

Solvothermal soft chemical synthesis and characterization of plate-like particles constructed from oriented BaTiO₃ nanocrystals

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Plate-like BaTiO₃ particles with a size of about 200 nm in thickness and 3 μm in width were prepared by using a novel solvothermal soft chemical process in ethanol and water-ethanol mixed solvents. A layered titanate of H_{1.07}Ti_{1.73}O₄ with a lepidocrocite-like structure and plate-like nanoparticle morphology was used as the precursor, and solvothermally treated in the Ba(OH)₂ solution to prepare the BaTiO₃ nanoparticles. The formation reaction, particle morphology, nanostructure, and crystal-axis-orientation of the plate-like BaTiO₃ nanoparticles were studied by XRD, FE-SEM, and TEM. The plate-like BaTiO₃ nanoparticles are formed by an *in situ* topotactic structural transformation reaction. The crystallinity and particle morphology can be controlled by changing the fraction of ethanol in the solvent, Ba(OH)₂ concentration, and reaction temperature. The plate-like BaTiO₃ nanoparticles are polycrystalline particles constructed from spherical nanocrystals which are arranged in the same crystal-axis orientation in each plate-like particle, and show a high degree orientation in [110] direction, being suitable for preparing oriented BaTiO₃ ceramic materials with high performance.

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1. Introduction

Barium titanate (BaTiO₃) is an important electronic material widely utilized for the manufacture of multilayer capacitors, thermistors, and electro-optic devices due to its high dielectric permittivity and ferroelectric properties.^{1–3)} Recently, BaTiO₃ attracts much attention as a candidate of lead-free piezoelectric material for replacing Pb(Zr,Ti)O₃ (PZT).^{4,5)} Up to now, a large number of studies on the preparation of BaTiO₃ particles have been carried out by using various methods, such as solid-state reaction,⁶⁾ hydrothermal method,^{7–10)} sol-gel method,^{11–13)} and metal-organic precursor decomposition method.^{14,15)} Recently, most of the studies focus on low-temperature synthesis and particle morphology control for BaTiO₃, and also on thin film preparations.^{16–19)} Although the high purity BaTiO₃ with controlled particles size can be prepared by the hydrothermal and sol-gel methods,¹⁾ but the BaTiO₃ particles obtained by these normal methods usually have cubic or spherical morphology, meaning that the particle shape is difficult to be controlled by these normal methods.

Since the ferroelectric materials show crystal-axis anisotropic properties, high performance devices can be achieved by using the crystal-axis-oriented materials.^{4,20,21)} The crystal-axis-oriented materials, however, are difficult to obtain from the spherical or cubic particles, because of their randomly oriented grains. The crystal-axis-oriented films can be prepared by using epitaxial crystal growth technique on a single crystal substrate, but it is high cost process. For the preparation of crystal-axis-

oriented materials, particles with special morphologies, such as plate-like and fibrous particles, are necessary, because they can be oriented easily by the mechanical methods, such as the doctor blade, tape casting, and spin coating methods.

Soft chemical synthesis is a useful method for the preparation of particles with special morphology. In the soft chemical synthesis, a compound with layered structure or other open structure can be used as the precursor.^{22–24)} The layered structure of the precursor can be transformed to a desired structure by an *in situ* topotactic structural transformation reaction, and the morphology of the precursor can be retained after the reaction. It means that the morphology of the product is dependent on that of the precursor, which is different from the normal methods like sol-gel and hydrothermal reaction methods where the crystal particle morphology are almost independent of the morphology of the precursor. By the normal methods, crystal morphology is controlled mainly in the crystal growth process, meaning control of growing plane of the crystal, but it is not easy.

Hydrothermal reaction is useful for the structural transformation in the soft chemical synthesis, and we call the method using the hydrothermal reaction for the soft chemical synthesis a hydrothermal soft chemical process.²⁵⁾ It has been reported that fibrous BaTiO₃ and PbTiO₃ can be prepared by hydrothermal treatment of a fibrous layered hydrous potassium titanate (2K₂O·11TiO₂·3H₂O) with Ba(OH)₂ and Pb₂O(OH), respectively.^{26,27)} The fibrous BaTiO₃ and PbTiO₃ particles show high degree crystal-axis-orientation and anisotropic dielectric properties. We have prepared plate-like anatase and BaTiO₃ particles by hydrothermal treatment of an H⁺-form lepidocrocite-like layered titanate with plate-like particle morphology.^{28,29)} The plate-like

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anatase and BaTiO₃ show high degree crystal-axis-orientation. The plate-like particles, however, are difficult to be used in the preparation of oriented ceramic, because of their large particle size of about 50 μm . Recently, we have prepared BaTiO₃ nanoparticles by using exfoliated layered titanate nanosheets as precursor.³⁰⁾ Although some sheet-like BaTiO₃ nanoparticles can be observed in the products, but the particle morphology is irregular.

In the present paper, we describe the preparation of crystal-axis-oriented plate-like BaTiO₃ nanoparticles by a novel solvothermal soft chemical process in ethanol and ethanol-water mixed solvents, the formation reaction mechanism, and the characterization of the nanoparticles. These plate-like BaTiO₃ particle is constructed from crystal-axis-oriented BaTiO₃ nanocrystals, which is suitable for preparing oriented BaTiO₃ ceramic material that has a potential application to the lead-free piezoelectric material due to its extremely large piezoelectric constant.³¹⁾

2. Experiment procedure

In the synthesis process, first a layered titanate of $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ (KTLO) with lepidocrocite-like layered structure was prepared by a hydrothermal reaction. 5.1 g of KOH, 0.6 g of LiOH·H₂O, 6.9 g of TiO₂ (anatase) and 25 mL of distilled water were sealed into a Hastelloy-C-lined vessel with internal volume of 45 mL, and then heated at 250°C for 24 h under stirring conditions. After the hydrothermal treatment, the sample was washed with distilled water, and dried at room temperature to obtain KTLO. KTLO (10 g) was treated with a 0.2 M HNO₃ solution (1 L) for 1 d under stirring conditions to exchange K⁺ and Li⁺ in the layered structure with H⁺, and then the sample was washed with distilled water. After 2 times of the acid-treatment, an H⁺-form layered titanate $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot n\text{H}_2\text{O}$ (HTO) was obtained.

A mixture of the H⁺-form titanate (0.147 g), a desired amount of Ba(OH)₂·8H₂O, and 15 mL solvent was sealed into a Teflon-lined, sealed stainless steel vessel (30 mL of inner volume), and then solvothermally treated at 120, 150, 200°C, respectively, for 12 h under stirring conditions. Water, ethanol, and water-ethanol mixed solvents were used in the reaction. The Ba(OH)₂ concentrations in the reaction system were adjusted to 0.1, 0.11, 0.12, and 0.15 M, respectively. Thus, the Ba/Ti mole ratios in the reaction system were controlled to be 1.0, 1.1, 1.2, and 1.5, respectively. After the solvothermal treatment, the product was filtered, washed with hot distilled water, and then dried at 80°C for 1 d.

The crystal structures of samples were investigated using a powder X-ray diffractometer (Shimadzu Co., XRD-6100) with Cu K α ($\lambda = 0.15418$ nm) radiation. The particle size and morphology were characterized by scanning electron microscopy (SEM, JEOL Ltd., JSM-5500S) or by field emission scanning electron microscopy (FE-SEM, JEOL Ltd., JSM-6700F). Transmission electron microscopy (TEM) observation and selected-area electron diffraction (SAED) were performed on a JEOL Ltd., JEM-3010 at 200 kV, and the nanoparticle sample was supported on a microgrid. In the crystal-axis-orientation study, plate-like particles were dispersed in ethanol solution by ultrasonication for 10 min, and then oriented on a silica glass slide by spin coating treatment at 4000 rpm.

3. Results and discussion

3.1 Synthesis of $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ and $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4$ nanoparticles

For the preparation of the plate-like BaTiO₃ nanoparticles by the soft chemical process, first layered titanate nanoparticles with

the plate-like morphology have to be prepared as the precursor. In the present study, we choose $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ (KTLO) with a lepidocrocite-like layered structure as the precursor. The large plate-like particles of KTLO can be prepared by a flux method.²⁸⁾ In the present study, KTLO was prepared by a hydrothermal method to obtain the plate-like nanoparticles. An XRD study revealed that single phase of KTLO with a basal spacing of 0.783 nm was obtained by hydrothermal treatment of the mixture of KOH, LiOH, and TiO₂ at 250°C. The KTLO prepared by the hydrothermal method has plate-like particle morphology with a size of about 200 nm in thickness and 3 μm in width.

K⁺ and Li⁺ in the KTLO structure can be exchanged with H⁺ in acid solution. An H⁺-form layered titanate $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot n\text{H}_2\text{O}$ (HTO) was obtained after the ion-exchange. XRD study indicated that HTO retained the lepidocrocite-like layered structure, while the basal spacing increased to 0.923 nm after the ion-exchange (Fig. 1(a)), owing to the increase of water content in the interlayer space of the layered structure. The plate-like particle morphology of KTLO retained after the ion-exchange reaction, as shown in Fig. 2(a).

3.2 Synthesis of BaTiO₃ in water solvent

For the preparation of BaTiO₃ nanoparticles, firstly the layered

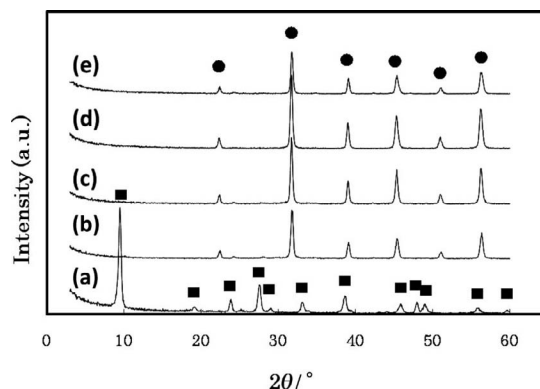


Fig. 1. XRD patterns of (a) H⁺-form layered titanate (HTO), and samples obtained by hydrothermal treatment of HTO at 120°C in (b) 0.10 M, (c) 0.11 M, (d) 0.12 M, and (e) 0.15 M Ba(OH)₂ solutions, respectively, in water solvent system. ■: HTO phase; ●: BaTiO₃ phase.

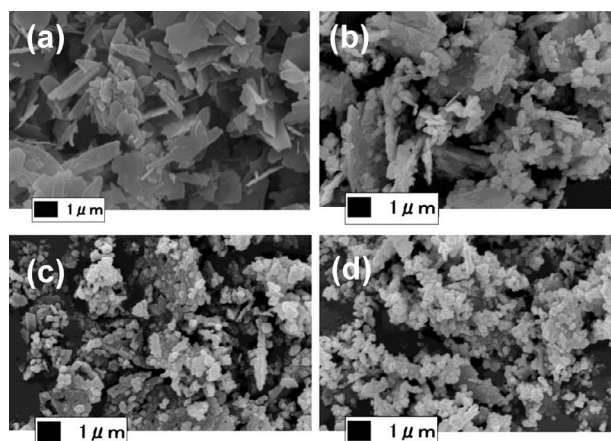


Fig. 2. SEM images of (a) HTO and BaTiO₃ samples prepared at 120°C in (b) 0.10 M, (c) 0.12 M, and (d) 0.15 M Ba(OH)₂ solution, respectively, in water solvent system.

titanate HTO was reacted with $\text{Ba}(\text{OH})_2$ in water solvent at 120, 150, and 200°C, respectively. Figure 1 shows XRD patterns of the products obtained at 120°C. The layered titanate was transformed into BaTiO_3 completely after the hydrothermal treatment, even at the low temperature conditions of 120°C. This result suggests the HTO shows high reactivity in the formation reaction of BaTiO_3 . The particle morphology of the products was investigated using SEM (Fig. 2). In the sample prepared in 0.10 M $\text{Ba}(\text{OH})_2$ solution, the particles partially retained the plate-like particle morphology of the HTO precursor and some small spherical nanoparticles were formed. The percentage of small spherical nanoparticle increased with increasing $\text{Ba}(\text{OH})_2$ concentration, and finally almost all particles changed to small spherical nanoparticles in 0.15 M $\text{Ba}(\text{OH})_2$ solution. The crystallinity of BaTiO_3 and the percentage of small spherical nanoparticle increased with increasing the reaction temperature and the $\text{Ba}(\text{OH})_2$ concentration in the reaction system.

In the BaTiO_3 formation process, the plate-like BaTiO_3 particles were formed by an *in situ* topotactic structural transformation reaction, while the small spherical BaTiO_3 particles were formed by destruction of the plate-like particles. The plate-like particle morphology was damaged by a dissolution-deposition reaction that occurs on the particle surface under the hydrothermal conditions, which increased with increasing the $\text{Ba}(\text{OH})_2$ concentration and reaction temperature, which will be discussed later in detail. This result suggests that the dissolution-deposition reaction occurs easily for the HTO nanoparticles; due to the nanoparticles have a large surface area. For the preparation of the plate-like BaTiO_3 nanoparticles, decrease of the dissolution-deposition reaction is very important.

3.3 Synthesis of BaTiO_3 in ethanol solvent

To decrease the dissolution-deposition reaction, we use ethanol as the reaction solvent instead of water solvent. A XRD analysis results revealed that the layered structure of HTO was partially transformed to BaTiO_3 structure after the solvothermal reaction at 120°C in the ethanol solvent. All of layered structure was transformed to BaTiO_3 structure at 200°C (Fig. 3). The crystallinity of BaTiO_3 increased with increasing the reaction temperature and the concentration of $\text{Ba}(\text{OH})_2$ solution similar to the case in water solvent. In comparison with the case in water solvent (Fig. 1), however, the diffraction peaks of BaTiO_3 phase were quite broad even under the high temperature conditions of 200°C, revealing that low crystallinity BaTiO_3 was formed in the

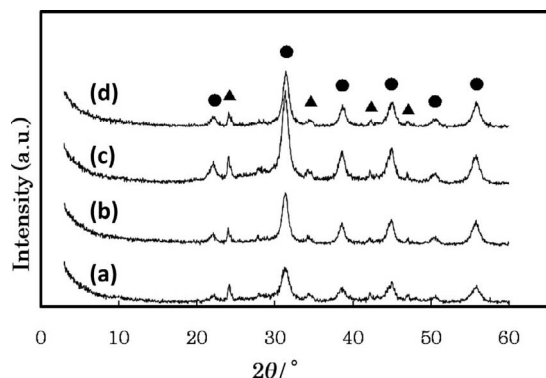


Fig. 3. XRD patterns of samples obtained by solvothermal treatment of HTO at 200°C in (a) 0.10 M, (b) 0.11 M, (c) 0.12 M, and (d) 0.15 M $\text{Ba}(\text{OH})_2$ solutions, respectively, in ethanol solvent system. ●: BaTiO_3 phase; ▲: BaCO_3 phase.

ethanol solvent. This result indicated that the ethanol solution has a lower reactivity than the water solution.

The products prepared in ethanol solution retained well the plate-like particle morphology of HTO precursor in the $\text{Ba}(\text{OH})_2$ concentration range studied here, as shown in Fig. 4, where almost without small spherical BaTiO_3 nanoparticles were observed. The ethanol solvent has a lower polarity than water, so that it shows a lower ability to dissolve HTO and $\text{Ba}(\text{OH})_2$ in the BaTiO_3 formation reaction, which decreases the dissolution-deposition reaction on the HTO particle surface and keep the particle morphology. The above results reveal that the selection of reaction solvent is effective for controlling the dissolution-deposition reaction and particle morphology.

3.4 Synthesis of BaTiO_3 in water-ethanol mixed solvent

Although the plate-like BaTiO_3 nanoparticles can be prepared in ethanol solvent, but the crystallinity is low. We tried to prepare the plate-like BaTiO_3 nanoparticles with high crystallinity by changing the polarity of the reaction solvent. A water-ethanol mixed solvent was chosen, because a series of solvent with different polarities can be obtained easily by changing fraction of water in the mixture. Figure 5 shows XRD patterns for the samples prepared in the water-ethanol mixed solvent with a volume ratio of $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/9$ at 200°C. The XRD peaks of BaTiO_3 phase were much sharper than those prepared in ethanol solution (Fig. 3). The SEM images for the samples indicated that plate-like BaTiO_3 nanoparticles were obtained in 0.10 and 0.12 M $\text{Ba}(\text{OH})_2$ solution, and the plate-like particle morphology changed to the spherical nanoparticle morphology in 0.15 M $\text{Ba}(\text{OH})_2$ solution at 200°C (Fig. 6).

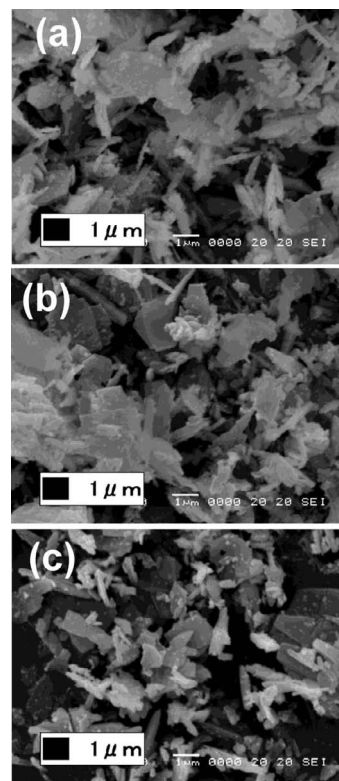


Fig. 4. SEM images of BaTiO_3 samples prepared at 200°C in (a) 0.10 M, (b) 0.12 M, and (c) 0.15 M $\text{Ba}(\text{OH})_2$ solution, respectively, in ethanol solvent system.

The preparation of BaTiO₃ was carried out also under other different conditions, such as different volume ratios of H₂O/C₂H₅OH and temperatures. The results indicate that the reactivity for the BaTiO₃ formation increases with increasing the ratio of H₂O/C₂H₅OH of the solvent, reaction temperature, and Ba(OH)₂ concentration. The plate-like BaTiO₃ nanoparticles with high crystallinity can be prepared at 200°C in 0.11 M Ba(OH)₂ solution of water-ethanol mixed solvent with volume ratio of H₂O/C₂H₅OH = 1/9.

3.5 Nanostructural study of BaTiO₃ nanoparticles

The nanostructure of the plate-like BaTiO₃ nanoparticles was

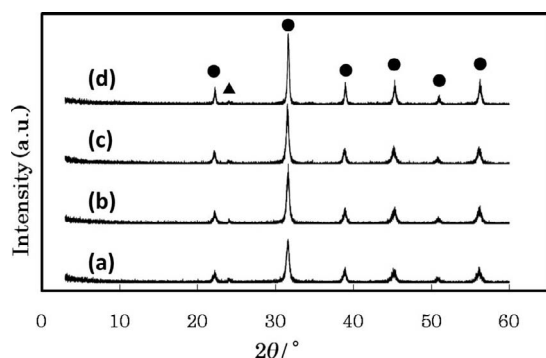


Fig. 5. XRD patterns of samples obtained by solvothermal treatment of HTO at 200°C in (a) 0.10 M, (b) 0.11 M, (c) 0.12 M, and (d) 0.15 M Ba(OH)₂ solutions, respectively, in water-ethanol mixed solvent system with water/ethanol volume ratio of 1/9. ●: BaTiO₃ phase; ▲: BaCO₃ phase.

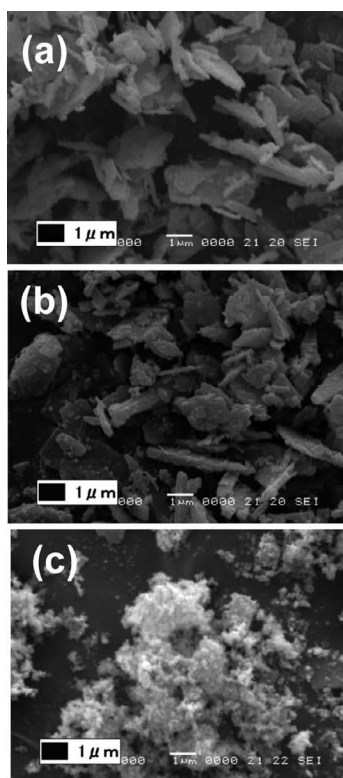


Fig. 6. SEM images of BaTiO₃ samples prepared at 200°C in (a) 0.10 M, (b) 0.12 M, and (c) 0.15 M Ba(OH)₂ solution, respectively, in water-ethanol mixed solvent system with water/ethanol volume ratio of 1/9.

investigated using FE-SEM and TEM. **Figure 7** shows the FE-SEM images of the BaTiO₃ prepared in water-ethanol (1/9) mixed solvent at 120, 150, and 200°C. The samples prepared at 120 and 150°C in 0.11 M Ba(OH)₂ solution have plate-like particle morphology, and the plate-like particles are constructed by connecting spherical nanoparticles, meaning that the plate-like particles are polycrystalline BaTiO₃. The size of the spherical nanoparticles in the plate-like particles is about 20 nm (Fig. 7(b), (c)). The plate-like particles are split into independent spherical nanoparticles with a size of about 50 nm after reaction at 200°C in 0.15 M Ba(OH)₂ solution (Fig. 7(d)). The disintegration of the plate-like particles is due to the crystal growth of the spherical nanoparticles with increasing reaction temperature and Ba(OH)₂ concentration.

Figure 8 shows TEM images and selected area electron dif-

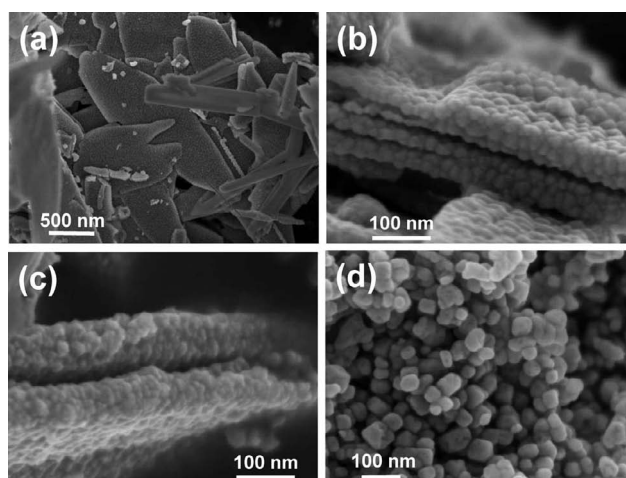


Fig. 7. FE-SEM images of BaTiO₃ samples prepared (a, b) at 120°C in 0.11 M Ba(OH)₂ solution, (c) at 150°C in 0.11 M Ba(OH)₂ solution, and (d) at 200°C in 0.15 M Ba(OH)₂ solution, respectively, in water-ethanol mixed solvent system with water/ethanol volume ratio of 1/9.

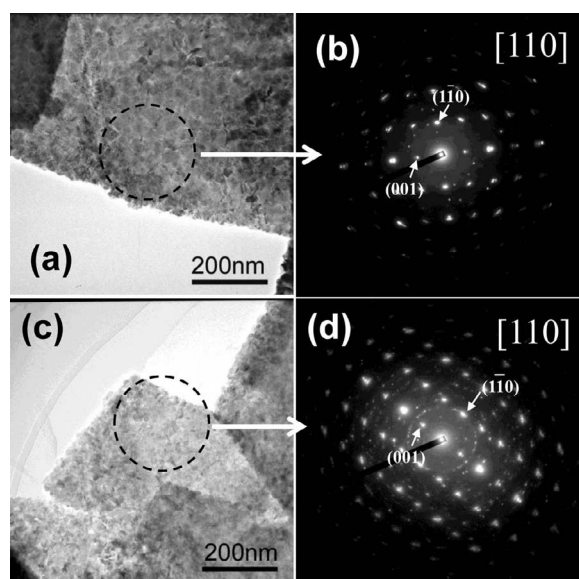


Fig. 8. TEM images and SAED patterns for the plate-like BaTiO₃ nanoparticles prepared (a, b) at 120°C in 0.11 M Ba(OH)₂ solution and (c, d) at 150°C in 0.11 M Ba(OH)₂ solution, respectively, in water-ethanol mixed solvent system with water/ethanol volume ratio of 1/9.

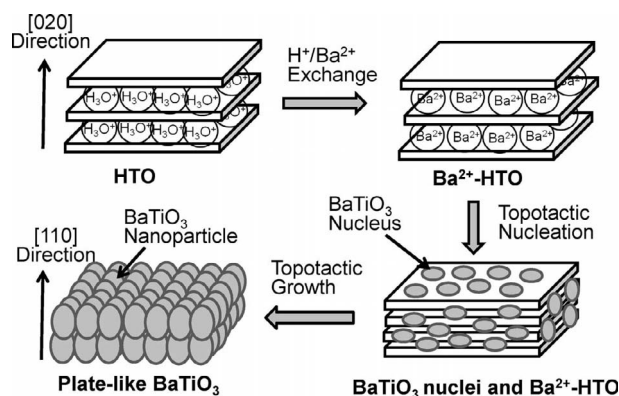


Fig. 9. Formation mechanism of the plate-like BaTiO₃ nanoparticle by topotactic structural transformation reaction.

fraction patterns (SAED) of the plate-like BaTiO₃ nanoparticles. It can be confirmed that the plate-like particles are constructed from the spherical nanoparticles by the TEM images, similar to the FE-SEM results. It is very interesting that although the plate-like BaTiO₃ nanoparticle prepared at 120°C is a polycrystalline particle, but it shows a SAED pattern similar to the BaTiO₃ single crystal (Fig. 8(b)). This result reveals that all small spherical nanoparticles in each plate-like particle are arranged in the same crystal-axis orientation, meaning perfectly oriented polycrystalline particle. The SAED pattern indicates that the [110] direction of the BaTiO₃ structure is vertical to the basal plane of the plate-like particle. The sample prepared at 150°C shows a similar SAED pattern to the sample prepared at 120°C, except some weak diffraction rings were observed (Fig. 8(d)). The diffraction rings are due to small amount of randomly arranged BaTiO₃ nanoparticles. The SAED results reveal that the plate-like BaTiO₃ particles show the crystal-axis-orientation in the [110] direction, and the orientation decreases with increasing reaction temperature.

3.6 Formation reaction mechanism for BaTiO₃ nanoparticles

The above results suggest that two types of reactions occur in the formation process of BaTiO₃ nanoparticles from the HTO precursor. One is the *in situ* topotactic structural transformation reaction, and the other is the dissolution-deposition reaction, as shown in Fig. 9. In the *in situ* topotactic structural transformation reaction, Ba²⁺ ions intercalate into the crystal bulk of the layered titanate through the interlayer pathway by a H⁺/Ba²⁺ exchange reaction. The Ba²⁺ ions react with the TiO₆ octahedral layers of HTO in the crystal bulk to form BaTiO₃ nuclei, and then the nuclei grow up to the BaTiO₃ nanocrystals by *in situ* topotactic mechanism, where the TiO₆ octahedra shift regularly from the positions of the layered structure to the positions of BaTiO₃ structure in a sub-nanometer order distance. The *in situ* topotactic mechanism causes the formation of the crystal-axis-oriented BaTiO₃ nanostructure. There is a definite crystallographic relationship between the layered structure of the HTO precursor and structure of the BaTiO₃ product in the topotactic transformation reaction, which determine the direction of crystal-axis-orientation of the BaTiO₃ crystals. In the present case, the [020] direction of the lepidocrocite-like layered structure of HTO²⁸⁾ corresponds to the [110] direction of BaTiO₃ structure.

In the dissolution-deposition reaction, the titanium oxide dissolves in the alkaline solution of Ba(OH)₂, reacts with Ba²⁺ in the

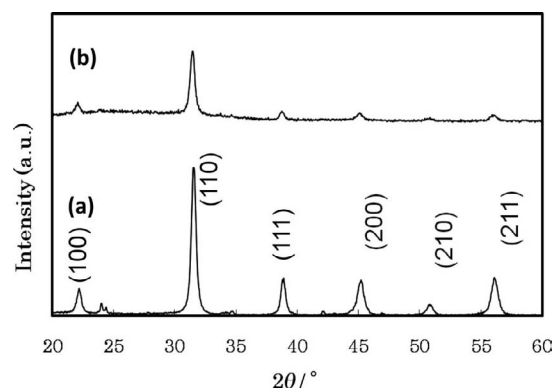


Fig. 10. XRD patterns of plate-like BaTiO₃ particles prepared at 200°C in 0.11 M Ba(OH)₂ solution in water-ethanol mixed solvent system with water/ethanol volume ratio of 1/9. (a) without and (b) with spin coating orientation treatment.

solution, and then forms BaTiO₃ on the particle surface. The dissolution-deposition reaction causes formation cracks on the plate-like particles, which split the plate-like BaTiO₃ particle into the spherical nanoparticles (Fig. 7). The dissolution-deposition reaction also causes the crystal growth of the spherical BaTiO₃ nanoparticles similar to the normal hydrothermal reaction, which increases the size of the spherical BaTiO₃ nanoparticles, and finally splits the plate-like particle into the independent spherical nanoparticles. The dissolution-deposition reaction increases with increasing solubility of titanium oxide in the solution, corresponding to the increase of the polarity of the reaction solvent, reaction temperature and Ba(OH)₂ concentration (Figs. 2, 4, 6). In the water-ethanol mixed solvent reaction system, the polarity increases with increasing water content in the solvent. Therefore, the control of these factors to decrease the dissolution-deposition reaction is the point for the preparation of plate-like BaTiO₃ with high crystallinity.

3.7 Orientation behavior of plate-like BaTiO₃ nanoparticles

The plate-like BaTiO₃ nanoparticles prepared by the solvothermal soft chemical process described above can be oriented on a silica glass slide surface by spin coating treatment. After the spin coating orientation treatment, the plate-like nanoparticles show a relatively higher intensity for (110) diffraction peak and lower intensities for other diffraction peaks than the sample without orientation treatment, as shown in Fig. 10. This result reveals that the plate-like BaTiO₃ nanoparticles are oriented on the glass slide surface after the spin coating treatment, where the basal plane of the plate-like particles, corresponding to the (110) plane of the BaTiO₃ structure, is parallel to the glass slide surface. The above results imply that the plate-like BaTiO₃ nanoparticles can be oriented easily by the mechanical methods, such as spin coating, doctor blade, and tape casting methods, in the preparation process for the oriented BaTiO₃ ceramic materials which have potential application to the high performance electronic devices.³¹⁾

4. Conclusion

Two types of simultaneous reactions occur in the formation of BaTiO₃ from HTO precursor under the solvothermal conditions. One is the *in situ* topotactic structural transformation reaction in the crystal bulk of the layered titanate, and the other is the

dissolution-deposition reaction on the surface of the particles. The crystal-axis-oriented plate-like BaTiO₃ nanoparticles are formed by the topotactic reaction, and the plate-like particles are split into small spherical BaTiO₃ nanoparticles by the dissolution-deposition reaction. The fraction of the dissolution-deposition reaction and the crystallinity of BaTiO₃ nanoparticles increase with increasing polarity of the reaction solvent, reaction temperature, and Ba(OH)₂ concentration. The control of the solvent polarity is an important factor to obtain the plate-like BaTiO₃ nanoparticles with high crystallinity. It is effective and convenient to use the water-ethanol mixed solvent for the polarity control. The plate-like BaTiO₃ nanoparticles with high crystallinity can be prepared in the water-ethanol mixed solvent, and those with low crystallinity in the ethanol solvent. The plate-like BaTiO₃ nanoparticles are polycrystalline particles constructed from spherical nanocrystals. All spherical nanocrystals in each plate-like particle are arranged in the same crystal-axis orientation, and show high degree crystal-axis-orientation in [110] direction.

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