Characteristics and Sintering Behavior of Barium Titanate Powder Synthesized by Emulsion Combustion Method

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Barium titanate (BaTiO₃) powder was synthesized using the emulsion combustion method (ECM) from a water-in-oil-type emulsion, in which a barium nitrate aqueous solution, a titania sol, kerosene and a surfactant were included, at a firing temperature of 850°C. Particle characteristics and sintering behavior of the synthesized particles were evaluated. The particles of the synthesized powder were nearly spherical in shape, 200-500nm in diameter and polycrystalline. The diameter of the particle was almost consistent with that calculated from the size of the aqueous microsphere in the emulsion, the concentration of metal ions and the density of BaTiO₃. The X-ray diffraction (XRD) pattern showed that the main product (over 95%) was BaTiO₃ and that a small amount of Ba₂TiO₄ was synthesized. The compact of the synthesized powder was densified up to 90% of the theoretical density at a sintering temperature of 1200°C, which was 100°C lower than that of the powder produced by the hydrothermal process. The fine polycrystalline structure of the ECM-made particles was considered to enhance the densification at a lower temperature. The sintered specimen showed a typical temperature dependence of dielectric constant in BaTiO₃, which included two peaks at 20 and 120°C, corresponding to orthorhombic-tetragonal and tetragonal-cubic phase transitions, respectively.

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1. Introduction

Barium titanate (BaTiO₃) and its related systems are some of the most important materials for multilayer ceramic capacitors (MLCs) due to their excellent dielectric properties. Recent demand for capacitors with a higher capacitance and a smaller size requires the thickness of each layer in MLCs to be 2 to 3 micrometers. A lower sintering temperature is also required for a decrease of production cost. The demand for fine reactive BaTiO₃ powder is very high. Many studies have been carried out to obtain fine reactive BaTiO₃ powder using various methods such as hydrothermal methods, a sol-gel method, a sol-crystal method, citric processes, a polymerized complex method, spray pyrolysis and combustion synthesis.

The emulsion combustion method (ECM), developed in our laboratory, is a novel particle synthesis technique. Figure 1 shows the schematic diagram of the ECM. The ECM consists of three principal steps; (1) preparing a w/o (water-in-oil)-type emulsion in which metal salts are dissolved in an aqueous phase, (2) atomizing and firing the prepared emulsion and (3) collecting the synthesized powder. The metal salts in the emulsion are decomposed and oxidized during the firing step. An oxide particle is synthesized from an aqueous microsphere in an emulsion by ECM, so that the diameter of the synthesized particle is small and controllable by changing the diameter of the aqueous microsphere. The synthesized particle is also chemically homogeneous, because the aqueous microsphere is heated by combustion of oil and quenched rapidly enough to maintain homogeneity of multiple metal ions in an aqueous solution.

In this study, BaTiO₃ powder was synthesized by ECM. Particle characteristics and sintering behavior of the synthesized powder were evaluated and compared with those of the powder prepared by a hydrothermal (HT) process.

Fig. 1. Schematic diagrams of ECM process.

2. Experiments

2.1 Synthesis and evaluation of a powder

A barium nitrate aqueous solution (0.3 mol/l) and a titania sol (Nissan Chemical Ind., TA-15) were used as barium and titanium sources, respectively. Primary titania particles (<10 nm) were agglomerated to form secondary particles (<100 nm) in the titania sol. A mixture of the barium and titanium sources (Ba/Ti=1/1 in molar ratio), kerosene and hexa (2-hydroxy-1,3-propylene-gricolic) diricinolate (Taiyo Kagaku, SUNSOFT818H) were prepared as aqueous
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The synthesis of the powder involved the use of an emulsion combustion method. The aqueous phase, oil phase, and surfactant were mixed and stirred to form an oil-in-water (o/w) emulsion. The diameter of the aqueous microspheres was about 1 to 2 micrometers. The emulsion was atomized and fired to synthesize BaTiO3 powder. The flame temperature was controlled to be about 850°C. The synthesized powder was collected using a bag filter with the aid of a vacuum pump.

The synthesized powder was die-pressed at 40 MPa and isostatically pressed at 300 MPa to form a green disc. The density of the sintered body was measured using the Archimedes method. The microstructure of the sintered body was observed by SEM. The crystalline phase was characterized by X-ray diffraction. The dielectric constant and its temperature dependence were measured using an impedance analyzer and a thermostatic chamber.

Figure 2 shows the SEM micrographs of the ECM and HT particles. The ECM particles were nearly spherical in shape, with an average particle size of 315 nm. The HT particles were also nearly spherical in shape, with an average particle size of 330 nm. The ECM particle size was smaller than that of the HT particles. The microstructure of the sintered bodies was observed by SEM. The crystalline phase was characterized by XRD. The dielectric constant and its temperature dependence were measured using an impedance analyzer and a thermostatic chamber.
3.2 Sintering behavior and characteristics of a sintered body

Figure 5 shows the densification behaviors of the ECM and HT specimens. In the ECM specimens, the increase of the relative density was clearly observed at 1000°C and the relative density reached 94.4% at the sintering temperature of 1200°C. The relative density of the HT specimen was lower than that of the ECM specimen at the sintering temperatures of 1000 to 1200°C and they were almost equal at the sintering temperatures of 1300 and 1400°C.

Figure 6 shows the SEM micrographs of the etched surfaces in the ECM specimens sintered at 1200, 1300 and 1400°C. The surfaces were over-etched to observe domain structures in the grains. The diameter of the grains increased as the sintering temperature increased. The average diameters were 1.8, 3.7 and 4.9 μm for the ECM specimens sintered at 1200, 1300 and 1400°C, respectively. The stripe patterns were slightly formed and clearly observed on the grain surfaces of the specimens sintered at 1300 and 1400°C, respectively, which may indicate that the domain structure is formed at the sintering temperature range of 1300–1400°C. Figure 7 shows the X-ray diffraction patterns of the specimens sintered at 1200, 1300 and 1400°C. All specimens were identified to be pure BaTiO$_3$.

Figure 8 shows the dielectric constant ($\varepsilon/\varepsilon_0$)-temperature curves of the specimens sintered at 1200–1400°C. They showed typical temperature dependences of $\varepsilon/\varepsilon_0$, which included two peaks at 20 and 120°C, corresponding to orthorhombic–tetragonal and tetragonal–cubic phase transitions of BaTiO$_3$, respectively. The $\varepsilon/\varepsilon_0$ at 20°C were 1780, 2320 and 2990 for the specimens sintered at 1200, 1300 and 1400°C, respectively. The $\varepsilon/\varepsilon_0$ increased at room temperature and the peaks of temperature dependences of $\varepsilon/\varepsilon_0$ at the phase transition temperatures became sharp, as the sintering temperature increased.

4. Discussion

4.1 Structure of particles

Assuming a spherical and solid BaTiO$_3$ particle, the diameter of the synthesized particle ($d_p$) is calculated by the equation $d_p = (M \cdot C / \rho)^{1/3} \cdot d_m$, where $M$ is the molecular weight of BaTiO$_3$, $C$ the concentration of metal, $\rho$ the theo-
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The theoretical density of BaTiO$_3$ and $d_m$ the diameter of the aqueous microsphere in the emulsion. The value calculated is 225 to 450 nm, which is consistent with that observed and also suggests that the particle is solid.

The SSA values are calculated from the average particle diameters and are 3.1 and 3.0 m$^2$/g for the ECM and HT powders, respectively, provided that the particles are spherical, solid with a smooth surface and uniform in sizes. The calculated value is about half of the measured one for the ECM powder, indicating that the polycrystalline structure of the particle clearly increases the SSA value. On the other hand, the calculated and measured SSA values are in good mutual agreement for the HT powder, which can be explained by the smooth surface of the particles.

4.2 Particle formation

Figure 9 shows the presumed mechanism of the BaTiO$_3$ particle formation by ECM, which consists of the following four steps; (1) the aqueous microsphere is rapidly heated by combustion of kerosene, (2) a precipitation occurs on the surface of the dispersed titania sol particles, (3) the nuclei grow and are sintered during firing and (4) the particle is quenched to form a polycrystalline structure. Our separate observation is consistent with this mechanism. In ECM, hollow particles are likely to be formed by precipitation of the nuclei on the aqueous microsphere surface by rapid heating, as well as in spray pyrolysis. On the other hand, solid alumina particles were obtained when sol particles were contained in aqueous microspheres of the emulsion, because the sol particles were considered to behave as the homogeneously dispersed nuclei and the precipitation occurred not only at the surface of the microsphere but also in it, interrupting the hollow shell formation. In this study, the solid particles were produced for the same reason as that in alumina particle synthesis by ECM.

The high content of Na in the ECM powder is from the surfactant. The measured value (300 ppm) is consistent with the one calculated (310 ppm) from the concentration of Na in the surfactant (700 ppm) and that in the emulsion.

4.3 Sintering behavior

The high surface energy of the ECM powder is responsible for the densification temperature that is lower than that of the HT powder. The polycrystalline structure of the ECM particles results in a high SSA value, which corresponds to the high surface energy and therefore high reactivity of the powder. The ECM powder is also partially chemically heterogeneous, which may enhance the diffusion of the elements and the densification of the specimen. The amount of Na in the ECM powder was found to be higher than that of the HT particles. Na ions may replace Ba ions to create oxygen vacancies and promote sintering in the case of the lead titanate system. However, we found no reports concerning the effects of Na ions on the sinterability of BaTiO$_3$.

The $\varepsilon/\varepsilon_0$ values of the specimens at 20°C are roughly consistent with the reported values, although the exact comparison of the $\varepsilon/\varepsilon_0$ in BaTiO$_3$ ceramics is difficult to determine because it can be affected by the preparation condition of the specimen. Arlt et al. showed that the domain structure was formed to release residual strain in the grains as they grew in BaTiO$_3$ ceramics and that $\varepsilon/\varepsilon_0$ increased with the grain growth by the formation of the mobile domain walls when the grains were less than 1 μm and decreased with the decrease of the domain wall density when the grain size exceeded 1 μm. In our study, sintering at a higher temperature enhanced the grain growth, which led to the formation of the domain structure for the same reason. The increase of $\varepsilon/\varepsilon_0$ can be explained by the formation of the domain structure with the grain growth, although the range of the grain size to increase $\varepsilon/\varepsilon_0$ is different from that reported by Arlt et al. This may result from the differences in the particle properties (e.g., impurity and Ba/Ti ratio). The increased sintering temperature also contributes to the improvement of the crystallinity and/or chemical homogeneity of the specimens, which sharpened the peak of the $\varepsilon/\varepsilon_0$-T curve.

5. Conclusion

Spherical and fine BaTiO$_3$ powder was synthesized by ECM. The synthesized powder exhibited excellent sintering behavior, compared to the commercial powder produced by
a HT process. The polycrystalline structure of the ECM particles was considered to enhance the densification of the specimen upon sintering.

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References