Stabilization of Size-Controlled BaTiO$_3$ Nanocubes via Precise Solvothermal Crystal Growth and Their Anomalous Surface Compositional Reconstruction

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ABSTRACT: Crystal growth of barium titanate (BaTiO$_3$) using a wet chemical reaction was investigated at various temperatures. BaTiO$_3$ nanoparticles were obtained at an energy-efficient temperature of 80 °C. However, BaTiO$_3$ nanocubes with a preferred size and shape could be synthesized using a solvothermal method at 200 °C via a reaction involving titanium tetraisopropoxide [(CH$_3$)$_2$CHO]$_4$Ti for nucleation and fine titanium oxide (TiO$_2$) nanoparticles for crystal growth. The BaTiO$_3$ nanocubes showed a high degree of dispersion without the use of dispersants or surfactants. The morphology of BaTiO$_3$ was found to depend on the reaction medium. The size of the BaTiO$_3$ particles obtained using water as the reaction medium was the largest among the particles synthesized using various reaction media. In the case of alcohol reaction media, the BaTiO$_3$ particle size increased in the order methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol. Furthermore, BaTiO$_3$ powder obtained using alcohol reaction media resulted in cubic shapes as opposed to the round shapes obtained when water was used as the medium. We found that the optimal condition for the synthesis of BaTiO$_3$ nanocubes involved the use of 1-butanol as the reaction medium, resulting in an average particle size of 52 nm, which is the average distance of the cubes measured diagonally from corner to corner, and a tetragonal crystal system as evidenced by the powder X-ray diffraction pattern obtained using high-energy synchrotron X-rays. The origin of the spontaneous polarization of the BaTiO$_3$ tetragonal crystal structure was clarified by a pair distribution function analysis. In addition, surface reconstruction of BaTiO$_3$ nanocubes led to an outermost surface comprising two layers of Ti columns.

INTRODUCTION

Barium titanate (BaTiO$_3$) is widely used in ceramic capacitors because of its ferroelectric and piezoelectric properties.$^{1,2}$ In addition, it exhibits high relative permittivity, enabling its use in sensors, actuators, power transmission devices, memory devices, and high energy storage devices.$^{1,3}$ However, further improvements to BaTiO$_3$ particles are necessary in order to enhance their dielectric constant. BaTiO$_3$ is generally synthesized at temperatures greater than 1000 °C via a solid-phase reaction although such a reaction makes controlling the morphology of the obtained powders difficult. However, a wet chemical reaction enables control of the morphology; moreover, it is a more energy-efficient process than a solid-phase reaction. Highly energy-efficient processes are those that can be performed at room temperature. A previous study demonstrated the synthesis of sub-10 nm BaTiO$_3$ nanocrystals at room temperature via the vapor diffusion sol–gel method and their subsequent characterization by Rietveld analysis of synchrotron X-ray diffraction (XRD) data, Raman spectroscopy, and a pair distribution function (PDF) analysis, which revealed non-centrosymmetric regions arising from the off-centering of Ti atoms.$^4$ By contrast, a different reaction occurred at 200 °C using a novel nonaqueous route for the preparation of nanocrystalline BaTiO$_3$.$^5$ The authors of this second paper reported obtaining nearly spherical BaTiO$_3$ nanoparticles with diameters ranging from 4 to 5 nm.

The ideal BaTiO$_3$ morphology is a single nano-sized crystal with a cubic shape.$^{5-10}$ A densely assembled ceramic can be created if uniform BaTiO$_3$ nanocubes are used as a base substance. The authors of previous studies have reported using platinum (Pt)$^{11}$ and palladium (Pd)$^{12}$ nanocubes as a base substance; however, the strain between the BaTiO$_3$ nanocubes led to a high dielectric constant in the densely assembled ceramic.$^{13}$ That is, BaTiO$_3$ nanocubes are necessary for the material design because of the surface properties of the particles. The synthesis of BaTiO$_3$ nanoparticles requires three
key points: (1) a method to control the particle size because nanoscale materials are desirable as a consequence of their large specific surface area; (2) a method to control the particle shape because cubes are desirable as a consequence of the wide contact area between nanocubes; and (3) a method to control the particle surface as strain between nanocubes is desirable because it eliminates the need for a dispersant or surfactant.

Controlling BaTiO₃ nucleation and crystal growth is essential for the formation of BaTiO₃ nanocubes. One technique for morphological control is a wet chemical reaction using a bottom-up approach that enables atomic-level control. Researchers have reported synthesizing BaTiO₃ with various morphologies, including cube-like, nanorod, nanowire, acicular, and hollow shapes, using wet chemical reactions. In the present study, we chose a solvothermal method as a wet chemical reaction method; this technique involves using reaction media at high temperatures and under high saturated vapor pressures in an autoclave. Specifically, we used the solvothermal method, which is a solvothermal method in which water is used as the reaction medium. We selected this...
method because it enables the dissolution of raw materials such as titanium oxide (TiO$_2$) while maintaining control of nucleation and crystal growth at $\sim$200 °C. From the viewpoint of morphological control, surface modification is not used in BaTiO$_3$ synthesis because the surface properties of BaTiO$_3$ particles directly affect their dielectric constant.

We used electron microscopy to investigate the surface of the obtained BaTiO$_3$ nanocubes. In particular, surface reconstruction was examined in detail. Surface reconstruction, where the atomic column arrangement at a crystal’s surface differs from the regular atomic column arrangement within the crystal, often occurs in one or two layers at the surface of metal oxide or oxynitride crystals. Previous studies have reported the occurrence of surface reconstruction on TiO$_2$,$^{21−23}$ SrTiO$_3$,$^{24−26}$ and LaTiO$_2$N$^{27}$ crystals. These studies have provided important information about the function expression. In the present study, we primarily focused on the size, shape, and surface of BaTiO$_3$ particles as well as on controlling their morphology during synthesis without modifying their surface.

## RESULTS AND DISCUSSION

### Raw Materials and Reaction Media

The type and concentration of raw material, reaction temperature and time, and reaction medium are important factors for morphological control; these parameters determine the solubility of the raw material, nuclei formation, and crystal growth of the obtained powders. In the present study, we used TiO$_2$ and/or [(CH$_3$)$_2$CHO]$^4$Ti and Ba(OH)$_2$·8H$_2$O as raw materials and water, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol as the reaction media.

Although TiO$_2$ is difficult to dissolve in all the chosen reaction media, [(CH$_3$)$_2$CHO]$^4$Ti is hydrolyzed in water and can be dissolved in methanol, ethanol, 1-propanol, 1-butanol, or 1-pentanol. Ba(OH)$_2$·8H$_2$O can dissolve in water but not in the alcohol media. Additionally, the relative permittivity at room temperature differs among the media used, with water having the largest relative permittivity, followed by methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol. The relative permittivity of the reaction medium is closely related to the solubility of the raw material.

### Synthesis of BaTiO$_3$ Particles Below 80 °C

Figure 1 shows XRD patterns for powders produced via solvothermal synthesis using TiO$_2$ as a raw material and different reaction temperatures. TiO$_2$ (10 mmol) and Ba(OH)$_2$·8H$_2$O (20 mmol) were the raw materials reacted for 72 h in water (40 mL) at room temperature, 40, 60, or 80 °C. The XRD pattern was assigned to a single phase of anatase-type TiO$_2$. No peaks attributable to BaTiO$_3$ were observed in the pattern for the product obtained after reaction at room temperature [Figure 1(a-1)]. However, the XRD pattern for the product obtained at 40 °C [Figure 1(b-1)] shows the formation of both anatase-type TiO$_2$ and BaTiO$_3$, with single phases of BaTiO$_3$ also confirmed in the products obtained at 60 and 80 °C [Figure 1(c-1),(d-1)]. The XRD peaks were assigned to BaTiO$_3$ with a tetragonal crystal system was executed using the RIETAN-Fp$^{37,38}$ and Z-Rietveld$^{39−41}$ software packages for XRD and neutron diffraction (ND) patterns, respectively. The R-weighted pattern ($R_w$) and R-pattern ($R_p$) are shown in Tables 1 and 2.

| Table 1. Rietveld Refinement of the Structural Parameters of the High-Energy Synchrotron XRD Pattern for the Same Sample Shown in Figure 1 |
|---|---|---|---|
| synthesis temperature (°C) | BaTiO$_3$ P4mm model | a/Å | c/Å | $R_w/%$ | $R_p/%$ |
| 40 | 4.00671(63) | 4.01753(110) | 1.66 | 1.07 |
| 60 | 4.01129 (43) | 4.02317(78) | 0.86 | 0.65 |
| 80 | 4.00643(39) | 4.02050(71) | 0.83 | 0.64 |

The XRD pattern for the product obtained at 40 °C [Figure 1(b-2)] indicates that the principal component was BaTiO$_3$, and that the peak intensity of anatase-type TiO$_2$ decreased. Notably, we obtained BaTiO$_3$ at 40 °C, which is an extremely low reaction temperature. When the synthesis temperature was increased, the amount of BaTiO$_3$ obtained increased [Figure 1]. The high-energy synchrotron XRD pattern for the product obtained at 80 °C [Figure 1(d-2)] clearly confirmed a single phase of BaTiO$_3$.

A shortcoming of XRD is its poor ability to detect light elements such as oxygen (O) because an element’s atomic scattering factor depends on its atomic number; that is, the atomic scattering factor increases with increasing atomic number. ND has an advantage in detecting light elements such as oxygen because the coherent neutron scattering length varies by element. Therefore, ND measurements and Rietveld refinement were performed to confirm the presence of oxygen defects in BaTiO$_3$. The corresponding $R_w$ and $R_p$ values are shown in Figure 1. All the $R_w$ and $R_p$ values from the Rietveld analysis were satisfactory [Figure 1(b-3,c-3,d-3)]. The ND pattern for the product obtained at 40 °C [Figure 1(b-3)] indicates that the principal component was BaTiO$_3$ and the intensity of the anatase-type TiO$_2$ decreased. When the synthesis temperature increased, the amount of BaTiO$_3$ increased [Figure 1(c-3,d-3)]. The ND pattern for the product obtained at 80 °C [Figure 1(d-3)] shows that a single phase of BaTiO$_3$ was obtained.

| Table 2. Rietveld Refinement of the Structural Parameters of the High-Energy Synchrotron ND Pattern for the Same Sample Shown in Figure 1 |
|---|---|---|---|
| synthesis temperature (°C) | BaTiO$_3$ P4mm model | a/Å | c/Å | $R_w/%$ | $R_p/%$ |
| 40 | 4.03033(3) | 4.03804(5) | 4.08 | 3.19 |
| 60 | 4.02466(9) | 4.04024(11) | 5.21 | 3.79 |
| 80 | 4.02259(8) | 4.04132(11) | 3.11 | 2.42 |

Tables 1 and 2 show the Rietveld refinement structural parameters corresponding to the high-energy synchrotron XRD and ND pattern for the samples [Figure 1(b-1,c-1,d-1)]. The lattice constants obtained from refinement of the high-energy synchrotron XRD data and ND data were approximately the same. In addition, the ND analysis revealed no oxygen defects.

Figure 2 shows secondary electron (SE) images of powders produced via solvothermal synthesis using TiO$_2$ as a raw
were observed in detail from HAADF–STEM and ABF–STEM. Also, elemental analyses of Ba and Ti were conducted using EELS peaks. Ba and Ti are indicated by green and red, respectively. Ti atomic columns were arranged in line with the surface of the BaTiO3 nanoparticle. Surface reconstruction of the BaTiO3 nanoparticle was confirmed from STEM observations and EELS analyses. In addition, EELS analysis of another BaTiO3 nanoparticle is shown in Figure S1. The surface reconstruction of the BaTiO3 nanoparticle is indicated in Figure S1.

One explanation for the formation of BaTiO3 at temperatures above 40 °C is the inclusion of larger TiO2 particles and their solubility characteristics. In general, TiO2 does not dissolve in water at room temperature; however, fine TiO2 particles can dissolve in water with a basic pH. Therefore, when Ba(OH)2·8H2O was dissolved more readily in water at higher temperatures, the solution acquired a basic pH that promoted solvation of the fine TiO2 particles.

**Synthesis of BaTiO3 Particles at Above 80 °C.**

**Solvothermal Synthesis Using TiO2 as a Ti Raw Material.** Following the solvothermal reaction of TiO2 and Ba(OH)2·8H2O between 100 and 200 °C for 72 h, the XRD pattern for the products revealed BaTiO3 with a tetragonal crystal system (JCPDS file: 5-0626). (Figures S2 and S3 in the Supporting Information). Regarding the effect of acetic acid treatment, the product remained unchanged at 200 °C for 72 h when compared with after the treatment (Figure S2 (f) and before (Figure S3). Rietveld refinement of the P4mm model of BaTiO3 in the tetragonal crystal system was performed using the Z-Rietveld software packages for the XRD pattern (Figure S3). Rietveld refinement revealed a single phase of BaTiO3 before acetic acid treatment. The R-weighted pattern (Rwp) and R-pattern (Rp) are shown in Table S1. All the Rwp and Rp values from the Rietveld analysis were satisfactory (Figure S3, Table S1). The SE images in Figure S reveals that the synthesized particles were smallest at 100 °C [Figure S5a] and became larger with increasing reaction temperatures [Figure S5b–f]. Furthermore, the particles acquired a cubic shape with increasing temperature, with BaTiO3 cubes forming at 200 °C [Figure S5f]. It was found that the reaction temperature was important for synthesis of BaTiO3 nanocubes. Regarding the previous reports, a metal based on one element such gold (Au)28–35 and palladium (Pd)12 can be synthesized with the use of dispersants or surfactants below 80 °C (at a low temperature). On the other hand, cesium lead halide (CsPbX3)36 can be prepared as a specimen with a perovskite structure being necessary below 160 °C (high temperature) for the nanocube synthesis. Therefore, the reaction temperature is the key point for the nanocube synthesis.

**Figure 2.** SE images of powders produced via the hydrothermal method using TiO2 as a raw material and different reaction temperatures. TiO2 (10 mmol), Ba(OH)2·8H2O (20 mmol) for 72 h, with a reaction medium of water (40 mL) at (a) room temperature, (b) 40 °C, (c) 60 °C, and (d) 80 °C.

**Figure 3.** TEM image and the corresponding nano-beam electron diffraction pattern for BaTiO3 produced via the solvothermal method at 80 °C, from the direction of [001] incidence. The accelerating voltage was 80 kV. TiO2 (10 mmol), Ba(OH)2·8H2O (20 mmol) for 72 h in 40 mL of water as a reaction medium. (a) Nano-beam diffraction of sample 1 and (b) nano-beam diffraction of sample 2.
We next examined the effect of varying the Ba(OH)$_2$·8H$_2$O concentration on the solvothermal synthesis of BaTiO$_3$. XRD patterns were assigned to the same tetragonal crystal system (JCPDS file: 5-0626) (Figure S4, Supporting Information); however, the shape changed dramatically as the Ba(OH)$_2$·8H$_2$O concentration was varied. Figure 6 shows SE images indicating that formless particles were synthesized from low-concentration Ba(OH)$_2$·8H$_2$O [Figure 6a], whereas the shape gradually became cube-like as the Ba(OH)$_2$·8H$_2$O concentration increased [Figure 6b,c]. We found that cube-shaped BaTiO$_3$ particles formed when the amount of Ba(OH)$_2$·8H$_2$O was greater than 20 mmol [Figure 6d–f], with no significant difference in shape, although their sizes were on the order of several hundred nanometers. Therefore, subsequent solvothermal syntheses were performed using 20 mmol of Ba(OH)$_2$·8H$_2$O as a raw material.

We next evaluated the effect of reaction time on the solvothermal synthesis. The XRD patterns were assigned to BaTiO$_3$ with a tetragonal crystal system (JCPDS file: 5-0626) (Figure S5, Supporting Information). Figure 7 shows SE images revealing aggregated particles resulting from a relatively short reaction time [Figure 7a–c], where the shape of the BaTiO$_3$ powder particles became gradually more cube-like as the reaction time was increased to 72 h [Figure 7d,e]. Moreover, we found no substantial difference in the shape of the BaTiO$_3$ products at reaction times longer than 72 h [Figure 7e,f], where the particle size was on the order of several...
hundred nanometers. Therefore, subsequent solvothermal syntheses were performed at a reaction time of 72 h.

We subsequently evaluated the effects of different media on the BaTiO₃ solvothermal synthesis. The XRD results indicate that the products crystallized in the same crystal system as those synthesized under the previously studied conditions (Figure S6, Supporting Information); however, the SE images indicate that the dielectric constant of the solvent affected the size and shape of the particles (Figure 8). Water is a hydrophilic solvent with the largest room-temperature dielectric constant among the tested solvents. By contrast, the alcohol-based solvents are hydrophobic, with small room-temperature dielectric constants that vary with the number of carbon atoms (i.e., methanol < ethanol < 1-propanol < 1-butanol < 1-pentanol). We found that cube-like BaTiO₃ crystals were obtained with particle sizes > 100 nm in water (Figure 8a), whereas the particle size was dramatically decreased in the alcohol-based solvents, with the smallest size observed in methanol and increasing according to the number of carbon atoms in the solvent (methanol < ethanol <
1-propanol < 1-butanol) [Figure 8b–c]. The particle shape was approximately the same between products synthesized in 1-butanol and 1-pentanol [Figure 8e,f]. Moreover, the shape became increasingly cubic under the same conditions in the alcohol solvents. Furthermore, electron microscopy observations were conducted at an acceleration voltage of 200 kV. The shape of nanocubes was clearly observed from the SE and bright-field transmission electron microscopy (BF−TEM) images [Figure 9a,b]. A single crystal of BaTiO₃ was confirmed from the selected area electron diffraction (SAED) pattern for the BF−TEM image [Figure 9c].

Solvothermal Synthesis Using [(CH₃)₂CHO]₄Ti and/or TiO₂ as the Raw Material for Ti. The solubility of the raw material is an important factor for morphological control because of its effect on nucleation and crystal growth. We aimed to enable the formation of a large number of BaTiO₃-nuclei to obtain nanoscale BaTiO₃. We used [(CH₃)₂CHO]₄Ti and TiO₂ as raw materials. The [(CH₃)₂CHO]₄Ti is soluble in methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol at room temperature; however, TiO₂ cannot dissolve in alcohol-based solvents at room temperature but rather requires heat treatment to enable Ti-related crystal growth. We found that using a mixture of [(CH₃)₂CHO]₄Ti and TiO₂ under solvothermal conditions led to BaTiO₃-nucleation and crystal growth, respectively, with the number of nuclei determining the particle size (a large number of nuclei resulted in small particles and vice versa) and crystal growth determining the particle shape. We therefore conducted solvothermal synthesis using [(CH₃)₂CHO]₄Ti and TiO₂ as raw materials to obtain BaTiO₃ nanocubes.

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Figure 9. SE images, BF−TEM image from the direction of [001] incidence, and the corresponding SAED pattern for powders produced via the solvothermal method using TiO₂ (10 mmol) and Ba(OH)₂·8H₂O (20 mmol) as raw materials at 200 °C for 72 h in 40 mL of reaction medium of water. (a) SE image, (b) BF−TEM image, and (c) SAED image of (b).

Figure 10. SE images of powders produced via the solvothermal method using [(CH₃)₂CHO]₄Ti as a raw material and various reaction media. [(CH₃)₂CHO]₄Ti (10 mmol), Ba(OH)₂·8H₂O (20 mmol) at 200 °C for 72 h in 40 mL of reaction medium of (a) water, (b) methanol, (c) ethanol, (d) 1-propanol, (e) 1-butanol, and (f) 1-pentanol.

Figure 11. SE images of powders produced via the solvothermal method using equal parts [(CH₃)₂CHO]₄Ti and TiO₂ as raw materials and various reaction media. [(CH₃)₂CHO]₄Ti (5 mmol), TiO₂ (5 mmol), Ba(OH)₂·8H₂O (20 mmol) at 200 °C for 72 h in 40 mL of reaction medium of (a) water, (b) methanol, (c) ethanol, (d) 1-propanol, (e) 1-butanol, and (f) 1-pentanol.
We predicted that the size of the obtained particles would increase in the alcohol-based solvents because of the high solubility of \((\text{CH}_3)_2\text{CHO}\)_4\text{Ti}\) decreasing the dielectric constant of the solvent. XRD patterns were assigned to \(\text{BaTiO}_3\) with a tetragonal crystal system (JCPDS file: 5-0626) (Figure S7, Supporting Information), and the SE images revealed cube-like shapes under all solvent conditions [Figure 10a-f]. However, the sizes of the products varied greatly according to each solvent, with water producing the largest particles [Figure 10a]. Hydrolysis of \((\text{CH}_3)_2\text{CHO}\)_4\text{Ti}\) in water resulted in its precipitation, whereas the alcohol-based solvents dissolved \((\text{CH}_3)_2\text{CHO}\)_4\text{Ti}\). Similar to the results of solvothermal synthesis using TiO\(_2\) as a raw material, we found that the sizes of the cube-like \(\text{BaTiO}_3\) crystals decreased in the alcohol-based solvents, with the smallest size observed in methanol increasing with increasing the number of carbon atoms in the solvent (methanol < ethanol < 1-propanol < 1-butanol < 1-pentanol) [Figure 10b-f]. The morphology of the particles synthesized in 1-butanol and 1-pentanol was approximately the same [Figure 10e,f].

We subsequently investigated the effects of different ratios of \((\text{CH}_3)_2\text{CHO}\)_4\text{Ti}\) and TiO\(_2\) in 1-butanol for the solvothermal synthesis of \(\text{BaTiO}_3\). The XRD patterns were again assigned to a tetragonal crystal system (JCPDS file: 5-0626) (Figure S9, Supporting Information), and SE images showed fine particles with cubic shapes [Figure 12a-e]. Regarding the effect of acetic acid treatment as shown in Figure 12d, there was a second phase of barium carbonate (\(\text{BaCO}_3\)) before acetic acid treatment (Figure S10). Rietveld refinement of the \(P4mm\) model of \(\text{BaTiO}_3\) in the tetragonal crystal system was performed using the Z-Rietveld\(^{39-41}\) software packages for XRD patterns. Rietveld refinement revealed the products of \(\text{BaTiO}_3\) and \(\text{BaCO}_3\) before acetic acid treatment. The \(R\)-weighted pattern (\(R_w\)) and \(R\)-pattern (\(R_p\)) are shown in Table S2. All of the \(R_w\) and \(R_p\) values from the Rietveld analysis were satisfactory. However, acetic acid treatment removed the second phase of \(\text{BaCO}_3\) and a single phase of \(\text{BaTiO}_3\) was obtained after acetic acid treatment [Figure 12d]. The \(\text{BaTiO}_3\) morphology changed to uniform-sized particles upon addition...
of \([(\text{CH}_3\text{CHO})_4\text{Ti}]\) to \(\text{TiO}_2\) [Figure 12b–d], with the optimal solvothermal condition for the \(\text{BaTiO}_3\) nanocubes determined to be 7.5 mmol \(\text{TiO}_2\) and 2.5 mmol \([(\text{CH}_3\text{CHO})_4\text{Ti}]\) [Figure 12d]. The average particle size of \(\text{BaTiO}_3\) nanocubes which were synthesized with the optimal solvothermal condition was 52 nm, which is the average distance of the cubes measured diagonally from corner to corner, and the average side length was 37 nm.

Figure 13 illustrates the formation mechanism for \(\text{BaTiO}_3\) nanocubes using mixtures of the raw materials \([(\text{CH}_3\text{CHO})_4\text{Ti}]\) and \(\text{TiO}_2\). Before solvothermal synthesis, \([(\text{CH}_3\text{CHO})_4\text{Ti}]\) dissolved in the reaction medium, whereas \(\text{TiO}_2\) was not. After solvothermal synthesis, nuclei of \(\text{BaTiO}_3\) were formed from the dissolved \([(\text{CH}_3\text{CHO})_4\text{Ti}]\), whereas the \(\text{TiO}_2\) nanoparticles became smaller because they slowly dissolved into the reaction medium as a consequence of their stability. Subsequently, the \(\text{BaTiO}_3\) crystals grew into a cubic shape. \([(\text{CH}_3\text{CHO})_4\text{Ti}]\) and \(\text{TiO}_2\) participate in nucleation and crystal growth, respectively. We obtained \(\text{BaTiO}_3\) nanocubes by controlling these processes.

**XRD and ND Analyses of the \(\text{BaTiO}_3\) Nanocubes.** Figure 14 shows high-energy synchrotron X-ray and neutron crystal structures of the \(\text{BaTiO}_3\) nanocubes. The high-energy synchrotron XRD pattern and its Rietveld refinement using the TOF method with a white neutron source. Regarding the Rietveld refinement, the recorded spectrum is shown as red cross marks and the light-blue solid line is the fit to the model for the \(\text{BaTiO}_3\) phase. Red cross marks, light-blue solid lines, and blue solid lines represent observed, calculated, and differing intensities, respectively. Green ticks represent positions of the calculated Bragg reflections of the \(\text{BaTiO}_3\) phase. On the basis of the XRD and ND data, we confirmed a single phase of \(\text{BaTiO}_3\) assigned to a tetragonal crystal system of the \(P4mm\) space group. In addition, Rietveld refinement showed highly similar estimated lattice constants between the XRD and ND data, with no oxygen-related defects in the \(\text{BaTiO}_3\) nanocubes according to analysis of the ND pattern (Table 3).

The PDF method was performed to analyze the radial distribution from disordered materials via the powder XRD pattern and to obtain information about the interatomic distances. Figure 15 shows a PDF analysis of the XRD pattern obtained using high-energy synchrotron X-rays [Figure 14a]. The PDF analysis of XRD data confirmed Ti–O interatomic distances of 1.9 and 2.1 Å, a Ba–O interatomic distance of 2.9 Å, a Ba–Ti interatomic distance of 3.5 Å, and a Ba–Ba interatomic distance of 4.0 Å. These results suggest displacement of the Ti atom from the center of the \(\text{BaTiO}_3\) unit cell, which caused spontaneous polarization of the \(\text{BaTiO}_3\) tetragonal crystal structure.

The atomic column arrangement and surface reconstruction phenomenon were observed using Cs-corrected HAADF–STEM and ABF–STEM. The contrast in HAADF–STEM depends on the atomic number of the observed elements, where the contrast of heavy elements is brighter than that of light elements, making the detection of light elements difficult. By contrast, ABF–STEM enables the detection of light elements such as oxygen; therefore, using both HAADF–STEM and ABF–STEM enables a more complete observation that overcomes the shortcomings of each detection method. Figure 16 shows atomic column observations of a \(\text{BaTiO}_3\) nanocube from the [001] incidence direction, as observed in the corresponding scanning electron microscopy (SEM) image used for analysis [Figure 12d]. The left-hand side of the pair is the HAADF–STEM image and the right-hand side is the ABF–STEM image. In Figure 16(a–1),(a–2), in the middle of the array is an overall view of the \(\text{BaTiO}_3\) nanocube. The particle size of the \(\text{BaTiO}_3\) nanocube was approximately 40 nm. Figure 16(b–1),(b–2),(d–1),(d–2),(h–1),(h–2),(f–1),(f–2) shows images of the four corners of the \(\text{BaTiO}_3\) nanocube. Figure 16(c–1),(c–2),(i–1),(i–2),(e–1),(e–2),(g–1),(g–2) shows images corresponding to the top, left, right, and bottom of the \(\text{BaTiO}_3\) nanocube, respectively. In the HAADF–STEM images, we observe two lines of atomic columns of differing contrast intensities: one line of spots is bright, and the other line of spots is very bright. Compared with the atomic number of \(^{42}\text{Ba}\) columns, that of \(^{56}\text{Ba}\) is greater, suggesting that the bright spots indicate \(^{22}\text{Ti}\) columns and that the very bright spots indicate \(^{56}\text{Ba}\) columns. Columns associated with O were not visible because of their poor contrast. The ABF–STEM images also show two lines of atomic columns although the Ti atomic columns were obscured by the O atomic columns. However, the ABF–STEM images also show O atomic columns between the Ba atomic columns.

Examination of the atomic column arrangements of the surface of the \(\text{BaTiO}_3\) nanocubes revealed a homogeneous internal structure although not at the surface, where surface reconstruction was clearly observed. If the \(\text{BaTiO}_3\) nanocrystal had been homogeneous throughout, the surface arrangement would have ended at the Ba or Ti atomic columns. However, our observations of the nanocrystal’s surface indicated the existence of atomic columns, which we theorized to be Ti layers, and a lack of Ba atomic columns; therefore, we examined the composition of the surface of the \(\text{BaTiO}_3\) nanocrystal in greater detail. Figure 17 shows an atomic
observation of a BaTiO₃ nanocube from the [001] incidence direction, which was used for analysis [Figure 16(i-1),(i-2)]. A regular arrangement of Ba and Ti columns was clearly observed inside the BaTiO₃ nanocube from HAADF−STEM and ABF−STEM. However, the atomic arrangement at the outermost

| atom  | site | x   | y   | z   | occupancy | Biso  | x   | y   | z   | occupancy | Biso  |
|-------|------|-----|-----|-----|-----------|-------|-----|-----|-----|-----------|-------|
| Ba    | 1a   | 0   | 0   | 0   | 1         | 1.297(14) | 0   | 0   | 0   | 1         | 0.127(14) |
| Ti    | 1b   | 1/2 | 1/2 | Z1  | 1         | 0.642(38)  | 1/2 | 1/2 | Z4  | 1         | 0.011(14) |
| O1    | 1b   | 1/2 | 1/2 | Z2  | 1         | 0.642     | 1/2 | 1/2 | ZS  | 1         | 0.392(32) |
| O2    | 2c   | 1/2 | 0   | Z3  | 2         | 0.642     | 1/2 | 0   | Z6  | 2         | 0.467(17) |

| a/Å   | 3.99243(18) | 4.00685(4) |
| c/Å   | 4.01542(23) | 4.02502(5) |
| Rwp/% | 9.34        | 5.79       |
| Rp/%  | 4.68        |            |

aZ₁ = 0.46851(96), Z₂ = 0.98840(487), Z₃ = 0.46557(177), Z₄ = 0.46693(68), Z₅ = -0.00955 (65), and Z₆ = 0.50577(65).

Figure 15. PDF analysis of the XRD pattern obtained using high-energy synchrotron X-rays and shown in Figure 14a. Regarding the PDF analysis, the recorded spectrum is shown as a black solid line and red circles are the fit to the recorded spectrum. The black solid line, red circle marks, and blue solid lines represent observed, calculated, and differing intensities, respectively.

Figure 16. Atomic column observations of a BaTiO₃ nanocube in the direction of [001] incidence. STEM images at an accelerating voltage of 200 kV, obtained with an instrument equipped with a Cs corrector. HAADF−STEM images: (a-1) whole particle, (b-1) top left-hand corner of the particle, (c-1) top of the particle, (d-1) top right-hand corner of the particle, (e-1) right-hand side of the particle, (f-1) bottom right-hand corner of the particle, (g-1) bottom of the particle, (h-1) bottom left-hand corner of the particle, and (i-1) left-hand side of the particle. ABF−STEM images: (a-2) whole particle, (b-2) top left-hand corner of the particle, (c-2) top of the particle, (d-2) top right-hand corner of the particle, (e-2) right-hand side of the particle, (f-2) bottom right-hand corner of the particle, (g-2) bottom of the particle, (h-2) bottom left-hand corner of the particle, and (i-2) left-hand side of the particle.

Figure 17. Observations of atomic columns in a BaTiO₃ nanocube in the direction of [001] incidence. STEM images were observed at an accelerating voltage of 200 kV using an instrument equipped with a Cs corrector. (a,b) Histogram of the areas surrounded by dotted lines of HAADF−STEM image of the left-hand side of the BaTiO₃ nanocube.
surface of the BaTiO$_3$ nanocube clearly differed from that inside the BaTiO$_3$ nanocube. Specific atomic columns were arranged at equal distances and built by surface reconstruction. We can understand the arrangement detail from the histogram. From the HAADF−STEM contrast results, Figure 17a,b shows the histograms representing Ti atomic columns and Ba atomic columns inside a BaTiO$_3$ nanocube, respectively. From the results of the histogram, we confirmed that the Ti atomic columns and the Ba atomic columns were arranged at equal distances inside BaTiO$_3$ nanocubes. However, the atomic column arrangement at the outermost surface of the BaTiO$_3$ nanocube clearly differed from that inside the BaTiO$_3$ nanocube. In addition, the peaks of the histogram were in the same positions for the Ba atomic columns [Figure 17a] and the Ti atomic columns [Figure 17b] at the outermost surface of the BaTiO$_3$ nanocube. Furthermore, the intensities in the histogram corresponding to the outermost surface of the BaTiO$_3$ nanocube were weak. That is, even though atomic columns were arranged with regularity at the outermost surface of the BaTiO$_3$ nanocube, lattice defects did exist. EELS analysis was performed to clarify the component elements of the outermost surface of the BaTiO$_3$ nanocube.

Surface reconstruction was investigated from the point of view of elemental analysis. BaTiO$_3$ comprises three elements (Ba, Ti, and O). Analysis of Ba and O is possible, whereas analysis of Ti is more difficult because the La lines of Ba overlap the Ka lines of Ti. However, EELS enables elemental analysis of Ti because its peaks do not overlap those of Ba in EELS spectra. Therefore, elemental analysis of the surface of a BaTiO$_3$ nanocube was conducted using EELS.

The surface of a BaTiO$_3$ nanocube before acetic acid treatment was also examined with electron microscopy. Figure S11 shows observations of a BaTiO$_3$ nanocube from the direction of [001] incidence before acetic acid treatment. A single crystal of BaTiO$_3$ was confirmed from the results of TEM and its nano-beam diffraction [Figure S11]. Figure S12 shows atomic column observations of a BaTiO$_3$ nanocube from the [001] incidence direction before acetic acid treatment, as observed in the corresponding TEM image used for analysis [Figure S11a]. Figure 12(a-1) is the HAADF−STEM image and Figure S12(a-2) is the ABF−STEM image. In Figure S12(a-1), (a-2), in the middle of the array is an overall view of the BaTiO$_3$ nanocube. Figure S12(b-1), (b-2), (d-1), (d-2), (h-1), (h-2), (f-1), and (f-2) shows images of the four corners of the BaTiO$_3$ nanocube. Figure S12(c-1), (c-2), (i-1), (i-2), (e-1), (e-2), (g-1), and (g-2) shows images corresponding to the top, left, right, and bottom of the BaTiO$_3$ nanocube, respectively.

Atomic column observations of HAADF−STEM and their EELS analyses of the top, right-side, bottom, and left-side of the BaTiO$_3$ nanocube before acetic acid treatment, as observed in corresponding pairs of TEM images used for analysis [Figure S11a], were performed as shown in Figures S12, S13. Ba and Ti are indicated by green and red, respectively. Each

Figure 18. Observations of a BaTiO$_3$ nanocube in the direction of [001] incidence. TEM and the corresponding nano-beam electron diffraction pattern and STEM images were observed at an accelerating voltage of 80 kV using an instrument equipped with a Cs corrector. (a) TEM image of a BaTiO$_3$ nanocube; (b) nano-beam diffraction of sample 3; (c,d) HAADF−STEM and ABF−STEM images; (e) HAADF−STEM observations of atomic columns in a BaTiO$_3$ nanocube the direction of [001] incidence and their EELS elemental mapping. Ba and Ti are indicated by green and red of EELS elemental mapping, respectively.
EELS spectrum is shown in Figure S14. A regular arrangement of Ba and Ti columns was clearly observed inside the BaTiO3 nanocube, along with surface reconstruction comprising Ti columns without Ba columns at the outermost surface on all sides of the BaTiO3 nanocube.

Figure 18 shows observations of a BaTiO3 nanocube after acetic acid treatment from the direction of [001] incidence. A single crystal of BaTiO3 was confirmed from the results of TEM and its nano-beam diffraction, HAADF–STEM, and ABF–STEM observation [Figure 18a–d]. Figure 18e shows a BaTiO3 nanocube as shown in sample 3 of Figure 18a,c,d. Atomic column observations of HAADF–STEM and their EELS analyses of the top, right-side, bottom, and left-side of BaTiO3 were performed as shown in Figure 18e. Ba and Ti are indicated by green and red, respectively. Each EELS spectrum is shown in Figure S15. A regular arrangement of Ba and Ti columns was clearly observed inside the BaTiO3 nanocube, along with surface reconstruction comprising Ti columns without Ba columns at the outermost surface on all sides of the BaTiO3 nanocube. In addition, EELS analysis of another BaTiO3 nanocube is shown in Figure S16. Figure S16a shows the observed atomic columns in a BaTiO3 nanocube from the direction of [001] incidence. Elemental analyses of Ba and Ti were conducted using the EELS peaks at Ti: 457.8−461.1 and Ba: 782.4−798.1 eV [Figure S16 (c-1, c-2)], respectively. As a result, the surface reconstruction of the BaTiO3 nanocube is indicated in Figure S16.

Comparing before and after acetic acid treatments, the surface reconstruction was clearly observed after acetic acid treatment. Therefore, further investigation is necessary to identify the mechanism for the formation of the surface reconstruction of the BaTiO3 nanocube.

Figure 19 shows observations of a BaTiO3 nanocube from the direction of [110] incidence. A single crystal of a BaTiO3 nanocube was obtained from the results of TEM and its nano-beam diffraction. Figure 20 shows HAADF–STEM and ABF–STEM observations of a BaTiO3 nanocube from the direction of [110] incidence. Note that one of the atomic positions of O overlaps on the atomic position of Ti in the direction of [001] incidence (Figures 16–18), whereas one of them overlaps on the atomic position of Ba in the direction of [110] incidence (Figure 20). Thus, we can clearly observe different atomic positions of some O atoms between the images in the direction of [001] and [110].

In this study, the internal structure of a BaTiO3 nanocube was confirmed to be homogeneous. However, we discovered that surface reconstruction resulted in two Ti layers (Figure 21). This phenomenon was theorized to be a consequence of the solvothermal method used to synthesize the BaTiO3 nanocubes. Surface reconstruction is dependent on ionic radius and/or binding energy forces. Ti4+ has an ionic radius of approximately one-half that of Ba2+, which enables easier arrangement of Ti4+ on the BaTiO3 nanocube surface. Ti has a higher binding-energy force than Ba, thus making the surface harder to split apart. The field of atomic arrangement is important and intriguing. In the present study, we confirmed the atomic arrangement of a BaTiO3 nanocube. Identifying an atomic arrangement, especially on the surface of a BaTiO3 nanocube, is challenging; however, our results are informative.

CONCLUSIONS

In summary, we described a wet chemical method for synthesizing BaTiO3 without dispersants of surfactants. This approach involves mixing fine TiO2 nanoparticles with Ba(OH)2:8H2O to form a single phase of BaTiO3 at 80 °C. Additionally, we obtained a high dispersion of BaTiO3 nanocubes using a solvothermal method at 200 °C. Moreover, we mediated BaTiO3 nanocube synthesis by controlling nucleation and crystal growth by altering the ratio of [(CH3)2CHO]4Ti and TiO2, as raw materials where the role of [(CH3)2CHO]4Ti promoted nucleation and the fine TiO2 nanoparticles promoted crystal growth. [(CH3)2CHO]4Ti was dissolved in a reaction medium of alcohol before the solvothermal reaction. Thereafter, uniform nuclei formed under the solvothermal reaction conditions. Uniform nuclei led to a narrow particle size distribution. In addition, the large number of nuclei resulted in fine nano-sized particles. On the other hand, fine TiO2 nanoparticles dissolved slowly in the reaction medium compared with [(CH3)2CHO]4Ti. The fine TiO2 nanoparticles led to crystal growth when the solvothermal synthesis was carried out at 200 °C.

The shape of the obtained powders in the present study depended on the crystal system of BaTiO3, which, in this case, is a tetragonal crystal system. During the solvothermal reaction, the crystals of BaTiO3 that grew depended on the crystal system. BaTiO3 particle sizes obtained using different reaction media increased in the order methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, water. The optimum condition for synthesizing BaTiO3 nanocubes was achieved with 1-butanol as the reaction medium. The average particles size was 52 nm, which is the average distance of the cubes measured diagonally from corner to corner, and the average side length was 37 nm, and the crystal system of BaTiO3 nanocubes was a tetragonal crystal system. In addition, the origin of the spontaneous polarization of the BaTiO3 tetragonal crystal structure was clarified from a pair PDF analysis. Detailed observations of a BaTiO3 nanocube were carried out using electron microscopy. The surface reconstruction of the BaTiO3 nanocube clarified that the outermost surface of the BaTiO3 nanocube was composed of Ti columns. Two layers of Ti columns at the surface of the BaTiO3 nanocubes were identified. By comparing the atomic ratio of Ba and Ti, we found that Ti was slightly richer than Ba. These data were reflected in the observation of surface reconstruction of Ti atomic columns.
To reiterate, BaTiO3 nanocubes were synthesized using a solvothermal method and the occurrence of surface reconstruction of Ti columns was revealed in the present work.

■ EXPERIMENTAL SECTION

Raw Materials. We used the following raw materials for BaTiO3 synthesis: anatase-type TiO2 (particle size: <25 nm; 99.7% purity; Sigma-Aldrich, St. Louis, MO, U.S.A.); titanium tetraisopropoxide [(CH3)2CHO]4Ti; >97.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan); barium hydroxide octahydrate [Ba(OH)2·8H2O; 99% purity; Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan]; acetic acid (CH3COOH; 99.7% purity; Kanto Chemical Co., Inc., Tokyo, Japan); acetone [CH3COCH3; 99.5% purity; Kanto Chemical Co., Inc., Tokyo, Japan]; methanol (CH3OH; 99.8% purity; Kanto Chemical Co., Inc., Tokyo, Japan); ethanol (C2H5OH; 99.5% purity; Kanto Chemical Co., Inc., Tokyo, Japan); 1-propanol (1-C3H7OH; 99.5% purity; Kanto Chemical Co., Inc., Tokyo, Japan); 1-butanol (1-C4H9OH; 99.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan); and 1-pentanol (1-C5H11OH; 98.5% purity; Kanto Chemical Co., Inc., Tokyo, Japan).

Acetic Acid Treatment. Acetic acid treatment was performed to remove the second phase. The concentration of the acetic acid aqueous solution was first adjusted to 0.69 mol·dm\(^{-3}\); 50 mL of this solution was then combined with 2 g of the product, and the resultant mixture was stirred at 350 rpm for 5 min.

Synthesis of BaTiO3 Particles Below 80 °C. BaTiO3 particles were synthesized at temperatures below 80 °C. First, 20 mmol of Ba(OH)2·8H2O and 10 mmol of fine anatase-type TiO2 (particle size: < 25 nm) were stirred in a Teflon reactor in 40 mL of water for 5 min, after which the Teflon reactor was placed in a stainless-steel autoclave with an internal volume of 100 mL, and a heat treatment was performed from room temperature to 80 °C for 72 h. After the autoclave cooled to room temperature, the product was collected by centrifugation at 10,000 rpm, rinsed with water for three cycles and acetone for two cycles, and then dried at room temperature. An acetic acid treatment was then performed, after which the product was again collected by centrifugation using a centrifugal separator at 10,000 rpm, rinsed with water for three cycles and then acetone for two cycles, and dried overnight at room temperature.

Synthesis of BaTiO3 Particles Above 80 °C. BaTiO3 nanocubes were synthesized using a solvothermal method. First, the raw materials were added to a Teflon reactor and stirred at 350 rpm for 5 min; the resultant mixture was placed into a stainless-steel autoclave with an internal volume of 100 mL. Solvothermal synthesis was then performed at 200 °C for 6 to 96 h, after which the autoclave was cooled to room temperature. The product was collected by centrifugation at 10,000 rpm, rinsed with water for three cycles and ethanol for two cycles, and then dried at room temperature. An acetic acid treatment was then performed, after which the product was collected using a centrifugal separator at 10,000 rpm, rinsed with water for three cycles and then acetone for two cycles, and dried overnight at 80 °C in a dryer.

Characterization of the Obtained Powders. XRD measurements were performed using an Ultima IV diffractometer (Rigaku Co., Tokyo, Japan) equipped with a Cu Kα radiation source (wavelength: 0.15418 nm) operating at 40 kV.
and 30 mA; samples were scanned at room temperature over the 2θ range from 10 to 80°. High-energy synchrotron XRD measurements were carried out at SPring-8 (Hyogo, Japan); data were collected in transmission mode at the SPring-8 BL22XU beamline using high-energy X-rays with a wavelength of 0.02015 nm. Short- and long-range structural parameters were refined using the Rietveld technique and the RIETAN-FP program. An ND pattern was obtained by the time-of-flight (TOF) method using white neutrons at J-PARC (Ibaraki, Japan). ND data were collected in a high-resolution bank (150° ≤ 2θ ≤ 175°) at beamline BL20 (iMATERIA) using neutron beams produced at the Materials and Life Science Experimental Facility (J-PARC) from megawatt-class high-power pulsed proton beams generated by a 3 GeV rapid-cycling synchrotron. The use of a white pulsed neutron source enabled ND measurement.

SE images of the powders were obtained by SEM using an instrument (SU-5000; Hitachi High-Tech Corporation, Tokyo, Japan) operating at an accelerating voltage of 3 kV and by STEM using an instrument (HD-2700; Hitachi High-Tech Corporation, Tokyo, Japan) operated at 200 kV acceleration voltage. BF-TEM observations were conducted and SAED patterns were obtained by TEM using an instrument (Tecnai Osiris; FEI; Thermo Fisher Scientific, Waltham, MA, U.S.A.) operating at an accelerating voltage of 200 kV. The BaTiO3 surface was analyzed by HAADF–STEM at beamline BL20 (iMATERIA) using a JEM-ARM200CF (JEOL Ltd., Tokyo, Japan) operating at an accelerating voltage of 80 and 200 kV and equipped with a cold field emission gun and a Cs corrector to observe atomic columns of BaTiO3. Elemental analysis was carried out using a JEM JEM-ARM200CF transmission electron microscope equipped with an electron energy loss spectroscope. Regarding the accelerating voltage, 200 kV has a higher resolution for the atomic column observation compared with 80 kV. On the other hand, 80 kV is suitable for EELS elemental mapping because it can be performed over a long period of time. A long duration observation time causes damage to the BaTiO3 nanocube if performed over a long period of time. A long duration observation compared with 80 kV. On the other hand, 80 kV is 200 kV has a higher resolution for the atomic column energy loss spectroscope. Regarding the accelerating voltage, 200 kV was a higher resolution. Therefore, in the STEM observations including the EELS elemental mapping, we used 80 kV with an accelerating voltage due to the lowered STem damage to the BaTiO3 nanocube.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05878.

XRD patterns, Rietveld analyses, TEM image, nano-beam diffraction, STEM images, and EELS analyses of BaTiO3 (PDF)

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Author Contributions
K.N. conceived and designed the overall project. TEM and STEM images were observed by K.N. The sample was synthesized and characterized by K.O.. The synchrotron XRD pattern was measured and its Rietveld refinement was carried out by Y.Y., ND patterns were measured by T.I., and Rietveld refinement was carried out by Y.I., Y.K., S.Y., M.K., and T.S. contributed to discussions and developed the concept of the present research.

Notes
The authors declare no competing financial interest.

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