Disordered off-center direction of Ti$^{4+}$ in pseudo-cubic type BaTiO$_3$ prepared by mixed hydroxide process

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Recently, perovskite-type BaTiO$_3$ showing sharp X-ray diffraction peak comparable to that synthesized by a conventional solid-state reaction was obtained by mixing Ba(OH)$_2$ and TiO$_2$ hydrous gel and by leaving the mixture at 323 K or less. However, the obtained BaTiO$_3$ was cubic crystal system, which was different from that synthesized by a conventional solid-state reaction. In this study, the structural analysis of cubic-BaTiO$_3$ obtained by this technique was conducted, and the factors to form cubic structure were investigated. Since no second harmonic generation signal was observed, the structure of BaTiO$_3$ was essentially different from that of traditional tetragonal-BaTiO$_3$. Rietveld analysis with the initial structure model of ideal cubic perovskite structure exhibited that Ti$^{4+}$ had exceptionally large isotropic atomic displacement parameter. A reasonable isotropic atomic displacement parameter was obtained by considering the static site disorder in the initial structural model, that is, Ti$^{4+}$ locates at off-center position in TiO$_6$ octahedron by displacing in a disordered direction, resulting in pseudo-cubic symmetry.

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1. Introduction

Perovskite-type titanate ATiO$_3$ exhibits various functions due to the polarizability of Ti$^{4+}$. Ferroelectric BaTiO$_3$$^1$ has spontaneous polarization because Ti$^{4+}$ displaces cooperatively in the oxygen octahedron, breaking the inversion symmetry.

Recently, we found that perovskite-type A$^{2+}$TiO$_3$ ($A$ = Sr, Ba; $M$ = Ti, Zr, Hf) was obtained by leaving the powder mixture of alkaline earth hydroxide $A$(OH)$_2$·8H$_2$O and MO$_2$ hydrous gel at near room temperature ($\sim$323 K) for several days. It is hereinafter referred to as a mixed hydroxide process. Unlike general low temperature synthesis methods such as hydrothermal synthesis method$^{6,7}$ and the solution method,$^8$ the mixed hydroxide process does not need a solvent or additional regents. As a driving force of this synthetic route, a neutralization reaction has been proposed. In this mechanism, alkaline earth hydroxide acts as a base and MO$_2$ hydrous gel acts as an acid. The mixed hydroxide method is similar to recently developed water assisted solid state reaction (WASSR)$^9$ method in the point of synthesizing ceramic materials by leaving a mixture of raw materials at low temperature. However, the reaction mechanism in these methods is different. In the WASSR method, a small amount of water is added to raw material mixture. It is considered that the reaction is promoted by “the water layer present on the surface” of the raw materials particles.$^{10}$ On the other hand, in mixed hydroxide process, additional water is not needed. The reaction is considered to proceeds through the “internal water” of hydrous gel.$^4$

The crystal system of BaTiO$_3$ synthesized by the mixed hydroxide process was cubic, though the crystal system of BaTiO$_3$ synthesized by conventional solid-state synthesis method (fired at $\sim$1473 K) is tetragonal. The structural analysis of the sample obtained by mixed hydroxide process has not been carried out, and therefore, the details of the crystal structure and the reason for the structural difference by synthesis method are still unknown.

BaTiO$_3$ undergoes a sequential phase transition of rhombohedral, orthorhombic, tetragonal, and cubic from low temperature. These crystal systems are related to the Ti displacement direction. Ti displaces toward [111], [110], and [001] in rhombohedral system, orthorhombic system, and tetragonal system, respectively. The cubic phase usually appears only at high temperature above $\sim$400 K as a non-quenchable phase. A quenchable cubic BaTiO$_3$ was
also obtained by hydrothermal synthesis at low temperature. In hydrothermal synthesis, a multiphase of cubic and tetragonal was obtained, and the proportion of cubic phase increased with decreasing the synthesis temperature. \(^{11}\) As for the reason for becoming cubic phase, there are many reports that investigated from the viewpoint of grain morphology \(^{12-14}\) and defects. \(^{15}\) However, there were very few reports of crystal structural analysis for these cubic BaTiO\(_3\). Rietveld analysis was used to determine the mixing ratio of cubic phase and tetragonal phase \(^{15-17}\) but the analysis focusing on the crystal structure has not been performed.

In this study, the crystal structure of BaTiO\(_3\) obtained by the mixed hydroxide process was investigated, focusing on the shift of Ti\(^{4+}\). The factors causing cubic structure was discussed. The optical second harmonic generation (SHG) measurement and Rietveld analysis were performed for accurate crystal structure evaluation. When the sample crystal is centrosymmetric, SHG does not show a signal. On the other hand, when sample has non-centrosymmetric point group such as 4\(_{mm}\) of tetragonal BaTiO\(_3\), light with half the wavelength of the incident laser is observed. \(^{18}\) There are two possible causes for the absence of XRD diffraction peaks splitting by tetragonal distortion. One is that the crystal symmetry is essentially cubic. The other is that the split width is smaller than the full width half maximum of the peaks and it does not seen to be split artificially. The SHG measurement makes it possible to distinguish between these causes and enables more accurate structural evaluation.

2. Experimental procedure

Ba(OH)\(_2\)-8H\(_2\)O (Fujifilm Wako Pure Chemical, 98\%) and TiO\(_2\) hydrous gel (hereinafter TiO\(_2\)-nH\(_2\)O) were used as raw materials for the mixed hydroxide process. For the synthesis of TiO\(_2\) hydrous gel, TiCl\(_4\) (Fujifilm Wako Pure Chemical, 16\% in HCl aq.) was added to 200 mL of cold water in ice bath. Then, a concentrated ammonia water was added until the pH reached 8.5 to precipitate the TiO\(_2\) hydrous gel. The obtained precipitation was filtered and washed with ultrapure water, and then dried at 373 K for 12 h. The \(n\) value in TiO\(_2\)-nH\(_2\)O was determined to be 1.68 by thermogravimetric analysis (TGA).

The perovskite type BaTiO\(_3\) was obtained by the mixed hydroxide process according to the following procedure. Ba(OH)\(_2\)-8H\(_2\)O and TiO\(_2\)-nH\(_2\)O were mixed using an alumina mortar with the stoichiometric ratio. The mixture was placed in a vial and sealed by closing the cap. These operations were performed in an Ar filled glove box to avoid the formation of carbonate due to CO\(_2\) in the air. The vial was kept at 323 K in a constant temperature bath for 3 to 10 days. The obtained powder was washed with 1.0 M acetic acid to remove unreacted hydroxide, and then was vacuum-dried for 24 h.

Powder XRD measurement was performed using a RIGAKU MiniFlex600 X-ray diffractometer (Cu K\(_\alpha\) radiation). Refinement of crystal structure by Rietveld analysis was performed using RIETAN-FP software. \(^{19}\) Electron density distributions were elucidated by maximum entropy method (MEM) using the code Dysnomia. \(^{20}\) The program VESTA was used for drawing crystal structures and electron density distributions. \(^{21}\) The optical SHG response was measured for ungraded powders using a Continuum Minilite YAG:Nd laser (\(\lambda = 1064\) nm). The SHG signal (\(\lambda = 532\) nm) was amplified by Hamamatsu H7415 photomultiplier and C6438 amplifier unit and then recorded by Rhode & Schwartz RTM1052 Oscilloscope. TGA (BRUKER AXS WS002) was performed by heating the powders in air at 5 K/min to 1273 K using \(\alpha\)-Al\(_2\)O\(_3\) as reference material. The composition analysis was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a SHIMADZU ICPE-9000. The particle shape was observed with the JEOL JSM-7600 field emission scanning electron microscope.

3. Results and discussion

Figure 1 shows the XRD patterns of BaTiO\(_3\) obtained by the mixed hydroxide process. BaTiO\(_3\) exhibited sharp diffraction peaks of perovskite phase. However, as in the previous report, no splitting of the diffraction lines due to tetragonal distortion was observed. \(^{4}\) Even if the reaction time was extended from 3 to 10 days, there was almost no change in the XRD pattern. From the composition analysis by ICP-AES, the Ba/Ti ratio was 0.781, 0.882, and 0.924 for reaction duration of 3, 5, and 10 days, respectively. It is noted that these values do not represent the Ba/Ti ratio in perovskite phase. Excess Ti content was considered to stem from unreacted TiO\(_2\) hydrous gel which was not detected by XRD measurement. The subsequent structural refinement was performed using the sample with 10 reaction days. Figure 2 shows the SEM image of BaTiO\(_3\) for reaction duration of 10 days. Aggregated particles were observed, and it was difficult to estimate the primary particle size. The crystallite size derived from Williamson-Hall method \(^{22}\) was about 200 nm, where the shape factor \(K = 4/3.\) \(^{23}\)
Figure 3 shows the SHG signals for BaTiO3 obtained by mixed hydroxide process and fired at 1473 K. The second harmonic signal at 532 nm was clearly observed in the tetragonal-BaTiO3. In contrast, the sample synthesized by mixed hydroxide process did not exhibit SHG signal, indicating centrosymmetric. Therefore, cubic-BaTiO3 obtained by mixed hydroxide process have essentially different crystal structure from that of synthesized by conventional solid-state reaction method. When a mixture of cubic and tetragonal phases is obtained as in the hydrothermal method, the SHG signal is supposed to be observed. Therefore, in the mixed hydroxide process, the cubic phase was obtained as a single phase.

Rietveld analysis of cubic-BaTiO3 obtained by mixed hydroxide process was performed with the ideal-cubic perovskite structure (space group Pm3m) as an initial structure model. Table 1 shows the resulted reliability factors (R factors) and structural parameters. R factors indicated that the fitting was successful. The obtained isotropic atomic displacement parameter, B, of Ti was exceptionally large value of 0.0170(2) nm². Table 2 shows the results of Rietveld analysis of tetragonal-BaTiO3 (space group P4mm) synthesized by firing at 1573 K. The atomic displacement parameter was 0.0039(2) nm² for Ti in the tetragonal-BaTiO3, though the element, the measured temperature, and the coordination environment are similar. This result indicated that the atomic displacement parameter of cubic-BaTiO3 was unusually large compared to the typical value.

The bond valence sum (BVS) of Ti⁴⁺ was calculated by following equation, where S_i is bond valence between Ti and i-th O atom, \( D_i \)’s are observed Ti–O distances and \( r_0 \) is a bond valence parameter of Ti⁴⁺ ion (1.815). The BVS values of Ti⁴⁺ were 3.731 for tetragonal-BaTiO3 and 3.469 for cubic-BaTiO3. In the cubic-BaTiO3, BVS value was much smaller than the formal charge, indicating that the Ti–O bond length obtained by Rietveld analysis is longer than that predicted by the valence state. Therefore, initial structure model for Rietveld analysis of ideal cubic perovskite structure was inaccurate.

The off-center state of Ti⁴⁺ is stabilized by second order Jahn–Teller (SOJT) effect. The SOJT effect, which are commonly found in ions with electronic configuration of \( d^0 \) or \( s^2 \), such as Ti⁴⁺, Nb⁵⁺, and Pb⁴⁺, is an anisotropic covalent bond by mixing empty d orbitals (or p orbitals) of metals and filled p orbitals of ligands. In the case of non-d⁰ configuration (for example, Sn⁴⁺ in BaSnO₃), electrons are supposed to occupy the antibonding orbital, and thus displacement of central metal is not induced. Even in SrTiO₃, which is generally regarded as an ideal-cubic perovskite structure with almost unity tolerance factor, Ti⁴⁺ was located off-center position in local structure. It is considered that in cubic-BaTiO3 obtained by mixed hydroxide process, the ideal-cubic perovskite structure model in which Ti⁴⁺ is located at the center of the oxygen octahedron is not reasonable because of SOJT effect, exceptionally large atomic displacement parameter, and the small BVS value of Ti⁴⁺.

### Table 1. Structural parameters for cubic BaTiO₃ synthesized by leaving the mixture for 10 days

| Atom | site | g | x | y | z | B/nm²  |
|------|------|---|---|---|---|--------|
| Ba   | 1a   | 1 | 0 | 0 | 0 | 0.0094(2) |
| Ti   | 1b   | 1 | 1/2 | 1/2 | 1/2 | 0.0170(2) |
| O    | 3c   | 1 | 1/2 | 1/2 | 0 | 0.0034(15) |

Cubic, space group Pm3m (No. 221), a = 0.403542(13) nm, \( V = 0.065715(4) \) nm³, \( R_{wp} = 5.243 \) %, \( S = 1.3067 \), \( R_B = 1.120 \) %, \( R_F = 0.444 \) %.

### Table 2. Structural parameters for tetragonal BaTiO₃ synthesized by firing at 1573 K

| Atom | site | g | x | y | z | B/nm²  |
|------|------|---|---|---|---|--------|
| Ba   | 1a   | 1 | 0 | 0 | 0 | 0.00487(15) |
| Ti   | 1b   | 1 | 1/2 | 1/2 | 0 | 0.0039(4) |
| O1   | 1b   | 1 | 1/2 | 1/2 | -0.021(4) | 0.0034(9) |
| O2   | 2c   | 0 | 0 | 0 | 0.488(4) | = B(O1) |

Tetragonal, space group P4mm (No. 99), a = 0.399048(9) nm, c = 0.402303(10) nm, \( V = 0.064063(3) \) nm³, \( R_{wp} = 9.578 \) %, \( S = 2.2236 \), \( R_B = 0.498 \) %, \( R_F = 0.441 \) %.
The reason for the exceptionally large atomic displacement parameter is generally considered to be inaccurate occupancy or static site disorder. We tried to refine the Ti occupancy in Rietveld analysis, but the value of anisotropic atomic displacement parameter did not improve. In the static site disorder model, each Ti\(^{4+}\) displaces from the center of oxygen octahedron toward disordered direction, and thus in average structure, Ti\(^{4+}\) is observed as if Ti\(^{4+}\) located at center of octahedron artificially.

There are some reports evaluating the crystal structure of cubic-BaTiO\(_3\) synthesized by the hydrothermal method, and all of them use the ideal-cubic perovskite structure as an initial structure model.\(^{15-17}\) However, structural analysis involving the static site disorder of Ti\(^{4+}\) has not been performed. In the hydrothermal method, a mixed phase of cubic- and tetragonal-BaTiO\(_3\) was obtained. Since most of the XRD peaks of these phases overlap, evaluation by the Rietveld method is quite difficult. Especially, the atomic displacement parameters are generally prone to include error. XRD measurement data with few overlapping peaks are required for accurate evaluation. As shown by the SHG measurement, cubic-BaTiO\(_3\) obtained by mixed hydroxide process was single phase, and thus it allowed Rietveld analysis accurately. For cubic-BaTiO\(_3\) obtained by mixed hydroxide process, structural analysis was performed using the structure model involving a static site disorder of Ti\(^{4+}\).

First, the off-center displacement direction of Ti\(^{4+}\) was examined by MEM analysis. Since the biases of the initial structure model are relatively few in MEM analysis, visualizing of the anisotropic expansion of electron density due to displacement of Ti\(^{4+}\) is expected even if the initial structure model which does not consider the displacement of Ti\(^{4+}\) is used. In fact, in trigonal (Ba\(_{0.65}\)Ca\(_{0.35}\))\(_2\)SiO\(_4\) (space group P\(_3m1\)), there was a report that the site splitting of oxygen was observed from the electron density distribution by MEM analysis.\(^{28}\)

Figure 4 shows the two-dimensional map of electron density distribution on the \{110\} plane of cubic-BaTiO\(_3\) obtained by mixed hydroxide process. A slight expansion of the electron density due to Ti\(^{4+}\) was observed in \{110\}, but there was no noticeable sign of anisotropic off-center displacement.

Next, the static site disorder of Ti\(^{4+}\) in cubic-BaTiO\(_3\) obtained by mixed hydroxide process was evaluated by Rietveld analysis using three initial structural models in which Ti\(^{4+}\) displaced to (100), (110), and (110). The Wyckoff positions of Ti\(^{4+}\) are 1b, 6f, 12j, and 8g for no displacement, displacing to (100), (110), and (110), respectively. Figure 5 shows the structural model with off-center displacement to the \{100\} direction and the fitting results. Table 3 shows the R factors, fractional coordinates and isotropic atomic displacement parameters obtained by Rietveld analysis. In all models, the R factors and the isotropic atomic displacement parameter of Ti\(^{4+}\) were reasonable values, indicating that the structure model of static site disorder of Ti\(^{4+}\) is reasonable in cubic-BaTiO\(_3\). The BVS of Ti\(^{4+}\) of these structural models were 3.581, 3.577, and 3.574 for displacing to (100), (110), and (110), respectively. These are closer to the formal charge value (4.000) than that in the ideal-cubic perovskite model (3.468), indicating that the static site disorder model is also reasonable in electrostatically. There are few differences in R factors by displacement direction. Displacement direction of Ti\(^{4+}\) was likely mixed of (100), (110), and (110), resulting in almost spherical symmetry distribution exhibited by electron density distribution analysis by MEM. Recently, Zhang et al. reported the shift direction of Ti in
BaTiO$_3$ by the first-principles quantum mechanics calculation.\textsuperscript{29)} They showed that all four phases (Rhombohedral, Orthorhombic, Tetragonal and Cubic) of BaTiO$_3$ had local Ti distortions toward (111). The orthorhombic, tetragonal, and cubic phases had antiferroelectric coupling in one, two, and three dimensions, respectively. Our analysis results are consistent with their report in which Ti had a shift in Cubic-BaTiO$_3$. But no specific distortion of Ti toward (111) was observed from the Rietveld analysis.

The reason for BaTiO$_3$ obtained by the mixed hydroxide process being a pseudo-cubic structure is discussed below. BaTiO$_3$ is known to have core–shell structure where core and shell layer are composed of tetragonal and cubic phase, respectively. The thickness of cubic shell layer was almost constant irrespective of particle size, and therefore, the smaller the particle size, the larger the proportion of cubic phase. Aoyagi et al.\textsuperscript{30)} and Kuroiwa et al.\textsuperscript{31)} reported that the thickness of cubic shell layer was about 8 nm in the BaTiO$_3$ particles of 100–700 nm synthesized by hydrothermal method and heat treatment. They estimate the critical size of a BaTiO$_3$ fine particle at approximately 15 nm, where the tetragonal core disappears and the cubic shell occupies the whole particle. Hoshina reported that the thickness of cubic core layer was 10–15 nm and critical size was 20–30 nm in the BaTiO$_3$ fine particles of 85–430 nm synthesized by a two-step decomposition method of barium titanyl oxalate.\textsuperscript{32)} Yasukawa et al. reported the thickness of cubic shell layer in Y, Mg, Mn doped BaTiO$_3$ synthesized by calcined in reduction atmosphere. In the particle size of 240 nm, thickness of cubic shell layer was 29 nm and volume fraction of cubic phase were 47%.\textsuperscript{33)} The crystallite size of our BaTiO$_3$ (about 200 nm) was obviously larger than critical size for core–shell model. In addition, the color of obtained sample powder was white, indicating that oxygen vacancy and reduction of Ti$^{4+}$ are very few. For these reasons, particle size was not dominant factor for being a pseudo-cubic structure in our sample. The lattice volume of previously reported and our cubic BaTiO$_3$ was about 0.0645–0.0657 nm$^3$, which were larger than that of tetragonal phase (0.0641 nm$^3$).\textsuperscript{6,15,30,32,34)} The large lattice volume may reflect the presence of some kind of defect.\textsuperscript{35)} In BaTiO$_3$ synthesized by hydrothermal method, it was reported that a cubic phase was formed by chemically adsorbed water or OH group in perovskite lattice. Hennings and Schreinemacher\textsuperscript{6)} reported that cubic-BaTiO$_3$ gradually transformed to tetragonal phase by annealing above 773 K to remove the H$_2$O or OH group. However, in our sample, these defects were not a factor to form cubic phase. Cubic-BaTiO$_3$ synthesized by mixed hydroxide process was annealed at 873 K for 1 h but remained on a cubic phase. The reason to form cubic structure for BaTiO$_3$ synthesized by mixed hydroxide process is still unknown, though different from particle size and defect originating in OH group or water.

4. Conclusion

BaTiO$_3$ was synthesized at a low temperature of 323 K by the recently developed mixed hydroxide process, and its crystal structure was evaluated by combining SHG and Rietveld analysis. Since no SHG signal was observed, cubic-BaTiO$_3$ obtained by this synthesis method is centrosymmetric as the average structure, and its structure is essentially different from the tetragonal-BaTiO$_3$ obtained by the conventional solid-state reaction method. Rietveld analysis using the initial structure model of static site disorder of Ti$^{4+}$ revealed that Ti$^{4+}$ was off-centered in a disordered direction and became pseudo-cubic as an average structure.

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