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Synthesis of nm-sized barium titanate crystallites using a new LTDS method and their characterization

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A new LTDS method was established to synthesize nm-sized barium titanate crystallites with particle sizes around 10 nm. This LTDS method was the following two features, i.e., (1) a heat of neutralization in a neutralization reaction between strong acid and base can be used as a driving force for a formation of barium titanate, and (2) barium titanate crystallites can be directly synthesized from Ti and Ba ions, not via intermediates. Therefore, using the LTDS method, it can be expected that there is no minimum limit in particle sizes, and also no contamination in barium titanate crystallites. At first, optimum conditions for a formation of barium titanate were screened at various reaction temperatures and Ba/Ti atomic ratios in the starting materials. As a result, the formation of barium titanate was found 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 ratios while under a constant Ba/Ti atomic ratio, particle sizes were independent of reaction temperatures. Finally, barium titanate crystallites with particle sizes below 10 nm were first prepared. These particles were also characterized using various methods. © *2000 Kluwer Academic Publishers*

1. Introduction

With miniaturization for electronic device, down-sizing of electronic component has been developed for past years and accelerated at present. As a result, in the electric devices such as multilayered capacitor, particle sizes of barium titanate ($BaTiO_3$) and barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$) raw materials also are down-sizing, and today, 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 [1–9]. Therefore, size effect for ferroelectrics such as $BaTiO_3$ and lead titanate ($PbTiO_3$) is one of the most important phenomena for an interest of industry and science. Size effect should be a phase transition caused by down-sizing, i.e., one of ferroelectric phase transitions caused by temperature, stress and electric field. To study intrinsic size effect in ferroelectrics, it is important to avoid other factors such as internal stress in ceramics and interfacial stress between film and substrate in thin film, which can affect significantly the phase transition. Thus, it is so difficult to understand intrinsic size effect using ceramics and thin film. We believe that the best way to study the size effect must be using fine single-crystal particles.

Ishikawa *et al.* prepared $PbTiO_3$ fine particles by a sol-gel 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 $PbTiO_3$ is around 10.7 nm, for which a paraelectric phase can become stable at room temperature [8]. McCauley *et al.* also prepared $BaTiO_3$-glass ceramics, i.e., $BaTiO_3$ 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 $BaTiO_3$ at room temperature is 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 sizes below their estimated critical sizes. Moreover, Hennings and Schreinemacher [10] and Wada *et al.* [7, 11, 12] revealed a "defect effect" in ferroelectrics, which despite no change of particle size, the structure of $BaTiO_3$ can be affected by a defect such as lattice hydroxyl group. Therefore, to study intrinsic size effect, defect-free nm-sized ferroelectric crystals with various sizes through the estimated critical size must be prepared.

Today, to synthesize $BaTiO_3$ fine particles, it was well-known that there were some ways such as sol-gel and hydrothermal method. Matsuda *et al.* prepared $BaTiO_3$ fine particles with sizes around 10 nm using sol-gel method, and found that in as-prepared $BaTiO_3$ fine particles, there were a lot of impurities such as hydroxyl group and hydrocarbon species originated from metal-alkoxides [13, 14]. Thus, 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 sol-gel method. On the other hand, hydrothermal method also had some problems for a preparation of $BaTiO_3$ fine particles. One is a existence of lattice hydroxyl group in as-prepared $BaTiO_3$ fine particles. Lattice hydroxyl group caused vacancies of barium and titanium in $BaTiO_3$ fine particles, and thus, affected their crystal structure and ferroelectricity significantly [10, 12, 15]. Another problem was a minimum limit in particle sizes. Wada *et al.* prepared $BaTiO_3$ fine particles with an average particle size around 20 nm using hydrothermal method, and reported that 20 nm was a minimum size in the hydrothermal $BaTiO_3$ fine particles [11, 12]. This is because that in hydrothermal synthesis, colloidal titanium tetrahydroxide $Ti(OH)_4$ gel was used as Ti source, and $Ti(OH)_4$ gel was composed of $Ti(OH)_4$ clusters with sizes from 10 to 50 nm [16]. This means that a size of hydrothermal $BaTiO_3$ fine particles can be limited by that of $Ti(OH)_4$ gel. Therefore, it is so difficult to prepare the defect-free nm-sized ferroelectric crystals using hydrothermal method. To prepare defect-free nm-sized $BaTiO_3$ crystals with sizes around 10 nm, a new innovative preparation method must be required.

Our final purpose is to investigate intrinsic size effect in $BaTiO_3$ crystals. In this study, we will propose a new innovative preparation method for this purpose. Moreover, using this method, $BaTiO_3$ crystallites will be synthesized under various conditions. Finally, their characterization will be also done here.

2. Experimental

2.1. LTDS methods

Fig. 1 shows a schematic concept proposed for a new innovative preparation method [17]. Ti ions in strong acid solution ($pH < 1.0$) is dropped slowly in strong basic solution ($pH > 13.0$) with excess Ba ions (Fig. 1a). Next, near an interface between Ti droplet and Ba solution, a neutralization reaction between strong acid and base occurs, and then there can be a lot of heat of neutralization (Fig. 1b). As a result, it can be expected to synthesize $BaTiO_3$ particles directly from Ti and Ba ions using the heat of neutralization as a driving force (Fig. 1c) as follows;

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

This new preparation method has two features as follows. One is the possibility that a heat of neutralization occurred in a neutralization reaction between a strong acid ($pH < 1.0$) and a strong base ($pH > 13.0$) can be expected as a driving force for a formation of $BaTiO_3$ fine particles. This means that $BaTiO_3$ crystallites can be synthesized at lower temperatures below 100°C. Another is the possibility that $BaTiO_3$ crystallites can be directly prepared from Ti and Ba ions in a solution, not via intermediates such as amorphous $Ti(OH)_4$ gel. This suggests that there is no minimum limit in particle sizes, and also no contamination. Therefore, using this new method, a formation of nm-sized and impurity-free $BaTiO_3$ crystallites can be expected. We named this new innovative method Low Temperature Direct Synthesis (**LTDS**) method through the manuscript.

2.2. Preparation procedure

Synthesis of $BaTiO_3$ fine particles using LTDS method was done as shown in Fig. 2. Titanium tetrachloride $TiCl_4$ (Kishida Chem., >99.9%) was dropped slowly

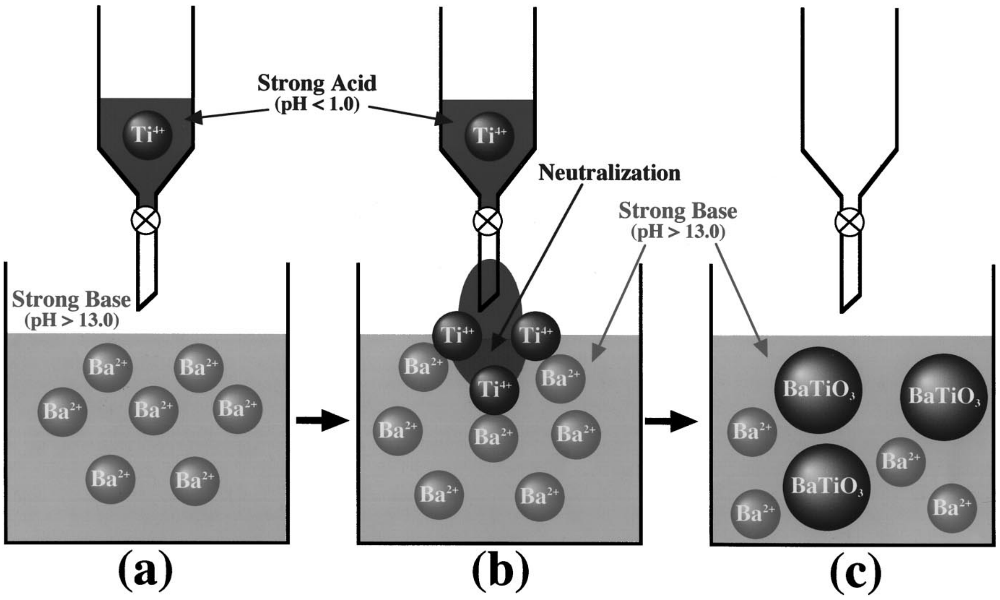

Figure 1 A schematic concept in a new preparation method for nm-sized $BaTiO_3$ fine particles.

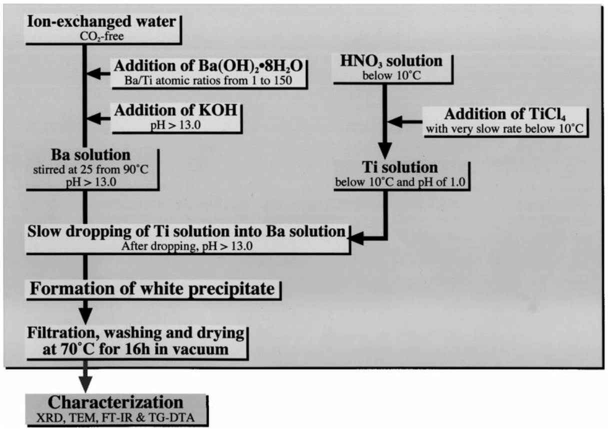

Figure 2 A schematic procedure for synthesis of $BaTiO_3$ fine particles using a LTDS method.

into ice-cooled nitric acid (Junsei Chem., EL grade) below 10°C, and this solution was used as Ti source. On the other hand, barium hydroxide $Ba(OH)_2 \bullet 8H_2O$ (Sakai Chem., >99.99%) was dissolved into CO_2-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 can depend simply only on Ba concentration in Ba solution. At a dropping of Ti solution into Ba solution, a instantaneous formation of white precipitation was observed. The white precipitation was filtered, washed, dried at 70°C for 16 h in vacuum, and used as products.

2.3. Characterization

The crystal structure of the products was investigated at room temperature using a powder X-ray diffractometer (XRD) (RAD-2C, Rigaku, Cu-k_α, 30 kV, 20 mA). The average particle sizes and crystallite sizes were estimated using a transmission electron microscope (TEM) (H-700H, Hitachi, 200 kV) and XRD. The impurity in the products was examined using a Fourier transform infrared spectrometer (FT-IR) (SYSTEM 2000 FT-IR, Perkin Elmer) and a differential thermal analysis with thermogravimetry (TG-DTA) (TG-DTA2000, Mac Science).

3. Results and discussion

At first, optimum conditions for a formation of $BaTiO_3$ using LTDS method was screened at various reaction temperatures from 25 to 90°C and Ba/Ti atomic ratios in the starting materials from 1 to 150. Fig. 3 shows a XRD pattern of products prepared at 70°C and Ba/Ti atomic ratio of 10, as a typical example. In Fig. 3, $BaTiO_3$ phase was observed as a main product while orthorhombic $BaCO_3$ phase (JCPDS No. 5-378) was also observed as a by-product. As above described, in LTDS method, at dropping of Ti solution into Ba solution, a white precipitation appeared instantaneously, which revealed that $BaTiO_3$ was directly synthesized from Ti and Ba ions. A crystal structure of an ideal $BaTiO_3$ crystal at room temperature is a tetragonal symmetry P4mm, and in the 2θ region from 44° to 46°, two peaks must be observed, i.e., (002) planes around 44.9° and (200) planes around 45.4°. However, in the XRD pattern assigned to $BaTiO_3$ in Fig. 3, there was only one symmetric-shaped peak around 45°, which suggested that a crystal structure of $BaTiO_3$ particles prepared using LTDS method can not be assigned to a tetragonal, but a cubic symmetry Pm3m. Thus, using the reported assignment as cubic $BaTiO_3$ (JCPDS No. 31-174), each $BaTiO_3$ peak in Fig. 3 was indexed. All of $BaTiO_3$ particles prepared in this study were also assigned to cubic Pm3m symmetry.

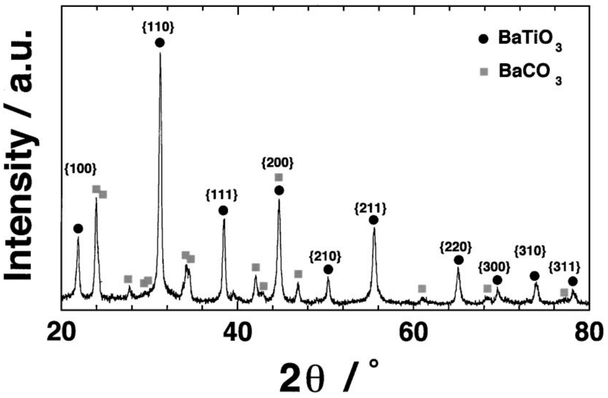

Figure 3 A XRD pattern in products prepared at 70°C and Ba/Ti atomic ratio of 10.

In this study, LTDS method was done in atmosphere, and under all of conditions, a formation of $BaCO_3$ was confirmed. Moreover, before dropping of Ti solution into Ba solution, a small formation of white precipitate was observed, which was assigned to $BaCO_3$ by XRD measurements. Now, we considered that $BaCO_3$ formed in LTDS method can be a product via a reaction between Ba ions in the solution and CO_2 in atmosphere as follows,

$$Ba^{2+} + CO_2 + 2OH^- \longrightarrow BaCO_3 + H_2O. \qquad (2)$$

This means that a formation of $BaTiO_3$ (Equation 1) was completely independent of that of $BaCO_3$ (Equation 2), and two reactions proceeded parallel. Therefore, if LTDS method can be done in CO_2-free atmosphere, it can be expected that there is no $BaCO_3$ formation, i.e., a formation of $BaTiO_3$ single phase.

Table I shows the optimum conditions for a formation of $BaTiO_3$ using LTDS method. Products were assigned by XRD measurements. A sign of "**O**" means a formation of $BaTiO_3$ while "**X**" means no formation of $BaTiO_3$. Formation of $BaTiO_3$ phase in products 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. To date, a minimum temperature for crystallization of $BaTiO_3$ in a wet process was reported around 70°C [12], except for sol-gel method, but in this study, a temperature for the crystallization of $BaTiO_3$ was lowered to 50°C for the first time using LTDS method.

TABLE I A $BaTiO_3$ formation diagram at various temperatures from 25°C and various Ba/Ti atomic ratios from 1 to 150

Temperature (°C)	Ba/Ti atomic ratio Ba/Ti = 1	Ba/Ti = 2	Ba/Ti = 5	Ba/Ti = 10	Ba/Ti > 35
25°C	X	X	X	X	-
50°C	X	X	O	O	O^1
70°C	X	X	O	O	O^2
90°C	X	O	O	O	O^3

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

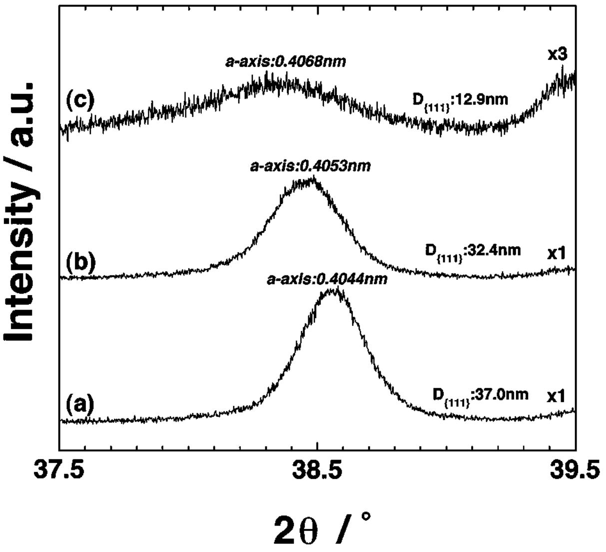

Figure 4 {111} planes in $BaTiO_3$ fine particles prepared at 70°C and various Ba/Ti atomic ratio of 5 (a), 10 (b) and 100 (c).

Next, in various $BaTiO_3$ particles prepared using LTDS method, their crystallite and particle sizes were investigated. At the same time, their lattice constants *a-axis* were also measured on the assumption that their crystal structure is a cubic symmetry Pm3m. Crystallite sizes and *a-axis* were evaluated using XRD measurement. For this measurement, among peaks assigned to $BaTiO_3$, {111} planes around 2θ of 38.5° was chosen. This is because there was no overlapping peaks between $BaTiO_3$ and $BaCO_3$. The *a-axis* was estimated from a peak top of {111} planes while a crystallite size of {111} planes ($D_{(111)}$) was estimated from FWHM of a slow scanned {111} peak using Scherrer's formula [18]. It should be noted that a position of peak top and FWHM of {111} planes were corrected using α-SiO_2 standard material. Fig. 4 shows {111} planes in $BaTiO_3$ particles prepared at fixed 70°C and various Ba/Ti atomic ratios from 5 to 100. With increasing Ba/Ti atomic ratios, peak tops of {111} planes shifted to lower 2θ while FWHM of {111} planes broadened significantly. This indicated that with increasing Ba/Ti atomic ratios, lattice parameter *a-axis* expanded and crystallite sizes $D_{(111)}$ decreased. In Fig. 4, with increasing Ba/Ti atomic ratios, *a-axis* changed from 0.4044 nm to 0.4068 nm while $D_{(111)}$ changed from 37.0 nm to 12.9 nm. Especially, a value of 12.9 nm is a minimum one among the reported ones, except for those using sol-gel method. Thus, to investigate a relationship between crystallite and particle sizes, TEM observation was done. Figs 5 and 6 show TEM bright-field and dark-field images in $BaTiO_3$ fine particles prepared at 70°C and Ba/Ti atomic ratio of 10 and 100, respectively. Both SAED patterns revealed that these particles were assigned to $BaTiO_3$ single crystal. From Figs 5 and 6, shape of particles was almost spherical, and a particle size of TEM bright-field image (Figs 5 (a) and 6 (a)) almost corresponded to that of TEM dark-field image (Figs 5 (b) and 6 (b)), which means that one particle must be a single-crystal particle. Moreover, this suggests that even if a surface of $BaTiO_3$ crystallite is covered with $BaCO_3$, its thickness must be below limit of detection in TEM equipment. Therefore, TEM observation revealed that formation of $BaTiO_3$ and $BaCO_3$ was completely independent. In all of $BaTiO_3$ fine particles prepared in this study, the similar results were observed.

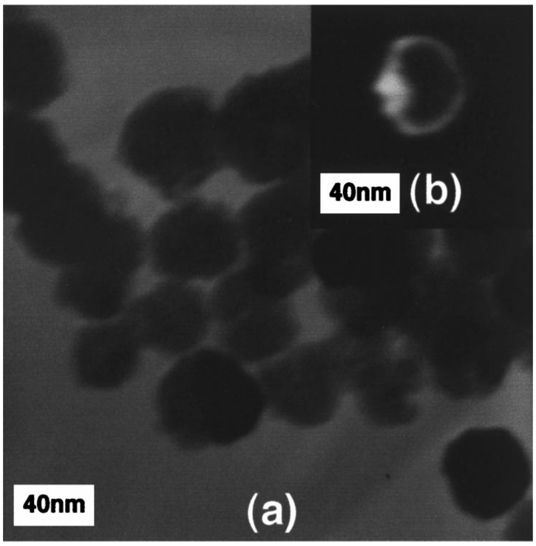

Figure 5 TEM bright-field (a) and dark-field (b) images in $BaTiO_3$ fine particles prepared at 70°C and Ba/Ti atomic ratio of 10.

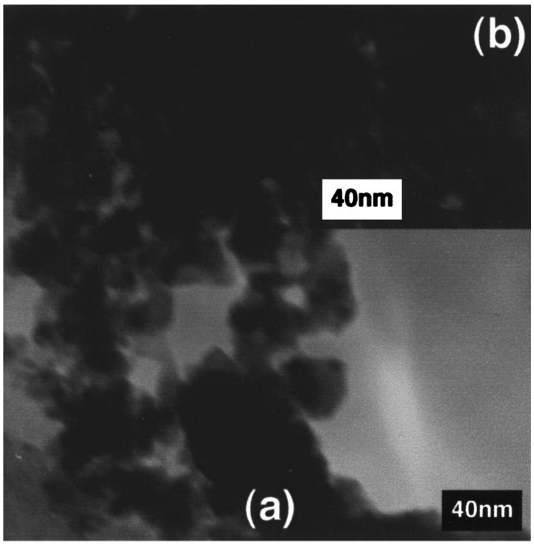

Figure 6 TEM bright-field (a) and dark-field (b) images in $BaTiO_3$ fine particles prepared at 70°C and Ba/Ti atomic ratio of 100.

On the other hand, from several TEM bright-field images, an average particle size was estimated at 43.2 nm in $BaTiO_3$ crystallites prepared at 70°C and Ba/Ti atomic ratio of 10 while that was estimated at 11.8 nm in $BaTiO_3$ crystallites prepared at 70°C and Ba/Ti atomic ratio of 100. The formation of $BaTiO_3$ single-crystal particles with a size of 11.8 nm is first report. These particle sizes of 43.2 nm and 11.8 nm were almost same as a crystallite sizes of 32.4 nm and 12.9 nm, respectively. Thus, it was confirmed that in $BaTiO_3$ fine particles prepared using LTDS method, particle sizes from TEM observation almost equal crystallite sizes from XRD measurement. Through this manuscript, all of $BaTiO_3$ fine particles were regarded as single-crystal particles.

Fig. 7 shows {111} planes in $BaTiO_3$ particles prepared at a fixed Ba/Ti atomic ratio of 10 and various temperatures from 50°C to 90°C. With increasing reaction temperatures, peak tops of {111} planes shifted to lower 2θ while FWHM of {111} planes did not changed. This indicated that with increasing reaction temperatures, lattice parameter *a-axis* expanded and crystallite sizes $D_{(111)}$ were unchanged. In Fig. 7, with increasing reaction temperatures, *a-axis* changed from 0.4044 nm to 0.4061 nm while $D_{(111)}$ was almost constant around 32 nm. There data were listed in Tables II and III. Table II shows particle and crystallite size dependence on reaction temperature and Ba/Ti atomic ratio, while Table III shows lattice constant *a-axis* dependence on reaction temperature and Ba/Ti atomic ratio. In Table II, upper values mean particle sizes from TEM observation, and lower values mean crystallite sizes from XRD measurement. It was confirmed that in most of $BaTiO_3$ particles, particle sizes almost equal crystallite sizes, which supported that LTDS method is effective to synthesize single-crystal particles. In Table II, at a fixed Ba/Ti atomic ratio, both sizes were almost constant despite change of reaction temperatures. On the other hand, at a fixed reaction temperature, both sizes decreased drastically with increasing Ba/Ti atomic ratios. This revealed that in LTDS method, particle sizes can be controlled using Ba/Ti atomic ratios. Moreover, under conditions above 50°C and Ba/Ti atomic ratio of 35, $BaTiO_3$ crystallites with sizes below 10 nm were synthesized here. This is the first report for preparation of $BaTiO_3$ crystallites with sizes below 10 nm. Therefore, it was confirmed that LTDS method is very effective for synthesis of nm-sized $BaTiO_3$ crystallites.

TABLE II Particle and crystallite sizes in $BaTiO_3$ crystallites prepared at various temperatures from 25°C to 90°C and various Ba/Ti atomic ratios from 1 to 150

	Ba/Ti atomic ratio				
Temperature (°C)	Ba/Ti = 1	Ba/Ti = 2	Ba/Ti = 5	Ba/Ti = 10	Ba/Ti > 35
25°C	X	X	X	X	-
50°C	X	X	- 31.1 nm	50.2 nm 31.7 nm	- 8.67 nm [1]
70°C	X	X	68.8 nm 37.0 nm	43.2 nm 32.4 nm	11.8 nm 12.9 nm [2]
90°C	X	- 52.3 nm	- 43.1 nm	35.5 nm 43.1 nm	- 9.72 nm [3]

*[1]: Ba/Ti atomic ratio of 35, [2]: Ba/Ti atomic ratio of 100, [3]: Ba/Ti atomic ratio of 150, upper: average particle sizes estimated from TEM bright-field images, lower: crystallite sizes $D_{\{111\}}$ estimated from FWHM of {111} planes.

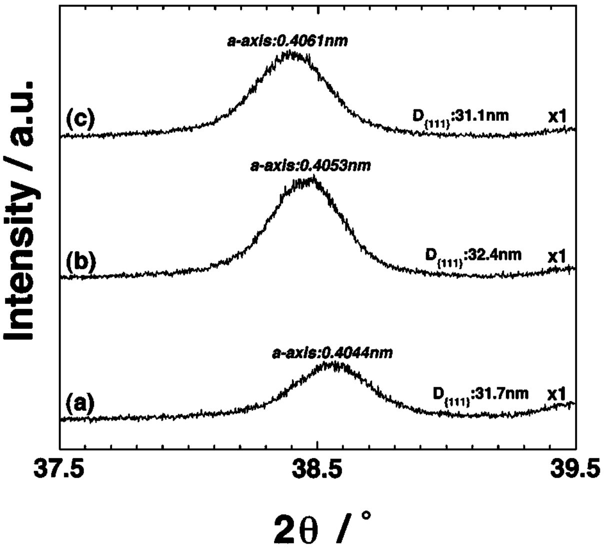

Figure 7 {111} planes in $BaTiO_3$ fine particles prepared at Ba/Ti atomic ratio of 10 and various temperatures of 50°C (a), 70°C (b) and 90°C (c).

TABLE III *a*-axis $BaTiO_3$ crystallites at various temperatures from 25°C to 90°C and various Ba/Ti atomic ratios from 1 to 150

	Ba/Ti atomic ratio				
Temperature (°C)	Ba/Ti = 1	Ba/Ti = 2	Ba/Ti = 5	Ba/Ti = 10	Ba/Ti > 35
25°C	X	X	X	X	-
50°C	X	X	0.4040 nm	0.4044 nm	0.4053 nm[1]
70°C	X	X	0.4043 nm	0.4053 nm	0.4058 nm[2]
90°C	X	0.4044 nm	0.4049 nm	0.4061 nm	0.4068 nm[3]

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

On the other hand, in Table III, all of lattice constants *a-axis* exhibited very large values, and especially, a maximum *a-axis* of 0.4068 nm was obtained in $BaTiO_3$ crystallites prepared at 90°C and Ba/Ti atomic ratio of 150. On the assumption that crystal structure of an ideal $BaTiO_3$ crystal at room temperature can be a cubic symmetry Pm3m, its *a-axis* can be estimated at 0.4005 nm by an extrapolation of *a-axis* of normal cubic $BaTiO_3$ above 130°C to 25°C using Kay and Vousden's data [19]. However, minimum *a-axis* in $BaTiO_3$ crystallites synthesized in this study was 0.4040 nm, which prepared at 50°C and Ba/Ti atomic ratio of 5, and is much larger than 0.4005 nm. This means that $BaTiO_3$ crystallites prepared using LTDS method (LTDS-prepared $BaTiO_3$ crystallites) have an extremely expanded unit lattice. In Table III, at a fixed Ba/Ti atomic ratio, *a-axis* increased with increasing reaction temperatures. On the other hand, at a fixed reaction temperature, *a-axis* also increased with increasing Ba/Ti atomic ratios. In general, it is well-known that in $BaTiO_3$ fine particles prepared using wet process such as hydrothermal method, there existed lattice hydroxyl group, which indicates that proton (H^+) can exist into some interstitial positions of a $BaTiO_3$ unit cell, and expands a unit cell volume. This phenomenon was reported by some researchers, who have investigated hydrothermal synthesis of $BaTiO_3$ fine particles [10, 12, 15]. Therefore, the lattice expansion as shown in Table III can suggest that there may be some impurities such as lattice hydroxyl group in an unit cell of LTDS-prepared $BaTiO_3$ crystallites. Thus, Table III suggested that in order to inhibit a substitution of impurity into a $BaTiO_3$ unit lattice, it is necessary to synthesize $BaTiO_3$ crystallites at lower temperatures and lower Ba/Ti atomic ratios. As to a reason why in LTDS method, *a-axis* can depend on both reaction temperatures and Ba/Ti atomic ratios, it is unclear now.

To investigate about kinds and amounts of impurities including in LTDS-prepared $BaTiO_3$ crystallites, FT-IR and TG-DTA measurements were done for all of LTDS-prepared $BaTiO_3$ crystallites. As a typical example, FT-IR spectrum and TG-DTA curves in products prepared at 70°C and Ba/Ti atomic ratio of 10 are shown in Figs 8 (a) and 9, respectively. It should be noted that as above mentioned, all of products were composed of both $BaTiO_3$ crystallites and $BaCO_3$. Thus, two other FT-IR spectra for commercial $BaCO_3$ (Wako Pure Chem., >99.9%) and $BaTiO_3$ (Kishida Chem., >99.8%) particles as a standard materials were also exhibited in Fig. 8b and c, respectively. Most of absorption bands in the FT-IR spectrum of the products (Fig. 8 (a)) can be assigned to those in standard $BaCO_3$ and $BaTiO_3$. However, since the products were mixture of both $BaTiO_3$ crystallites and $BaCO_3$, it is very difficult to discuss about impurities in only LTDS-prepared $BaTiO_3$ crystallites here. In Fig. 8 (a), there existed only one absorption band around 3501 cm^{-1} completely different from those of standard $BaCO_3$ and $BaTiO_3$. It is well-known that in very wide wave number region from 2500 cm^{-1} to 3560 cm^{-1}, an absorption band assigned to various O-H stretching vibrational modes can be observed [20]. As to standard materials, there was no band in commercial $BaTiO_3$ while in commercial $BaCO_3$, there was a symmetric broad band with peak top around 3426 cm^{-1}. On the other hand, in Fig. 8a, the absorption band assigned to O-H stretching vibration was composed of two peaks, i.e., (a) a very broad peak with a peak top around 3426 cm^{-1} and (b) a very sharp peak with a peak top around 3501 cm^{-1}. Kapphan and Weber reported that proton of the lattice hydroxyl group can exist in five sites around lattice oxygen in $BaTiO_3$ lattice, and their sharp absorption bands for stretching vibration appear in the narrow range from 3462.5 to 3509.5 cm^{-1} [21]. Therefore, the peak with a top around 3501 cm^{-1} in Fig. 8a can be assigned to O-H stretching vibration of lattice hydroxyl group, which suggests that in LTDS-prepared $BaTiO_3$ crystallites, there can exist lattice hydroxyl group. The peak with a top around 3501 cm^{-1} was observed in all of LTDS-prepared $BaTiO_3$ crystallites, and its intensity increased with expanding *a-axis*.

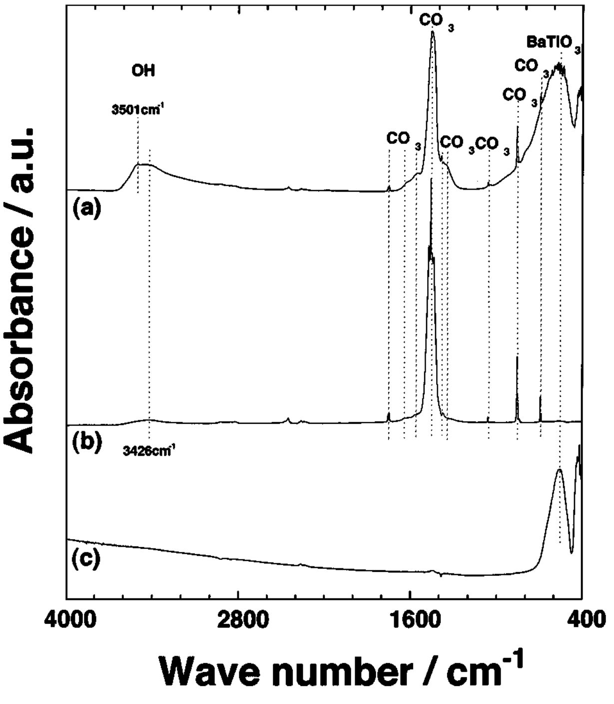

Figure 8 FT-IR spectra of (a) products prepared at 70°C and Ba/Ti atomic ratio of 10, (b) $BaCO_3$ (Wako Pure Chem., >99.9%) and (c) $BaTiO_3$ (Kishida Chem., >99.8%).

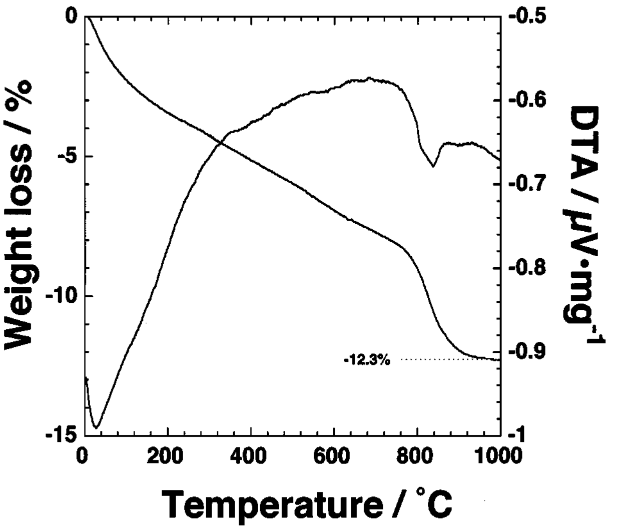

Figure 9 TG-DTA curves in products prepared at 70°C and Ba/Ti atomic ratio of 10.

TG-DTA curves in products prepared at 70°C and Ba/Ti atomic ratio of 10 (Fig. 9) revealed a large weight loss of 12.3% up to 1000°C. This weight loss can be divided into the following two stages, i.e., (a) a weight loss around 8% with a gentle slope from room temperature to 800°C, and (b) a weight loss around 4% with a steep slope from 800°C to 900°C. The weight loss behavior with two stage was observed in all of products prepared using LTDS method. This products (70°C and Ba/Ti atomic ratio of 10) was annealed at various temperatures up to 800°C for 1 h in atmosphere, and after that, XRD measurements were done at room temperature. As the result, below 800°C, XRD patterns assigned to $BaCO_3$ did not changed, but at 800°C, its intensity decreased remarkably, which revealed that at 800°C, a part of $BaCO_3$ decomposed. Thus, it is possible to assign the weight loss (a) to desorption of H_2O and the weight loss (b) to desorption of CO_2. However, as above described, since the products were mixture of both $BaTiO_3$ crystallites and $BaCO_3$, it is very difficult to discuss about amounts of impurities in only LTDS-prepared $BaTiO_3$ crystallites here.

FT-IR and TG-DTA measurements revealed that there were only hydroxyl group and carbonate group as impurities in all of products prepared using LTDS method. At present, we can not discuss about kinds and amounts of impurities including in only LTDS-prepared $BaTiO_3$ crystallites. To do this, we must synthesize $BaTiO_3$ crystallites under CO_2-free atmosphere using LTDS method. After this preparation, various detailed characterization will be done using $BaTiO_3$ crystallites synthesized under CO_2-free atmosphere.

4. Conclusion

In this study, a new LTDS method was established to synthesize $BaTiO_3$ crystallites with particle sizes around 10 nm. Using this method, $BaTiO_3$ crystallites were directly synthesized from Ti and Ba ions in solution, not via intermediates. Screening of optimum conditions for a formation of $BaTiO_3$ at various reaction temperatures from 25 to 90°C and Ba/Ti atomic ratios from 1 to 150 resulted in the formation of $BaTiO_3$ under the conditions with higher reaction temperatures than 50°C and higher Ba/Ti atomic ratios than 5. For all of LTDS-prepared $BaTiO_3$ crystallites, the comparison of TEM bright-field images with dark-field images revealed that one particle was a $BaTiO_3$ single-crystal particle. Under a constant reaction temperature, particle sizes decreased with increasing Ba/Ti atomic ratio while under a constant Ba/Ti atomic ratio, particle sizes were independent of reaction temperatures. Finally, $BaTiO_3$ crystallites with particle sizes below 10 nm were first prepared under the conditions with higher reaction temperatures than 50°C and higher Ba/Ti atomic ratios than 35. These particles were also characterized using FT-IR and TG-DTA and there were impurities over 10% such as hydroxyl group and carbonate group. At present, we can not assign all of hydroxyl group to lattice, surface-absorbed hydroxyl group or water in $BaCO_3$. Therefore, we will synthesize $BaTiO_3$ crystallites using the LTDS method under CO_2-free atmosphere to neglect a formation of $BaCO_3$ as a by-product.

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