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Preparation of barium titanate powders by microwave-assisted liquid phase process at ambient pressure

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Fine barium titanate ($BaTiO_3$) powders were prepared by a microwave-assisted liquid phase process at ambient pressure. The process is simple, ecologically friendly, and economical. Titanium dioxide (TiO_2) and Barium hydroxide octahydrate ($BaOH_2{\cdot}8H_2O$) were the only starting materials used, in order to avoid contamination. $BaTiO_3$ powders were obtained as a single cubic phase from both microwave-assisted and conventional liquid phase processes. $BaTiO_3$ powders synthesized by conventional liquid phase process were nonuniform in size. In contrast, $BaTiO_3$ powders made by the microwave-assisted process consisted of fine uniform particles with a narrow size distribution. TGA analysis revealed that the lattice OH group content in $BaTiO_3$ powders synthesized by the microwave-assisted process decreased with increasing reaction time.

Key-words : Barium titanate, Microwave synthesis, Liquid phase, Lattice hydroxyl groups, Morphology

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From an environmental viewpoint, lead-free materials have become a focus of significant attention. In recent years, the EU WEEE and RoHS directives have drawn the attention of electronics manufacturers to more environmentally benign technologies.[1] A key technological challenge for the electronics industry is the adoption of lead-free systems, and many studies have been reported on the development of lead-free materials such as $BaTiO_3$.[2] Currently, $BaTiO_3$ is one of the most important raw materials used in the electronic ceramics industry because of its excellent ferroelectric and piezoelectric properties. In particular, recent advancements in thin multilayer ceramic capacitors (MLCCs) have required fine, high-purity $BaTiO_3$ powders with a uniform particle size distribution. There are many methods of synthesizing such powders: fine, high-purity $BaTiO_3$ powders have been synthesized by liquid phase methods, hydrothermal methods, sol–gel processing, the oxalate route, microwave heating, and a polymeric precursor method.[3)–6)] Of these, the microwave-heating process has been recognized as a time and energy saving approach, due to its fine crystal kinetics.[7] Recently, fine high-purity $BaTiO_3$ was synthesized by a microwave-hydrothermal process,[8] but there have been no reports to date of a liquid phase method at ambient pressure, which should allow for milder conditions than the hydrothermal process. For this study, we prepared fine $BaTiO_3$ powders by a microwave-assisted liquid phase process at ambient pressure, and the resulting material was compared with that obtained by a conventional liquid phase method.

TiO_2 powder (Degussa p–25) and $Ba(OH)_2{\cdot}8H_2O$ (98% purity, Wako Pure Chemical Industries, Ltd.) were used as starting materials with no alkali hydroxide present, to avoid contaminants such as sodium or potassium.[9] These mixtures were added to 80 ml of pure water in a round tetrafluoroethylene-perfluoro alkyl vinyl ether copolymer (PFA) flask. The initial concentration of Ti was 0.5 mol/dm^3, and the Ba/Ti molar ratio was 1.5. The reacting solution was irradiated with microwaves, at a frequency of 2.45 GHz, from a system capable of operation at 0–100% of its full power of 700 W. A reflux apparatus was fitted to the system so that recovered vapor dropped back down into the reacting solution. The process was carried out for 10–600 min with stirring at a fixed microwave power of 420 W. After microwave irradiation, the reacting solution was centrifuged at 3000 rpm for 3 min and washed several times with pure water and aqueous acetic acid. The washed particles were dried at 90°C and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA). TGA was performed with a thermal analyzer. Typically, about 10–20 mg sample was heated from room temperature to 700°C with a heating rate of 10°C/min in air-flow condition. For comparison, conventional liquid phase syntheses were also conducted. This process was carried out on a conventional heating under vigorous stirring, and the reacting solution was boiled for 10–600 min.

Figures 1 and **2** show XRD patterns of powders synthesized by conventional liquid phase and microwave-assisted processes with varying reaction times from 10 to 600 min. For 10 min reactions, $BaTiO_3$ peaks appeared using both methods. With increasing reaction time, the intensity of the $BaTiO_3$ peaks increased. With a reaction time of 240 min, the TiO_2 peaks disappeared, and single-phase cubic $BaTiO_3$ was obtained. For powders synthesized over 600 min, only pure cubic $BaTiO_3$ was obtained from both processing methods. TEM images of $BaTiO_3$ powders synthesized by both methods are shown in **Figs. 3** and **4**. Particles prepared by both methods had a cubic shape, but with a different size distribution for each process. The conventional liquid phase process produced uniform 80 nm $BaTiO_3$ particles when the reaction time was 10 min (Fig. 3), but a wide size distribution of particles ranging from 20 to 150 nm when reaction time was 240 min or longer. Electron beam diffraction indicated that each $BaTiO_3$ particle was a single crystal. In contrast, the particles synthesized by the microwave-assisted process were uniform in size, and the average particles were 100 nm for all reaction times, as shown in Fig. 4. This implies that rapid nucleation and growth,

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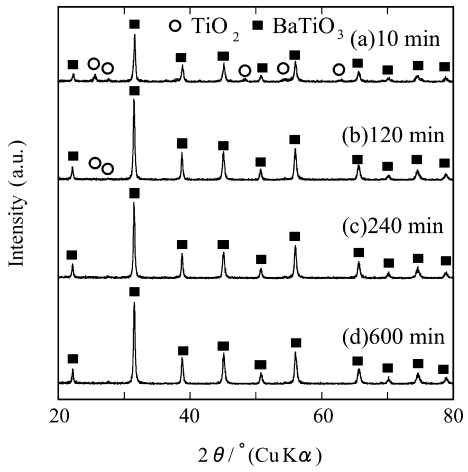

Fig. 1. XRD patterns of samples synthesized by conventional liquid phase process.

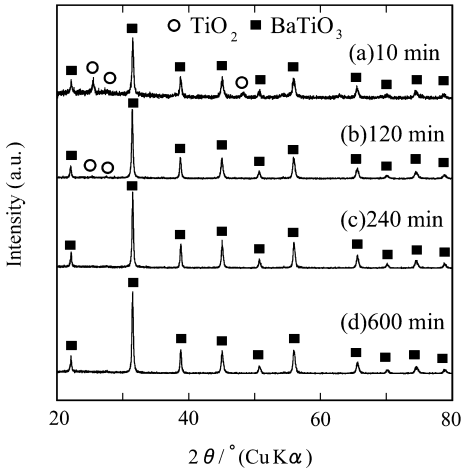

Fig. 2. XRD patterns of samples synthesized by microwave-assisted process.

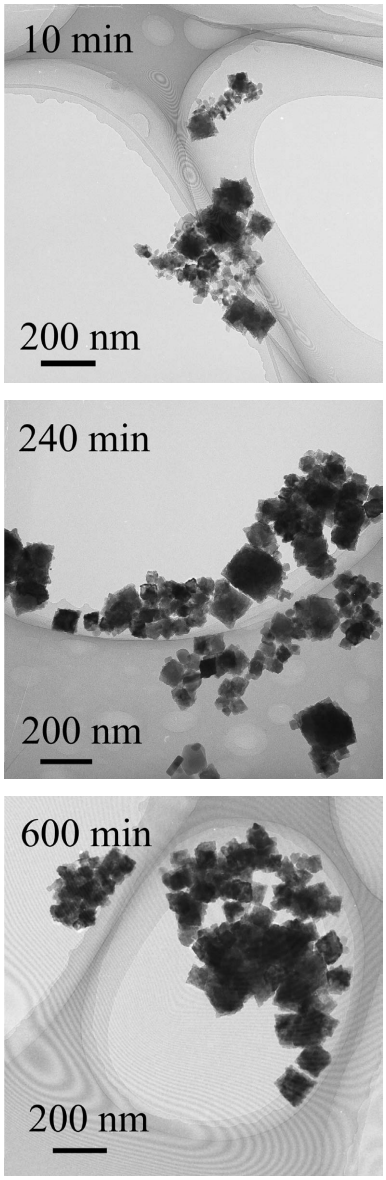

Fig. 3. TEM images of samples synthesized by conventional liquid phase process.

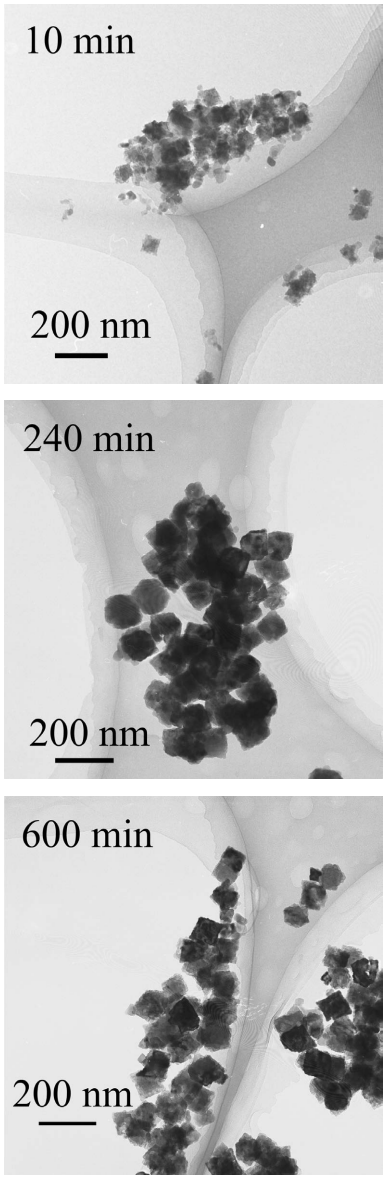

Fig. 4. TEM images of samples synthesized by microwave-assisted process.

induced by fast microwave heating, was completed within the first 10 min. The particles synthesized by the microwave-assisted process clearly had a narrower size distribution than the particles synthesized by the conventional liquid phase process. The reason for the difference in $BaTiO_3$ particle size distributions is discussed as follows; Conventional heating is external, with heat transferred to the reacting solution from a heat source underneath the reaction mixture. Because the reacting solution was heated heterogeneously, there was a temperature gradient from the top of the solution to the bottom, which resulted in uneven nucleation and the growth of particles of various sizes. On the other hand, microwave heating can be very fast and uniform, through a self-heating process that arises from the direct absorption of microwave energy into the reaction mixture. This rapid homogeneous heating, not possible by conventional heating, provides uniform nucleation.[10] Because of homogeneous nucleation, uniform-sized particles could be prepared. It is well-known that the liquid phase process performed at low temperature yields cubic $BaTiO_3$, even though the tetragonal structure is thermodynamically stable at room temperature. Several researchers have reported that this is because of residual OH groups in the oxygen sublattice.[11–13] In this study, the $BaTiO_3$ powders synthesized by both processes were cubic, according to XRD results. To investigate the differences in the residual OH groups contained in the $BaTiO_3$, TGA was performed. **Figures 5** and **6** show TGA curves

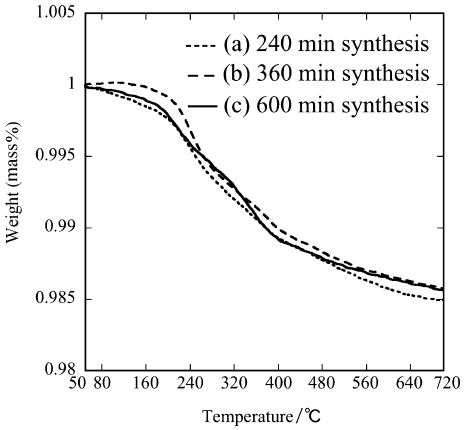

Fig. 5. TGA curves for $BaTiO_3$ powders synthesized by conventional liquid phase process.

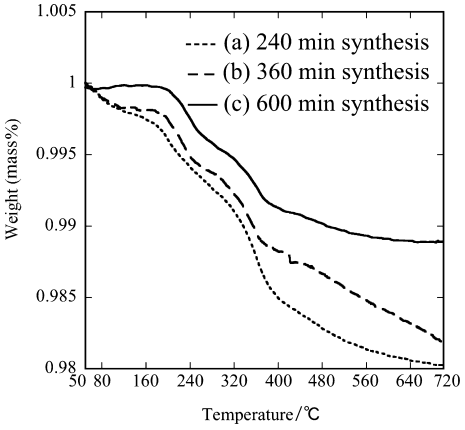

Fig. 6. TGA curves for $BaTiO_3$ powders synthesized by microwave-assisted process.

for $BaTiO_3$ powders prepared by conventional liquid-phase and microwave-assisted processes. It has been reported that weight loss below 200°C corresponds to the amount of water attached to sample, and between 200 and 600°C corresponds to the amount of lattice OH groups retained in $BaTiO_3$.[9),14)] The amounts of lattice OH groups were 1.20, 1.23 and 1.16 mass% for $BaTiO_3$ powders synthesized by the conventional liquid-phase method for 240, 360 and 600 min, respectively, and 1.56, 1.34 and 1.05 mass% for $BaTiO_3$ powders synthesized by the microwave-assisted method for 240, 360 and 600 min, respectively. The OH group content of the $BaTiO_3$ powders synthesized by the microwave-assisted method showed a decreasing trend with increasing reaction time. There are some reports that microwave-hydrothermal process has advantages over the hydrothermal process in terms of enhanced the crystallization kinetics.[8),15),16)] Ma et al.[15)] have reported their study on direct synthesis of tetragonal $BaTiO_3$ by microwave-hydrothermal process at 170°C for several days. They turned out that microwave-hydrothermal process showed advantages of shortened crystallization time, increased *c/a* ratio. Sun et al.[8)] have observed that microwave-hydrothermal $BaTiO_3$ powders contain a lower concentration of lattice OH groups than hydrothermal $BaTiO_3$. $BaTiO_3$ powders which they synthesized contain only 0.02 mass% lattice OH groups, by contrast 0.14 mass% for the conventional hydrothermal one. They also have been reported that the content of lattice OH groups in microwave-hydrothermal $BaTiO_3$ powders shows a decreasing trend as a function of reaction time and are much less than that in hydrothermal $BaTiO_3$ sample.[16)] According to their results, the content of lattice OH groups are 0.06 and 0.03 mass% for the microwave-hydrothermal $BaTiO_3$ powders synthesized for 12 and 20 h. Our result seems to agree with their reports. In the microwave-assisted process, the microwaves probably act on the lattice OH groups, enhancing their removal. On the other hand, in the hydrothermal synthesis, it is reported that tetragonality of prepared $BaTiO_3$ powders shows a increasing trend as a function of reaction time.[16)] However, the OH group content of the $BaTiO_3$ powders synthesized by conventional liquid phase method showed no change with reaction time, which might be attributed to our reaction condition. To our knowledge, there is no report to date of the decrease of OH group content in these liquid phase conditions at ambient pressure. The mechanism by which microwaves act on lattice OH groups is unclear, but it does seem that the microwaves not only supply energy to heat the reaction mixture as effectively as conventional liquid phase heating methods, but also act on the $BaTiO_3$.

$BaTiO_3$ powders were synthesized by a simple microwave-assisted liquid phase synthesis at ambient pressure. This process is ecologically friendly and economical because no organic materials and no alkali hydroxides were used, the reaction was performed at ambient pressure, microwave heating saved energy, and the method is suitable for wide application. Obtained $BaTiO_3$ powders synthesized by this microwave-assisted process were finer and more uniform than powders synthesized by a conventional process, and the average particle size was 100 nm after a 240 min synthesis. According to TGA analysis, the lattice OH group content decreased with increasing of reaction time in $BaTiO_3$ powders prepared by the microwave-assisted process. This is probably because the microwaves act on the lattice OH groups.

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