

Preparation of barium titanate ultrafine particles from amorphous titania by a hydrothermal method and specific dielectric constants of sintered discs of the prepared particles

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Barium titanate ultrafine particles were synthesized from amorphous titania by a hydrothermal method. The mean size of the barium titanate particles prepared at a hydrothermal treatment time of 4 h, was nearly equal to $0.045\ \mu\text{m}$ in the range of barium-to-titanium molar ratio (BT) ≥ 2 , and approximately agreed well with the crystallite size. At a BT molar ratio of 1.0, the mean particle size increased to $0.2\ \mu\text{m}$, while the crystallite size remained constant at $0.045\ \mu\text{m}$. When the particle size ranged from $0.12\text{--}0.20\ \mu\text{m}$, prepared for the BT molar ratio of 1.0–1.4, the specific dielectric constant for a sintered disc composed of these particles attained a value of 5000 or more. As the BT molar ratio increased to exceed 1.5, when the mean particle size decreased from $0.13\ \mu\text{m}$ to $0.045\ \mu\text{m}$, the specific dielectric constant for the sintered disc was decreased greatly. The specific dielectric constant for the sintered disc can be correlated well with the size of the composing particles.

1. Introduction

Barium titanate (BaTiO_3), which has been employed for dielectric materials, can be produced by a hydrothermal method. In this method, an aqueous $\text{Ba}(\text{OH})_2$ solution with suspended TiO_2 fine particles is treated hydrothermally, and the extremely fine powders can be formed with high crystallinity, high purity and narrow size distribution. The dissolution–deposition scheme is met here, and hence the rate of dissolution of TiO_2 particles tends to affect the rates of nucleation and crystal growth of barium titanate. The dissolution rate of titania may greatly depend on whether titania is amorphous or crystalline. In our preceding work [1], barium titanate fine particles of the cubic system were synthesized hydrothermally from aqueous barium hydroxide solutions with suspended amorphous and crystalline (rutile) titania fine particles. The mean size of the barium titanate particles prepared from amorphous titania ranged from $0.04\text{--}0.11\ \mu\text{m}$, depending on the hydrothermal conditions. The particle size for a barium-to-titanium molar ratio above 2 approximately agreed with the crystallite size ($0.05\ \mu\text{m}$). On the other hand, the mean size of barium titanate particles prepared from rutile titania ranged from $0.2\text{--}0.7\ \mu\text{m}$, which were about one order of magnitude larger than the mean size of those prepared from amorphous titania, though the crystallite size remained constant at $\sim 0.05\ \mu\text{m}$.

In the present work, ultrafine particles of barium titanate were synthesized hydrothermally from aqueous solutions of barium hydroxide with suspended amorphous titania fine particles. The relations of the particle size to such operating conditions as barium-to-titanium (BT) molar ratio, hydrothermal temperature and reaction time were investigated systematically. Prepared ultrafine barium titanate particles were compressed into a disc, and subsequently the disc was sintered at $1300\ ^\circ\text{C}$ for 4 h. The specific dielectric constant of the sintered disc was measured, and correlated with the size of the composing particle.

2. Experimental procedure

A stainless steel autoclave (Nitto, UN-4) equipped with a paddle-type stirrer (Nitto, NS-8) was used as a reactor for hydrothermal synthesis. The autoclave, internal diameter and height 4.6 and 14.0 cm, respectively, was the same as that used in our preceding work [1, 2]. Barium titanate fine particles were produced from aqueous solutions of barium hydroxide with suspended titania fine particles. Two kinds of titania particle were used: amorphous and crystalline (rutile) titania. Amorphous titania particles were produced by controlled hydrolysis of titanium tetrathoxide in ethanol [3]. Amorphous titania particles thus prepared are spherical and mono-dispersed, with a mean size of $0.65\ \mu\text{m}$. Rutile titania particles, which

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were produced by a gas-phase method and whose mean size was 0.49 μm , were kindly supplied from Ishihara Sangyo Kaisha Ltd, Japan.

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 mounted in the autoclave. The heating rate up to the hydrothermal treatment temperature was maintained at 4 $^\circ\text{C min}^{-1}$. The temperature for the hydrothermal treatment ranged from 150–300 $^\circ\text{C}$. 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 almost independent of the stirring speed in the range 100–600 r.p.m. Thus, the stirring speed was maintained mainly at 300 r.p.m. The hydrothermal treatment was for 8 h.

The prepared fine particles were rinsed with distilled water several times and dried at 80 $^\circ\text{C}$ in a vacuum oven. Afterwards, the particles were characterized by 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 $\text{CuK}\alpha$ radiation. The crystallite size of barium titanate powders was estimated from the half-value width of the diffraction peak on the (200) face in terms of Scherrer's equation [4]. The mean particle size and the size distribution were determined from TEM and SEM images, in which the number of particles for determining the size distribution was about 300.

The dielectric characteristic of the sintered disc composed of ultrafine particles was measured, and correlated with the size of the composing particles.

3. Results and discussion

The effect of barium to titanium molar ratio (BT molar ratio or BT) on the particle size was examined under a constant temperature of 300 $^\circ\text{C}$, an amorphous titania loading of 0.5 kmol m^{-3} and a treatment time of 4 h. The relations of mean particle size and crystallite size to BT molar ratio are shown in Fig. 1. In the range of BTs above 1, the mean particle size determined from TEM images decreased with increasing BT, and in the range of BT > 2, it approached the

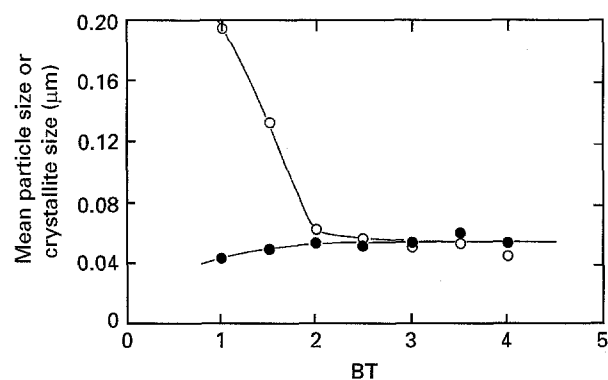


Figure 1 Dependences of BT molar ratio on (○) mean size and (●) crystallite size for barium titanate particles prepared from amorphous titania.

TABLE I Specific dielectric constants of sintered discs of barium titanate particles prepared at different BT molar ratios^a

BT	Specific dielectric constant	Mean particle size (μm)
1.0	3800	0.226
1.1	5320	0.201
1.2	5590	0.169
1.5	4600	0.0980
2.0	430	0.0622
3.0	420	0.0456
4.0	440	0.0456

^a Treatment temperature, 300 $^\circ\text{C}$; treatment time, 4 h.

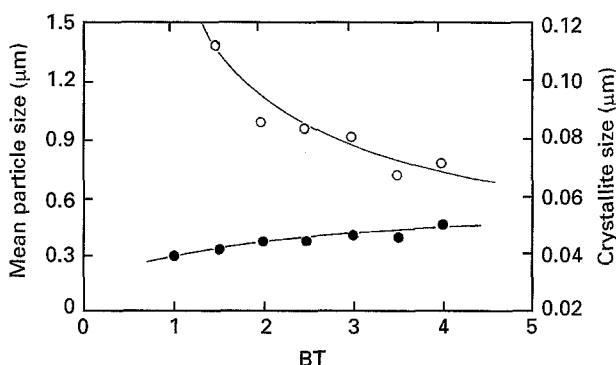


Figure 2 Dependences of BT molar ratio on (○) mean size and (●) crystallite size for barium titanate particles prepared from rutile titania.

crystallite size determined by powder XRD, which was about 0.045 μm . The dissolution of titania, which is in an amorphous state, 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 increases. The particle size can readily be controlled by the BT molar ratio. The values of the specific dielectric constants of sintered discs of barium titanate prepared at different BTs are listed in Table I. In the same table, the mean sizes of BaTiO_3 particles comprising the sintered discs are presented. For the BT molar ratios of 1.0–1.2, where the size of prepared particles ranges from 0.15–0.2 μm , the specific dielectric constant for the sintered disc composed of the prepared particles, reaches 5000 or more. As the BT molar ratio exceeds 1.5, at which the mean particle size decreases to 0.045 μm , the specific dielectric constant is greatly decreased. For the sake of comparison with the preparation of BaTiO_3 ultrafine particles from amorphous TiO_2 , the mean particle size and the crystallite size of BaTiO_3 particles prepared from rutile TiO_2 are shown as a function of BT molar ratio in Fig. 2. The crystallite size here is estimated to be 0.045 μm , and approximately agrees with that in the case of preparation from amorphous TiO_2 . The mean particle size has been shown to decrease with BT molar ratio. Even at a BT molar ratio of 4, the mean particle size is only decreased to 0.7 μm , which is larger by an order of magnitude than the crystallite size. High dielectric constant materials are seemingly realized, when the size of composing powders lies in the range of 0.15–0.20 μm . It is difficult to produce BaTiO_3

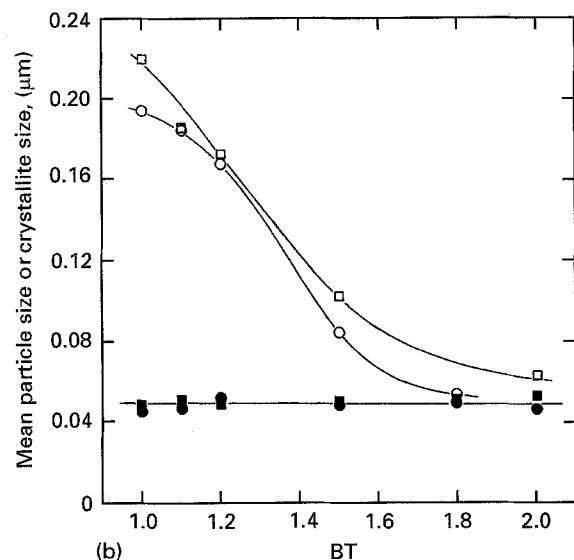
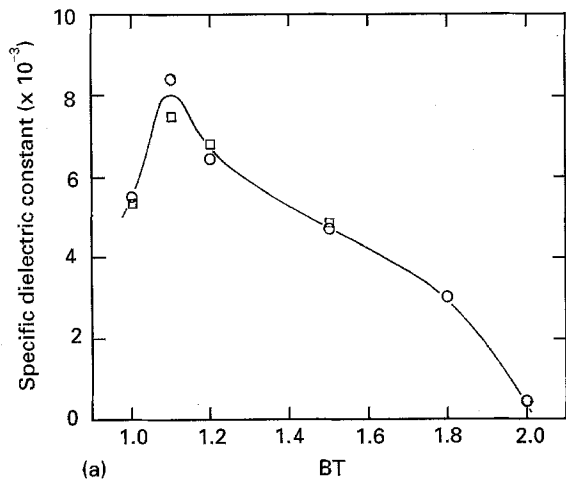


Figure 3 Dependences of (a) (○, □) specific dielectric constant and (b) (○, □) mean particle size and (●, ■) crystallite size on BT molar ratio when prepared from amorphous titania at (○, ●) 200 and (□, ■) 250 °C.

particles of such sizes, when rutile TiO_2 is employed as a starting material.

Fig. 3 shows the dependences of the mean particle size and specific dielectric constant on BT molar ratio, when the BaTiO_3 particles were prepared from amorphous TiO_2 particles for 4 h at 200 and 250 °C. The crystallite size also remains constant at $\sim 0.045 \mu\text{m}$. The particle size decreases with increasing BT molar ratio, and approaches the crystallite size. The specific dielectric constant for the sintered disc attains a maximum value of 8400 at $\text{BT} = 1.1$, and subsequently decreases with increasing BT. In the range of BTs of 1.0–1.4, the dielectric constant attains a value above 5000.

Fig. 4 shows the relations of mean size and crystallite size for BaTiO_3 particles prepared from amorphous TiO_2 and specific dielectric constants of sintered discs composed of the prepared particles to the treatment time, where the treatment temperature is fixed at 300 °C, the initial loading of titania is 0.5 kmol m^{-3} , and the BT molar ratio is fixed at 1.0. It has been found that the high specific dielectric constant can be realized, when the composing particles prepared at $\text{BT} = 1.0$ are employed. Table II, gives the specific dielectric constants of sintered discs of barium titanate

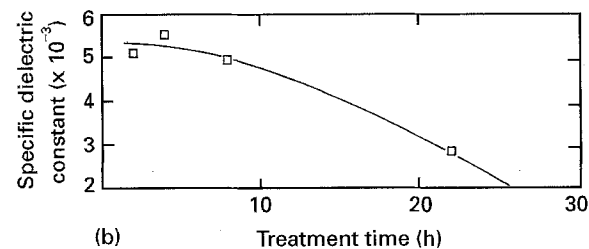
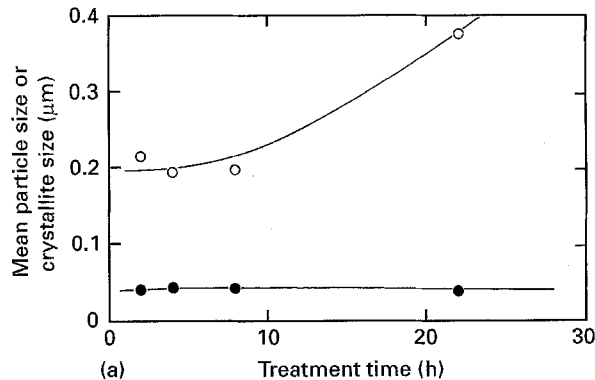


Figure 4 Time dependences of (a) (○) mean size and (●) crystallite size for barium titanate particles prepared from amorphous titania at 300 °C, and (b) specific dielectric constants of sintered discs composed of the prepared particles.

TABLE II Specific dielectric constants of sintered discs of barium titanate particles prepared at different hydrothermal treatment times^a

Time (h)	Specific dielectric constant	Mean particle size (μm)
2	5080	0.215
4	5520	0.194
8	4940	0.198
22	2920	0.376

^a BT, 1.0; treatment temperature, 300 °C.

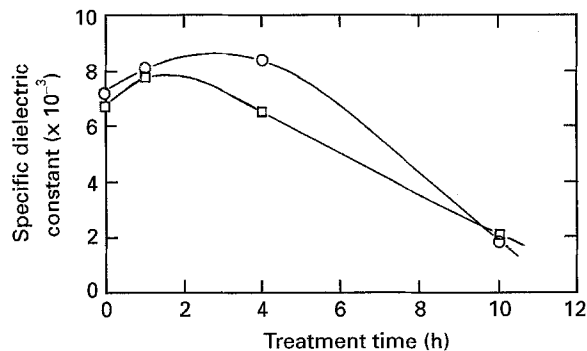


Figure 5 Relationship between specific dielectric constant of a sintered disc of barium titanate particles and treatment time during hydrothermal synthesis of the particles at 200 °C for 4 h. BT: (○) 1.1, (□) 1.2.

particles prepared at different hydrothermal treatment times. The mean particle size is approximately kept constant at $0.20 \mu\text{m}$, when the hydrothermal treatment time is less than 4 h. At a treatment time of 22 h, the mean particle size increased up to $0.376 \mu\text{m}$. The specific dielectric constant of the sintered disc composed of BaTiO_3 particles of $0.376 \mu\text{m}$ in size

TABLE III Specific dielectric constants of sintered discs of barium titanate particles prepared at different treatment temperatures^a

Temperature (°C)	Specific dielectric constant	Mean particle size (μm)
150	4730	—
200	8400	0.168
250	7500	0.185
300	5320	0.201

^a BT, 1.1; treatment time, 4 h.

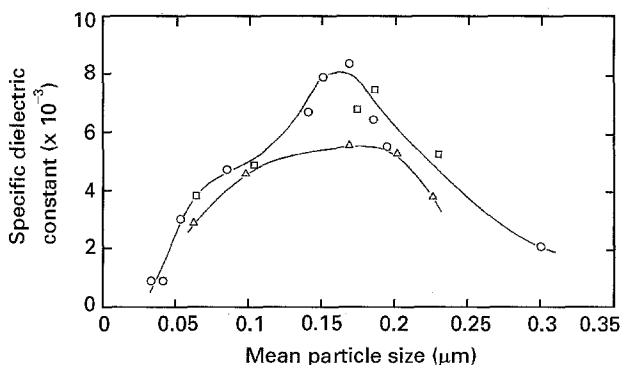


Figure 6 Relationship between specific dielectric constant of sintered discs of barium titanate particles and the mean size of the composing particles, at (○) 200 °C, (□) 250 °C, (▲) 300 °C.

decreased to 2920. Fig. 5 shows the relations with treatment time of specific dielectric constants for the sintered discs of BaTiO₃ particles prepared under a treatment time of 4 h and BT molar ratios of 1.1 and 1.2. The particle grows with treating time, resulting in a decrease in the specific dielectric constant.

Next, BaTiO₃ powders were prepared at different treatment temperatures, when the treatment time was fixed at 4 h. In Table III the specific dielectric constants are listed for the sintered discs of prepared BaTiO₃ particles. The specific dielectric constant attained a maximum value of 8400 for BaTiO₃ particles prepared at 200 °C. At this point the mean size of composing particles was 0.168 μm.

In summary, the correlation of the specific dielectric constant with the particle sizes composing the disc is shown in Fig. 6. It is found from the correlation at 200

and 250 °C that the specific dielectric constant attains a value larger than 5000 in the range of the particle size of 0.10–0.22 μm. The value of the dielectric constant reaches ~ 8400, when the particle size is 0.168 μm. From the correlation at 300 °C, the specific dielectric constant exceeds 5000 for the particle sizes ranging from 0.11–0.20 μm.

4. Conclusion

Barium titanate ultrafine particles were synthesized hydrothermally from amorphous titania. The mean size of the barium titanate particles prepared at a treatment time of 4 h, was nearly equal to 0.045 μm in the range of barium-to-titanium molar ratio (BT) ≥ 2, and agreed reasonably well with the crystallite size. At a BT molar ratio of 1.0, the mean particle size increased to 0.2 μm, whereas the crystallite size remained constant at 0.045 μm. When the particle size ranged from 0.12–0.20 μm, prepared for the BT molar ratio of 1.0–1.4, the specific dielectric constant for the sintered disc composed of the particles reached 5000 or more. As the BT molar ratio increased above 1.5, when the mean particle size decreased from 0.13 μm to 0.045 μm, the specific dielectric constant for the sintered disc was decreased greatly. The specific dielectric constant for the sintered disc attained a maximum value of 8400, when the sintered disc was composed of BaTiO₃ particles prepared under a BT molar ratio of 1.1, treatment temperature of 200 °C and treatment time of 4 h. The specific dielectric constant for the sintered disc correlated well with the size of the composing particles.

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