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Direct Synthesis of nm-sized Barium Titanate Crystallites using a New Preparation Method

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A new preparation method was established to synthesize nm-sized barium titanate crystallites with particle sizes around 10 nm. This method had the following two features, *i.e.*, (1) a heat of neutralization in a neutralization reaction between strong acid and base is used as a driving force for the formation of barium titanate, and (2) barium titanate crystallites are directly synthesized from Ti and Ba ions, not via intermediates. Therefore, using this method, it is expected that there is no minimum limit in particle sizes, and also no contamination in barium titanate crystallites. At first, optimum conditions for the formation of barium titanate were investigated at various reaction temperatures and Ba/Ti atomic ratios in the starting materials. As a result, barium titanate was formed at higher reaction temperatures than 50°C and higher Ba/Ti atomic ratios than 5. Under a constant temperature, particle sizes decreased with increasing Ba/Ti atomic ratio. Finally, barium titanate crystallites with particle sizes around 10 nm were first prepared.

Key word: barium titanate, crystallites, LTDS method, size effect, nm-sized particles

1. INTRODUCTION

With miniaturization of electronic devices, downsizing of electronic components has been developed for past years and accelerated at present. As a result, in the electric devices such as multilayered capacitors, particle sizes of barium titanate (BaTiO₃) and barium strontium titanate (Ba_{1,x}Sr,TiO₃) raw materials also need downsizing, and ferroelectric fine particles with sizes below 100 nm are required. However, in ferroelectric fine particles, a phenomenon was known well that ferroelectricity decreased with decreasing particle and grain sizes, and disappeared below certain critical sizes, which called "size effect" in ferroelectrics [1-7]. Therefore, the size effect for ferroelectrics such as BaTiO₃ and lead titanate (PbTiO₃) is one of the most important phenomena in the industry and science. Ishikawa et al. prepared PbTiO₃ fine particles by a solgel method, and studied its size effect using both Raman scattering and XRD [8]. As a result, Curie temperature (Tc) and c/a ratio (tetragonality) decreased with reducing size, and they estimated that a critical size of PbTiO₃ is around 10.7 nm, for which a paraelectric phase becomes stable at room temperature [8]. McCauley et al. also prepared BaTiO₃-glass ceramics, i.e., BaTiO₃ fine particles dispersed in glass, and studied its size effect using a dielectric measurement [9]. As a result, Tc decreased with reducing size, and they estimated that the critical size of BaTiO₃ at room temperature was around 17 nm [9]. The above critical sizes were just estimated values, and there is no experimental critical size because of difficulty in preparation of ferroelectric particles with sizes around 10 nm. Thus, it is very important to prepare ferroelectric crystals with a size below their critical

sizes.

There were some ways to synthesize BaTiO₃ fine particles, such as sol-gel and hydrothermal methods. Matsuda et al. prepared BaTiO₃ fine particles with sizes around 10 nm using sol-gel method, and found that asprepared BaTiO, fine particles contain a lot of impurities such as hydroxyl group and hydrocarbon species originated from metal-alkoxides [10-11]. To remove the impurities, a heat-treatment at 700°C was required, and this heat-treatment made particle sizes larger over 50 nm. Therefore, it seems to be very difficult to prepare the defect-free nm-sized ferroelectric crystals using solgel method. On the other hand, hydrothermal method also had some problems for a preparation of BaTiO₃ fine particles. One of the problems was a minimum limitation in particle sizes. Wada et al. prepared BaTiO₃ fine particles with an average particle size of around 20 nm using hydrothermal method, and reported that 20 nm was a minimum size in the hydrothermal BaTiO₃ fine particles [12-13]. This is because that in hydrothermal synthesis, colloidal titanium tetrahydroxide Ti(OH)₄ gel was used as Ti source, and Ti(OH), gel was composed of Ti(OH)₄ clusters with sizes around 10 nm. This means that a size of hydrothermal BaTiO, fine particles can be limited by that of Ti(OH)₄ gel. Therefore, it is very difficult to prepare the defect-free nm-sized ferroelectric crystals using hydrothermal method. To prepare defect-free nm-sized BaTiO, crystals with sizes around 10 nm, a new innovative preparation method must be required. In this study, we proposed a new preparation method for nm-sized BaTiO₃ fine particles.

2. EXPERIMENTAL

Figure 1 shows a schematic concept proposed as a



Fig. 1 A schematic concept in a new preparation method for nm-sized BaTiO₃ fine particles.

new preparation method. Ti ions in a strong acid solution (pH < 1.0) is dropped slowly in a strong basic solution (pH > 13.0) with excess Ba ions (Fig. 1-a). Next, near an interface between Ti droplet and Ba solution, a neutralization reaction between strong acid and base occurs, and then there is a lot of heat of neutralization (Fig. 1-b). As a result, it is expected to synthesize BaTiO₃ particles directly from Ti and Ba ions using the heat of neutralization as a driving force (Fig. 1-c) as follows;

$Ba^{2*} + Ti^{4*} + 6OH^{-} \rightarrow BaTiO_3 + 3H_2O$ (1).

This new preparation method has the following two features. One is the possibility that $BaTiO_3$ crystallites are synthesized at lower temperatures below 100°C because of a heat of neutralization as a driving force. Another is the possibility that there is no minimum limitation in particle sizes, and also no contamination in $BaTiO_3$ crystallites. This is because nm-sized and impurity-free $BaTiO_3$ crystallites are directly prepared from Ti and Ba ions in a solution, not via intermediates. We named this new innovative method Low Temperature Direct Synthesis (**LTDS**) method.

BaTiO₃ fine particles were prepared using a LTDS method as follows. Titanium tetrachloride TiCl₄ (Kishida Chem., >99.9%) was dropped slowly into icecooled nitric acid (Junsei Chem., EL grade) below 10°C, and this solution was used as Ti source. On the other hand, barium hydroxide Ba(OH)₂•8H₂O (Sakai Chem., >99.99%) was dissolved into CO₃-free ion-exchanged water, and its pH was adjusted above 13.0 using potassium hydroxide KOH (Wako Pure Chem., >98%). Ba solution was stirred at various temperatures from 25 to 90°C, and this solution was used as Ba source. Ice-cooled Ti solution below pH of 1.0 was dropped slowly into Ba solution with various Ba/Ti atomic ratios in the starting materials from 1 to 150. In this study, an amount of added Ti ions was always fixed. Thus, Ba/Ti atomic ratios in the starting materials depend simply only on Ba concentration in Ba solution. At a dropping of Ti solution into Ba solution, a white precipitation was formed instantaneously. The white precipitation was filtered, washed and then dried at 70°C for 16h in vacuum.

3. RESULTS AND DISCUSSION

At first, optimum conditions for the formation of BaTiO₃ using the LTDS method were investigated at various reaction temperatures from 25 to 90°C and Ba/Ti atomic ratios from 1 to 150. Table 1 shows this result. Products were assigned by XRD measurements. A sign of "NO" means the formation of BaTiO, while "YES" means no formation of BaTiO₃. The formation of BaTiO, phase was confirmed under the conditions over 50°C and Ba/Ti atomic ratios of 5, except for one condition at 90°C and Ba/Ti atomic ratio of 2. As above described, in the LTDS method, at dropping of Ti solution into Ba solution, a white precipitation appeared instantaneously, which revealed that BaTiO₃ was directly synthesized from Ti and Ba ions. Figure 2 shows a XRD pattern of BaTiO, particles prepared at 70°C and Ba/Ti atomic ratio of 10, as a typical example. In Fig. 2, BaTiO₃ phase was observed as a main product while orthorhombic BaCO₃ phase (JCPDS No. 5-378) was also observed as a by-product. In this study, the LTDS method was done in atmosphere. Hence, before dropping of Ti solution into Ba solution, the slight formation of white precipitate was observed, which was assigned to BaCO₃ by XRD measurements. Now, we believe that BaCO₃ formed in the LTDS method is a product via a reaction between Ba(OH), and CO, in atmosphere. Therefore, if the LTDS method is done in CO₂-free atmosphere, it is expected that there is no

| Temperature (°C) | Ba/Ti atomic ratio | | | | |
|---------------------|--------------------|-----------|-----------|------------|--|
| | Ba/Ti = 1 | Ba/Ti = 2 | Ba/Ti = 5 | Ba/Ti = 10 | Ba/Ti > 35 |
| 25°C | NO | NO | NO | NO | cienzis vitai sunta a mili 1964 viti viden scala con cata cata manera cata sporta sunta di |
| 50°C | NO | NO | YES | YES | YES ¹ |
| 70°C | NO | NO | YES | YES | YES ² |
| 90°C | NO | YES | YES | YES | YES ³ |

Table 1 A BaTiO, formation diagram at various temperatures from 25°C to 90°C and various Ba/Ti atomic ratios from 1 to 150.

* 1: Ba/Ti atomic ratio of 35, 2: Ba/Ti atomic ratio of 100, 3: Ba/Ti atomic ratio of 150

BaCO₃ formation. Among peaks assigned to BaTiO₃ in Fig. 2, {111} planes around 20 of 38.5° were chosen in order to estimate a crystallite size of {111} planes (D₍₁₁₁₎) using Scherrer's formula [14]. On the basis of FWHM of a slow scanned {111} peak, as shown in Fig. 3, D₍₁₁₁₎ was estimated at 32.4 nm. It should be noted that FWHM of a slow scanned {111} peak was corrected using α -SiO₂ standard material. Figure 4 shows TEM bright-field and dark-field images in BaTiO₃ fine particles prepared at 70°C and Ba/Ti atomic ratio of 10. A SAED pattern revealed that this particles were assigned to BaTiO₃. From Fig. 4, shape of particles was almost spherical, and a particle size of TEM bright-field image (Fig. 4-a) almost corresponded



Fig. 2 A XRD pattern in $BaTiO_3$ fine particles prepared at 70°C and Ba/Ti atomic ratio of 10.



Fig. 3 $\{111\}$ planes in BaTiO₃ fine particles prepared at 70°C and Ba/Ti atomic ratio of 10.

to that of TEM dark-field image (Fig. 4-b), which means that one particle must be a single-crystal particle. Moreover, this average particle size was estimated at 43.2 nm from TEM bright-field images. This particle size of 43.2 nm was almost same as a crystallite size of 32.4 nm.

On the other hand, Fig. 5 shows a XRD pattern of BaTiO₃ particles prepared at 70°C and Ba/Ti atomic ratio of 100. Both BaTiO, and BaCO, phase were observed in Fig. 5. It should be noted that all of FWHMs assigned to BaTiO, were much broader than those in Fig. 2, which means that crystallite sizes in Fig. 5 are much smaller than those in Fig. 2. In fact, on the basis of FWHM of a slow scanned {111} peak, as shown in Fig. 6, $D_{(11)}$ was estimated at 12.9 nm. Figure 7 shows TEM bright-field and dark-field images in BaTiO₂ fine particles prepared at 70°C and Ba/Ti atomic ratio of 100. A comparison between bright-field and dark-field images indicated that one particle is a singlecrystal particle, and an average particle sizes was estimated at 11.8 nm from bright-field images. This study is the first report for the formation of BaTiO₃



Fig. 4 TEM bright-field (a) and dark-field (b) images in BaTiO₃ fine particles prepared at 70° C and Ba/Ti atomic ratio of 10.

single-crystal particles with a size of 11.8 nm. Therefore, it was confirmed that the LTDS method is very effective for the synthesis of nm-sized $BaTiO_3$ crystallites.

4. CONCLUSION

In this study, the new LTDS method was established to synthesize nm-sized BaTiO₃ crystallites. Using this LTDS method, BaTiO₃ crystallites were directly synthesized from Ti and Ba ions in solution, not via intermediates. Finally, BaTiO₃ crystallites around 10 nm were first prepared at 70°C and a Ba/Ti atomic ratio of 100. These particles will be characterized using various methods such as FT-IR, Raman scattering, TG-DTA, and chemical analysis.

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Fig. 5 A XRD pattern in BaTiO₃ fine particles prepared at 70° C and Ba/Ti atomic ratio of 100.



Fig. 6 $\{111\}$ planes in BaTiO₃ fine particles prepared at 70°C and Ba/Ti atomic ratio of 100.



Fig. 7 TEM bright-field (a) and dark-field (b) images in BaTiO₃ fine particles prepared at 70° C and Ba/Ti atomic ratio of 100.