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Effects of dopants on grain growth of nano-sized $BaTiO_3$ powders prepared by citric acid-assisted spray pyrolysis

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Nano-sized $BaTiO_3$ powders doped with Y, Eu and La components were prepared by ultrasonic spray pyrolysis from a spray solution with citric acid. The precursor $BaTiO_3$ powders had a large size, fractured and hollow structures irrespective of the type of dopant. The calcined $BaTiO_3$ powders with and without dopants had nanometre sizes after a simple milling by hand using an agate mortar. The mean size of La-doped $BaTiO_3$ powders measured from the transmission electron microscope (TEM) images was 38 nm at a calcination temperature of 700 °C. The mean crystallite sizes of the doped and undoped $BaTiO_3$ powders changed from 20 to 33 nm according to the type of dopant at a calcination temperature of 700 °C. An effective grain growth inhibition took place with the doped $BaTiO_3$ ceramics. The average grain sizes of La and Eu-doped $BaTiO_3$ ceramics were each 380 and 400 nm at a sintering temperature of 1280 °C.

Key words: Spray pyrolysis, Nano particle, Barium titanate.

Introduction

With further developments in electronics, the miniaturization of electronic parts has proceeded quickly and the desire to increase the capacity of multilayer ceramic capacitors (MLCC) has also become more and more urgent [1, 2]. For MLCC fabrication, a dielectric layer thickness approaching 1 μm that can be co-fired with electrode materials is desired [3, 4]. For this reason, current MLCC industries prefer to use $BaTiO_3$ powders that are nano-sized, structured with regular morphologies, have a narrow size distribution, and show no excessive grain growth after sintering.

Some additives as dopant have been reported to effectively prevent discontinuous grain growth [5, 6]. Effective grain-growth inhibition for donor-doping occurs between 0.20 and 0.40 mol% with materials such as La_2O_3 [7, 8] and Sb_2O_3 [9]. The critical concentration has been conveniently termed the grain-growth inhibition threshold (GGIT) [6]; beyond which, grain growth in donor-doped $BaTiO_3$ ceramics is effectively hindered, the microstructure refined and semiconductivity sharply reduced. Donor-doped $BaTiO_3$ powders with a nanometre size have mainly been prepared by liquid phase reaction methods. Cui et al. prepared Nb-doped $BaTiO_3$ nanocrystalline powders and ceramics by a simple sol-gel process [10]. Nb-doped $BaTiO_3$ ceramics calcined at 1000 °C for 2 h and sintered at 1250 °C for 2 h had a regular microstructure with the maximum dielectric constant of 10,298. Zhao et al. prepared nano-sized $BaTiO_3$ doped with La by sol-gel process [11]. The powder size and grain size decreased with adding dopants.

Nano-sized $BaTiO_3$ powders have also been prepared by gas phase reaction methods. Lee et al. prepared nano-sized $BaTiO_3$ powders by spray pyrolysis from a spray solution containing an organic additive [12]. Xia et al. developed a new preparation strategy for spray pyrolysis to efficiently produce nano-sized $BaTiO_3$ powders, the so called 'salt-assisted' spray pyrolysis process [13]. Submicrometre size powders prepared by salt-assisted spray pyrolysis changed into nano-sized $BaTiO_3$ powders with non-agglomeration characteristics after a repeated washing process using distilled water. However, the donor-doped $BaTiO_3$ powders were not well studied to the gas phase reaction methods.

In this study, donor-doped $BaTiO_3$ powders with a nanometre size were prepared by ultrasonic spray pyrolysis from a spray solution with citric acid. The effects of the type of donor on the characteristics of nano-sized $BaTiO_3$ powders, such as mean size, crystallite size, and morphology, were investigated. The sintering characteristics of the donor-doped $BaTiO_3$ powders were also investigated.

Experimental Procedure

The spray pyrolysis system consisted of a droplet generator, a quartz reactor, and a teflon bag filter. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large amount of droplets, which were carried into the high temperature tubular reactor by a carrier gas. The flow rate of air used as a carrier gas was 45 $Lminute^{-1}$. Droplets and powders evaporated, decomposed, and/or crystallized in the quartz reactor. The

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length and diameter of the quartz reactor were 1200 and 50 mm, respectively.

Barium carbonate and titanium tetra-iso-propoxide (TTIP) were used as starting materials to prepare $BaTiO_3$ powders. The starting materials were added into a mixed solution of water and nitric acid to form a clear solution. The concentration of Ba and Ti was fixed at 0.1 M. The concentration of citric acid used as an organic additive was 0.4 M. Various doping materials such as Y_2O_3, Eu_2O_3, and La_2O_3 were added into the spray solution. The doping concentration of Y, Eu, and La components was 0.02 mol% of $BaTiO_3$. The as-prepared powders obtained by spray pyrolysis were calcined at 700 °C for 2 h in an air atmosphere. The calcined powders were pelletized at 2.45×10^7 Pa pressure into 15 mm diameter pellets. The pellets were then sintered at 1280 °C for 5 h and cooled naturally to room temperature by turning off the furnace power.

The crystal structures of the doped-$BaTiO_3$ calcined at 700 °C for 2 h were investigated using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 Å). The mean crystallite sizes of the $BaTiO_3$ powders were calculated using Scherrer's equation. The morphological characteristics of the powders and pellets were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The calcined powders were milled by hand using an agate mortar for the preparation of TEM samples.

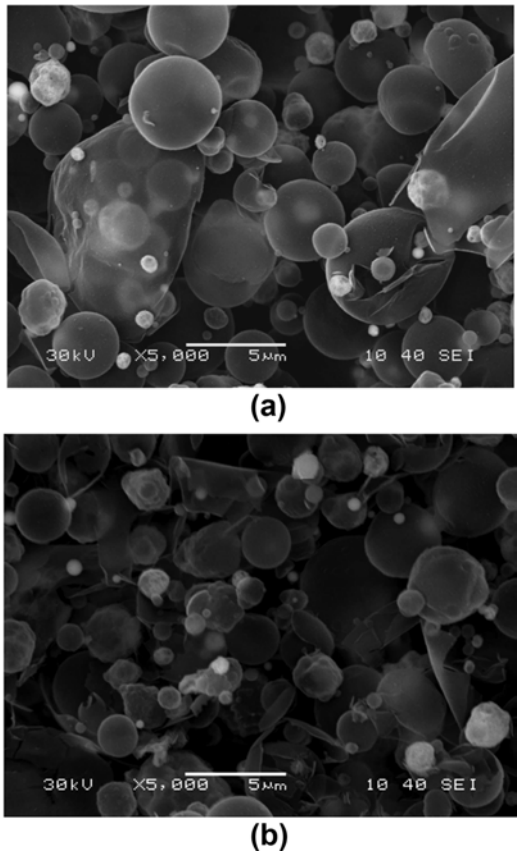

Fig. 1. SEM images of $BaTiO_3$ precursor powders; (a) undoped, (b) La-doped.

Results and Discussion

In spray pyrolysis, hollow powders can be formed when a solute concentration gradient is created during evaporation of droplet. The solute precipitates first at the more highly supersaturated surface if sufficient time is not available for solute diffusion in the droplet. Thus, the morphology of powders is strongly influenced by the preparation conditions in spray pyrolysis. The organic additives added into the spray solution also affect the morphology of the powders prepared by spray pyrolysis by controlling the drying and decomposition stages of the droplets or powders. In this study, $BaTiO_3$ powders with a hollow and porous morphology were prepared by spray pyrolysis from the spray solution with citric acid under severe preparation conditions. The residence time of the powders inside the hot wall reactor was 0.6 s. Figure 1 shows SEM images of precursor $BaTiO_3$ powders with and without La dopant.

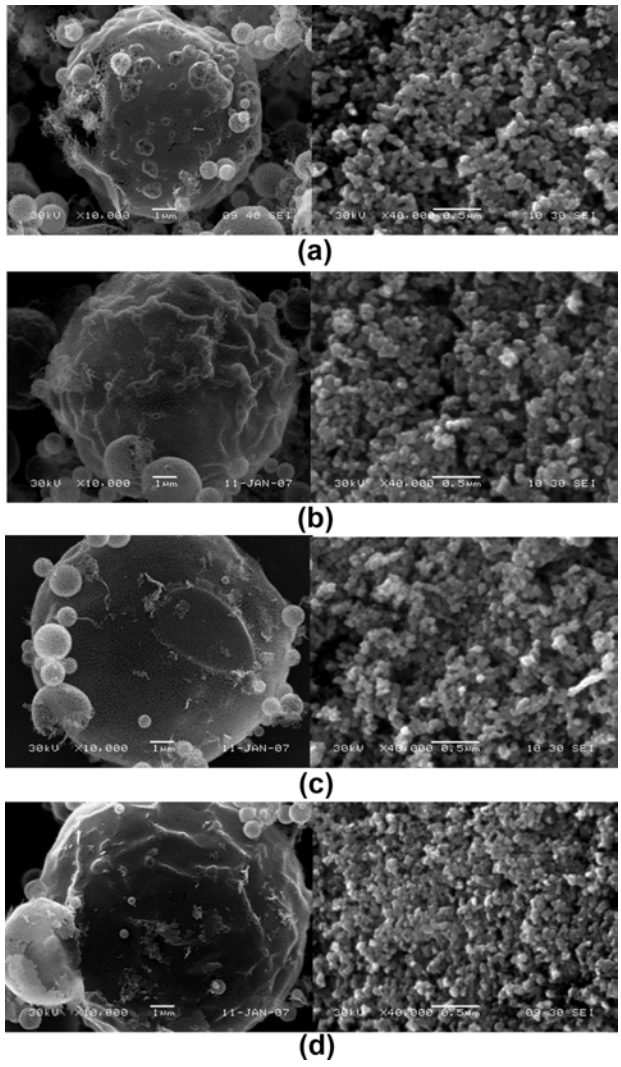

Fig. 2. SEM images of calcined $BaTiO_3$ powders; (a) undoped (b) Y-doped (c) Eu-doped and (d) La-doped.

The precursor $BaTiO_3$ powders with and without the dopant had a large size, with fractured and hollow structures irrespective of the type of dopant. Gas evolution generated by the decomposition of the citric acid caused the powders to be hollow and with thin wall structures. The mechanism of formation of powders with hollow and thin wall structures in spray pyrolysis from a spray solution with organic additives has been described in a previous paper [12].

Figure 2 shows SEM images of the doped and undoped $BaTiO_3$ powders calcined at a temperature of 700 °C for 2 h. The morphologies of the doped and undoped $BaTiO_3$ powders before (left) and after (right) the milling process are shown. The calcined powders were milled by hand using an agate mortar. The spherical shape and several micrometre size of the precursor powders were maintained after calcination. The micrometre-sized $BaTiO_3$ powders had an aggregated morphology of primary powders with a nanometre size irrespective of the dopant. The neck strength between the nano-sized primary powders was weak. Therefore, it was easy to disintegrate the nano-structured $BaTiO_3$ powders into non-aggregated powders with a nanometre size by the simple milling process. The spherical shape and micrometre sizes of the calcined $BaTiO_3$ powders disappeared after this simple milling process. The microstructures of the doped $BaTiO_3$ powders calcined at a temperature of 700 °C are shown in Fig. 3. The calcined $BaTiO_3$ powders had slightly the aggregated morphology of the primary powders with a nanometre size. The mean size of La-doped $BaTiO_3$ powders measured from the TEM images was 38 nm.

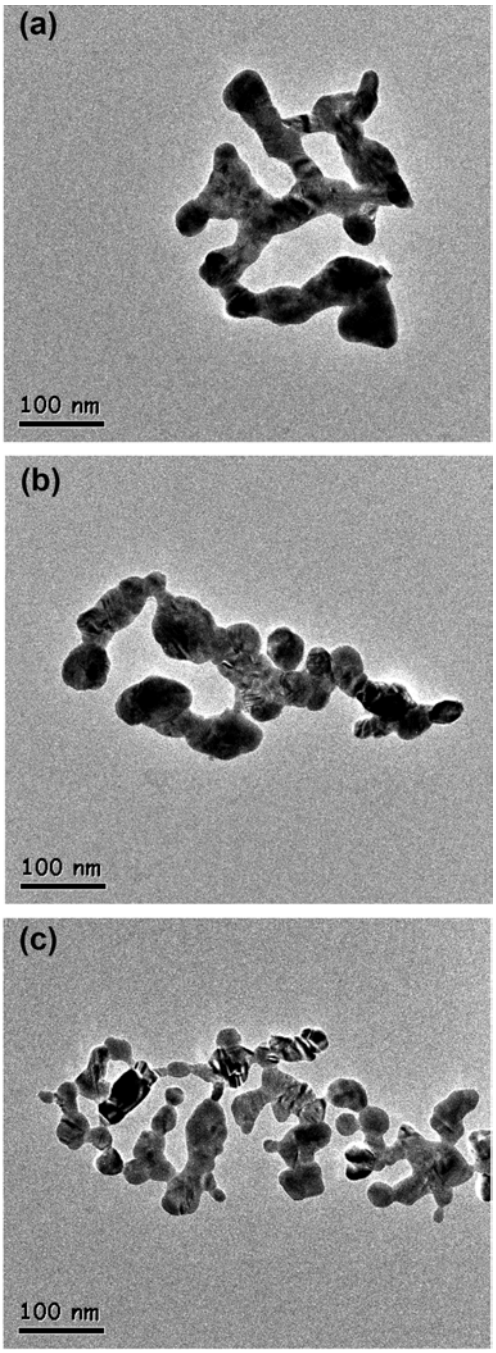

Fig. 3. TEM images of calcined $BaTiO_3$ powders; (a) Y-doped, (b) Eu-doped, (c) La-doped.

Figure 4 shows the XRD patterns of the doped and undoped $BaTiO_3$ powders calcined at a temperature of 700 °C for 2 h. The calcined $BaTiO_3$ powders had a pure cubic phase regardless of the type of dopant. However, the crystallinities of the powders were affected by the type of dopant. The mean crystallite size of the doped and undoped $BaTiO_3$ powders changed from 20 to 33 nm according to the type of dopant. The mean crystallite size of the powders were calculated using Scherrer's equation from the width of the XRD peaks located at $2\theta = 31.7°$.

The type of dopant affected the characteristics of the sintered $BaTiO_3$ pellets. Figure. 5 shows SEM images of the surfaces of sintered $BaTiO_3$ ceramics. From the SEM images, it can be seen that the grains have grown well with a regular and dense crystal shape. Interestingly, an effective grain growth inhibition took place with the doped $BaTiO_3$ ceramics, while the pure $BaTiO_3$ has a large grain size of 3-4 μm. This result is similar to the

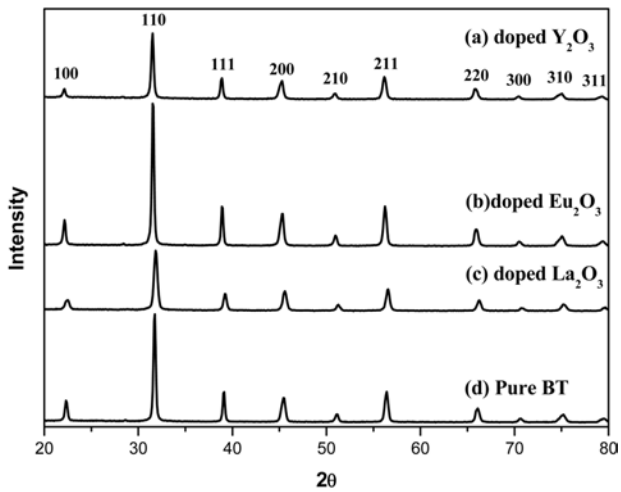

Fig. 4. X-ray diffraction patterns of calcined $BaTiO_3$ powders.

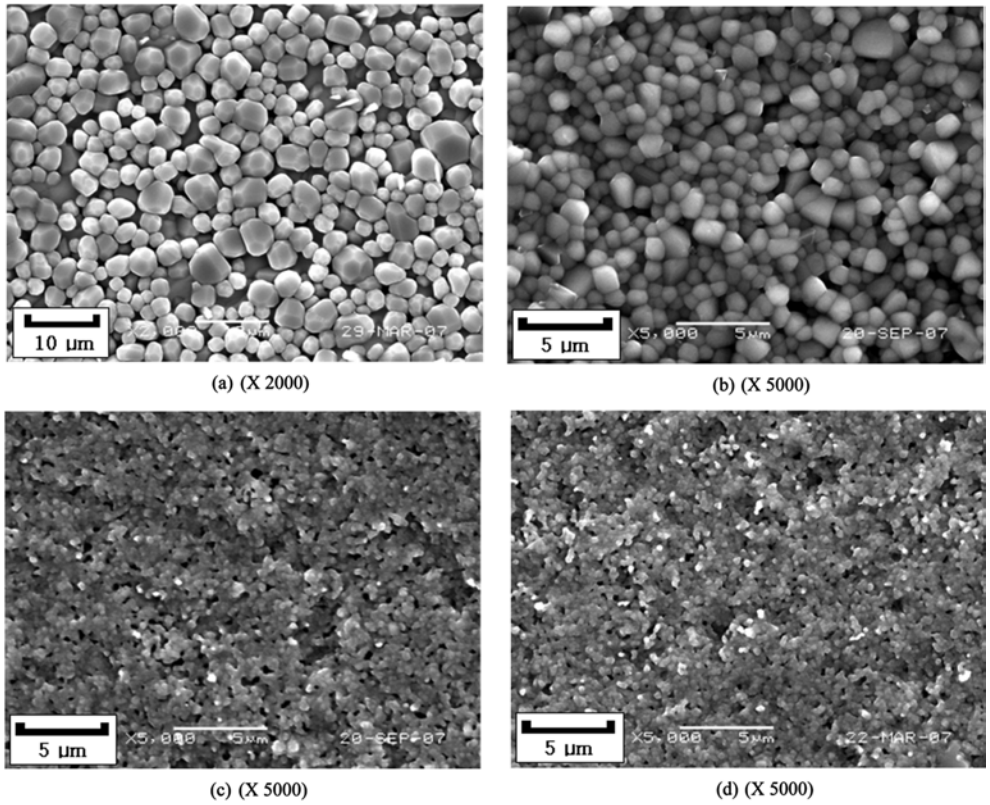

Fig. 5. Microstructures of $BaTiO_3$ pellets; (a) undoped, (b) Y-doped, (c) Eu-doped, (d) La-doped.

Ti-excess $BaTiO_3$ powders with donor oxides [7, 14-16]. Suppressed growth microstructures below 500 nm are shown in Fig. 5(c), (d). The average grain sizes of La and Eu-doped $BaTiO_3$ ceramics, estimated from SEM images, were 380 and 400 nm respectively.

Conclusions

The type of dopant affected the characteristics of nano-sized $BaTiO_3$ powders prepared by ultrasonic spray pyrolysis, such as the mean size, mean crystallite size, and morphology. The type of dopant also affected the characteristics of the sintered $BaTiO_3$ ceramics. The grains of $BaTiO_3$ ceramics grew well densely with a regular shape. The pure $BaTiO_3$ ceramic had a large grain size of 3-4 μm. However, doped $BaTiO_3$ ceramics had fine grain sizes below 500 nm and regular microstructures after sintering at a temperature of 1280 °C in an air atmosphere.

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