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Accelerated formation of barium titanate by solid-state reaction in water vapour atmosphere

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Abstract

Barium titanate ($BaTiO_3$) powders were synthesized from commercially available raw materials ($BaCO_3$ and rutile) without particular mechanochemical processing by solid-state reactions in water vapour atmosphere. The formation rate of $BaTiO_3$ was accelerated by water vapour and single phase of $BaTiO_3$ was obtained by calcination at 700 °C for 4 h in water vapour atmosphere, though high temperature (850 °C for 2.5 h) was required by calcinations in air to complete the reaction. The formation kinetics followed the Valensi–Carter equation, which suggested that the reaction proceeded by a diffusion controlled process. The apparent activation energy for the formation of $BaTiO_3$ in air and water vapour atmosphere was estimated to be 361 ± 20 kJ/mol and 142 ± 17 kJ/mol, respectively. Water vapour is considered to enhance thermal decomposition of $BaCO_3$ and formation of $BaTiO_3$ by attacking surface Ti–O–Ti bonds in TiO_2, increasing partial pressure of $Ba(OH)_2$, and producing vacancies in the $BaTiO_3$ structure.

Keywords: Powders solid-state reaction; $BaTiO_3$ and titanates; Water vapour

1. Introduction

Barium titanate ($BaTiO_3$) is well-known electroceramics widely utilized for manufactures of piezoelectric actuators and multilayer ceramic capacitors (MLCCs) due to its excellent dielectric properties. $BaTiO_3$ powders are conventionally prepared by solid-state reactions of barium carbonate ($BaCO_3$) and titanium dioxide (TiO_2) at temperatures above 1000 °C. The high calcination temperature required by the solid-state reaction process leads to many disadvantages of the $BaTiO_3$ powders, such as large particle size with a wide size distribution and high degree of particle agglomeration. Recent studies have clearly shown that the reduction of the particle size of the raw materials ($BaCO_3$ and TiO_2) to submicrometer or even to nanoscale results in a significant decrease of the calcination temperatures.[1–3] By using the submicrometer $BaCO_3$ ($d_{50} = 0.17\ \mu m$) and fine TiO_2 ($d_{50} = 0.2\ \mu m$), single phase of $BaTiO_3$ was almost obtained at 900 °C for 6 h.[1] The formation of $BaTiO_3$ by solid-state reactions of nanocrystalline $BaCO_3$ and TiO_2 powders was completed at 700–800 °C.[2,3] In addition, mechanochemical effects are known to be quite effective to reduce the calcination temperatures for solid-state reactions.[4–7] Kong et al.[7] milled the starting mixture in a planetary mill in air and obtained $BaTiO_3$ by calcination of the milled mixture at 800 °C for 2 h. The decrease of the calcination temperature provides the fine particle but usually lowers the crystallinity of the products.

On the other hand, it has been shown that the thermal decomposition of calcium carbonate ($CaCO_3$) is accelerated by water vapour.[8–11] It is expected that the thermal decomposition of $BaCO_3$ is also promoted by water vapour and the subsequent formation of $BaTiO_3$ by solid-state reactions with TiO_2 is accelerated. The aim of this study is to prepare $BaTiO_3$ powders at low temperatures in water vapour atmosphere by solid-state reactions using commercially available raw materials without particular mechanochemical processing. In this paper, the influence of water vapour on the formation kinetics of $BaTiO_3$ is reported and its formation mechanism is discussed.

2. Experimental procedures

The commercially available $BaCO_3$ (Wako pure chemical industries, Japan, 99% purity, $S_{BET} = 1.68\ m^2/g$, $d_{BET} =$

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0.83 μm) and TiO_2 (rutile, Wako, 99% purity, $S_{BET} = 5.60\ m^2/g$, $d_{BET} = 0.25$ μm) with stoichiometric quantities were mixed in a stainless ball mill for 6 h at 280 rpm. The mixed powder (0.1 g) was calcined at 650–1000 °C for 0.5–12 h in air and water vapour atmosphere by a tubular furnace equipped with a water evaporator. Calcinations in air atmosphere were performed in stagnant condition. In water vapour atmosphere, distilled water was introduced at a flow rate of 2 mL/min into the evaporator without a carrier gas to generate 100% water vapour atmosphere in the furnace. Flow rate of water vapour was estimated to be 2.5 L/min.

Crystalline phases in the products were identified by powder X-ray diffractions (XRD) obtained by a Rigaku Rotaflex RAD-RC diffractometer using Cu Kα radiation operating at voltage and current of 40 kV and 100 mA, respectively. Data were collected in the range of 5–80° in $2\theta/\theta$ scanning mode with a 0.02° step and scanning speed of 4°/min.

The amount of $BaTiO_3$ in each sample was determined from XRD peak areas of $BaTiO_3$ (1 0 1) (1 1 0) and silicon (1 1 1) diffraction. Silicon (Sigma–Aldrich, USA, 99.999% purity) was used as an internal standard. The calibration curve was previously obtained from the mixtures of silicon and pure $BaTiO_3$ which was prepared by solid-state reaction at 800 °C for 12 h, followed by calcination at 1200 °C for 6 h in air. TiO_2 was used as a dilution agent. Data were collected in the range of 27–33° in $2\theta/\theta$ scanning mode with a 0.006° step and scanning speed of 0.5°/min.

The lattice constants were calculated by the least square method using silicon as an internal standard. Data were collected in the range of 65–135° in $2\theta/\theta$ scanning mode with a 0.006° step and scanning speed of 0.5°/min. Specific surface area, S_{BET}, was measured by the BET method using nitrogen with a Yuasa-ionics NOVA-1200 instrument. The equivalent BET diameter, d_{BET}, was calculated by the following equation:

$$d_{BET} = \frac{6}{\rho_{S_{BET}}} \qquad (1)$$

where ρ is the density of $BaCO_3$ 4.306 g/cm^3, rutile type TiO_2 4.250 g/cm^3 and $BaTiO_3$ 6.012 g/cm^3.

3. Results and discussion

3.1. Preparation of $BaTiO_3$ powders by solid-state reactions

The formation of $BaTiO_3$ by solid-state reactions of $BaCO_3$ and TiO_2 involves the thermal decomposition of $BaCO_3$, so that the forcible removing of CO_2 gas from the reaction field might be accelerated the formation of $BaTiO_3$. The preliminary experiments for solid-state reactions of $BaCO_3$ and TiO_2 were conducted at 750 °C for 2 h in stagnant air and N_2 flowing atmosphere. N_2 gas was introduced to generate 100% N_2 gas flowing atmosphere in the furnace at the same flow rate of 2.5 L/min with that for 100% water vapour atmosphere. As shown in Fig. 1, the products obtained in stagnant air and N_2 flowing atmosphere gave the similar XRD patterns which showed that a large amount of $BaCO_3$ remained and a small amount of $BaTiO_3$ was formed. We considered that a gas flow for forcible removing of CO_2 gas had little effects on the decomposition of $BaCO_3$. Consequently, we examined the effect of water vapour atmosphere on the formation of $BaTiO_3$ comparing with stagnant air atmosphere.

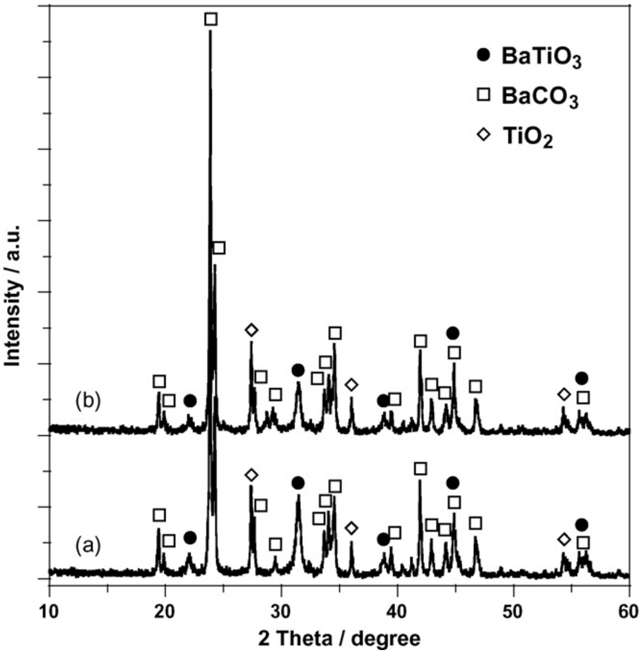

Fig. 1. XRD patters of the samples obtained by solid-state reaction at 750 °C for 2 h in (a) stagnant air and (b) N_2 atmosphere.

Fig. 2 shows the XRD patterns of the samples obtained by calcinations in air and water vapour atmosphere at 750 °C and 800 °C for 2 h. In air atmosphere, the raw materials remained in large quantities even at 800 °C. In contrast, the solid-state reaction of $BaCO_3$ and TiO_2 was accelerated by the injection of water vapour. $BaTiO_3$ was obtained as a single phase at 750 °C for 2 h in water vapour atmosphere. Water vapour accelerated the thermal decomposition of the $BaCO_3$ and then $BaTiO_3$ was synthesized at lower temperatures.

In order to investigate the reaction kinetics and formation mechanism of $BaTiO_3$, quantitative analysis of $BaTiO_3$ in each sample was conducted by the XRD using the internal standard method. The formation ratios of $BaTiO_3$ (fraction reacted: α) are plotted against calcination time at various temperatures in Fig. 3. The single phase of $BaTiO_3$ was obtained in water vapour atmosphere by calcinations at 700 °C for 4 h and 750 °C for 2 h. However, the $BaTiO_3$ (1 0 1) (1 1 0) XRD peak area of these samples was slightly lower than that of fully crystallized $BaTiO_3$, which results in lower formation ratios of these samples than 100%. The formation ratios of $BaTiO_3$ always increased with increase in calcination temperatures and times. The formation ratio by the calcinations in air has not reached 50% at 750 °C for 12 h, while that in water vapour atmosphere approached 100% at 700 °C within 12 h.

Tagawa and Igarashi[12] examined the kinetics of the solid-state reaction of strontium carbonate ($SrCO_3$) and TiO_2 to form strontium titanate ($SrTiO_3$) by the Jander[13] model and Valensi–Carter[14,15] model based on the diffusion controlled pro-

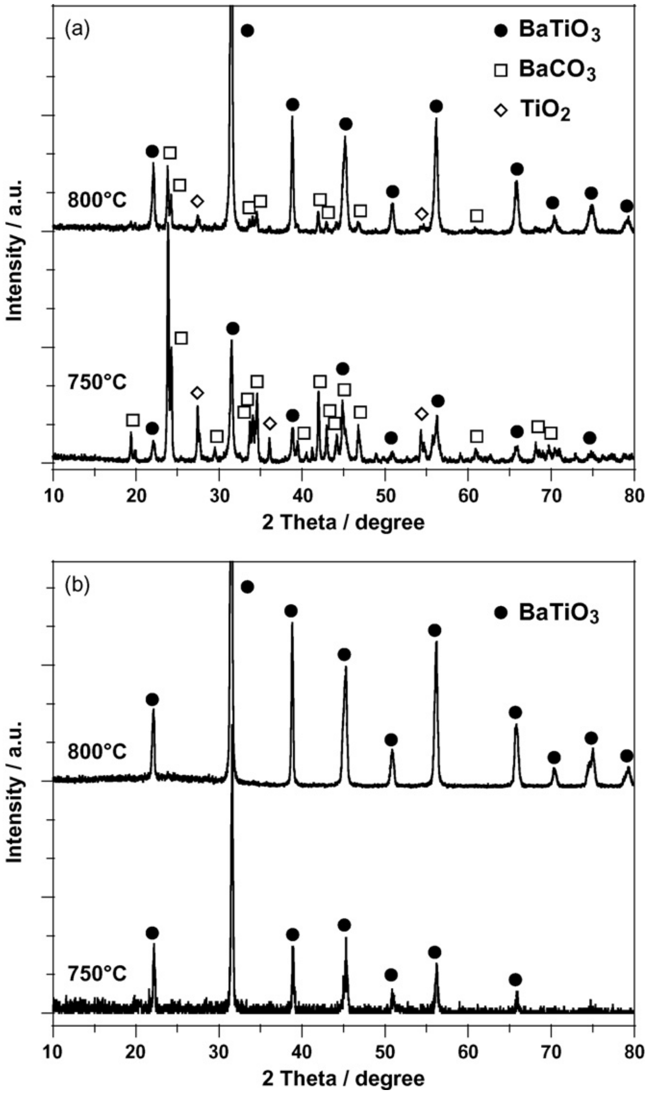

Fig. 2. XRD patterns of the samples obtained by solid-state reactions at 750 °C and 800 °C for 2 h in (a) air and (b) water vapour atmosphere.

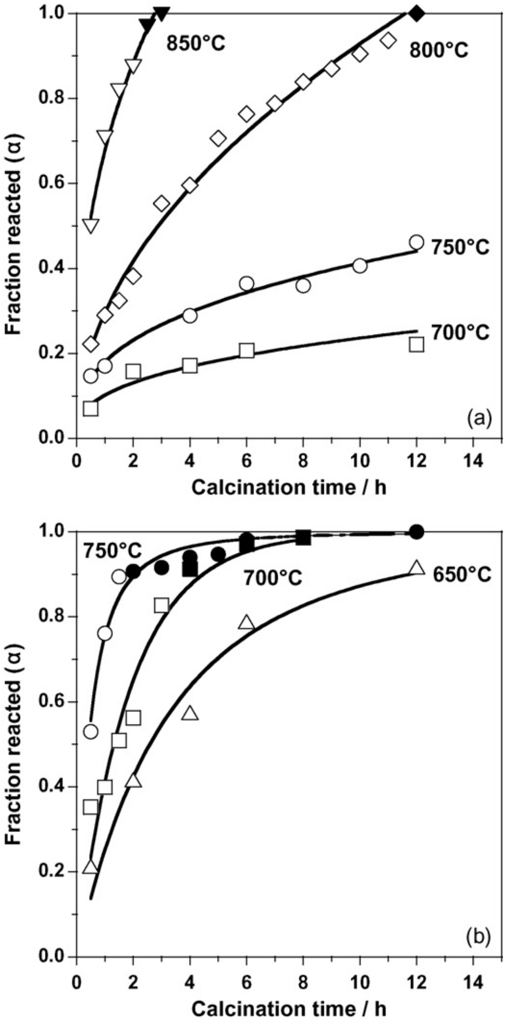

Fig. 3. Plots of fraction reacted of $BaTiO_3$ (α) obtained in (a) air and (b) water vapour atmosphere versus calcination time at various temperatures. Solid symbols show that the product is the $BaTiO_3$ single phase according to XRD.

cess. The reaction mechanism proposed by Jander is the simple model of powder reactions by diffusion but the equation proposed by Valensi and Carter was derived without simplification. We applied the Valensi–Carter equation to our experimental data and determined the mechanism for the solid-state reaction between $BaCO_3$ and TiO_2 to form $BaTiO_3$.

The Valensi–Carter equation is given as following:

$$\frac{z-[1+(z-1)a]^{2/3}-(z-1)(1-a)^{2/3}}{z-1}=kt \qquad (2)$$

where z represents the volume of product formed per unit volume of reactant consumed, α the fraction reacted, k the reaction rate constant, and t the reaction time. In the case of the reaction of $BaCO_3$ and TiO_2 to form $BaTiO_3$, z is 0.600. Fig. 4 shows the Valensi–Carter plots for the reaction of $BaCO_3$ and TiO_2. The linear relation was obtained for all data, which suggests that it is reasonable to conclude that the formation mechanism of $BaTiO_3$ in both atmospheres is diffusion controlled process following the Valensi–Carter equation. From the slopes in Fig. 4, the reaction rate constant, k, was obtained. Arrhenius plots of $\ln k$ versus $1/T$ as shown in Fig. 5 gave the apparent activation energy, E_a, for the formation of $BaTiO_3$ by the solid-state reactions and it was estimated to be 361 ± 20 kJ/mol and 142 ± 17 kJ/mol in air and water vapour atmosphere, respectively. By introducing water vapour, the apparent activation energy was drastically decreased. In other words, the diffusion of Ba^{2+} and O^{2-} ions through the $BaTiO_3$ layer was accelerated by water vapour.

3.2. *Mechanism of accelerated reaction by water vapour*

The results shown in Fig. 2 clearly indicated that water vapour accelerated the thermal decomposition of $BaCO_3$. Wang and Thomson[10] described that adsorbed water vapour weakened Ca–CO_3 bond and the thermal decomposition of $CaCO_3$ was accelerated by water vapour. Water vapour atmosphere similarly might play an important role to weaken the Ba–CO_3 bond, which resulted in acceleration of $BaCO_3$ decomposition in water vapour atmosphere at lower temperatures in comparison with that in air. Furthermore, the lower CO_2 partial pressure

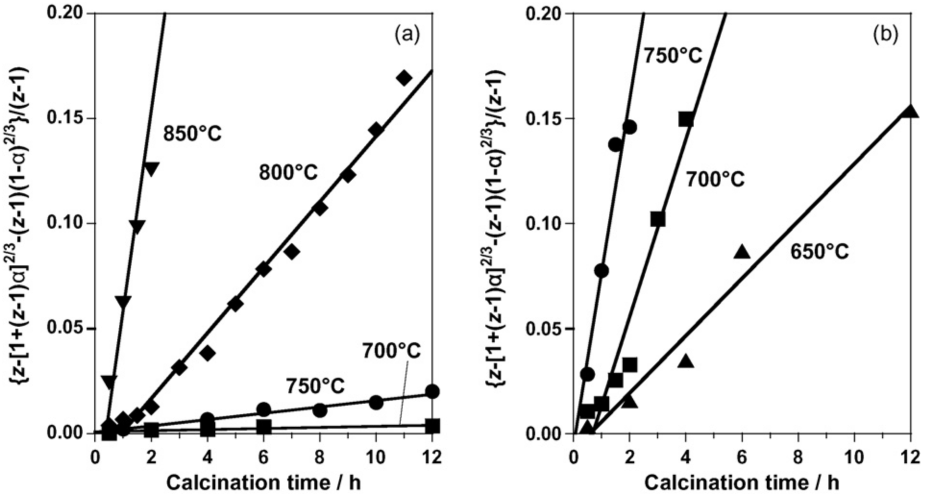

Fig. 4. Kinetics according to Valensi–Carter equation for reaction of $BaCO_3$ and TiO_2 in (a) air and (b) water vapour atmosphere.

in the water vapour might enhance the decomposition of $BaCO_3$ decomposition.

We previously showed that water adsorbed on the surface of amorphous titania particles catalyzed the rearrangement of the TiO_6 octahedra to accelerate the crystallization of amorphous titania to anatase.[16,17] MacKenzie[18] reported that water vapour assisted sintering of rutile type TiO_2 and presented an assumption of the formation of transient hydroxy-species such as $Ti(OH)_2{}^{2+}$ on the surface of the particles. The same effect is expected for the calcinations in water vapour atmosphere in this study. It is considered that water vapour attacks Ti–O–Ti bonds of rutile surface to promote rotation and movement of TiO_6 octahedra, and Ba^{2+} and O^{2-} ions which have already formed by the decomposition of $BaCO_3$, easily react with TiO_6 octahedra to form $BaTiO_3$. Most of formed hydroxyl groups are simultaneously eliminated as H_2O molecule by the rearrangement of TiO_6 octahedra to the perovskite structure of $BaTiO_3$.

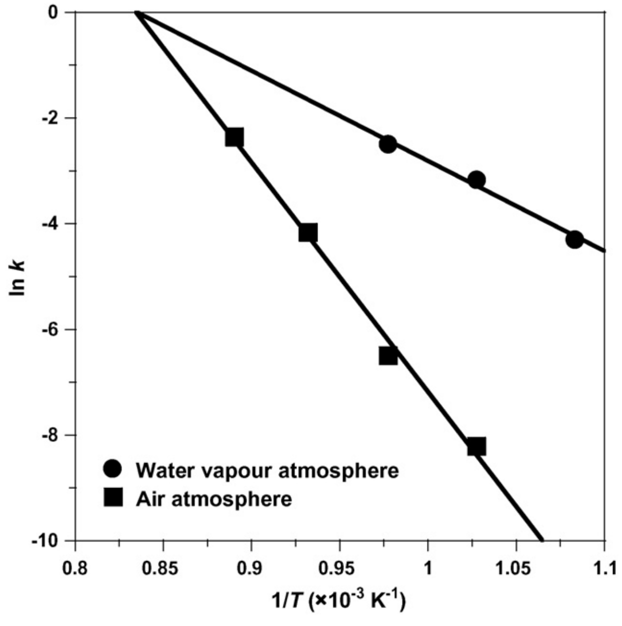

Fig. 5. Arrhenius plot for $BaTiO_3$ formation.

The formation of $BaTiO_3$ must be limited to the $BaCO_3/TiO_2$ contact points. The observed decrease of the reaction temperature in water vapour atmosphere even by using the relatively coarse particles ($BaCO_3$ 0.83 μm and TiO_2 0.25 μm) may imply that a Ba species is efficiently supplied over the entire TiO_2 particle surface in water vapour atmosphere. One possible mechanism is gas phase transport. It is reported that the volatility of the barium oxide (BaO) is greatly increased by the presence of water vapour due to the formation of volatile hydroxide ($Ba(OH)_2$) vapour[19–21] and $Ba(OH)_2$ vapour pressure is given as following[21]:

$$\ln K_\mathrm{p} = \frac{-16792.3}{T} + 4.94 \tag{3}$$

where $K_\mathrm{p} = p(Ba(OH)_2)/p(H_2O)$. Though the Eq. (3) was obtained at high temperatures over 1000 °C, we can estimate $Ba(OH)_2$ partial pressure to be 2.2×10^{-5} atm at 800 °C from the Eq. (3). This value is not negligible and gas phase transport of $Ba(OH)_2$ could become important when the solid-state reaction occurs in water vapour atmosphere. Accordingly, the surface diffusion of barium may be enhanced in water vapour atmosphere.

The formation of $BaTiO_3$ by solid-state reactions is diffusion controlled process as described above, and is explained by coupled diffusion of Ba^{2+} and O^{2-} ions in the $BaTiO_3$ crystal lattice.[3,22–24] Mutin and Niepce[23] suggested vacancy mechanism for diffusion of Ba^{2+} and O^{2-} ions. It is reported that the $BaTiO_3$ powders prepared by hydrothermal method contain a large amount of proton in the oxygen sublattice and the proton defects are compensated by the simultaneously formation of barium and titanium vacancies.[25] These defects might be formed by the solid-state reactions in water vapour atmosphere, which can explain the enhanced solid-state diffusion of barium. Ba^{2+} vacancies ($(Ba_{1-x}H_{2x})TiO_3$) might be formed in the $BaTiO_3$ structure when Ba^{2+} ions are diffused into the space between TiO_6 octahedra with hydroxyl groups, though most of formed hydroxyl groups are simultaneously eliminated as H_2O molecule by the rearrangement of TiO_6 octahedra to form $BaTiO_3$. As a

Table 1
Specific surface area and corresponding particle size of $BaTiO_3$ powders.

Sample	Calcination conditions	Atmosphere	S_{BET} (m^2/g)	d_{BET} (μm)
1	800 °C/12 h	Air	3.36	0.30
2	850 °C/3 h	Air	4.07	0.25
3	750 °C/2 h	Water vapour	4.14	0.24
4	750 °C/12 h	Water vapour	2.99	0.33
5	800 °C/2 h	Water vapour	4.04	0.25

result, the formation of Ba^{2+} vacancies facilitates the diffusion of Ba^{2+} ions by vacancy mechanism. On the other hand, it is also well known that sintering of $BaTiO_3$ in reducing atmosphere forms O^{2-} ion vacancy ($BaTiO_{3-x}$) with a valence reduction of titanium from Ti^{4+} into Ti^{3+}. In water vapour atmosphere that gives a reducing atmosphere compared with in air atmosphere, O^{2-} ion vacancy with the reduction of titanium ion might be formed in the $BaTiO_3$ structure. This O^{2-} vacancy also promotes the diffusion of O^{2-} ions. Thus, it is considered that the diffusion of Ba^{2+} and O^{2-} ions to the TiO_2 reaction front through the $BaTiO_3$ layer is accelerated by vacancy mechanism with three different vacancies formed in water vapour atmosphere.

3.3. *Powder properties and tetragonality*

The specific surface area and particle size of selected $BaTiO_3$ powders prepared in this study are shown in Table 1. The results show that $BaTiO_3$ powders with the same or smaller particle size in comparison with those obtained in air were prepared in water vapour atmosphere by calcinations at lower temperatures for a shorter time. For example, the particle size of $BaTiO_3$ powder obtained by calcination at 750 °C for 2 h in water vapour atmosphere was estimated to be 0.24 μm from its specific surface area, but 0.25 μm by calcination at 850 °C for 3 h in air.

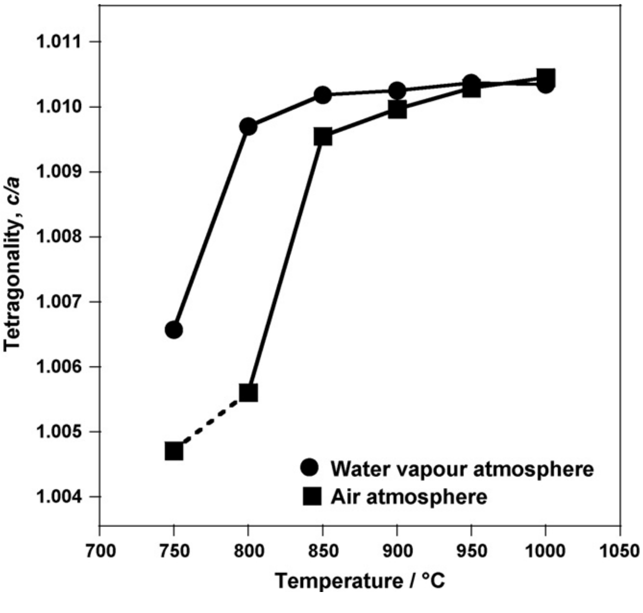

Fig. 6. Tetragonality of $BaTiO_3$ as a function of calcination temperature for 12 h.

Fig. 6 shows the tetragonality (*c*/*a*) of $BaTiO_3$ obtained by calcinations at various temperatures for 12 h in air and water vapour atmosphere. $BaTiO_3$ was obtained as a single phase except for the sample obtained by calcination at 750 °C in air. In both atmospheres, the tetragonality of $BaTiO_3$ increased with an increase in the calcination temperatures, which is explained by the increase of $BaTiO_3$ crystallinity with increasing calcination temperatures. On the other hand, the tetragonality of $BaTiO_3$ obtained in water vapour atmosphere was higher than that in air, and reached 1.0105, close to 1.011 of the $BaTiO_3$ single crystal (JCPDS No. 05-0626), by calcination at 850 °C. This result indicates that the crystallinity of $BaTiO_3$ is increased by water vapour.

4. Conclusions

$BaTiO_3$ powders were prepared by solid-state reactions of $BaCO_3$ and TiO_2 in air and water vapour atmosphere. The formation of $BaTiO_3$ was accelerated by water vapour and $BaTiO_3$ powders with the same or smaller particle size in comparison with those obtained in air were prepared in water vapour atmosphere by calcinations at lower temperatures for a shorter time. The solid-state reaction to form $BaTiO_3$ obeyed the Valensi–Carter equation, which suggested that the reaction proceeded by a diffusion controlled process. The apparent activation energy for the formation of $BaTiO_3$ in water vapour atmosphere was estimated to be 142 ± 17 kJ/mol, much lower than that in air (361 ± 20 kJ/mol). It is considered that water vapour has following effects to accelerate the formation of $BaTiO_3$; (1) acceleration of $BaCO_3$ decomposition, (2) acceleration of $BaTiO_3$ formation by surface attacking of water at the TiO_2 reaction front and by gas phase transport of $Ba(OH)_2$, and (3) acceleration of the diffusion of Ba^{2+} and O^{2-} ions in the $BaTiO_3$ layer by formation of vacancies in the $BaTiO_3$ structure.

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