Spherical shape BaNd$_2$Ti$_5$O$_{14}$ powders prepared by spray pyrolysis

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Spherical shape BaNd$_2$Ti$_5$O$_{14}$ (BNT) powders were prepared by post-treatment of the precursor powders obtained by spray pyrolysis. The mean size and geometric standard deviation of the powders prepared at a low flow rate of the carrier gas as 5 L/min were 0.73 μm and 1.30. The powders post-treated at a temperature of 1000°C had a single phase of BNT without impurity peaks. The BNT powders had similar compositions to that of the spray solution. Necking between the powders occurred at a sintering temperature of 1100°C. The BNT powders with spherical shape changed to the rod-like crystals after sintering at temperatures above 1200°C. The aspect ratio of the rod-like crystals increased with increasing the sintering temperatures.

1. Introduction

BaNd$_2$Ti$_5$O$_{14}$ (BNT), which is one of the important compound of Ba–Nd–Ti–O system, has been known as an important microwave dielectric material because of high dielectric constant, low dielectric loss and a near-zero temperature coefficient of resonant frequency. However, the high sintering temperatures above 1300°C are required to sinter the BNT ceramic. Therefore, lowering the sintering temperature of BNT is required to cofire BNT with metal electrode such as silver. Glass or glass-ceramic systems were widely studied to lower the sintering temperatures of the BNT ceramic. The sintering characteristics of the BNT ceramic were also affected by the mean sizes and morphologies of the BNT powders.

BNT powders were mainly prepared by solid-state reaction method. Phase pure BNT powders were prepared by solid-state reaction method at high sintering temperatures above 1200°C. Therefore, the BNT powders prepared by solid-state reaction method had large size and irregular morphologies. Liquid solutions methods including pechini method were applied to prepare the powders of Ba–Nd–Ti–O system at low sintering temperatures. Xu et al. prepared the powders of Ba–Nd–Ti–O system by the modified pechini method using ethylenediaminetetraaceticacid (EDTA). BNT powders prepared by liquid solution methods had fine sizes and non-spherical shapes. However, gas phase-reaction methods were not well applied to prepare the powders of Ba–Nd–Ti–O system.

Spray pyrolysis, which is one of the gas phase reaction method, has been successfully applied to synthesize the ceramic powders because it is a simple, continuous process, and produces powders with spherical shape, narrow size distributions, and high phase purity. The morphologies of powders prepared by spray pyrolysis are affected by the preparation conditions such as flow rate of the carrier gas, concentration of the spray solution, residence time of powders inside the reactor, temperature of the reactor, and temperature profile of the reactor. The powders prepared at the severe preparation conditions such as high flow rate of the carrier gas and short residence time of powders inside the reactor have more hollow and/or porous structure because of high solvent drying rate and lack of time for solute diffusion and powder densification. However, Ba–Nd–Ti–O system was not well studied in the spray pyrolysis. In this study, BNT powders were prepared by spray pyrolysis. The effects of flow rate of the carrier gas on the morphological characteristics of the as-prepared and post-treated powders were investigated. The spherical shape of the precursor powders obtained by spray pyrolysis maintained after post-treatment at a temperature of 1000°C. The sintering characteristics of the prepared BNT powders were investigated.

2. Experiments

The spray pyrolysis equipment used consisted of droplet generator, quartz reactor, and a teflon bag filter (powder collector). A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large amount of droplets, which are carried into the high temperature tubular reactor by a carrier gas. The length of the heating zone maintained at a temperature of 900°C was 80 cm. The length and diameter of the quartz reactor were 1,000 mm and 50 mm, respectively. The flow rates of air used as a carrier gas were changed from 10 to 40 L/min. The spray rate of the spray solution was 500 ml/h. The starting materials used in the synthesis of BNT powders were barium carbonate, neodymium nitrate, titanium tetra-iso-propoxide (TTIP). A small amount of nitric acid was used to peptize the hydrolyzed TTIP and form a clear solution. The total concentrations of Ba, Nd and Ti components were 0.07 and 0.5 mol/L. The precursor powders obtained by spray pyrolysis were post-treated at temperatures between 600 and 1000°C for 3 h in air atmosphere. The prepared BNT powders were pelletized at 320 MPa pressure into a 15 mm diameter. The pellets were then sintered at temperatures between 1100 and 1400°C for 3 h and cooled naturally to room temperature while furnace power was off.

The crystal structures of the precursor and post-treated BNT powders were investigated using X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5418 × 10–10 m). The morphological characteristics of the powders were investigated using scanning electron microscopy. The dielectric permittivity and loss were measured using a HP 4194A impedance analyzer (4 Hz–1 MHz).
electron microscopy (SEM). The specific surface areas and pores size distributions were measured by Brunauer-Emmet-Teller (BET) method using N₂ adsorption.

3. Results and discussion

The morphologies of the powders prepared by spray pyrolysis were strongly affected by the preparation conditions. Flow rate of the carrier gas is a key factor in large production of powders with controlled morphology. Figure 1 shows the SEM images of the precursor powders prepared at different flow rate of the carrier gas. The total concentration of metal components was 0.5 mol/L. The precursor powders had spherical shape irrespective of the flow rate of the carrier gas. However, the mean sizes and size distributions of the precursor powders were affected by the flow rate of the carrier gas. Figure 2 shows the size distributions of the precursor powders measured from the SEM images. In order to minimize errors, the mean sizes of the powders were determined from their SEM images by counting more than 500 powders in each sample. The mean size and geometric standard deviation of the precursor powders as shown in Fig. 1(a) were 0.73 μm and 1.30. On the other hand, the mean size and geometric standard deviation of the precursor powders as shown in Fig. 1(d) were 0.90 μm and 1.62. The different morphologies of the powders prepared at low and high flow rates of the carrier gas affected the mean sizes and size distributions of the precursor powders. The precursor powders prepared at a high flow rate of the carrier gas had more hollow morphology than those prepared at a low flow rate of the carrier gas because of high drying and decomposition rates of droplets and powders. Figure 3 shows the pore size distributions of the precursor powders as shown in Figs. 1(a) and (d). The precursor powders had meso (2 nm–10 nm).
nm) and macro pores (10 nm >) irrespective of the flow rate of the carrier gas. However, the pore volumes of the precursor powders were affected by the flow rate of the carrier gas. The precursor powders prepared at a high flow rate of the carrier gas had large pore volume of 0.076 cm$^3$/g. On the other hand, the precursor powders prepared at a low flow rate of the carrier gas had small pore volume of 0.025 cm$^3$/g. The BET surface areas of the precursor powders as shown in Figs. 1(a) and (d) were 7.7 and 17.8 m$^2$/g.

Figure 4 shows the XRD patterns of the precursor and post-treated powders. The precursor powders obtained by spray pyrolysis were post-treated at temperatures between 600 and 1000°C. The precursor powders obtained by spray pyrolysis had amorphous phase without crystal structure because of short residence time of the powders inside the hot wall reactor. The flow rate of the carrier gas was 40 L/min. The powders post-

![Figure 3: Pore size distributions of the precursor powders prepared by spray pyrolysis.](image)

![Figure 4: XRD patterns of the BNT powders post-treated at various temperatures.](image)

![Figure 5: SEM images of the BNT powders post-treated at a temperature of 1000°C.](image)
treated at temperatures of 800 and 860°C had XRD peaks of Nd₂Ti₃O₈.7 crystal structure. The powders had a single phase of BNT without impurity peaks after post-treatment at temperatures of 900 and 1000°C. However, the post-treated powders at a temperature of 1000°C had sharp crystal peaks. Therefore, the morphologies of the powders post-treated at a temperature of 1000°C were investigated.

Figure 5 shows the SEM images of the post-treated powders at a temperature of 1000°C for 3 h. The spherical shapes of the precursor powders maintained after post-treatment irrespective of the flow rate of the carrier gas. The powders obtained at a high flow rate of the carrier gas had more porous structure than those obtained at a low flow rate of the carrier gas. Figure 6 shows the XRD patterns of the post-treated powders. The post-treated powders had a single phase of BNT without impurity peaks irrespective of the flow rate of the carrier gas. The high mixing degrees of the Ba, Nd and Ti components in the precursor powders obtained by spray pyrolysis produced the single phase BNT powders without impurity phase. Figure 7 shows the EDX spectra of the post-treated BNT powders as shown in Fig. 5(a) and (d). The compositions of the BNT powders measured from the EDX spectra were described in Table 1. The BNT powders had similar compositions to that of the spray solution.

Figure 8 shows the SEM images of the precursor and post-treated powders prepared from the spray solution with low concentration. The concentration of the spray solution was 0.07 mol/L. The mean size of the precursor powders as shown in Fig. 8(a) was 0.4 μm. In this study, one powder was formed from one droplet. Therefore, the mean sizes of the precursor powders decreased with decreasing the concentrations of the spray solution. The spherical shape of the precursor powders obtained from the spray solution with low concentration was maintained after post-treatment as shown in Fig. 8(b). However, slight aggregation between the powders occurred.
Figure 9 shows the surface characteristics of the pellets sintered at various temperatures. Necking between the powders occurred at a sintering temperature of 1100°C. The BNT powders with spherical shape changed to the rod-like crystals after sintering at temperatures above 1200°C. The aspect ratio of the rod-like crystals increased with increasing the sintering temperatures. The densities and microstructures of the sintered pellets are strongly affected by the morphologies and mean sizes of the BNT powders. BNT powders with fine size and spherical shape are required to obtain the sintered pellet with high density and fine grain size. In the spray pyrolysis, the mean size of the BNT powders with spherical shape could be controlled by changing the concentrations of the spray solutions. However, in this study, the preliminary study of the sintering characteristics of the BNT powders prepared by spray pyrolysis was performed. Glass powders should be used to improve the sintering characteristics of the BNT powders. Therefore, the sintering characteristics of the BNT powders will be investigated by further studies.

4. Conclusions

BNT powders with submicron size and spherical shape were prepared by spray pyrolysis. The precursor powders prepared at
a low flow rate of the carrier gas had more dense morphology than those prepared at a high flow rate of the carrier gas. The different morphologies of the powders prepared at low and high flow rates of the carrier gas affected the mean sizes and size distributions of the precursor powders. The spherical shapes of the precursor powders maintained after post-treatment irrespective of the flow rate of the carrier gas. The BNT powders with spherical shape changed to the rod-like crystals after sintering at high temperatures.

References