JOURNAL OF MATERIALS SCIENCE 30 (1995) 4740–4744

Hydrothermal synthesis of barium titanate fine particles from amorphous and crystalline titania

H. KUMAZAWA*, S. ANNEN, E. SADA
Department of Chemical Engineering, Kyoto University, Kyoto 606-01, Japan

Barium titanate fine particles of cubic system were synthesized hydrothermally from aqueous barium hydroxide solutions with fine particles of either amorphous or crystalline (rutile) titania in suspension. The mean size of barium titanate particles prepared from amorphous titania ranged from 0.03 µm to 0.11 µm, depending on hydrothermal conditions. The particle size approximately agreed with the crystallite size (0.04–0.09 µm). On the other hand, the mean size of barium titanate particles prepared from rutile titania ranged from 0.2 to 0.7 µm, which was about six times as large as the crystallite size. The difference of sizes of barium titanate particles prepared might be ascribed to the difference in dissolution rates of amorphous or crystalline titania particles.

Nomenclature

$\bar{a}$	mean particle size, µm
BT	barium to titanium molar ratio
d	crystallite size, µm
K	shape factor appearing in Equation 3
β	half value breadth of diffraction peak
η	lattice strain
θ	Bragg diffraction angle, degree
λ	wave length of X-ray, µm
σ_g	geometric standard deviation defined by 84.1%-size/50%-size in a log normal size distribution

1. Introduction

Barium titanate ($BaTiO_3$) has been well-known as a dielectric material. $BaTiO_3$ powders are produced by use of solid-state and liquid phase reactions. The hydrothermal method in the category of liquid phase reactions has features of producing extremely fine particles with high crystallinity, high purity and narrow size distribution. In that method, an aqueous $Ba(OH)_2$ solution with suspended TiO_2 fine particles is treated hydrothermally, and barium titanate is formed through dissolution of TiO_2 particles followed by deposition, i.e. dissolution–deposition scheme. It is easy to conceive that the rate of dissolution of TiO_2 particles affects the rates of nucleation and crystal growth of barium titanate, and accordingly the final particle size. The dissolution rate of titania may greatly depend on whether the titania is amorphous or crystalline.

In the present work, fine particles of barium titanate were synthesized hydrothermally from aqueous solutions of $Ba(OH)_2$ with suspended amorphous and rutile titania fine particles. The relations of the particle size and shape to such operating variables as $Ba(OH)_2$ concentration, titania loading, stirring speed of autoclave, hydrothermal temperature and reaction time were investigated systematically. A mechanism of particle growth was deduced by observed dependences of particle size on the above operating variables. Ultrafine barium titanate particles of about 0.04 µm were prepared by use of amorphous titania.

2. Chemistry of barium titanate formation under a hydrothermal condition

Barium hydroxide reacts with titania under hydrothermal conditions to form barium titanate. The reaction can be written stoichiometrically as

$$Ba(OH)_2 + TiO_2 \rightarrow BaTiO_3 + H_2O \qquad (1)$$

Barium hydroxide is present as barium ion, whereas titania exists as a solid phase beforehand and dissolves into the liquid phase to participate in the reaction (Equation 1). The barium titanate formation reaction, thus, is of the dissolution–deposition type. The rates of nucleation and growth of barium titanate are affected by the rate of titania dissolution. Accordingly, the dissolution rate greatly depends on whether titania is amorphous or crystalline, and the final size of formed particles may possibly be altered.

3. Experimental details

A stainless steel autoclave (Nitto, UN-4) equipped with a paddle-type stirrer (Nitto, NS-8) was used as a reactor operated under hydrothermal conditions. The autoclave whose internal diameter and height are 4.6 and 14.0 cm, respectively, is the same one as in our

---

* Author to whom correspondence should be addressed.

preceding work [1,2]. Barium titanate fine particles were synthesized from aqueous solutions of barium hydroxide with suspended titania fine particles. Two kinds of titania particles were used: amorphous and crystalline (rutile) titania (hereafter aTiO_2 and rTiO_2 used in figures). Amorphous titania particles were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol [3]. Amorphous titania particles prepared thus are spherical and monodisperse. The mean size was 0.65 μm. Rutile titania particles were produced by a gas phase method and their mean size was 0.49 μm. The procedure for the synthesis of barium titanate was as follows; first, an aqueous solution of barium hydroxide with a prescribed concentration was prepared, and subsequently a prescribed amount of titania particles was added to the solution. A 50 cm^3 portion of the resultant slurry was poured into a pot made of titanium and was placed into the autoclave. The heating rate to the hydrothermal treatment temperature was maintained at 4 °C min^{-1}. The temperature of hydrothermal treatment ranged from 150 to 300 °C. The stirring speed of the autoclave was varied up to 600 r.p.m. The size of prepared particles had previously been found to be independent of the stirring speed in the range 100–600 r.p.m. Thus, the stirring speed was maintained at 300 r.p.m. The hydrothermal treatment was continued for 8 h.

Prepared fine particles were rinsed with distilled water several times and dried at 80 °C in a vacuum oven. Afterwards, the particles were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Powder XRD was performed with a diffractometer (Rigaku Corp., RAD-B) with CuKα radiation. The crystallite size of barium titanate powders was estimated from the half value breadth of the diffraction peak on the (2 0 0) face in terms of Scherrer's equation [4]. The crystallinity of particles was estimated from the intensity of the (1 1 0) diffraction peak. The mean particle size and the size distribution were determined from TEM and SEM images. The number of particles counted for determining the size distribution was about 300.

4. Experimental results and discussion

The X-ray diffraction patterns of fine particles prepared hydrothermally from amorphous and crystalline (rutile) titania are demonstrated in Fig. 1. From X-ray diffraction measurements, crystalline barium titanate is proved to be produced from both amorphous and rutile titania. The barium titanate particle is shown to be cubic system, because the (2 0 0) diffraction peak is not split. In order to examine the strain of prepared particles, the plots based on Hall's relation [5]

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{d} + \frac{\eta\sin\theta}{\lambda} \tag{2}$$

were made. In the above equation, β is half the value of the breadth of the diffraction peak, θ is the Bragg diffraction angle, d is the crystallite size, η is the lattice strain and λ is the wavelength of X-ray. Fig. 2 shows such plots where a single straight line can be drawn. The lattice strain equivalent to the slope of the straight line is judged to be negligibly small. The crystallite size was estimated from the half value breadth of the (2 0 0) diffraction peak in terms of Scherrer's equation [4].

$$d = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

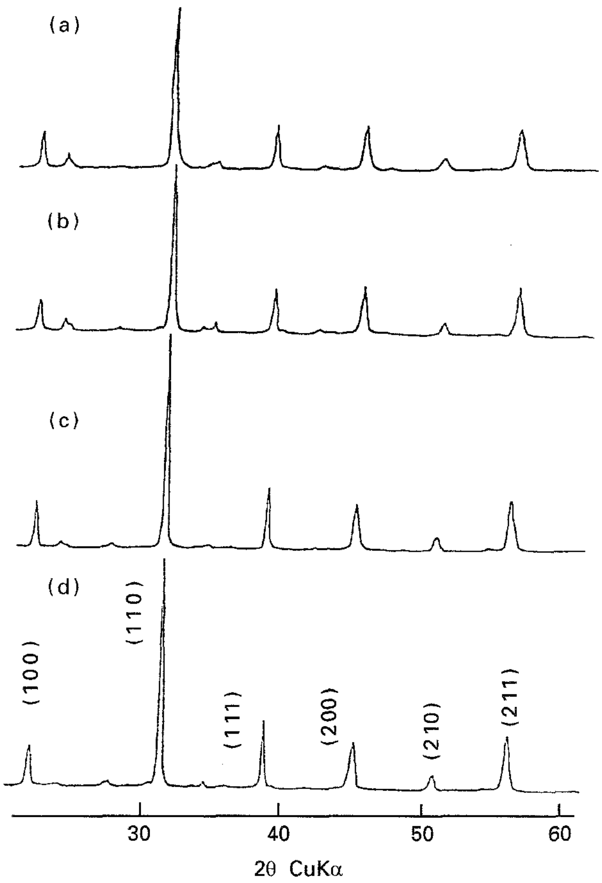

Figure 1 X-ray diffraction patterns of barium titanate fine particles prepared from amorphous ((a), (b)) and rutile ((c), (d)) titania under 200 °C ((a), (c)) and 300 °C ((b), (d)), initial titania loading of 0.5 kmol m^{-3}, BT molar ratio of 2 and stirring speed of 300 r.p.m. for 4 h.

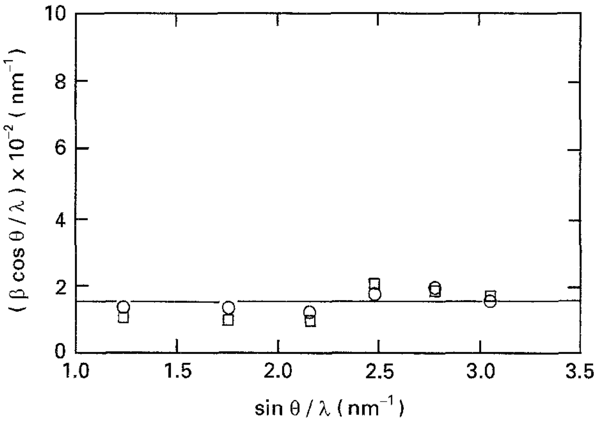

Figure 2 Relations of β cos θ/λ versus sin θ/λ after Hall's equation for barium titanate particles prepared from amorphous (○) and rutile (□) titania under 300 °C, initial titania loading of 0.5 kmol m^{-3}, BT molar ratiо of 2 and stirring speed of 300 r.p.m. for 4 h.

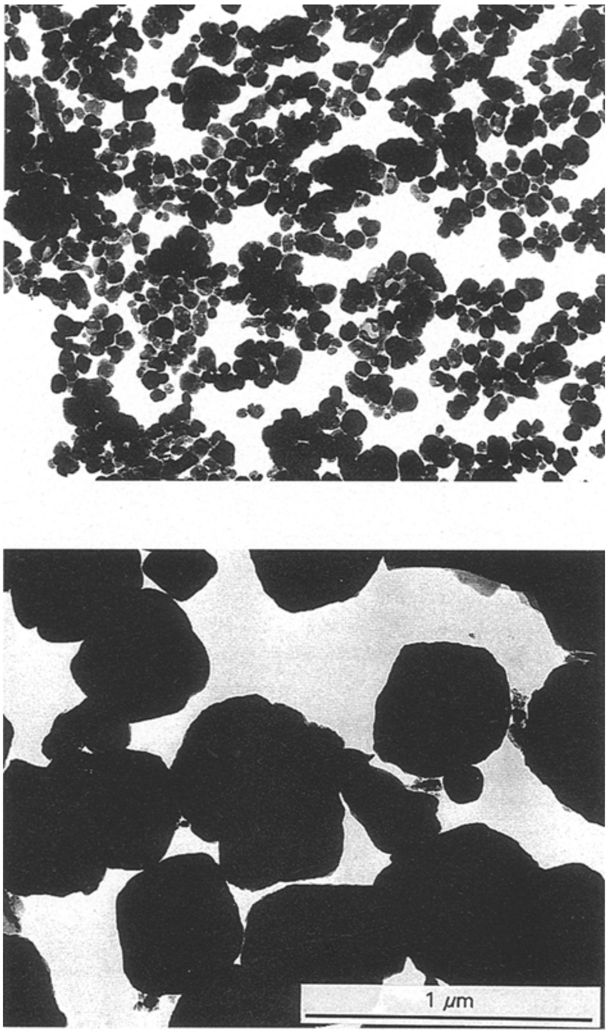

Figure 3 Transmission electron micrographs of barium titanate particles prepared from amorphous (upper) and rutile (lower) titania under 200 °C, initial titania loading of 0.5 kmol m^{-3}, BT molar ratio of 2 and stirring speed of 300 r.p.m. for 4 h.

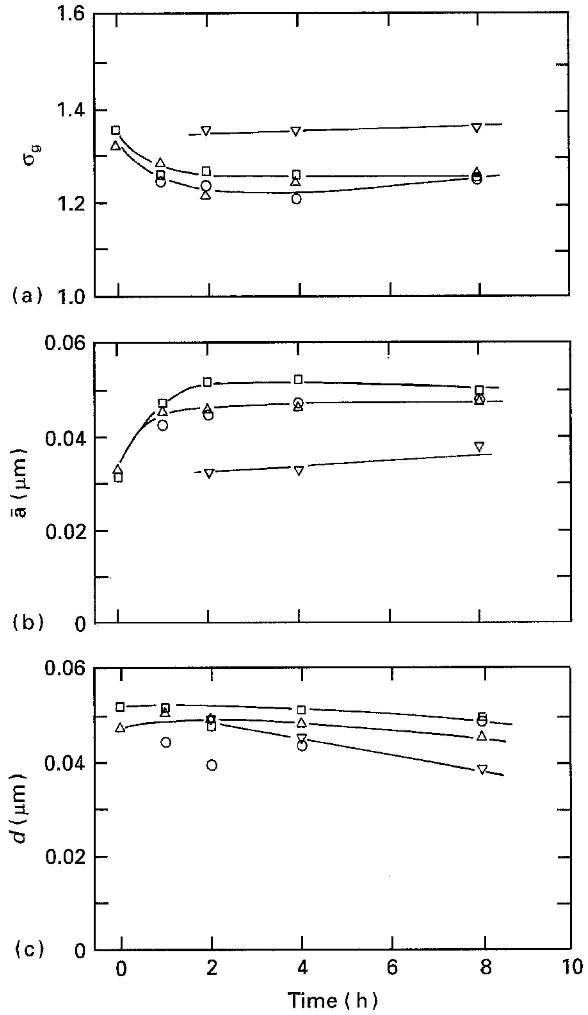

Figure 4 Time dependences of (a) geometric standard deviation of particle size distribution, (b) mean particle size and (c) crystallite size for barium titanate prepared from amorphous titania at different temperatures, initial titania loading of 0.5 kmol m^{-3}, BT molar ratio of 2 and stirring speed of 300 r.p.m. ▽ 150 °C; ○ 200 °C; △ 250 °C; □ 300 °C.

where K refers to a shape factor (= 0.9). The crystallite size was estimated to be about 0.05 μm, independent of whether the starting titania was amorphous or crystallite (rutile).

The transmission electron micrographs (TEM) of barium titanate particles whose XRD patterns were revealed in Fig. 1(a) and (c), are demonstrated in Fig. 3. The upper photo shows ultrafine particles prepared hydrothermally from amorphous titania, whereas the lower one shows fine particles from rutile titania. The mean size of barium titanate particles prepared from amorphous titania is about 0.048 μm, in close agreement with the crystallite size estimated from Scherrer's equation, whereas the mean size of barium titanate particles prepared from crystalline titania is read out as about 0.33 μm, which is about six times as large as the crystallite size. The hydrothermal conditions for preparing both kinds of barium titanate particles were the same, but the particle sizes were different by about six times, depending on whether the starting titania was amorphous or crystalline. The difference in the dissolution rates for amorphous and crystalline titania particles may be responsible for the difference in the final particle size. That is, amorphous titania particles dissolve more readily in water than do crystalline titania particles. Accordingly, the nucleation rate with amorphous titania as the starting material is higher than that with crystalline titania as a starting material. When the same amount of titania is put into suspension, the nuclei generated for the former case are more numerous than for the latter case. As a result, the final size for the former case is smaller than for the latter case.

The influence of the stirring speed in the autoclave was investigated. In the range of stirring speeds of 150 to 600 r.p.m, the mean size was found to be almost independent of the stirring speed. The hydrothermal synthesis hereafter was performed at a constant stirring speed of 300 r.p.m.

4.1. Preparation of barium titanate ultrafine particles from amorphous titania

Fig. 4 shows the time dependences of the mean size of barium titanate particles prepared at different temperatures ranging from 150 to 300 °C. The initial loading of amorphous titania was 0.5 kmol m^{-3}, and the BT

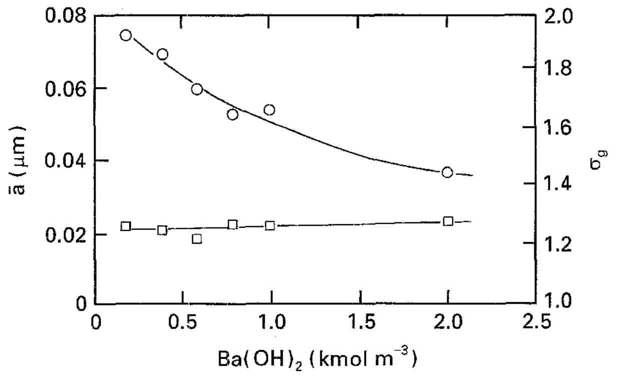

Figure 5 Relations of mean particle size and geometric standard deviation of particle size distribution to initial $Ba(OH)_2$ concentration for barium titanate prepared from amorphous titania under 300 °C, BT molar ratio of 2 and stirring speed of 300 r.p.m. for 4 h. ○ ā; □ σ_g.

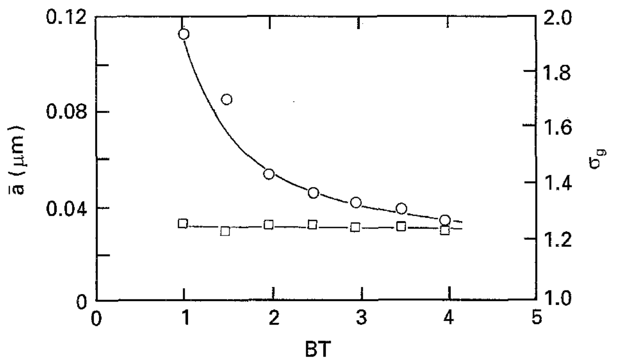

Figure 6 Relations of mean particle size and geometric standard deviation of particle size distribution to BT molar ratio for barium titanate prepared from amorphous titania under 300 °C, initial titania loading of 0.5 kmol m^{-3} and stirring speed of 300 r.p.m. for 4 h. ○ ā; □ σ_g.

molar ratio (barium to titanium molar ratio) was fixed at 2. The lower figure presents the variation of the crystallite size with treatment time. The upper figure presents the time dependences of the mean size and the geometric standard deviation of particle size distribution determined from TEM images. It should be emphasized that the mean particle size determined from TEM images approximately agrees with the crystallite size determined by powder XRD.

The intensity of the diffraction peaks which reflect the relative crystallinity increased with hydrothermal treatment temperature as would be expected. At treatment temperatures of 200, 250 and 300 °C, the particle size increases until two hours have passed, and afterwards it remains almost constant. The final size increases with rising temperature. Though in the early stage of hydrothermal treatment, nucleation and particle growth coexist, particles at longer times grow presumably via Ostwald ripening. The geometric standard deviation decreases to about 1.25 with increasing treatment time and temperature.

The influence of initial $Ba(OH)_2$ concentration on the particle size was investigated when prepared under constant temperature of 300 °C and BT molar ratio of 2 for 4 h. Fig. 5 shows the relation of initial $Ba(OH)_2$ concentration to mean particle size. It is apparent that the mean size decreases with increasing initial loading. Amorphous titania can readily dissolve into water to increase the degree of supersaturation when the initial loading of titania is increased. Accordingly, the nucleation rate or the number of nuclei generated increases with increasing titania loading. As nuclei generated in the early stage become numerous, the final particle size decreases.

The effects of BT molar ratio on the particle size was examined under constant temperature of 300 °C, titania loading of 0.5 kmol m^{-3}, and treatment time of 4 h. The relationship between mean particle size and BT molar ratio is shown in Fig. 6. The maximum mean particle size can be attained at a BT molar ratio of 1. In the range of BT molar ratios above 1, the particle size decreases with BT molar ratio. In a barium-rich environment, barium titanate formation reaction can be promoted. The dissolution of titania, which is amorphous, can readily follow the reaction, and hence the number of nuclei generated increases. As a result, smaller particles are formed as the BT molar ratio is increased.

4.2. Preparation of barium titanate fine particles from rutile titania

The variations of the particle and crystallite sizes with treatment time at various temperatures are presented in Fig. 7. The initial loading of crystalline (rutile) titania was 0.5 kmol m^{-3} and the BT molar ratio was fixed at 2. In the upper figure, the geometric standard deviation of particle size distribution was plotted against treatment time. The crystallite size amounts to about 0.045 μm, while the final particle size determined from SEM images is constant to be 0.34 μm irrespective of treatment temperature above 200 °C. At a treatment temperature of 150 °C, the final size was 0.29 μm. The final particle size was about six times as large as the crystallite size. The geometric standard deviation exhibits 1.25, a value slightly smaller than that (1.3) for the same particles prepared from amorphous titania. The diffraction strength was not varied with treatment temperature in the temperature range of 150 to 300 °C.

The influence of initial $Ba(OH)_2$ loading on the particle size was investigated at constant temperature of 300 °C, BT molar ratio of 2 and treatment time of 4 h. Fig. 8 indicates the relationship between mean particle size and initial $Ba(OH)_2$ concentration. The particle size increases with an increase in $Ba(OH)_2$ concentration. The dissolution rate for crystalline titania particles is very low in itself, and hence the dissolved amount of titania is not increased enough to increase the degree of supersaturation, even when the initial concentration of titania particles increases. Thus, the amount of dissolved titania consumed by particle growth increases and the final particle size increases.

Fig. 9 shows the effect of BT molar ratio on the particle size, where the mean sizes of particles prepared under a constant temperature of 300 °C and initial loading of 0.5 kmol m^{-3} for 4 h are plotted against BT molar ratio. The particle size has shown to

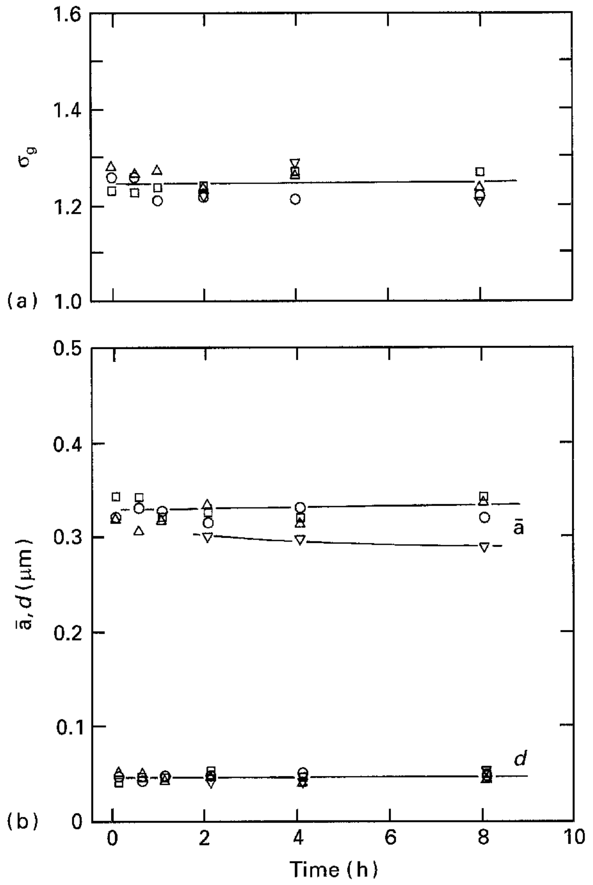

Figure 7 Time dependence of (a) geometric standard deviation of particle size distribution, (b) mean particle size and crystallite size for barium titanate prepared from rutile titania at different temperatures, initial titania loading of 0.5 kmol m^{-3}, BT molar ratio of 2 and stirring speed of 300 r.p.m. ▽ 150 °C; ○ 200 °C; △ 250 °C; □ 300 °C.

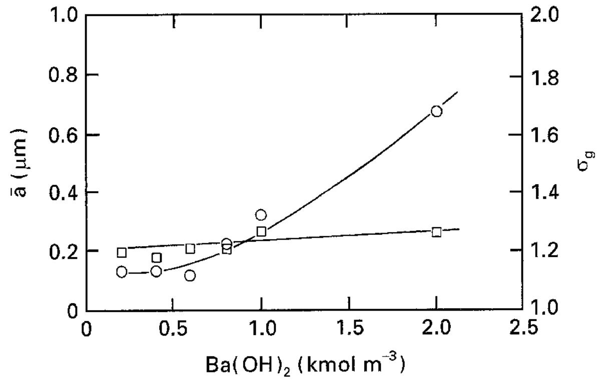

Figure 8 Relations of mean particle size and geometric standard deviation of particle size distribution to initial $Ba(OH)_2$ concentration for barium titanate prepared from rutile titania under 300 °C, BT molar ratio of 2 and stirring speed of 300 r.p.m. for 4 h. ○ ā; □ σ_g.

increase with BT molar ratio. Such a result cannot readily be understood, but may be interpreted as follows. The rate of dissolution of titania, which is crystalline, does not change greatly with increasing barium ion concentration, but the nucleus generation media may considerably be affected by the concentration of barium ion present. The number of nuclei generated in the early stage becomes different, depending on the concentration of barium ion or BT molar ratio.

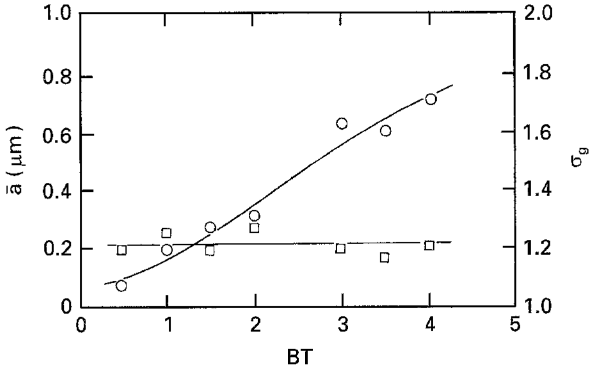

Figure 9 Relations of mean particle size and geometric standard deviation of particle size distribution to BT molar ratio for barium titanate prepared from rutile titania under 300 °C, initial titania loading of 0.5 kmol m^{-3} and stirring speed of 300 r.p.m. for 4 h. ○ ā; □ σ_g.

5. Conclusions

Barium titanate fine particles of cubic system were synthesized hydrothermally from amorphous and crystalline (rutile) titania. The following findings were yielded. The mean size of barium titanate particles prepared from amorphous titania ranges from 0.03 to 0.11 μm, depending on hydrothermal conditions. The particle size approximately agrees with the crystallite size (0.04–0.09 μm). The particle size increases with rising hydrothermal temperature and decreases with increasing $Ba(OH)_2$ concentration and BT molar ratio. On the other hand, the mean size of barium titanate particles prepared from rutile titania ranges from 0.2 to 0.7 μm. The particle size amounts to about six times as large as the crystallite size. The particle size is not much influenced by treatment temperature and time, but increases with increasing $Ba(OH)_2$ concentration and BT molar ratio. The difference of sizes of particles prepared from amorphous and crystalline titania may be ascribed to the difference of dissolution rates of both titania particles.

References

1. E. SADA, H. KUMAZAWA and H.-M. CHO, *Ind. Eng. Chem. Res.* **30** (1991) 1319.
2. H. KUMAZAWA, K. OKI, H.-M. CHO and E. SADA, *Chem. Eng. Commun.* **115** (1992) 25.
3. H. KUMAZAWA, H. OTSUKI and E. SADA, *J. Mater. Sci. Lett.* in press.
4. H. P. KLUG and L. E. ALEXANDER, "X-Ray diffraction procedures" (John Wiley and Sons, New York, 1974) p. 618.
5. W. H. HALL, *Proc. Phys. Soc.* **A62** (1949) 741.

Received 19 April 1993
and accepted 22 *March* 1995