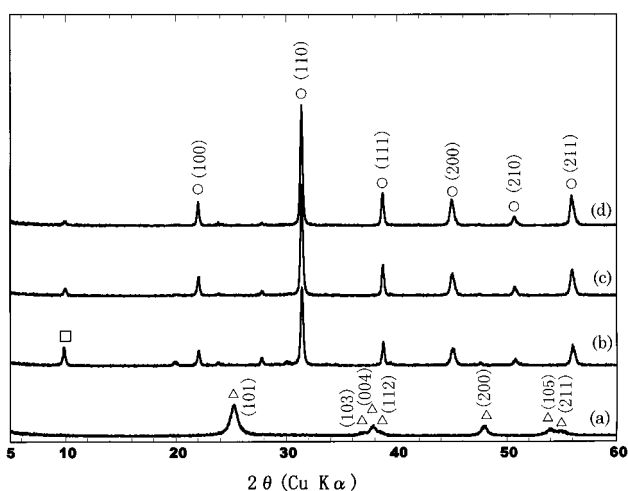


Figure 4. X-ray diffraction patterns of products obtained by hydrothermal treatment of HTO in (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3 M Ba(OH)₂ solutions, respectively, at 150 °C for 1 day: △, anatase phase; ○, BaTiO₃ phase; □, layered titanate phase.

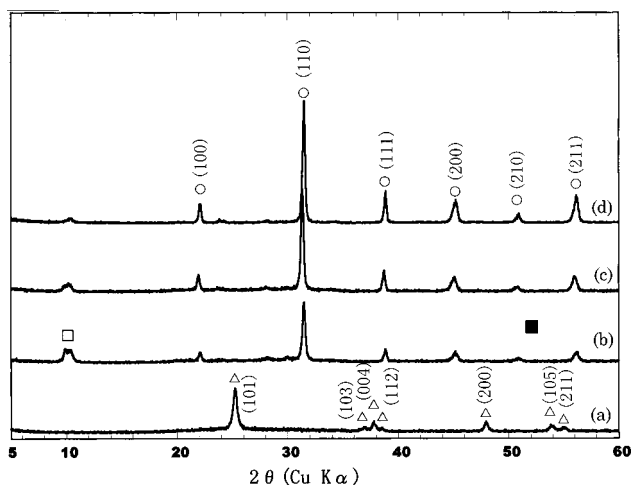


Figure 5. X-ray diffraction patterns of products obtained by hydrothermal treatment of HTO in (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3 M Ba(OH)₂ solutions, respectively, at 200 °C for 1 day: △, anatase phase; ○, BaTiO₃ phase; □, layered titanate phase.

sample oriented on the silica glass slide (Figure 8) and $IFS_{(hkl)}$ refers to a standard intensity factor calculated from the JCPDS card (BaTiO₃ No. 31-174 and anatase No. 21-1272). The $OI_{(hkl)}$ and $IFO_{(hkl)}$ values for BaTiO₃

and anatase samples prepared at 200 °C and $IFS_{(hkl)}$ values are given in Table 1. The $OI_{(110)}$ values for all BaTiO₃ samples are larger than 1 and decrease with increasing concentration of Ba(OH)₂ used in the hydrothermal treatment (Table 1), while $OI_{(100)}$ and $OI_{(111)}$ values are smaller than 1 and increase with increasing concentration of Ba(OH)₂ solution. These results indicate that the platelike BaTiO₃ particles show a high crystal-axis orientation along the [110] direction. The orientation decreased with the increase of the concentration of the Ba(OH)₂ reaction solution. The platelike anatase particles show a larger $OI_{(103)}$ value than 1, and other $OI_{(hkl)}$ values are smaller than 1, meaning high orientation along the [103] direction.

Structural Transformation Reaction. On the basis of the above results, we propose a reaction model, as shown in Figure 9, for the formation reaction of BaTiO₃. In the first step, K⁺ in the interlayer space and Li⁺ in the host octahedral layer of the KTLO layered structure are exchanged with H₃O⁺ by the acid-treatment, forming HTO. In a Ba(OH)₂ solution, H₃O⁺ in the interlayer space of HTO is exchanged with Ba²⁺ but still retains the layered structure in this stage. Under the hydrothermal conditions, the layered structure transforms to the perovskite structure of BaTiO₃. There are two simultaneous mechanisms in the formation of BaTiO₃ under the hydrothermal conditions. One is an in situ topotactic transformation reaction in the crystal bulk of the layered titanate, and we call it a hydrothermal soft chemical reaction. Another is a dissolution–deposition reaction on the surface of the particles. In the hydrothermal soft chemical reaction, Ba²⁺ in the interlayer space can react with the TiO₆ octahedral layers of HTO in the crystal bulk to form BaTiO₃ in situ, in which the TiO₆ octahedra shift regularly from the positions of the layered structure to the positions of the BaTiO₃ structure in a sub-nanometer order distance. BaTiO₃ formed by the hydrothermal soft chemical reaction retains the morphology of the precursor. Since the H⁺/Ti mole ratio is 1.07/1.73 in HTO, only about one third of the Ba²⁺ can be supplied to the formation reaction of BaTiO₃ by the ion-exchange reaction of Ba²⁺/H⁺. This suggests that another Ba²⁺ insertion reaction also occurs simultaneously to supply more Ba²⁺, accompanying the transformation reaction from the layered structure to the perovskite structure. Since Ba²⁺

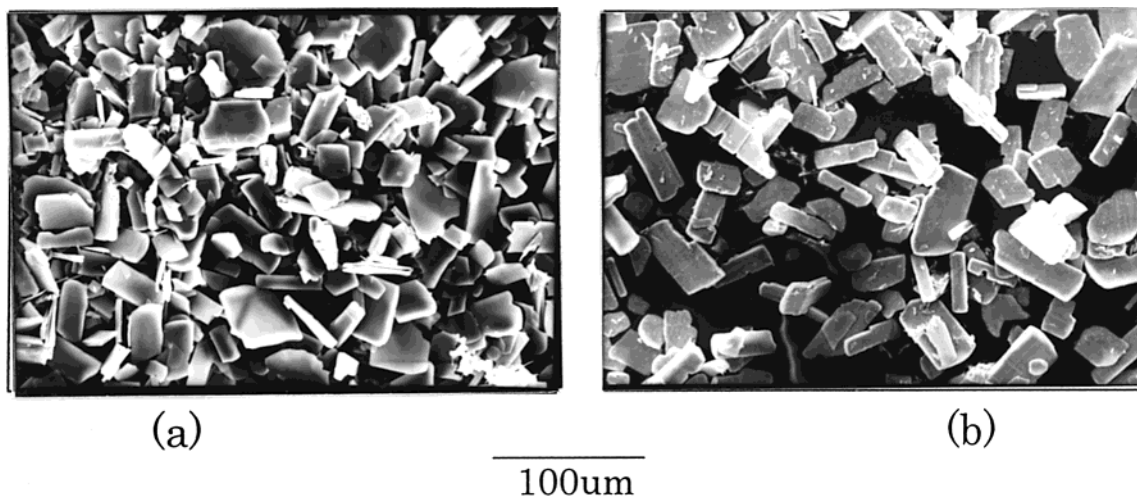


Figure 6. SEM photographs of platelike particles obtained by hydrothermal treatment of HTO in (a) distilled water and (b) 0.3 M $\text{Ba}(\text{OH})_2$ solution, respectively, at 200 °C for 1 day.

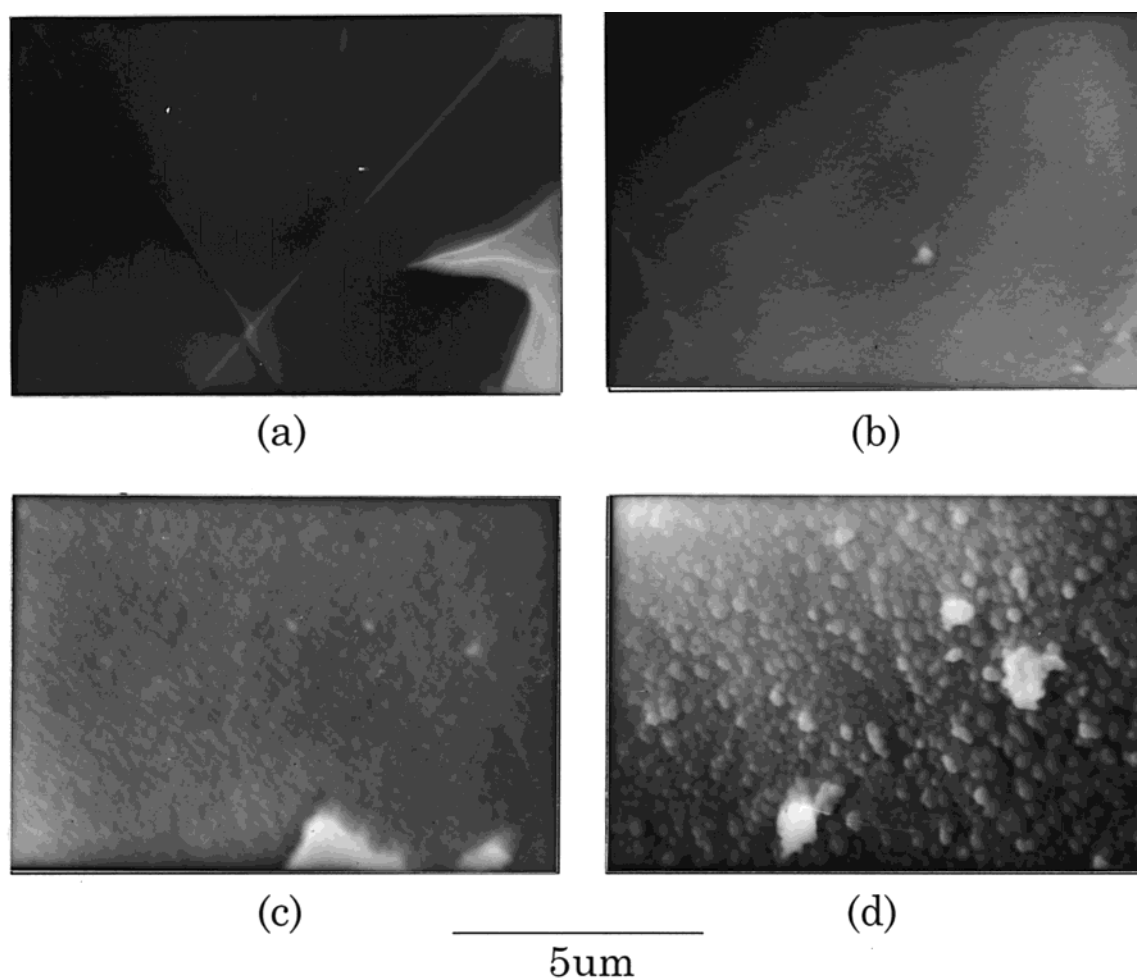


Figure 7. SEM photographs of platelike particle surfaces of (a) HTO used as the precursor and products obtained by hydrothermal treatment of HTO in (b) 0, (c) 0.1, and (d) 0.3 M $\text{Ba}(\text{OH})_2$ solutions, respectively, at 200 °C for 1 day.

can migrate into the crystal bulk through the interlayer pathway and react with the octahedral layers in the crystal bulk, the formation of BaTiO_3 is easy at the mild hydrothermal conditions and even the precursor has a large particle size.

The formation of fine BaTiO_3 particles (Figure 7) on the platelike particles is due to a dissolution–deposition reaction on the surface of the particles. The titanium oxide dissolves in an alkaline solution, and the dissolved

titanium reacts with Ba^{2+} in the solution near the surface of the precursor particles, forming the fine BaTiO_3 particles on the particle surface. The dissolution–deposition reaction is similar to the normal hydrothermal reaction. The fine BaTiO_3 particles formed by the dissolution–deposition reaction may not show a crystal-axis orientation property. The decrease of the crystal-axis orientation of BaTiO_3 with increasing $\text{Ba}(\text{OH})_2$ concentration (Table 1) is due to the increase of

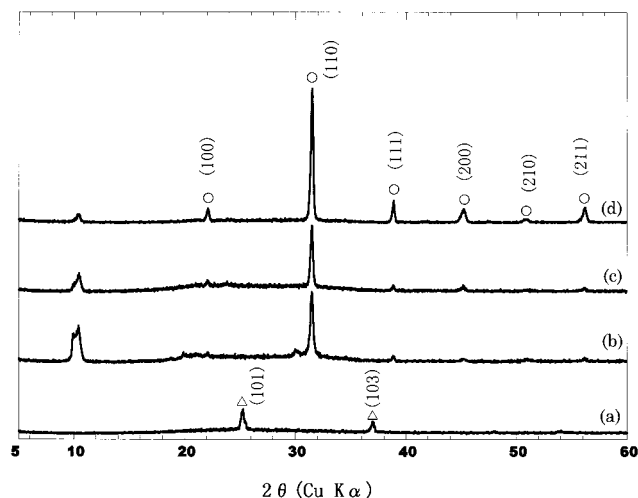


Figure 8. X-ray diffraction patterns of platelike particles oriented on a silica glass slide. The samples were prepared by hydrothermal treatment of HTO in (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3 M Ba(OH)₂ solutions, respectively, at 200 °C for 1 day: Δ , anatase phase; \circ , BaTiO₃ phase.

Table 1. Orientation Index and Intensity Factor of BaTiO₃ and Anatase Platelike Particles Prepared at 200 °C

sample	IFO(hkl)	IFS(hkl)	OI(hkl)
Standard BaTiO ₃ (JCPDS No. 31-174)			
(100)		0.0972	1
(110)		0.694	1
(111)		0.208	1
Platelike BaTiO ₃			
0.1 M Ba(OH) ₂			
(100)	0.0710		0.730
(110)	0.871		1.26
(111)	0.0547		0.263
0.2 M Ba(OH) ₂			
(100)	0.0728		0.749
(110)	0.844		1.22
(111)	0.0830		0.399
0.3 M Ba(OH) ₂			
(100)	0.0741		0.762
(110)	0.807		1.16
(111)	0.119		0.572
Standard Anatase (JCPDS No. 21-1272)			
(101)		0.606	1
(103)		0.0606	1
(004)		0.121	1
(200)		0.212	1
Platelike Anatase			
(101)	0.553		0.913
(103)	0.372		6.14
(004)	0.00		0.00
(200)	0.0746		0.352

the dissolution–deposition reaction in the high-concentration solution of Ba(OH)₂.

The transformation from HTO to anatase is a dehydration reaction. SEM study (Figure 7) reveals that the platelike particles of the anatase have a smooth particle surface, suggesting that most of the transformation progressed by an in situ topotactic reaction under the hydrothermal conditions. A fine particle was not observed on the platelike anatase particles, because of the low solubility of titanium in the neutral solution. On the basis of the mechanisms of the transformation reactions, it is easy to understand that the suppression of the dissolution–deposition reaction is important to

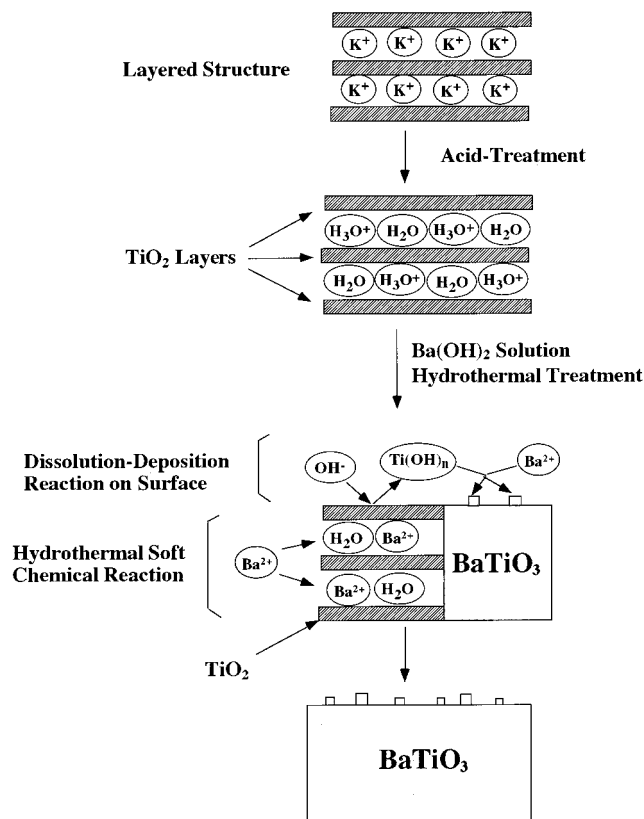


Figure 9. Model of formation reactions of BaTiO₃ from the layered titanate.

obtain perfect platelike particles of crystal-axis orientation.

The studies on the fibrous BaTiO₃ particles prepared from fibrous layered hydrous potassium titanate (2K₂O·11TiO₂·3H₂O) indicated that the fibrous BaTiO₃ particles show a crystal-axis orientation, and the fiber axis is perpendicular to the (001) plane of BaTiO₃.^{15,16} The different orientation directions of the platelike particles prepared here and the fibrous particles are due to different structures of the HTO and fibrous layered hydrous potassium titanate, which were used as the precursors. HTO has a flat TiO₆ octahedral layered structure, while fibrous layered hydrous potassium titanate has a stepped TiO₆ octahedral layered structure.^{24,29} The different orientation behavior also suggests that the transformation from the layered structures to the BaTiO₃ perovskite structure is the in situ topotactic reaction, and orientation direction can be controlled by using the precursors with different structures.

A crystallographic description of the relationship between the layered structures of titanates and the orientation directions of BaTiO₃ particles is important to predict the orientation direction of BaTiO₃ particles from the structure of the precursor. From the perovskite structure of BaTiO₃, it can be understood that Ba²⁺ ions are located on the (001) and (110) planes. This fact suggests that [001] or [110] direction-oriented BaTiO₃ particles may be formed easily from layered titanates. In the transformation reactions from the layered structures to the BaTiO₃ structure, Ba²⁺ and TiO₆ octahedra

(29) Sasaki, T.; Watanabe, M.; Fujiki, Y.; Kitami, Y. *Chem. Mater.* **1994**, *6*, 1749.

have to shift from the positions of the layered structures to the positions of the BaTiO₃ structure. The structural change from the layered titanates to BaTiO₃ will be smallest, when [001] or [110] direction-oriented BaTiO₃ particles are formed.

Conclusion

The results of this study indicate that the hydrothermal soft chemical process can be used for the synthesis of the crystal-axis-oriented BaTiO₃ and anatase particles, and the particle morphology of the products is

dependent on that of the precursor. The transformations from the layered structure of HTO to the structures of BaTiO₃ and anatase progress mainly by an in situ topotactic reaction. The crystal-axis orientation direction of BaTiO₃ particles is dependent on the structure of the precursor. The method used in this study will not be limited to the preparations of BaTiO₃ and anatase but will also be useful for the preparation of other materials with special morphologies.

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