JOURNAL OF MATERIALS SCIENCE 21 (1986) 757–762

Preparation of rod-shaped $BaTiO_3$ powder

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Rod-shaped $BaTiO_3$ powder particles have been prepared from rod-shaped $TiO_2 \cdot nH_2O$ and $BaCO_3$ in molten chloride. The morphology of $BaTiO_3$ particles was studied referring to the effects of the chemical species of the starting titanium compound, amount of chloride, particle size of the titanium compound and reaction conditions, and the preparation condition of rod-shaped $BaTiO_3$ has been determined: i.e., large $TiO_2 \cdot nH_2O$ particles were heated at 700° C in molten salt with an equal amount of $BaTiO_3$. This condition was effective in suppressing the formation of $BaTiO_3$ by a solution–precipitation process as well as the deformation of either $TiO_2 \cdot nH_2O$ or $BaTiO_3$, which are responsible for the formation of equiaxed $BaTiO_3$ particles. The obtained rod-shaped $BaTiO_3$ particles had a cubic symmetry. Electron diffraction analysis showed that the following topotactic relation is retained;

$$\langle 0\,1\,0\rangle_{\text{potassium tetratitanate}} \parallel \langle 0\,1\,0\rangle_{\text{hydrated titania}} \parallel \langle 1\,0\,0\rangle_{\text{anatase}} \parallel \langle 1\,0\,0\rangle_{\text{barium titanate}}$$

1. Introduction

Recent trends of ceramic powder preparation are toward either the preparation of ultrafine particles or the control of particle shape and agglomeration state [1, 2]. The particle shape is mainly determined by the formation process. As the conventional method by solid state reaction hardly controls the particle shape, novel techniques have been developed in which powders are prepared from a liquid or gas phase and nucleation and growth rates are controlled to develop a specific particle shape [3, 4]. These methods have been applied to simple oxides and a variety of powders with characteristic particle shapes have been prepared. Direct preparation of complex oxides is rather difficult and they are prepared via other compounds such as hydroxides and oxalates [5]. Conversion of these compounds into oxides by thermal decomposition causes agglomeration, the degree and strength of which depend on the precursor compound and decomposition condition.

One of the simple preparation methods of complex oxides is molten salt-synthesis, in which molten salts are used as solvent [6]. In this method, the control of the nucleation rate is rather difficult, because complex oxide particles are formed in the presence of solid reactant particles and the product nucleates usually on the reactant particles. Growth rate, on the other hand, can be controlled by selecting preparation conditions, such as salt species, heating temperature and duration. Beacuse of the highly anisotropic nature of growth in molten salt, particle growth in molten salt tends to have a characteristic shape reflecting crystal symmetry [7]. Oxides with high symmetry such as cubic ferrites tend to be equiaxed, i.e. octahedron in the ferrite case. However, close examination of reaction mechanisms has enabled us to prepare plate-like ferrite particles [8].

This paper deals with the preparation of rod-shaped $BaTiO_3$ particles. Rod-shaped TiO_2 particles were heated with $BaCO_3$ in a NaCl–KCl mixed salt. The effects of various titanium starting sources and reaction conditions on the $BaTiO_3$ particle shape have been studied, and the mechanism of $BaTiO_3$ formation was discussed.

2. Experimental procedure

Rod-shaped TiO_2 was prepared from rod-shaped $K_2Ti_4O_9$. Mixtures of K_2CO_3, TiO_2 and K_2MoO_4* in a molar ratio of 6:24:70 were heated at 1000° C for 18 h [9], and then washed with hot water several times to remove K_2MoO_4. The main product was $K_2Ti_4O_9$ with a small amount of $K_2Ti_6O_{13}$ detected by X-ray diffraction analysis. The product was refluxed in boiling 1N HCl solution for 2 h to extract K_2O. The resultant phase was $TiO_2 \cdot nH_2O$, which changes to anatase and rutile on heating for 1 h at 700° C and 1000° C, respectively [10]. Weight loss of $TiO_2 \cdot nH_2O$ by a constant rate heating of 10° C min^{-1} occurred between 100 and 500° C and was 7.6 wt % at 700° C, indicating that n is 0.38. Fig. 1 shows SEM photographs of $K_2Ti_4O_9$, $TiO_2 \cdot nH_2O$ and products obtained by heating $TiO_2 \cdot nH_2O$ at 700 and 1000° C for 1 h. $K_2Ti_4O_9$ consisted of rod-shaped particles and this shape was preserved during the conversion to anatase. The transformation to rutile, however, changed the particle shape to spheroid.

Potassium tetratitanate, $TiO_2 \cdot nH_2O$ or anatase, which was obtained by heating $TiO_2 \cdot nH_2O$ at 700° C for 1 h, was wet-mixed with a stoichiometric quantity of $BaCO_3$ using a blender. The mixture was admixed with chloride flux (50 NaCl–50 KCl, m.p.: 650° C) and heated in a furnace kept at a desired temperature. The amount of the chloride mixture (designated by W) is defined by the weight ratio of the chloride to $BaTiO_3$.

*K_2MoO_4 acts as a molten solvent to produce rod-shaped $K_2Ti_4O_9$.

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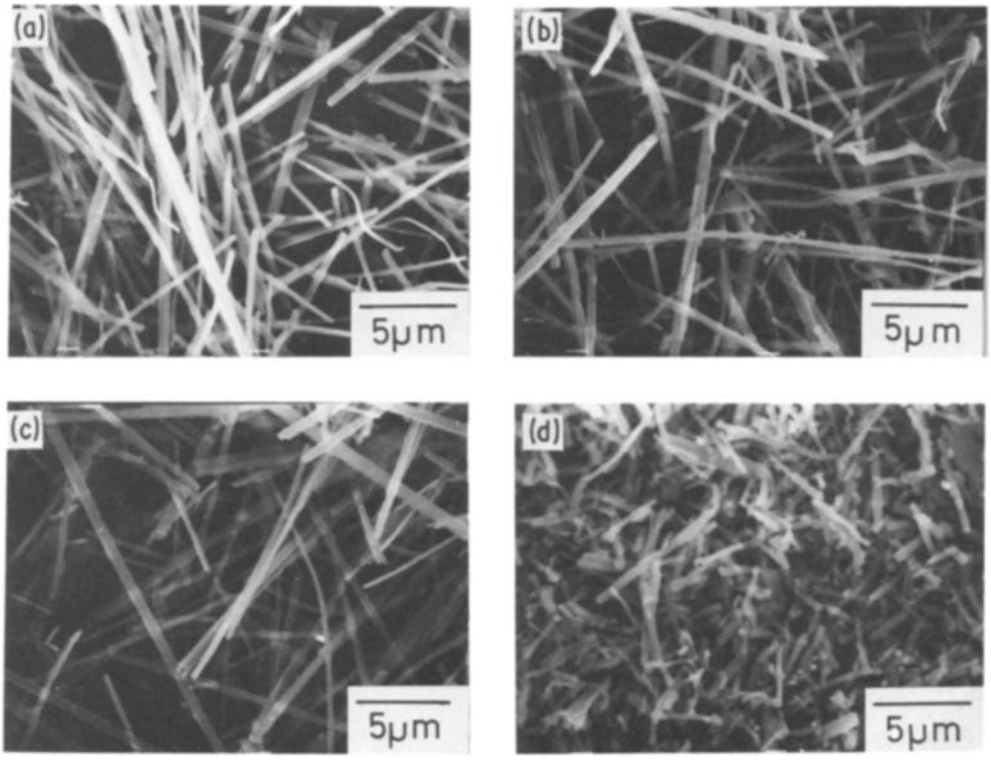

Figure 1 SEM photographs of (a) $K_2Ti_4O_9$, (b) $TiO_2 \cdot nH_2O$ and products obtained by heating $TiO_2 \cdot nH_2O$ for 1 h at (c) 700° C and (d) 1000° C.

After heating for a desired duration, the material was withdrawn from the furnace, cooled in air and washed with hot water several times. The resultant products were examined by X-ray diffraction analysis and scanning electron microscopy. The fractional reaction, was determined by the intensity ratio of the X-ray diffraction lines;

$$\alpha = I_{BT}/(I_{BT} + I_{BC}) \quad (1)$$

where I_{BT} and I_{BC} are peak areas of $BaTiO_3$ (1 1 0) + (1 0 1) and of $BaCO_3$ (1 1 1), respectively.

3. Results and discussion

3.1. Preparation condition of rod-shaped $BaTiO_3$ particles

Potassium tetratitanate, $TiO_2 \cdot nH_2O$ and anatase (shown in Fig. 1) were used as the titanium source and heated with $BaCO_3$ in the molten salt ($W = 1.0$) at 700° C for 1 h. The product phase was always $BaTiO_3$ but the particle shape was dependent on the titanium source. Fig. 2 shows the particle shape and the fraction reacted. When $K_2Ti_4O_9$ and anatase were used, the obtained $BaTiO_3$ powders were the mixture of small equiaxed and large rod-shaped particles. The rod shape in the titanium source was preserved only when $TiO_2 \cdot nH_2O$ was used. The $BaTiO_3$ formation was completed by heating $TiO_2 \cdot nH_2O$ for 1.5 h at 700° C in molten salt ($W = 1.0$), but no significant change in particle shape was observed.

As the $BaTiO_3$ powder composed of rod-shaped particles was obtained from $TiO_2 \cdot nH_2O$, the effects of reaction conditions on the shape of the resultant $BaTiO_3$ were examined. Studies on the effect of salt on the reaction rate at 700° C showed that the salt accelerated the reaction regardless of the flux amount

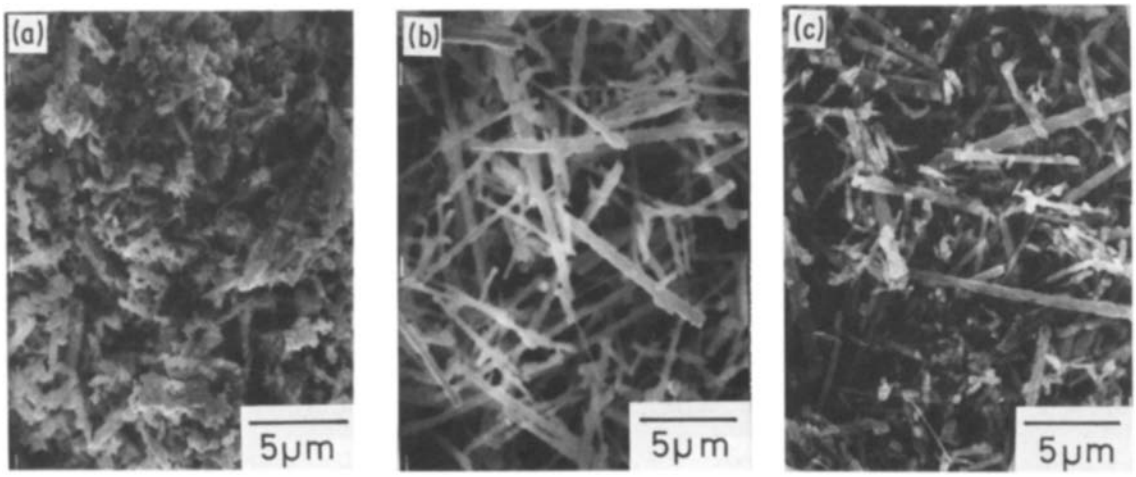

Figure 2 SEM photographs of reaction products between $BaCO_3$ and (a) $K_2Ti_4O_9$, (b) $TiO_2 \cdot nH_2O$ (c) anatase, heated at 700° C for 1 h ($W = 1.0$). The fractional reactions (α) were 1.00, 0.90 and 0.94 respectively.

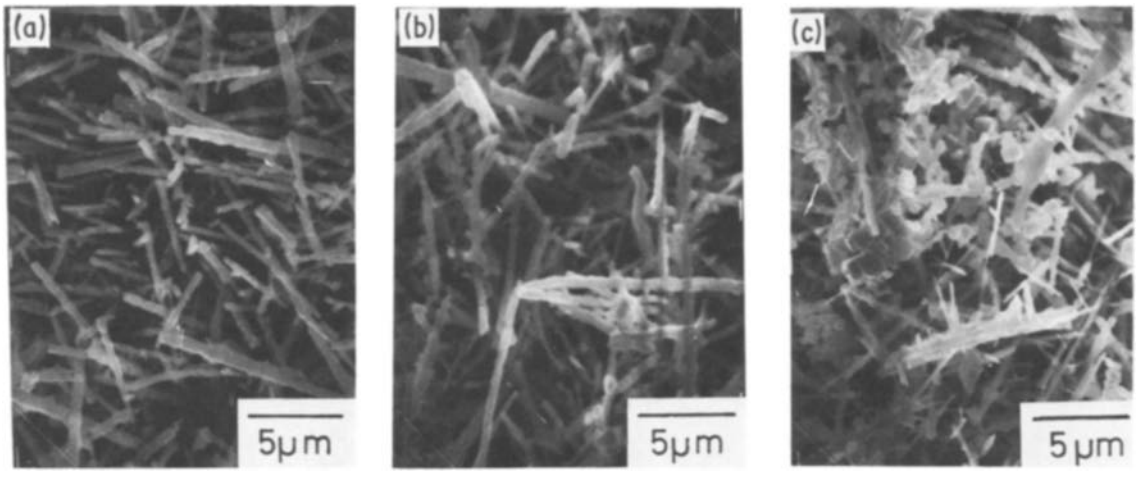

Figure 3 The effect of amount of salt on the product shape. $BaTiO_3$ powders obtained by heating $TiO_2 \cdot nH_2O$ at 700° C for 1 h with (a) $W = 0.1$ ($\alpha = 0.89$), (b) $W = 2.0$ ($\alpha = 0.91$) and (c) $W = 4.0$ ($\alpha = 0.89$).

employed. Fig. 3 shows the particle shape of the obtained products. Rod-shaped $BaTiO_3$ powders were prepared at W between 0.1 and 2.0, and some large equiaxed particles were present with increasing amount of salt (Fig. 3c). Fig. 4 shows the effect of $TiO_2 \cdot nH_2O$ particle size on the shape of $BaTiO_3$ particles. $BaTiO_3$ was obtained by heating small particles of $TiO_2 \cdot nH_2O$ with $BaCO_3$ at 700° C for 1 h ($W = 1.0$). The resultant powder (Fig. 4b) contained equiaxed particles as well as rod-shaped ones. Fig. 5 shows the effect of heating temperature on the particle shape ($W = 1.0$) of the product. The reaction was completed above 800° C by heating for 1 h. The increase in temperature promoted the formation of equiaxed $BaTiO_3$ particles.

3.2. Reaction mechanisms in molten salt

The formation of rod-shaped $BaTiO_3$ particles implies that barium ions diffuse through the $BaTiO_3$ layers formed on the surface of titanium source particles. When no other reaction mechanisms are operative, rod-shaped $BaTiO_3$ particles should be obtained as shown in Fig. 2b. First, we discussed the formation of equiaxed $BaTiO_3$ particles at 700° C in the case using anatase and $K_2Ti_4O_9$. When rod-shaped $BaTiO_3$ particles obtained at 700° C (Fig. 2b) were heated with molten salt at 700° C for another 1 h, no shape change occurred. This fact indicates that equiaxed $BaTiO_3$ particles were formed before or during the reaction. The conversion of anatase to rutile gave equiaxed TiO_2 particles as shown in Fig. 1d. This conversion was accelerated when the anatase particles were heated in molten salt. Possibly, the equiaxed rutile particles were formed before the reaction with $BaCO_3$, resulting in the equiaxed $BaTiO_3$ particles. The amount of rutile formed is probably much larger for anatase than $TiO_2 \cdot nH_2O$ under the same temperature–time condition. The equiaxed particles in Fig. 2c may have been formed by "break-up" of the rod-shaped titanium source particles before the reaction. The "breaking up" of $K_2Ti_4O_9$ is not probable, because the rod-shaped $K_2Ti_4O_9$ alone is stable in molten salt. Thus, the equiaxed $BaTiO_3$ particles in Fig. 2a would be formed during the reaction: i.e., $K_2Ti_4O_9$ and $BaCO_3$ dissolve into molten salt and $BaTiO_3$ precipitates out (solution–precipitation process). When the dissolution rate of the titanium source into the molten salt is smaller than that of $BaCO_3$, a $BaTiO_3$ layer is formed on the surface of the titanium source particles and suppresses the dissolution of titanium. When the dissolution rate of titanium source particles is larger, on the other hand, $BaCO_3$ reacts with dissolved titanium in the molten salt and no $BaTiO_3$ layer is formed. The latter case should yield equiaxed, spherical or polyhedron particles, the faces of which are composed of low Miller indices, since the crystal structure of $BaTiO_3$ at 700° C is cubic.

The amount of molten salt and particle size of

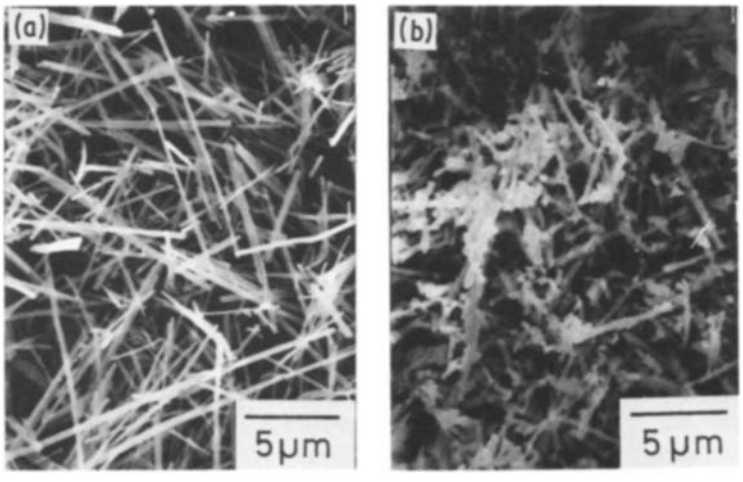

Figure 4 SEM photographs of (a) small starting particles of $TiO_2 \cdot nH_2O$ and (b) $BaTiO_3$ obtained by heating at 700° C for 1 h ($W = 1.0$), $\alpha = 0.96$.

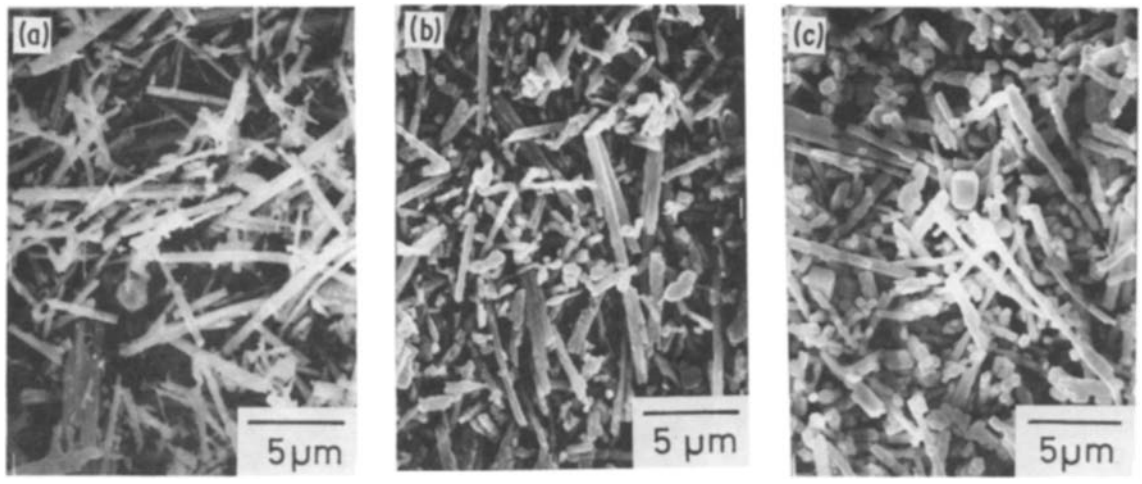

Figure 5 The effect of reaction temperature on the product shape, heated for 1 h (W = 1.0) at (a) 700° C, (b) 800° C and (c) 900° C.

$TiO_2 \cdot nH_2O$ affect the relative dissolution rate of $TiO_2 \cdot nH_2O$. The larger amount of salt would require a longer time for saturation with the barium ion. $TiO_2 \cdot nH_2O$ particles have a larger chance of dissolution, resulting in the increase in the amount of equiaxed particles (Fig. 3c). As small particles have a larger dissolution rate than larger ones, the equiaxed particles in Fig. 4b were formed probably by the solution–precipitation process.

Increasing the heating temperature also promoted the formation of equiaxed particles in the products. In order to understand the equiaxed particle formation at high reaction temperature, the particle shape change during 900° C-heating (W = 1.0) was examined as shown in Fig. 6. The $BaTiO_3$ formation was completed in 4 min at 900° C. The products obtained by heating within 4 min-heating consisted of only rod-shaped particles (Figs. 6a and b). Many equiaxed particles appeared in the 10 min-heated specimen (Fig. 6c). This fact indicates that rod-shaped $BaTiO_3$ particles break up into equiaxed ones after being formed. Thus, at high heating temperatures the "break-up" of rod-shaped $BaTiO_3$ particles could be a possible mechanism of equiaxed particle formation.

In summary, there are three possible mechanisms for the formation of equiaxed particles.

1. Rod-shaped titanium source particles break up into small equiaxed particles before reacting with $BaCO_3$. When a substance has a high crystal symmetry, the rod is not stable and breaks up into an equiaxed particle [11] as in the case of cylindrical void in sintered ceramics [12].
2. $TiO_2 \cdot nH_2O$ and $BaCO_3$ dissolve into molten salt and $BaTiO_3$ precipitates out (solution–precipitation process).
3. Rod-shaped $BaTiO_3$ particles once formed break up into small equiaxed particles by the same reason as in Mechanism (1).

3.3. Solid state method to prepare rod-shaped $BaTiO_3$ particles

The solid state reaction between $BaCO_3$ and TiO_2 proceeds by diffusion of barium ions, so that $BaTiO_3$ particles with a shape similar to that of TiO_2 are obtained [13]. It is possible to prepare the rod-shaped $BaTiO_3$ particles by solid state reaction, if the same mechanism operates. The rod-shaped $TiO_2 \cdot nH_2O$ particles were mixed with $BaCO_3$ and heated at various temperatures for 1 h. The reaction was completed at 1000° C and the shape of the product is shown in Fig. 7. The $BaTiO_3$ particles were rod-shaped and similar to those obtained in molten salt (Fig. 5a).

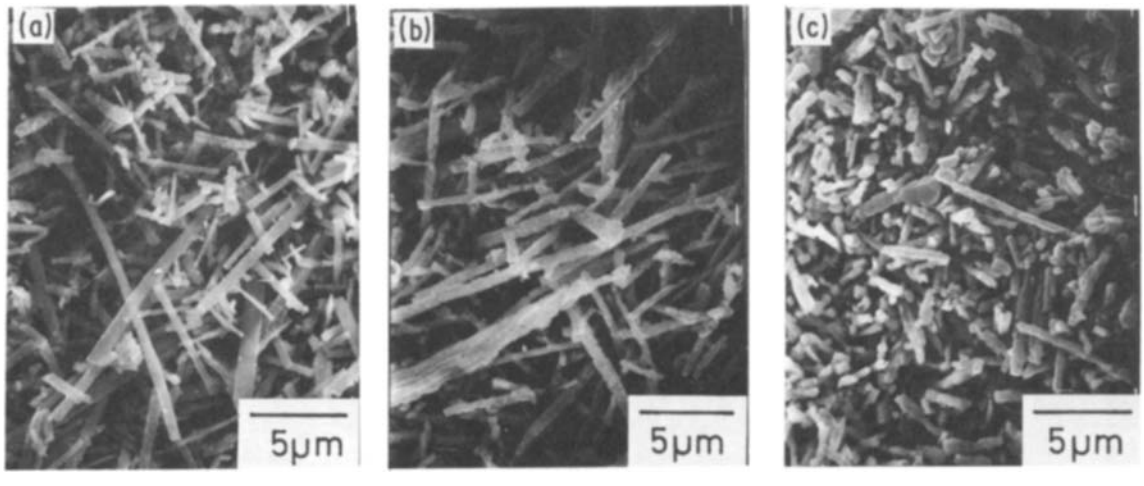

Figure 6 Particle shape changes during heating at 900° C in salt (W = 1.0) for (a) 2 min (α = 0.62), (b) 4 min (α = 1.00) and (c) 10 min (α = 1.00). Samples in (a) was washed with 0.5 N HCl to remove unreacted $BaCO_3$.

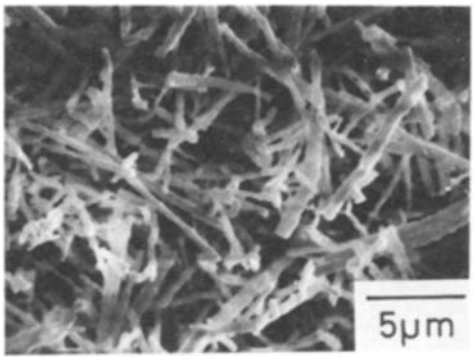

Figure 7 SEM of the product obtained by the conventional method.

Fig. 8 shows the particle size distribution of the product heated at 700° C for 1 h in molten salt (Fig. 5a) and that heated at 1000° C for 1 h by solid state reaction (Fig. 7). Particles were ultrasonically dispersed in water and the size was determined by the sedimentation method. The fraction of small sized particles obtained in molten salt is larger than that obtained by solid state reaction. As the particles are far from spherical, Stokes' law is not applicable and the obtained size does not correspond to the true particle size. However, this size distribution could reflect the size of the agglomerates, and consequently, the strength of the agglomerates in product powders. Thus, Fig. 8 implies that the powder obtained by solid state reaction contained larger and harder agglomerates. The reason why the powder prepared in the molten salt does not contain hard agglomerates is because the molten salt accelerates the reaction, lowering the reaction temperature. Moreover, the molten salt penetrates between the solid particles and prohibits the bonding of particles.

3.4. Characteristics of rod-shaped $BaTiO_3$ particles

In Section 3.2, we showed that the rod-shaped $BaTiO_3$ particles are unstable and change into equiaxed ones on prolonged heating at high temperature. Hence it is predicted that the tetragonality (c/a) of rod-shaped $BaTiO_3$ powder is different from that of equiaxed

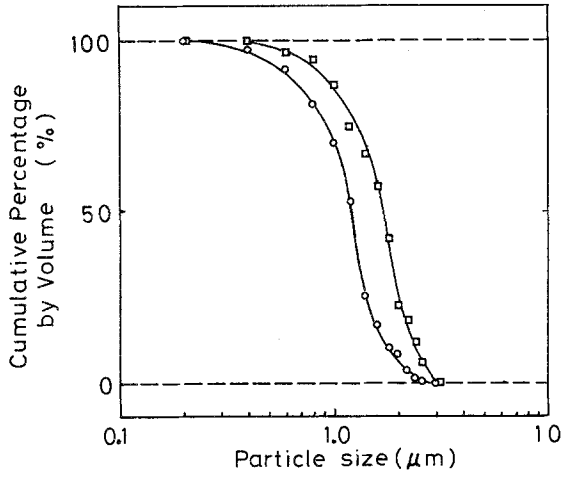

Figure 8 Particle size distribution of the rod-shaped $BaTiO_3$ powders obtained by heating for 1 h at (–○–) 700° C in salt (W = 1.0) and (–□–) 1000° C without salt.

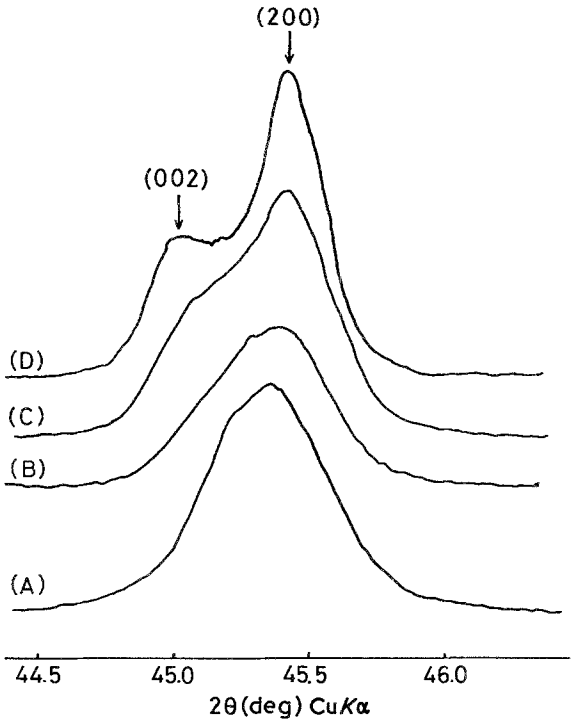

Figure 9 X-ray powder diffraction patterns showing tetragonal splitting of (2 0 0) and (0 0 2) lines. Profiles A, B and C correspond to diffraction lines of the $BaTiO_3$ powders shown in Figs. 5a, b and c. Profile D corresponds to the diffraction line of equiaxed $BaTiO_3$ powder with 0.8 μm diameter.

powder. Fig. 9 shows X-ray powder diffraction profiles of $BaTiO_3$ showing the effect of particle shape on the tetragonality. Profiles A, B and C correspond to the diffraction lines of $BaTiO_3$ powders shown in Figs. 5a, b and c, respectively. Profile D corresponds to the diffraction line of equiaxed $BaTiO_3$ powder with 0.8 μm-diameter, which was obtained from equiaxed $TiO_2 \cdot nH_2O$ powder. No tetragonal splitting was observed in Profile A. Tetragonal splitting becomes significant with increasing fraction of equiaxed particles in $BaTiO_3$ powders. These facts reveal that the tetragonal deformation is suppressed in rod-shaped $BaTiO_3$ particles. Fig. 10 shows the transmission electron microscopic photographs and electron diffraction patterns of rod-shaped $TiO_2 \cdot nH_2O$ and $BaTiO_3$ particles shown in Figs. 1b and 5a, respectively. The TEM observation indicates that a particle of $BaTiO_3$ is deformed. But the observed diffraction pattern of $BaTiO_3$ shows that the orientation is retained in the rod-shaped particle; the particle axis is parallel to the cubic a-axis. By electron diffraction analysis of rod-shaped titanium source particles reveals that the particle axes are parallel to the monoclinic b-axes [14] of $K_2Ti_4O_9$ and of $TiO_2 \cdot nH_2O$ and to the tetragonal a-axis of anatase. Thus, the orientation relation between titanium-source and $BaTiO_3$ particles is expressed as follows

$$\langle 0\,1\,0\rangle_{\text{potassium tetratitanate}} \parallel \langle 0\,1\,0\rangle_{\text{hydrated titanate}} \parallel \langle 1\,0\,0\rangle_{\text{anatase}} \parallel \langle 1\,0\,0\rangle_{\text{barium titanate}}$$

The structures of $K_2Ti_4O_9$, $TiO_2 \cdot nH_2O$, anatase and barium titanate contain TiO_6 octahedra [15, 16]. The observed directions of their particle axes coincide

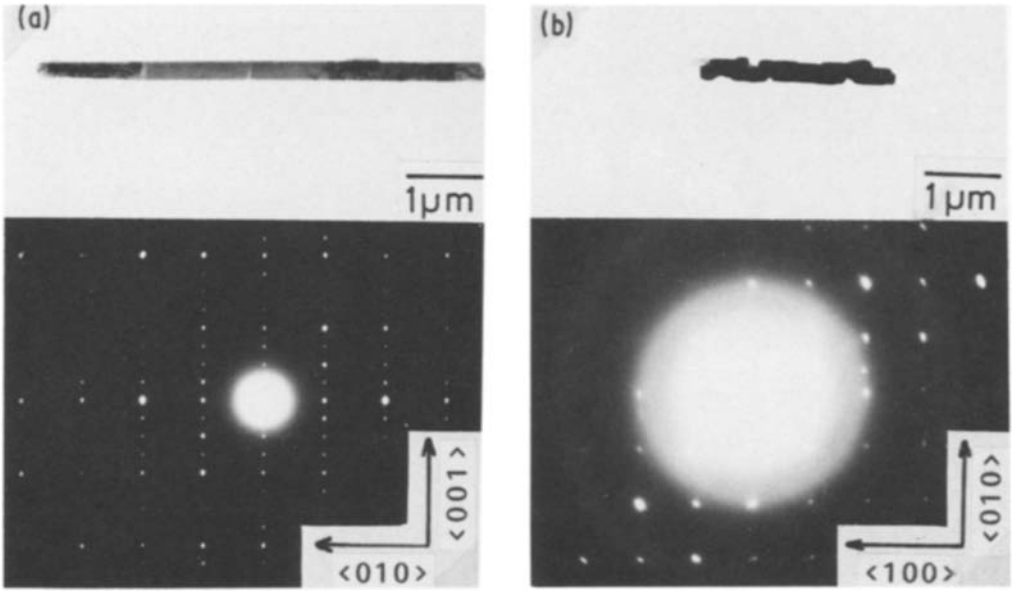

Figure 10 TEM and electron diffraction patterns of the rod-shaped (a) $TiO_2 \cdot nH_2O$ and (b) $BaTiO_3$ particles (shown in Fig. 1b and 5a.)

with the orientation of their TiO_6 octahedra, implying that $BaTiO_3$ formation takes place by topotactic reaction. Jonker [17] described that the tetragonal deformation is suppressed with decreasing crystallite size. The obtained rod-shaped $BaTiO_3$ particle is probably polycrystalline containing very small crystallites. The very small crystallites in the obtained rod-shaped $BaTiO_3$ particle might have been responsible for the suppression of cubic–tetragonal transition on cooling.

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Received 25 March
and accepted 2 April 1985