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Hydrothermal synthesis of ferroelectric barium and strontium titanate extremely fine particles

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$BaTiO_3$, $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$ fine particles were synthesized from amorphous TiO_2 fine particles by a hydrothermal method. The relationship between the specific dielectric constant of the sintered disk and the mean size of composing particles has been investigated. The specific dielectric constants of the sintered disks of $BaTiO_3$ and $SrTiO_3$ particles attain values exceeding 6000 in the range of the particle size of 0.10–0.17 μm. The specific dielectric constant for the sintered disk of $(Ba_{1-x}Sr_x)TiO_3$ particles synthesized at various atomic fractions of Sr (x) attains maximum values at both atomic fractions of 0.08 and 0.95. It has been suggested that the size of particles composing the disk should considerably affect the specific dielectric constant of the sintered disk. © *2000 Kluwer Academic Publishers*

1. Introduction

$BaTiO_3$ and $SrTiO_3$ ultrafine particles with perovskite structure and their compounds are desired in electronics industry applications; multilayer capacitor, ferroelectric memories, surface acoustic wave devices and so on [1]. Various chemical methods have been employed for the production of such fine particles, i.e., coprecipitation [2, 3], alkoxide hydrolysis [4, 5], sol-gel method [6], metallo-organic processing [7] and hydrothermal treatment [8, 9]. Among these, the hydrothermal method seems to be very promising due to the ability to control chemical homogeneity, purity, morphology, shape and phase composition of the powders [10, 11]. This method is, therefore, especially attractive for synthesis of both single- and multi-component powders.

In our preceding work [9], $BaTiO_3$ fine particles of cubic system were synthesized by the hydrothermal treatment of aqueous $Ba(OH)_2$ solutions with suspended amorphous and crystalline (rutile) TiO_2 fine particles. The mean size of $BaTiO_3$ particles prepared from amorphous TiO_2 ranged from 0.04 to 0.11 μm, depending on the hydrothermal treatment condition. The particle size increases with rising hydrothermal temperature and decreases with increasing $Ba(OH)_2$ concentration and barium-to-titanium (BT) atomic ratio. The particle size for BT atomic ratio above 2 approximately agreed with the crystallite size (0.05 μm). On the other hand, the mean size of $BaTiO_3$ particles prepared from rutile TiO_2 ranged from 0.2 to 0.7 μm, though the crystallite size remained constant at ca. 0.05 μm. Such a difference in the particle size was supposed to be caused by the difference in the dissolution rate of TiO_2, because the dissolution rate may greatly depend on whether TiO_2 is amorphous or crystalline. That is, amorphous titania particles dissolve more readily in water than crystallite titania ones. 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 one. Consequently, the final size for the former case is smaller than for the latter one. In the other work [12], when the size of the particles prepared from amorphous TiO_2, ranged from 0.12 to 0.20 μm, the specific dielectric constant of the sintered disk composed of the particles reached 5000 or more (max. 8400). The specific dielectric constant of the sintered disk was found to be correlated well with the size of the composing particles. But the range of the hydrothermal treatment condition where the correlation was met, was not clarified, and besides the reproducibility and reliability of the correlation could not be checked completely.

In the present work, furthermore, extremely fine particles of $BaTiO_3$, $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$ were synthesized by taking the reproducibility into account. The relations of the particle size to such operating conditions as barium-to-titanium (BT) or strontium-to-titanium (ST) atomic ratio, hydrothermal treatment temperature and time, were investigated systematically.

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Prepared titanate particles were compressed into a disk and subsequently the disk was sintered at temperatures ranging from 800 to 1300 °C for 0.5 h to measure the specific dielectric constant. The effect of the sintering temperature on the dielectric constant was investigated, and an optimum sintering temperature was searched for. The specific dielectric constant of the sintered disk was correlated well with the size of the composing particles.

2. Experimental section

2.1. Materials

Titaniumtetraethoxide, $Ti(OC_2H_5)_4$ (Soekawa Chem. Co., Ltd, Japan, Research grade), barium hydroxide, $Ba(OH)_2{\cdot}H_2O$ (Wako Pure Chem. Ind., Ltd, Japan, Research grade, Purity $>$ 98%) and $Sr(OH)_2{\cdot}H_2O$ (Wako Pure Chem. Ind., Ltd, Japan, Research grade) were used as starting materials. Most impurities in $Ba(OH)_2{\cdot}8H_2O$ are $BaCO_3$. The purity of cation Ba^{2+} is much higher than 98%, and is believed to approach 100%. Amorphous TiO_2 particles were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol. Amorphous TiO_2 particles prepared thus are spherical and monodisperse. The mean size was 0.65 μm. Barium and strontium titanate fine particles were synthesized hydrothermally from aqueous solutions of barium and strontium hydroxide with suspended amorphous TiO_2 fine particles.

2.2. Experimental equipment and procedures

A stainless steel autoclave (Nitto, UN-4) equipped with a paddle-type stirrer (Nitto, NS-8) was as a reactor for hydrothermal synthesis. The autoclave whose internal diameter and height are 4.6 and 14.0 cm, respectively, is the same one as in our preceding work [9]. Barium and strontium titanate fine particles here were produced from aqueous solutions of barium and strontium hydroxide with suspended amorphous titania fine particles.

First, an aqueous solution of barium and strontium hydroxide with a prescribed concentration was prepared, and subsequently a prescribed amount of amorphous titania particles was added to the solution. A 50 cm^3 portion of the resultant slurry 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 °C/min. The temperature for the hydrothermal treatment ranged from 150 to 300 °C. The size of prepared particles had previously been found to be almost independent of the stirring speed in the range 100–600 rpm. Thus, the stirring speed was maintained mainly at 300 rpm. Prepared fine particles were rinsed with distilled water several times, dried in a vacuum oven overnight at 80 °C, and used as samples.

2.3. Instrumental analyses

The crystal structure of the particles was investigated by the X-ray diffraction (XRD) method using CuK_α radiation. H_2O and OH^- in the particles were measured using FT-IR (Shimadzu FTIR-8501) and by a differential thermal analysis with thermogravimetry (DT-TGA: SDT-2960). For the FT-IR measurement, we prepared pellets of the samples by diluting the particles with KBr powder to 1 mass% and drying them at 100 °C in a vacuum oven overnight. Their FT-IR spectra were measured in dry air at room temperature. The mean particle size and the size distribution were determined from particle analyzer (Malvern 3600), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), wherein the number of particles for determining the size distribution was about 300. Chemical purity of the powders was determined by energy-dispersive spectroscopy (EDS: Link-10-85S).

A 2 g powder sample without added any binders was pressed into a disk of 20 mm diameter and 1 mm height under 4 ton/cm^2. The sintering temperature of pressed disks ranged from 800 to 1400 °C with $BaTiO_3$, and from 800 to 1300 °C with $SrTiO_3$ and (Ba, Si)TiO_3. The duration for which a disk was maintained at a sintering temperature, was 30 min. The heating rates were 100 °C/h up to 600 °C and afterwards 233 °C/h from 600 °C to the sintering temperature, whereas the cooling rate was maintained at 167 °C/h.

The specific dielectric constant of the sintered disk was determined from the capacitance which was measured at 1 kHz while sweeping through a volatage level (1.0 V) to obtain the capacitance-voltage characteristics using Precision LCR Meter (Yokogawa-Hewlette-Packard, 4284A). The electrodes of Al-thin film with a diameter of 2 mm were sputtered onto both sides of the disk. The measurement was made in a constant temperature room of 25 °C.

3. Experimental results and discussion

The X-ray diffraction (XRD) patterns of barium and strontium titanate fine particles prepared hydrothermally from amorphous titania are shown in Fig. 1. From XRD measurements, the barium titanate particle is

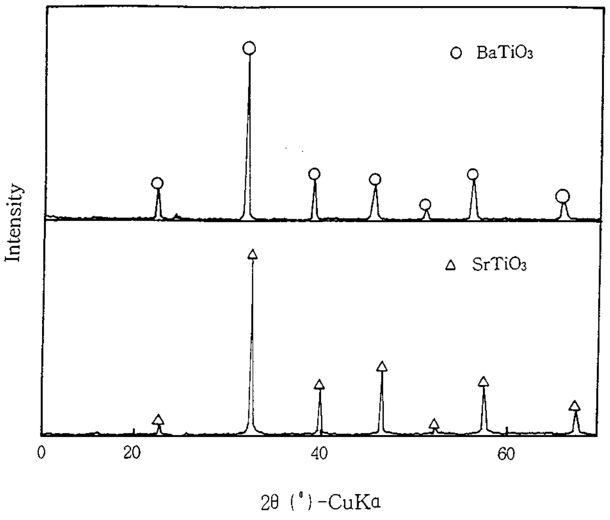
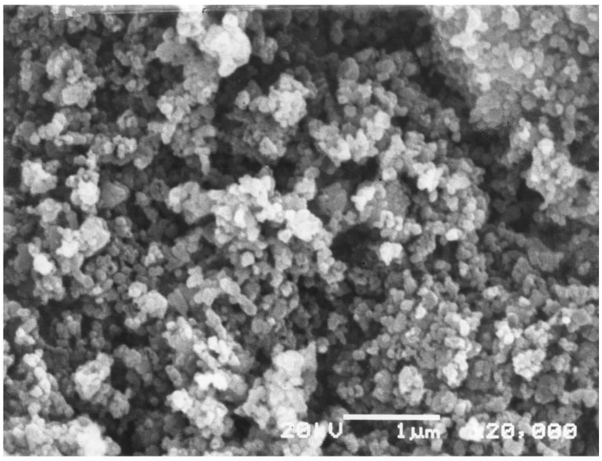


Figure 1 X-ray diffraction patterns of barium and strontium titanate fine particles prepared from amorphous titania with BT and ST ratios of 1.2 and 0.5, respectively, by hydrothermal treatment at 225 °C for 3 h.

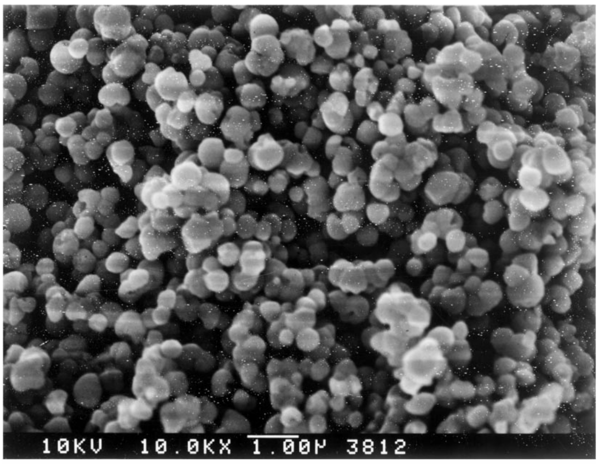
exhibited to be cubic system, because the (200) diffraction peak is not split. With strontium titanate particles, there appears no difference with respect to barium titanate particles exepting a shift of Bragg angle. This shifting is considered to be caused by the difference in ionic radii of Ba^{2+} and Sr^{2+}. EDS analysis of barium and strontium titanate particles prepared at 225 °C is summerized in Table I, which reveals only barium, strontium and titanium peaks. The molar ratios of BaO and SrO to TiO_2 are estimated to be 1.05 and 0.96, respectively. SEM micrographs of $BaTiO_3$ and $SrTiO_3$ particles prepared at 225 °C are presented in Fig. 2. Both particles are found to be of round shape and some are agglomerated. Fig. 3 indicates the FT-IR spectra of $BaTiO_3$ and $SrTiO_3$ particles prepared from amorphous TiO_2 at 225 °C for 3 h with barium-to-titanium (BT) and strontium-to-titanium (ST) atomic ratios of 1.2 and 0.5, respectively. A broad absorption band in the range of 2700 to 3600 cm^{-1} suggests the presence of considerable amounts of H_2O and OH^- in the particle. In particular, the sharp absorption band observed at ca. 550 cm^{-1} was ascribed to the bonding vibration of an O_6 octahedron deformation mode, which was assigned by Slater [13] and confirmed by Spitzer *et al.* [14]. The amounts of H_2O and OH^- included in the particles increased with increasing BT and ST atomic ratios. Thus, the amount of water included in the particle was measured by thermogravimetric analysis (TGA) experiments, and typical examples of measured TGA curves were presented in Fig. 4.

TABLE I Chemical analysis of $BaTiO_3$ and $SrTiO_3$

Composition (%)		Mole ratio of BaO/TiO_2	Composition (%)		Mole ratio of SrO/TiO_2
BaO	TiO_2		SrO	TiO_2	
66.82	33.18	1.05	55.38	44.62	0.96



(a) $BaTiO_3$



(b) $SrTiO_3$

Figure 2 Scanning electron micrographs of barium and strontium titanate fine particles prepared from amorphous titania with BT and ST ratios of 1.2 and 0.5, respectively, by hydrothermal treatment at 225 °C for 3 h.

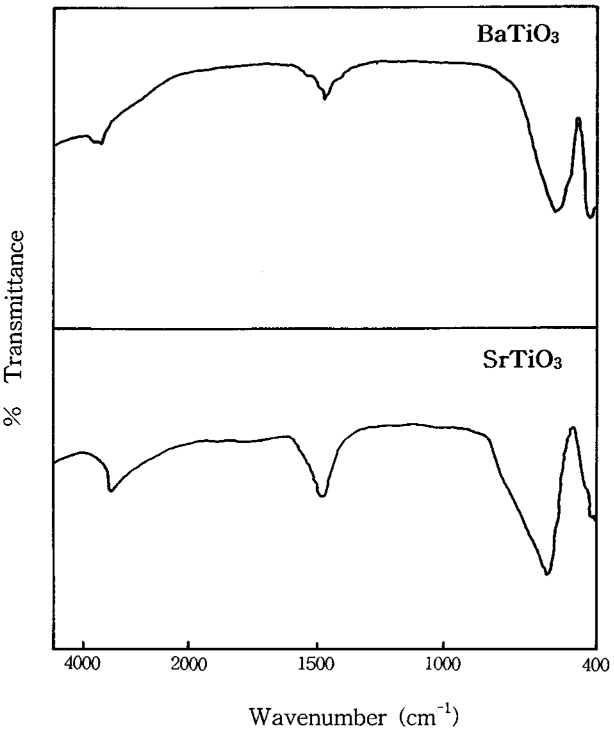


Figure 3 FT-IR spectra of barium and strontium titanate fine particles prepared from amorphous titania with BT and ST ratios of 1.2 and 0.5, respectively, by hydrothermal treatment at 225 °C for 3 h.

The relations of specific dielectric constants of sintered disks composed of $BaTiO_3$ and $SrTiO_3$ particles to the treatment time are shown in Fig. 5, where the treatment temperature is fixed at 225 °C. The value of tan δ of sintered disk ranged from 0.8 to 2.2%, while the specific dielectric constant lay in 3000 to 8000. In every run, the particles tend to grow progressively with treatment time. The particle growth with the treatment time has been observed for hydrothermal preparation of $BaTiO_3$ from amorphous TiO_2, while the crystallite size remains constant at 0.045 μm [9, 12]. Fig. 5 shows that the specific dielectric constants for $BaTiO_3$ and $SrTiO_3$ increase with treatment time until 4 and 3 h have passed, respectively, and afterwards they decrease with the time. The maximum values of specific dielectric constant for $BaTiO_3$ and $SrTiO_3$ formed at 4 and 3 h, respectively, amount to 8030 and 7130. The particles grow with treatment time, so the specific dielectric constant tends to attain a maximum value at a certain size of composing particles. Fig. 6 indicates the values of specific dielectric constants for sintered disks of $BaTiO_3$

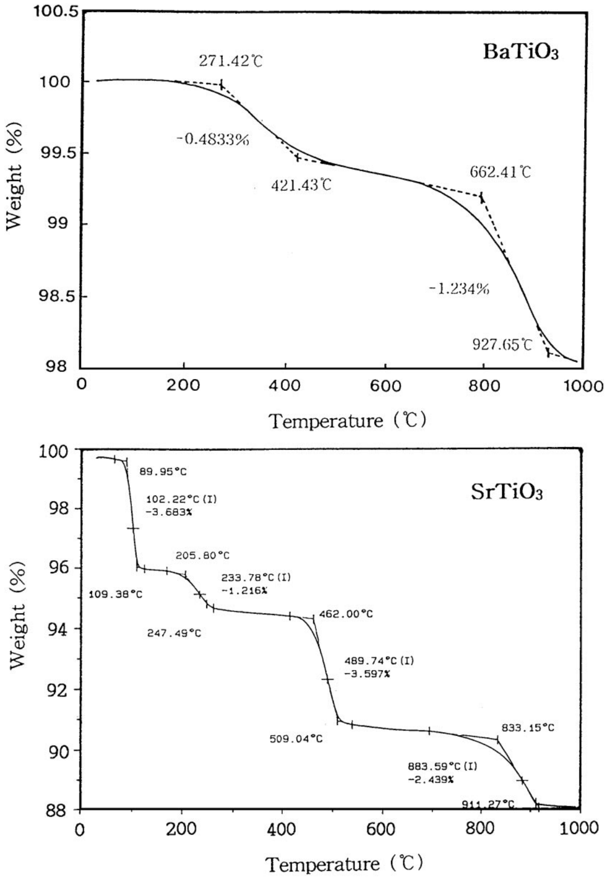


Figure 4 TGA curves of barium and strontium titanate fine particles prepared from amorphous titania with BT and ST ratios of 1.2 and 0.5, respectively, by hydrothermal treatment at 225 °C for 3 h.

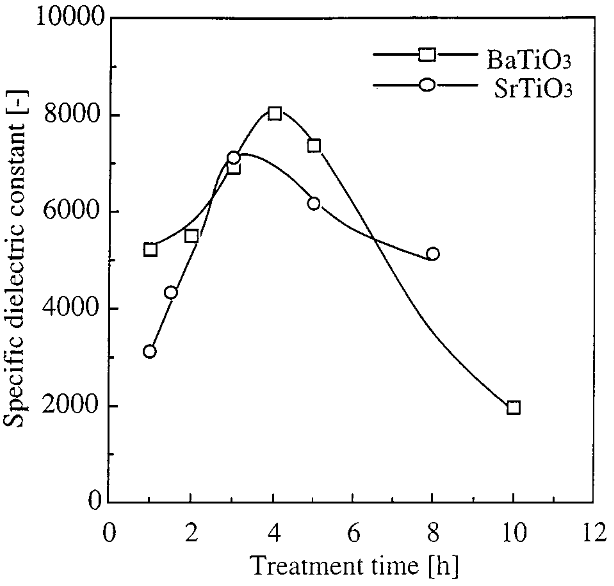


Figure 5 Specific dielectric constants of sintered disks of barium and strontium titanate fine particles prepared at 225 °C and different treatment times. (□) BT = 1.2; (○) ST = 1.0.

and $SrTiO_3$ particles prepared at different temperatures. It has been found that the particles grow progressively with rising treatment temperature [9]. Hence, this figure also suggests that the specific dielectric constant should tend to realize large values within a range of composing particle sizes. Fig. 7 shows the dependencies of the specific dielectric constants on BT and ST atomic ratios for preparations of $BaTiO_3$ and $SrTiO_3$ particles. With $BaTiO_3$, the particle size has been shown to decrease monotonically with increasing BT atomic ratio and to approach the crystallite size, which is independent of the atomic ratio and is ca. 0.045 μm [12]. The maximum values of the specific dielectric constant may be realized at certain sizes of composing particles.

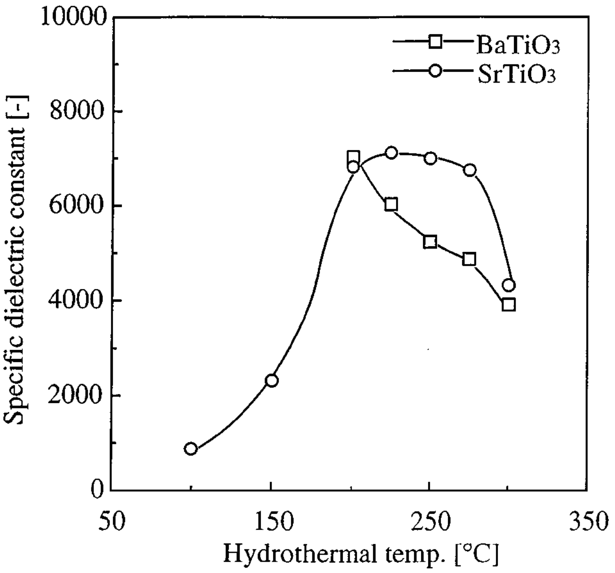


Figure 6 Specific dielectric constants of sintered disks of barium and strontium titanate fine particles prepared at different treatment temperatures. (□) BT = 1.0, Treatment time = 4 h, Sintering temp. = 1300 °C; (○) ST = 1.0, Treatment time = 3 h, Sintering temp. = 1200 °C.

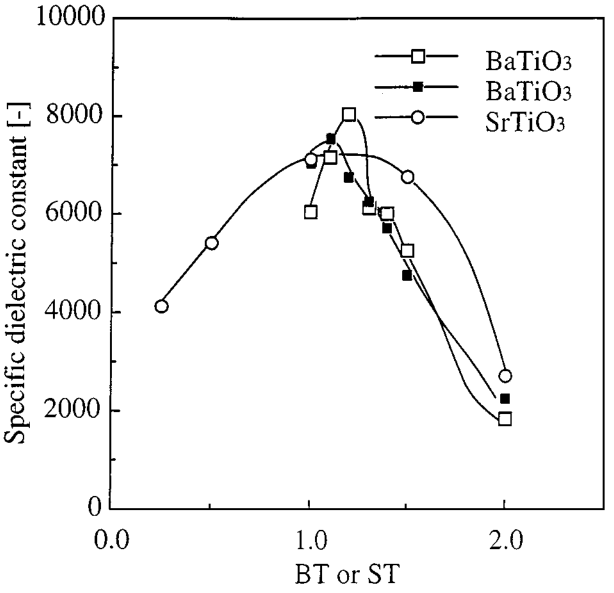


Figure 7 Dependencies of specific dielectric constant on BT and ST atomic ratios at preparation temperatures of (■) 200 °C and (□, ○) 225 °C.

Fig. 8 shows the values of specific dielectric constant for $(Ba_{1-x}Sr_x)TiO_3$ prepared at various atomic fractions of Sr (x). Both $BaTiO_3$ and $SrTiO_3$ particles are shown to exhibit respective high specific dielectric constants, but the specific dielectric constant attains maximum values at both the atomic fractions of 0.08 and 0.95. Fig. 9 exhibits XRD patterns of (Ba, Sr)TiO_3 fine particles prepared at 225 °C for 3 h with various Sr to Ba atomic ratios. As this atomic ratio was varied

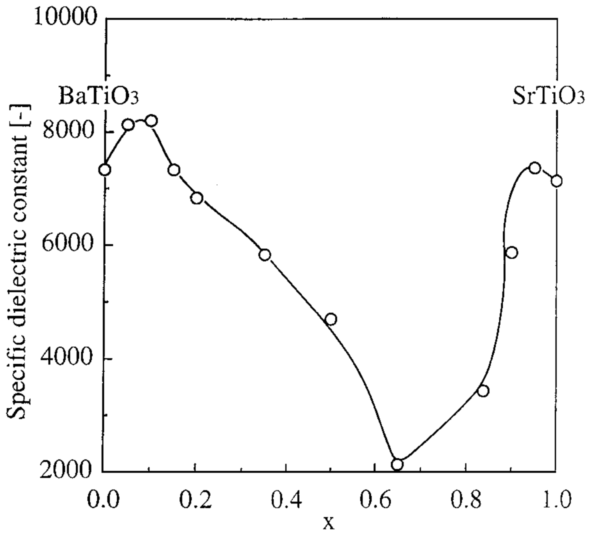


Figure 8 Dependence of specific dielectric constant on x for $Ba_{1-x}Sr_xTiO_3$.

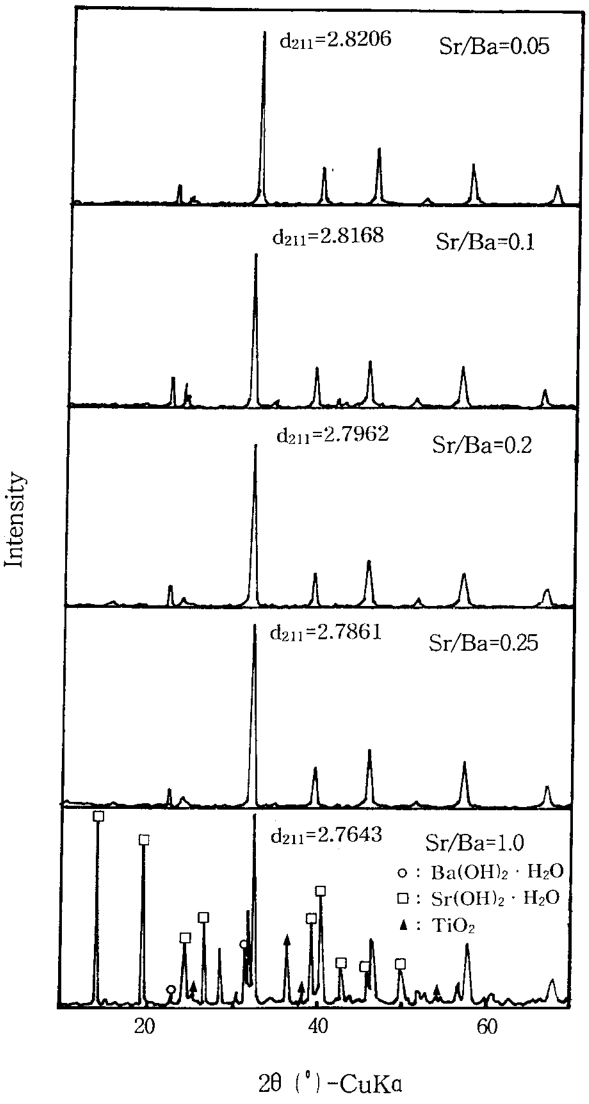


Figure 9 X-ray diffraction patterns of (Ba, Sr)TiO_3 fine particles prepared at 225 °C for 3 h under various Sr to Ba atomic ratios.

from 0.05 to 0.25, there appeared no difference in XRD patterns excepting a shift of 2θ. Also peaks for barium and strontium hydroxide were observed in case of Sr/Ba atomic ratio of 1.0.

Thus far, the disks of $BaTiO_3$, $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$ particles were sintered at 1300 and 1200 °C, respectively. The effect of sintering temperature for disks of $BaTiO_3$, $SrTiO_3$ and $(Ba_{0.95}Sr_{0.05})TiO_3$ particles on the specific dielectric constant was investigated. Fig. 10 shows the dependence of the specific dielectric constant on the sintering temperature for the three composing particles. It is shown to be desirable that the sintering temperature for $BaTiO_3$ disk is 1300 °C, whereas that for $SrTiO_3$ and $(Ba_{0.95}Sr_{0.05})$ TiO_3 disks is 1200 °C.

It has been suggested that the particle size should depend on the operational conditions such as BT (or ST) atomic ratio, hydrothermal treatment temperature and time, and besides the particle size composing the disk should considerably affect the value of specific dielectric constant. That is, it has been shown that the particle size increases with increasing treatment temperature

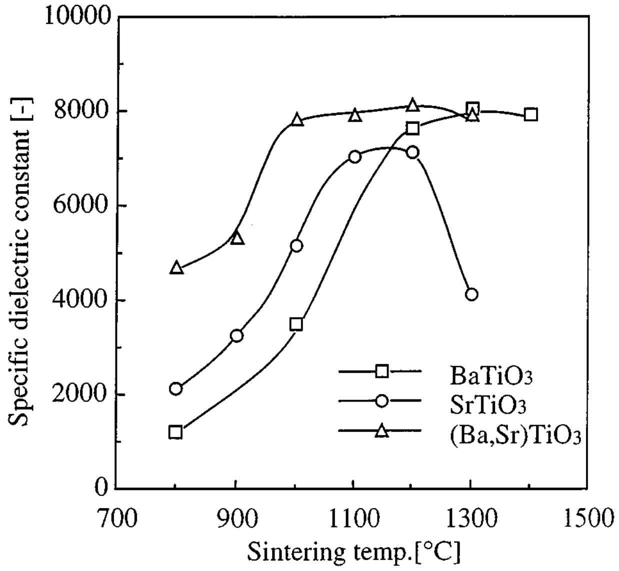


Figure 10 Dependence on sintering temperature of specific dielectric constants of sintered disks of $BaTiO_3$, $SrTiO_3$ and $Ba_{0.95}Sr_{0.05}TiO_3$.

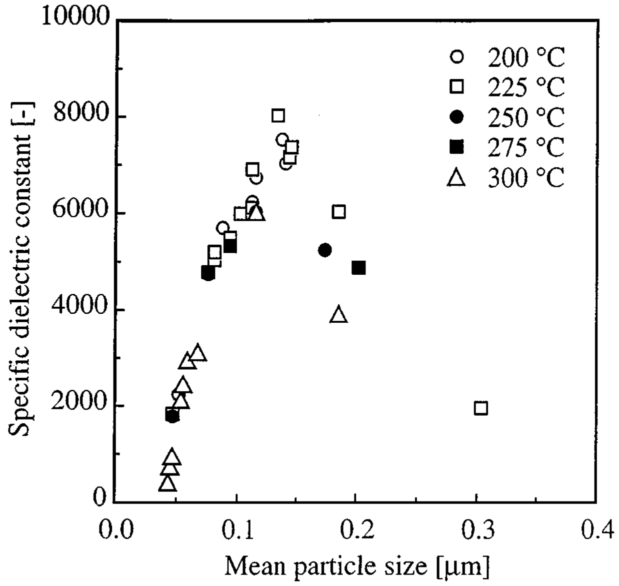


Figure 11 Relationship between specific dielectric constant of sintered disks of barium titanate particles and mean size of composing particles.

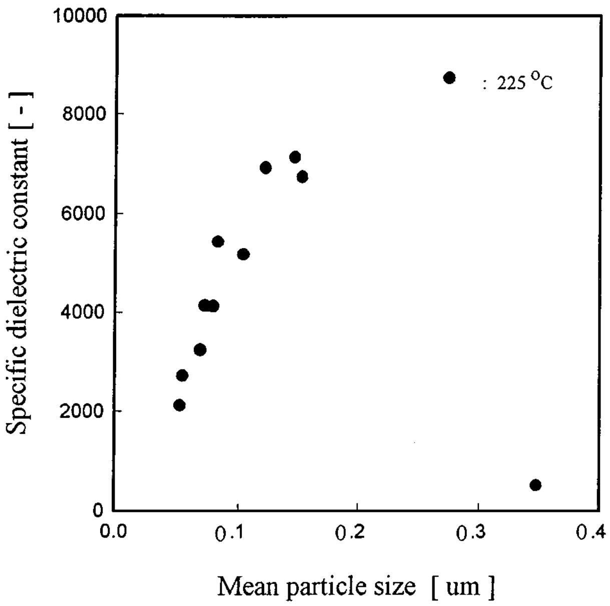


Figure 12 Relationship between specific dielectric constant of sintered disks of strontium titanate particles and mean size of composing particles prepared at 225 °C.

and time, whereas it decreases with BT or ST atomic ratio. In Fig. 11, the correlation of the specific dielectric constant with the mean size of composing particles was plotted in case of $BaTiO_3$. Fig. 12 shows similar correlations for $SrTiO_3$ prepared at 225 °C. It is apparent from both figures that the specific dielectric constant actually realizes values larger than 6000 in the range of composing particle sizes of 0.10–0.17 μm.

4. Conclusion

$BaTiO_3$, $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$ fine particles were synthesized hydrothermally from amorphous TiO_2 fine particles in aqueous barium and strontium hydroxide solutions. Especially, the relation of the specific dielectric constant of sintered disk to composing particle size has been investigated. The following findings were yielded.

(1) With $BaTiO_3$, the specific dielectric constant realized large values above 6000, for composing particles ranging from 0.10 to 0.17 μm in size.

(2) The specific dielectric constant attained a maximum value of 8400 and 7400 for $BaTiO_3$ and $SrTiO_3$, respectively.

(3) The specific dielectric constants of sintered disks of $BaTiO_3$, and $SrTiO_3$ particles could be correlated well with the sizes of composing particles.

(4) With $(Ba_{1-x}Sr_x)TiO_3$, the specific dielectric constant attained maximum values at both atomic fractions (x) of 0.08 and 0.95.

(5) The optimum sintering temperature for $BaTiO_3$ disk was 1300 °C, whereas those for $SrTiO_3$ and $(Ba_{0.95}Sr_{0.05})TiO_3$ disks were 1200 °C.

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