

Characteristics of BaTiO₃ powders synthesized by hydrothermal process

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Monodisperse BaTiO₃ powder was prepared by a hydrothermal process from a mixture of Ba(OH)₂ and Ti(OH)₄. In the process, the best synthesis conditions were a Ba(OH)₂/Ti(OH)₄ mole ratio of 1, the reaction temperature 180°C, which produced the cubic crystal structure of BaTiO₃ with 0.3 μm size. The effects of synthesis conditions and the dispersion stability of powder were investigated. The reaction kinetics was also discussed from the experimental results. © 2000 Kluwer Academic Publishers

1. Introduction

Barium titanate has been widely used in the ceramic capacitors industry. Although the electrical properties of BaTiO₃ depend on the sintering conditions, it is important to control the characteristic of powder in the early stage of reaction during the powder processing. Because the powder properties are profoundly affected by the particle size, the morphology, the particle size distribution and the crystal structure [1–6]. Specially, since high purity ultrafine BaTiO₃ powder which has been used for thermistors, multilayer capacitors and electro-optic devices are interested in synthesis and processing with increasing needs for miniaturization of integrated circuits, the powders are focused to be a low sintering temperature material due to the increased surface energy of powder [1]. Hydrothermal synthesis, one of wet chemical processing of BaTiO₃ powder, has been used with several reasons of high purity, homogenization of chemical composition, finer particle size and regular particle size distribution [2–4]. In spite of more benefits on the hydrothermal process, it has still remained some problems such as a solid-liquid reaction (TiO₂/Ba(OH)₂) with lacking thermodynamics data on the reaction, the corrosion problem (caustic solution) of chloride salt, and the formation of agglomerates [5]. One purpose of the research is to explore the use of the high surface activity of the powders. It needs to study thoroughly the nucleation and crystallization of BaTiO₃ powder to control the condition of processing for solving the agglomeration. In this study, the hydrothermal process was applied to prepare of fine and high purity BaTiO₃ powders and the processing parameters to affect powder size, morphology and particle distribution were investigated in order to understand the powder grain growth and the agglomeration. Finally, it was considered to apply surfactants to either powder processing or the synthesized powder to solve the agglomeration of powder.

2. Experimental procedure

As a precursor, Ti(OH)₄ was prepared using TiCl₄ solution and NH₄OH. In hydrothermal process, TiCl₄, NH₄OH and Ba(OH)₂ were used for this work. The powder synthesized was treated by washing, filtering and drying. During the reaction, a rotation speed of 500 rpm was maintained and the sampling of solution was done at certain intervals. X-ray diffractometer (XRD, Rigaku, 2028), scanning electron microscopy (SEM, Akashi, DS-130), differential scanning calorimetry (DSC, Dupont), particle size analyzer (Malvern), and surface analyzer (Quanta Chrom) were used for the characterization of powder. A zeta potentiometer (ZM80) was used for measuring the electrokinetic mobility of powders to find a repulsive condition of the synthesized and a commercial powders. The dispersion stability was observed for the powders treated with several surfactants (concentration 10⁻²–10⁻⁶ M/l).

3. Results and discussion

The synthesis condition, reaction products and grain size of the powder are represented in Table I. Under the condition of fixed Ba/Ti mole ratio of 1, the final crystal structure of BaTiO₃ was found to be a cubic irrespective of reaction temperatures. Fig. 1 shows the powder morphology as a function of reaction temperature. The powder with average sizes of 0.5 μm has a homogenous particle size distribution. Comparison of the powders prepared at 120 and 180°C as shown in SEM photographs (Fig. 1a and c) suggest that the powder synthesized at the lower temperature has a larger particle size, which is related to the poor crystallization at these temperature. Since a lower reaction temperature is known to hinder the particle growth so that the powders are agglomerated. This phenomena can be clearly found in Fig. 1a) showing necking between particles.

TABLE I The synthesis conditions and final products synthesized by the hydrothermal process

Ba(OH) ₂ (mole)	Ti(OH) ₄ (mole)	Temp. (°C)	Time (h)	Products (phases)*	Particle size (μm)
1	1	180	1	BaTiO ₃ (c)	0.31
1	1	150	1	BaTiO ₃ (c)	0.31
1	1	120	1	BaTiO ₃ (c)	0.34
0.5	1	180	2	BaTiO ₃ (c), TiH ₂	0.29
0.5	1	150	2	BaTiO ₃ (c), TiH ₂ , Ba(Ti _{1.48} Ti _{1.52})O _{2.76}	0.2
1	3	180	1	BaTiO ₃ (c), TiO ₂ , TiH ₂ , Ba(Ti _{1.46} Ti _{1.52})O _{2.76}	0.2
1.1	1	180	1	BaTiO ₃ (c), (t)	0.4
1.3	1	180	1	BaTiO ₃ (c)	0.34
1.5	1	180	1	BaTiO ₃ (c)	0.34
1	1.1	180	1	BaTiO ₃ (c)	0.34

* (c) and (t) mean a cubic and a tetragonal structure respectively.

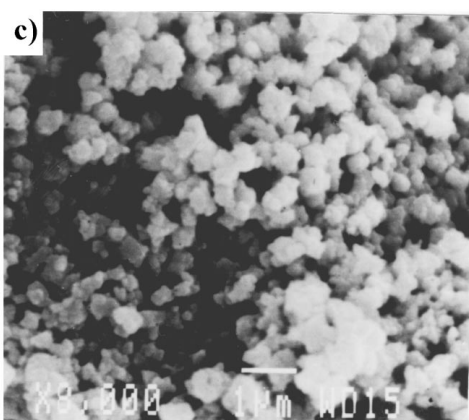
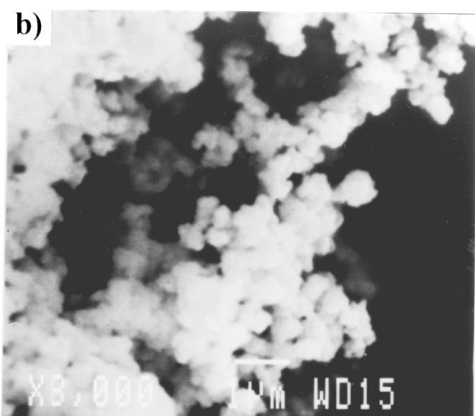
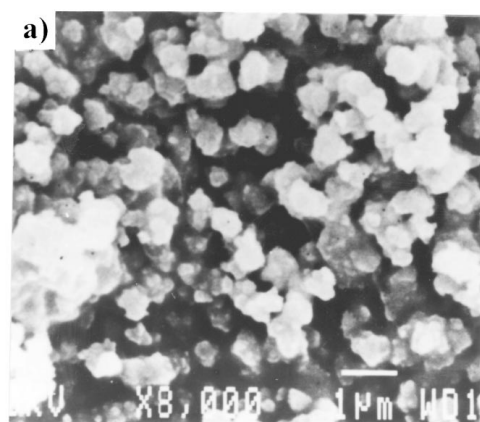


Figure 1 SEM micrographs of the product at various temperature (mole ratio of Ba(OH)₂/Ti(OH)₄ = 1, reaction time 1 h). a) 120°C; b) 150°C; c) 180°C.

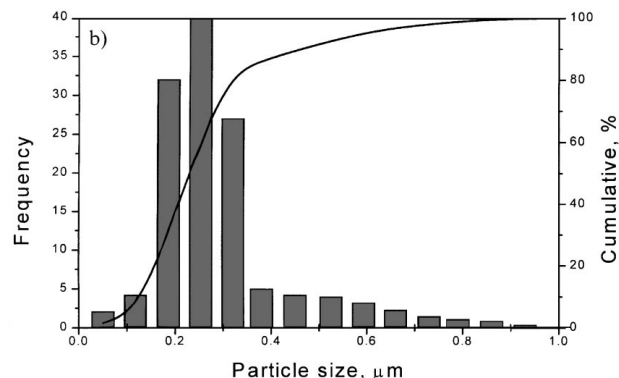
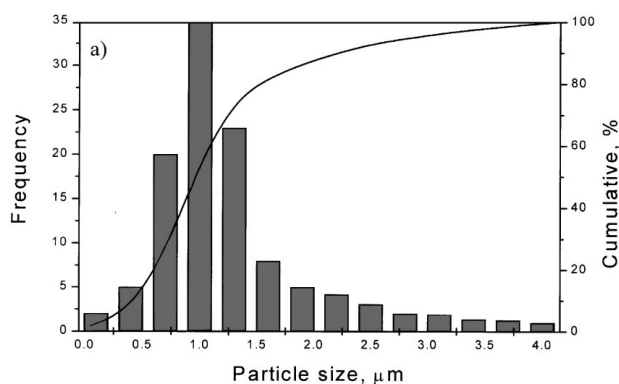


Figure 2 Particle size distribution of BaTiO₃ at various reaction time. a) 1 hr; b) 3 hrs.

The powder synthesized at 180 °C, therefore, resulted in monodisperse particle because of faster rate of growth at the higher temperature. As shown in Fig. 2, the effect of reaction time is sensitive to the powder size: the longer time at the constant reaction temperature resulted in a smaller powder size. This is related to a crystal formability, which is that the reaction at lower temperatures needs much longer time to complete the crystal growth.

In the formation of BaTiO₃ from Ba(OH)₂ and Ti(OH)₄, two mechanism are suggested: (1) Ba²⁺ ion is absorbed on the surface of Ti(OH)₄ particle and diffuse into the powder, and finally after the chemical reaction inside and BaTiO₃ forms (a consolidation mechanism); (2) a precipitation by dissolution-recrystallisation mechanism, in which Ti(OH)₄ is

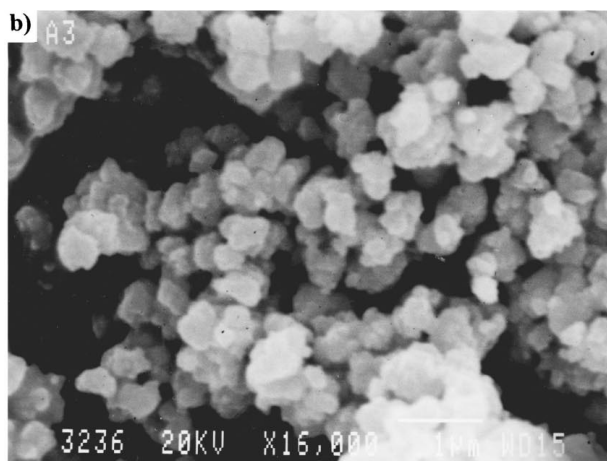
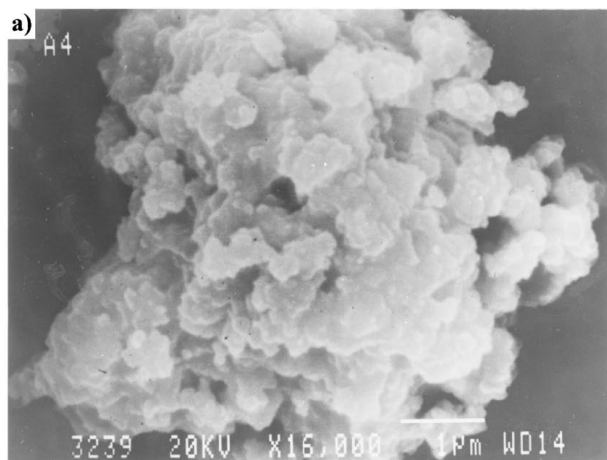


Figure 3 SEM micrographs of the product at various Ba/Ti mole ratio. a) 0.5 mole; b) 1.5 mole.

dissolved and BaTiO_3 forms directly under a saturated condition [6]. In fact, both the reaction mechanisms operate together during the reaction because the reaction temperature is low (80–180 °C) so that the nucleation is controlled by the consolidation and the crystal growth by the precipitation caused by dissolution-recrystallisation mechanism. For the reason of the mechanisms, as shown in Fig. 3, in case of excess concentration of $\text{Ti}(\text{OH})_4$, Ba^{+2} ion concentration is low so that the crystal growth occurs since the dissolution-recrystallisation mechanism predominates. It causes a slow growth rate with a crystal habit and results in faceted morphology in powder and severe agglomeration (Fig. 3a). On the other hand, the excess of $\text{Ba}(\text{OH})_2$ in the reaction showed a higher nucleation rate due to the so that the number of nuclei increases and the effect of dissolution-recrystallisation is less. Finally a smaller spherical powder was obtained as shown in Fig. 3b.

In order to observe the reaction kinetic, the Ba^{+2} content of the solution was determined at regular intervals. BaTiO_3 yielded as a function of reaction time at various temperature is presented in Fig. 4. After 3 min, the precipitation of BaTiO_3 was found to be above 96% in the reaction temperature range (80–180 °C). In the early stage of reaction, Ba^{+2} ion absorbed on the surface of $\text{Ti}(\text{OH})_4$ particle then diffused and a number of nuclei were formed. XRD confirmed the precipitate phase to be BaTiO_3 . As a conclusion, a combination long time at

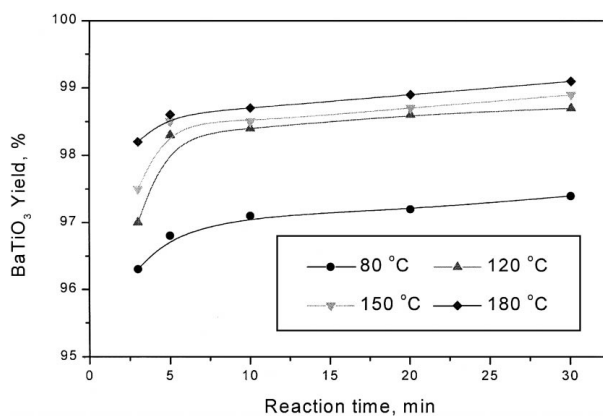


Figure 4 Yield of BaTiO_3 with respect to reaction time (Ba/Ti = 1).

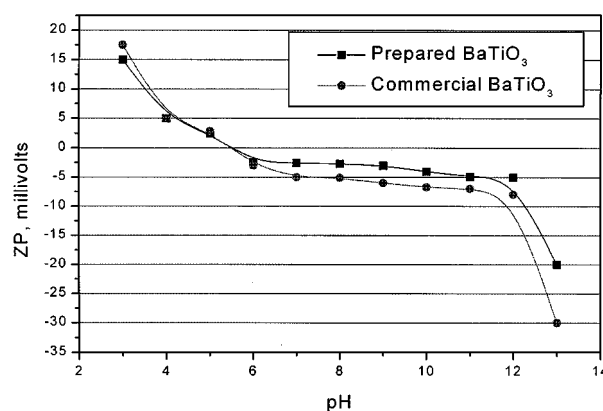


Figure 5 Electrophoretic mobility of prepared and commercial BaTiO_3 powders.

low temperature is required to produce a powder with good degree of crystallinity.

To compare the degree of dispersion of the synthesized powder and a commercial powder, the surface potential of two powders have been compared in Fig. 5. The ξ potential was calculated from the electrophoretic mobility, using the Helmholtz-Smoluchowski equation [7]. The ZPC (zero point charge) thus calculated was pH 5.5 for both of them and the ξ potential of the powder were nearly the same as in the overall range of pH. Considering that the greater the magnitude of the zeta potential, the higher is the dispersion stability, two different, cationic (SDS, PEX) and anionic (DACL) surfactant were used for strongly charging the surface of powder. The results are presented in Table II. As shown in Fig. 6a), application of PEX surfactant to the raw materials for hydrothermal synthesis did not improve the dispersion stability of the synthesized powder. Also, after completing the synthesis reaction, the surfactant was mixed for 24 h to the BaTiO_3 powder synthesized.

TABLE II Monodispersed phenomena of the products with various surfactants

Surfactant	Concentration	Reaction condition	Dispersing ability
SDS (-)	10^{-2} – 10^{-6} M/L	Ba/Ti = 1	Moderate
DACL (+)	10^{-2} – 10^{-6} M/L	Temp. 150 °C	Moderate
PEX (-)	10^{-2} – 10^{-3} M/L	Time = 1 hr	Strong

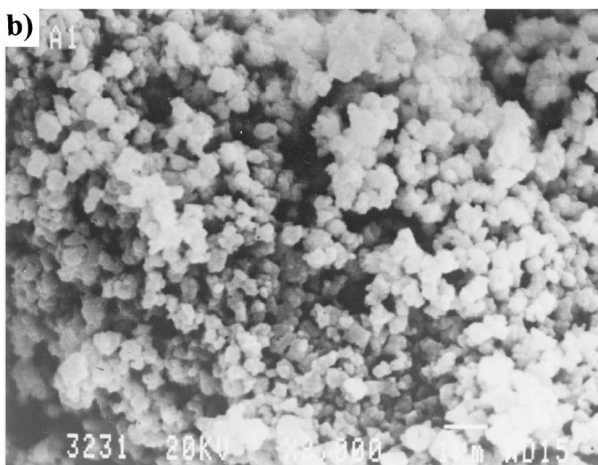
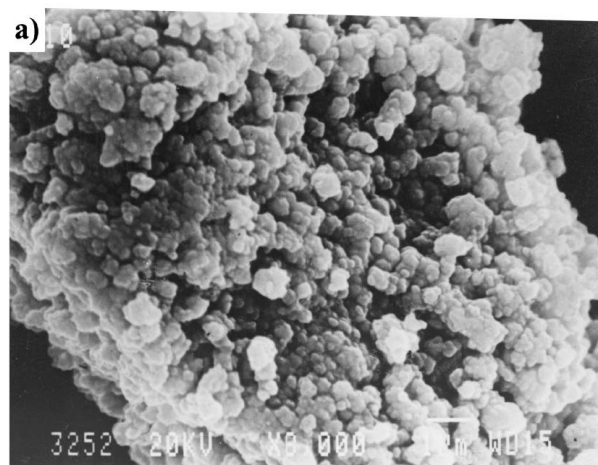


Figure 6 SEM micrographs of the product treated with PEX surfactant (10^{-4} M/l mole). a) Before reaction; b) After reaction.

This longer mixing time significantly improve the degree of dispersion (Fig. 6b). Thus, in the hydrothermal synthesis, the dispersion stability of powder could be controlled not with surfactants during reaction but by

processing conditions such as concentration, temperature and time which affect the reaction rate and grain growth of powder.

4. Conclusion

The BaTiO_3 powder was prepared by a hydrothermal process and the effects of syntheses conditions and the dispersion stability of powder were investigated. In the process, the best synthesis conditions were a $\text{Ba}(\text{OH})_2/\text{Ti}(\text{OH})_4$ mole ratio of 1, the reaction temperature 180°C , which produced the cubic crystal structure of BaTiO_3 with $0.3\ \mu\text{m}$ size. The dispersion stability of powder synthesized was not improved by application of the surfactants (cationic and ionic) during reaction. However, the agglomeration of the synthesized powder could be controlled by the processing conditions and long mixing time of the surfactant after hydrothermal reaction.

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