

## Fine-sized $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ powders prepared by spray pyrolysis from polymeric precursors

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$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT) powders with nanometre and micrometre sizes were prepared by an ultrasonic spray pyrolysis process. The BNT powders obtained from the spray solution without citric acid had a spherical shape and micrometre size. On the other hand, the BNT powders obtained from a spray solution with 0.4 M citric acid had nanometre size at a calcination temperature of 700 °C. Single phase BNT powders with a rhombohedral structure were obtained at a calcination temperature of 700 °C. The sintering of pellets obtained from the micrometre sized BNT powders started at a temperature of 900 °C. On the other hand, sintering and grain growth of the pellet obtained from the nanometre sized BNT powders occurred even at the low temperature of 850 °C. The relative densities of the pellets obtained from the nanometre sized BNT powders were 95 and 96% of the theoretical density of BNT at sintering temperatures of 950 and 1000 °C. The mean grain sizes of the pellets sintered at temperatures of 950 and 1000 °C were the same at 1.10  $\mu\text{m}$ .

**Key Words:** spray pyrolysis, nano powder.

### Introduction

At present, the most widely used piezoelectric materials are  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT)-based ceramics because of their superior piezoelectric properties. However, the toxicity of lead oxide and its high vapor pressure during sintering processing cause a serious ecological problem. To reduce and eliminate lead pollution and replace PZT-based ceramics, lead-free piezoelectric materials have been studied [1-3].

Bismuth sodium titanate,  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT), is considered to be an excellent candidate for use in lead-free piezoelectric ceramics [1-3]. With a perovskite structure of rhombohedral symmetry at room temperature [4-6], it shows a strong ferroelectric property with a relatively high Curie temperature of 320 °C and a large remnant polarization ( $\sim 38 \mu\text{Ccm}^{-2}$ ) [2, 7-10]. Therefore, BNT ceramics have great potential for use in a wide range of applications such as for surface acoustic wave (SAW) substrates, ultrasonic generators, ferroelectric random access memory (FRAM), etc.

To improve the properties of BNT ceramics, the use of a low sintering temperature is desired to obtain a close stoichiometric or nominal composition, apart from an energy cost consideration. This is because at high temperature the presence of intrinsic point defects as well as the loss of volatile compounds usually occurs [11].

To reduce the sintering temperature or improve the densification of ceramics, various techniques have been

adapted. These include the use of non-conventional sintering processes such as spark plasma sintering, microwave sintering, multi-step sintering, and reactive sintering. Another method is to fabricate ceramics by utilizing fine particles in submicrometre or nanometre range, which are prepared by high energy ball milling or by some chemical routes.

Spray pyrolysis as an aerosol process has been successfully applied to prepare ceramic powders, because it is simple, inexpensive, and a continuous process, and the powders prepared have narrow size distributions and high phase purity [12, 13]. In this process, a misted stream of precursor solution containing various compositions is dried, precipitated, and decomposed in a tubular furnace reactor continuously. The as-prepared powders obtained from the spray solution with organic additives under severe preparation conditions such as a high flow rate of carrier gas have hollow and thin walled structures [12, 13]. The powders with hollow and thin walled structures turn into the nano-sized powders after post-treatment at high temperature. Therefore, nano-sized powders prepared by spray pyrolysis have good crystallinity and high purity.

In this study, nano-sized BNT powders were prepared by an ultrasonic spray pyrolysis process. The effects of citric acid as an organic additive on the mean size and morphology of the BNT powders obtained after calcination were investigated. The effects of nano-sized BNT powders on the sintering characteristics were also investigated.

### Experimental Procedure

The spray pyrolysis equipment used consisted of droplet generator, quartz reactor, and a Teflon bag filter. A 1.7 MHz ultrasonic spray generator having six vibrators was used

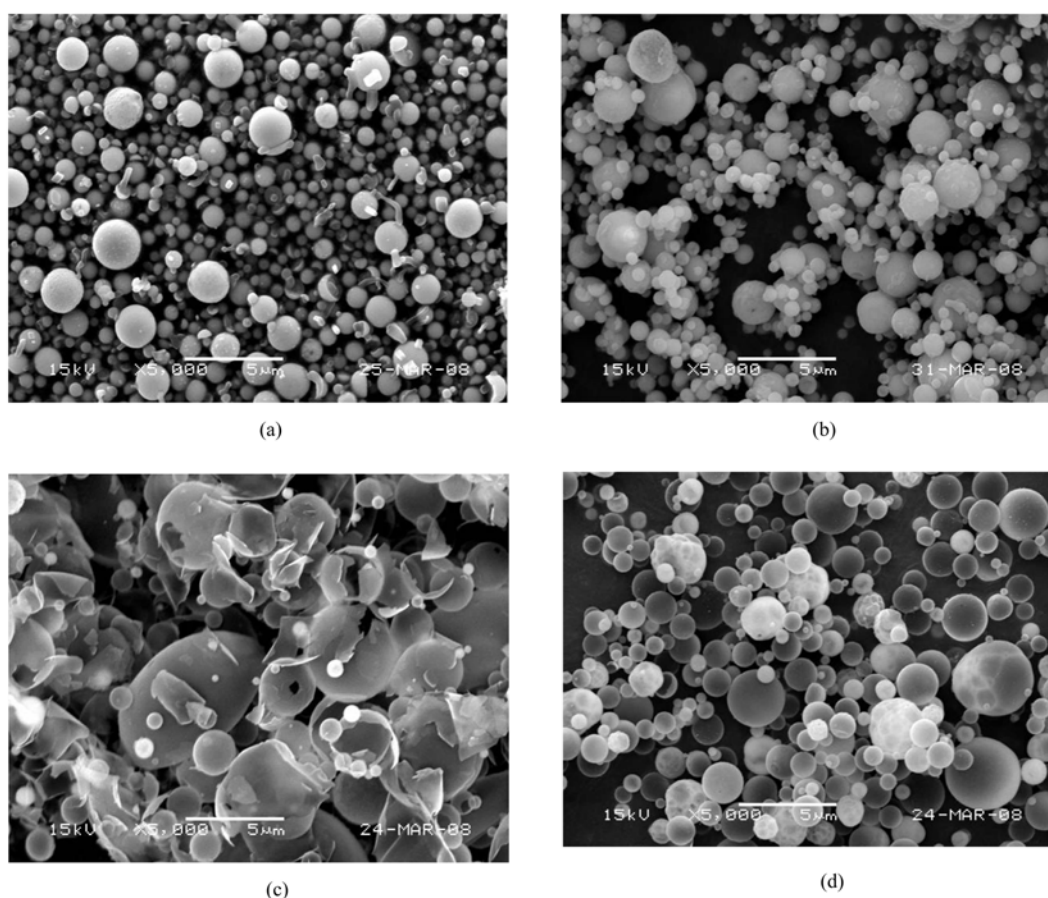
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to generate a large amount of droplets, which were carried into the high temperature tubular reactor by a carrier gas. The flow rate of air used as a carrier gas was  $40 \text{ Lmin}^{-1}$ . The length and diameter of the quartz reactor were 600 and 50 mm, respectively. Bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and titanium tetra-iso-propoxide ( $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ) were used as starting materials to prepare the BNT powders. The overall solution concentration of Bi, Na and Ti components was fixed as 0.2 M. The concentration of citric acid monohydrate used as an organic additive was changed from 0.1 to 0.8 M. The precursor powders obtained by spray pyrolysis were calcined at temperatures between 500 and  $900^\circ\text{C}$  for 3 h in an air atmosphere. The calcined powders were milled by hand using an agate mortar. The crystal structures of the precursor and calcined BNT powders were investigated using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The mean crystallite sizes of the BNT powders were calculated using Scherrer's equation. Measurement of the thermal properties of the precursor powders was performed in a thermo-analyzer (TG-DSC, Netzsch, STA409C, Germany) in the temperature range from 40 to  $900^\circ\text{C}$  ( $10^\circ\text{Cmin}^{-1}$ ). The powders calcined at  $700^\circ\text{C}$  were pelletized at 24.5 MPa pressure into an 18.2 mm diameter. The pellets were then sintered from

$800$  to  $1000^\circ\text{C}$  for 3 h and cooled naturally to room temperature with the furnace power off. The morphological characteristics of the powders and sintered ceramics were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060). Sample densities were measured by the Archimedes' method.

## Results and Discussion

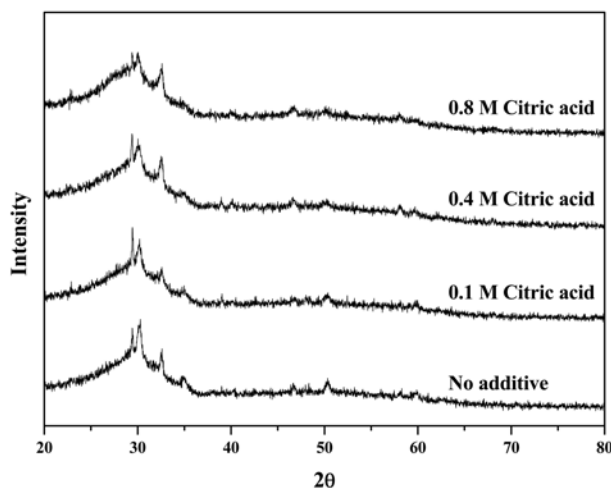
In spray pyrolysis, hollow powders can be formed when a solute concentration gradient is created during evaporation of droplets. The solute precipitates first at the more highly supersaturated surface if sufficient time is not available for solute diffusion in the droplet. Thus, the morphology of powders 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. The BNT precursor powders with filled or hollow structures were prepared by spray pyrolysis from the spray solutions with and without citric acid. The effect of the concentration of citric acid added to the spray solutions on the morphology of the BNT precursor powders is shown in Fig. 1. The precursor powders obtained from the spray solution without citric acid had some irregular and distorted shapes. On the order



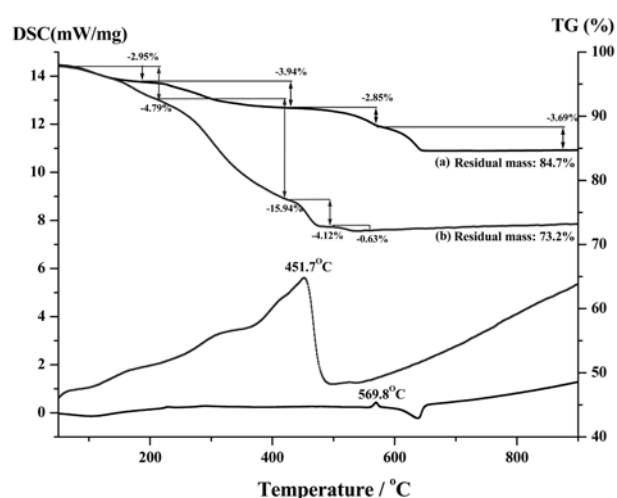
**Fig. 1.** SEM images of the precursor powders prepared by spray pyrolysis from spray solutions with different concentrations of citric acid. (a) No additive; (b) 0.1 M CA; (c) 0.4 M CA; (d) 0.8 M CA.

hand, the powders prepared from the spray solutions with citric acid had different morphologies, according to the concentration of citric acid. The precursor powders obtained from the spray solution with a low concentration of citric acid as 0.1 M were several micrometres in size, had a spherical shape and filled morphology. The BNT precursor powders with large size, hollow and thin walled structures were prepared from the spray solution with an optimum concentration of citric acid at 0.4 M. The high drying and decomposition rates of particles and the gas evolution from the decomposition of the citric acid generated BNT precursor particles with a non-spherical shape, hollow and thin wall structures. The hollow wall of the BNT precursor powders (Fig. 1c) had a low thickness below 50 nm in the high magnification SEM image. However, the precursor powders (Fig. 1d) obtained from the spray solution with a high concentration of citric acid had a spherical shape and slightly filled morphology. The high concentration of citric acid within the droplet formed a highly viscous gel during the drying and decomposition processes of the droplets. The viscous gel promoted the volume precipitation of precursors within the droplets and decreased the mean size of the precursor powders with a spherical shape.

Fig. 2 show the XRD patterns of the precursor powders obtained from the spray solutions with and without citric acid. The precursor powders consist of mostly of an amorphous phase and a small amount of nanocrystals irrespective of the spray solutions because of the short residence time of the powders inside the hot wall reactor as 0.3 s. The thermal properties of the BNT precursor powders prepared by spray pyrolysis from the spray solution with and without citric acid are shown in Fig. 3. The concentration of citric acid was 0.4 M. The TG curve of the precursor powders prepared from the spray solution without citric acid shows several weight losses at temperatures below 700 °C. The first pronounced weight loss region below 200 °C resulted from the loss of adsorbed water. The losses of weight between 200 and 650 °C were caused by incomplete



**Fig. 2.** XRD patterns of the precursor powders prepared by spray pyrolysis.

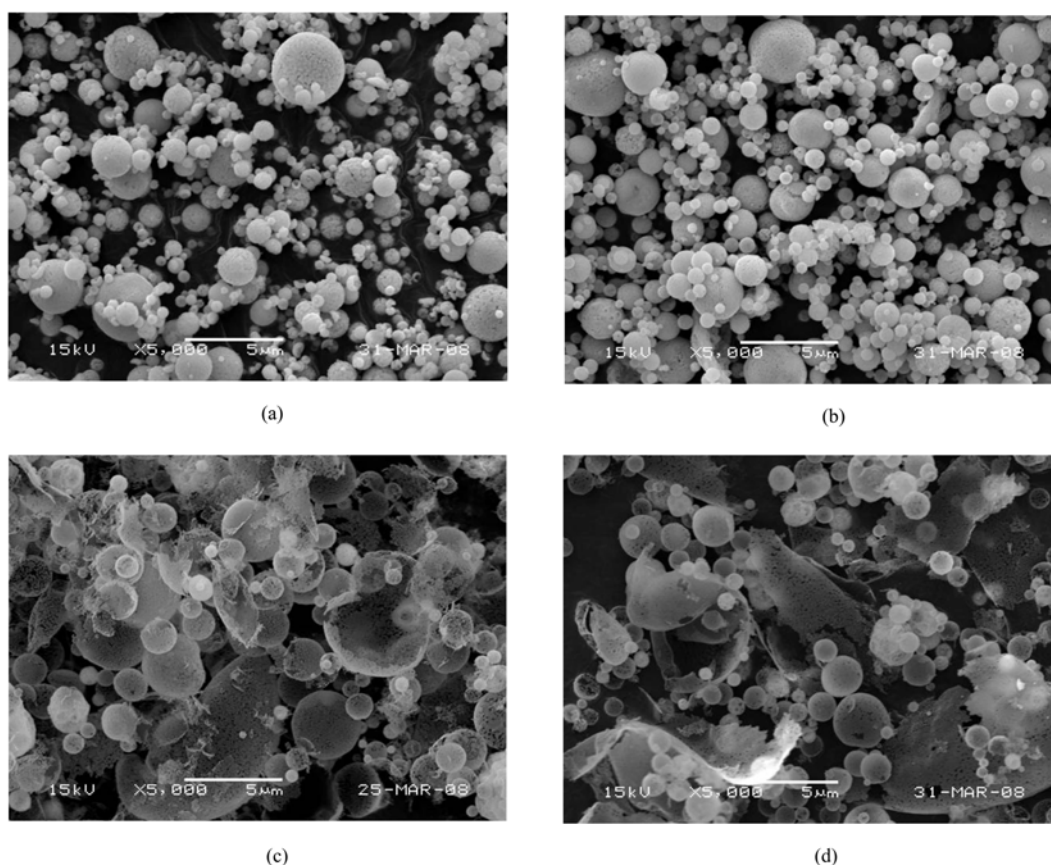


**Fig. 3.** TG/DSC curves of the precursor powders prepared by spray pyrolysis from spray solutions with and without citric acid. (a) No additive; (b) 0.4 M CA.

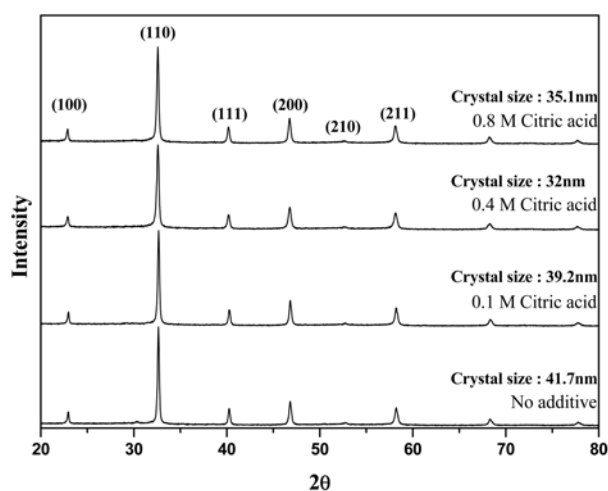
decomposition of the precursors. However, the precursor powders obtained from the spray solution with citric acid had a large weight loss compared to those obtained from the spray solution without citric acid. The complicated exothermic peaks and weight loss of the precursor powders obtained from the spray solution with citric acid appeared at temperatures between 200 and 500 °C. The large weight loss region from 200 to 500 °C is related to the decomposition of residual carbon components. The exothermic peak at 451.7 °C in the DSC curve corresponds to the decomposition of a residual carbon component.

The effect of the concentration of citric acid added into the spray solution on the morphologies of the calcined powders were investigated by SEM. Fig. 4 shows the SEM images of the BNT powders calcined at a temperature of 700 °C. The BNT powders obtained from the spray solution without citric acid and with low a concentration of citric acid had sizes of several micrometre and spherical shapes. On the other hand, the BNT powders obtained from the spray solution with adequate concentrations of citric acid had slightly aggregated morphologies of the primary powders with nanometre sizes. The precursor powders with hollow and thin walled structures formed slightly aggregated BNT powders with nanometre sizes after calcination.

Fig. 5 shows the XRD patterns of the calcined BNT powders obtained from the spray solutions with and without citric acid. The BNT powders calcined at 700 °C for 3 h were single phase with a rhombohedral structure, in agreement with the patterns reported in the literature [14]. The mean crystallite sizes of the BNT powders changed from 32 to 41.7 nm according to the concentration of citric acid added into the spray solutions. The powders obtained from the spray solution with 0.4 M citric acid had the smallest mean crystallite size of 32 nm. Fig. 6 shows the XRD patterns of the BNT powders calcined at different temperatures. The powders obtained from



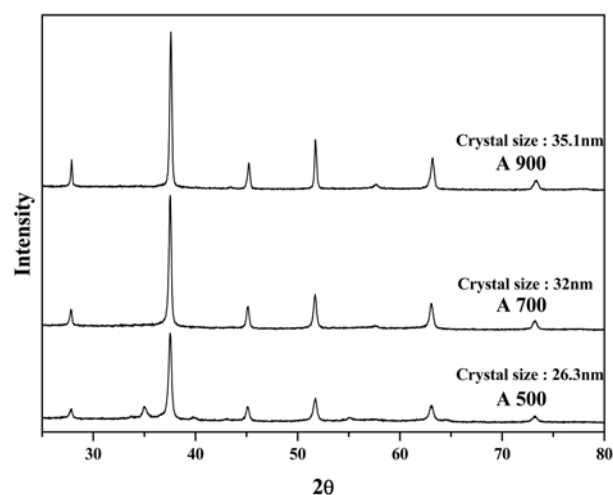
**Fig. 4.** SEM images of the BNT powders calcined at a temperature of 700 °C. (a) No additive; (b) 0.1 M CA; (c) 0.4 M CA; (d) 0.8 M CA.



**Fig. 5.** XRD patterns of the BNT powders calcined at 700 °C.

the spray solution with 0.4 M citric acid were calcined at various temperatures. The single BNT phase started to show up at 700 °C and the mean crystallite size increased with an increase in the calcination temperature.

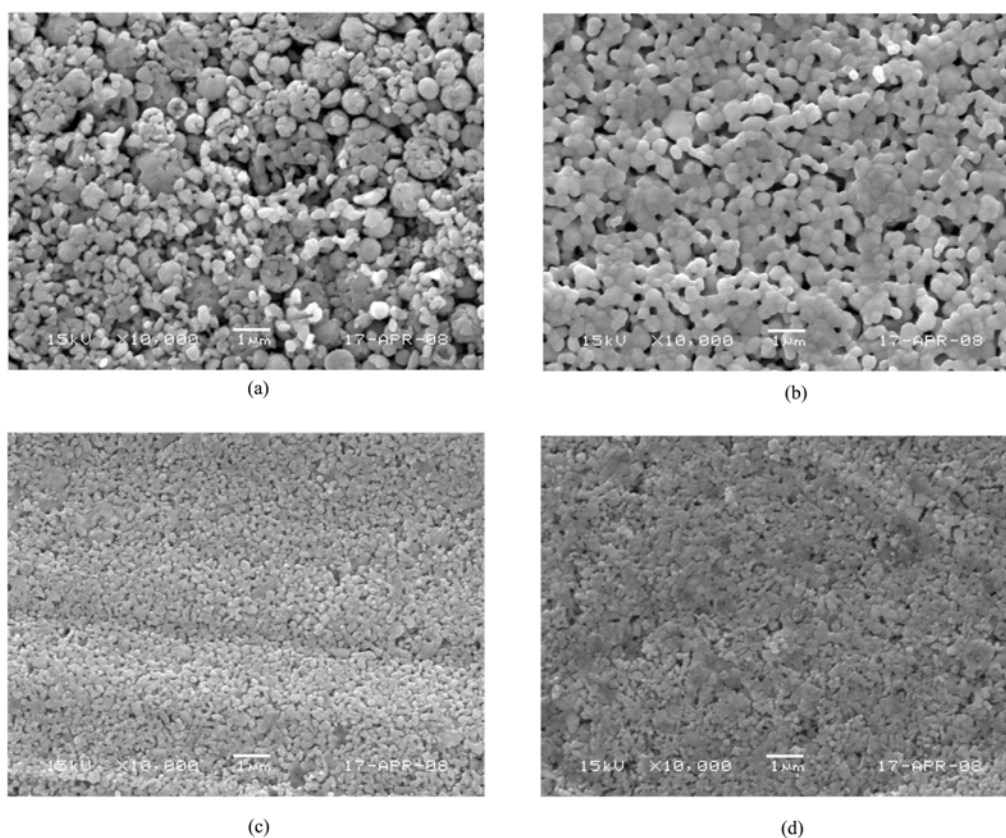
Fig. 7 shows the surface morphologies of the sintered BNT pellets. The BNT powders as shown in Fig. 4 were pelletized and then sintered at 800 °C for 3 h. The sintering of the powders obtained from the spray solution without citric acid did not occur at a sintering temperature of 800 °C.



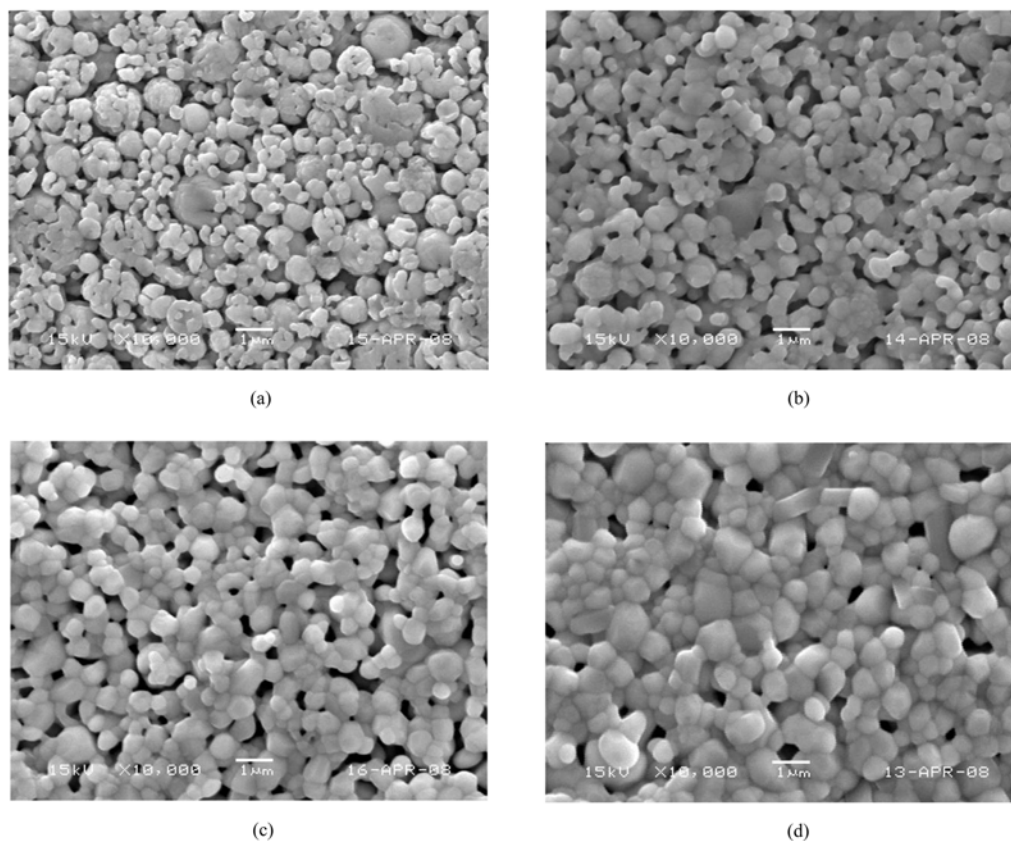
**Fig. 6.** XRD patterns of the BNT powders calcined at different temperatures.

On the other hand, sintering between the powders obtained from the spray solutions with citric acid occurred at the same sintering temperature. The pellets obtained from the powders with nanometre sizes had dense structures and fine grain sizes.

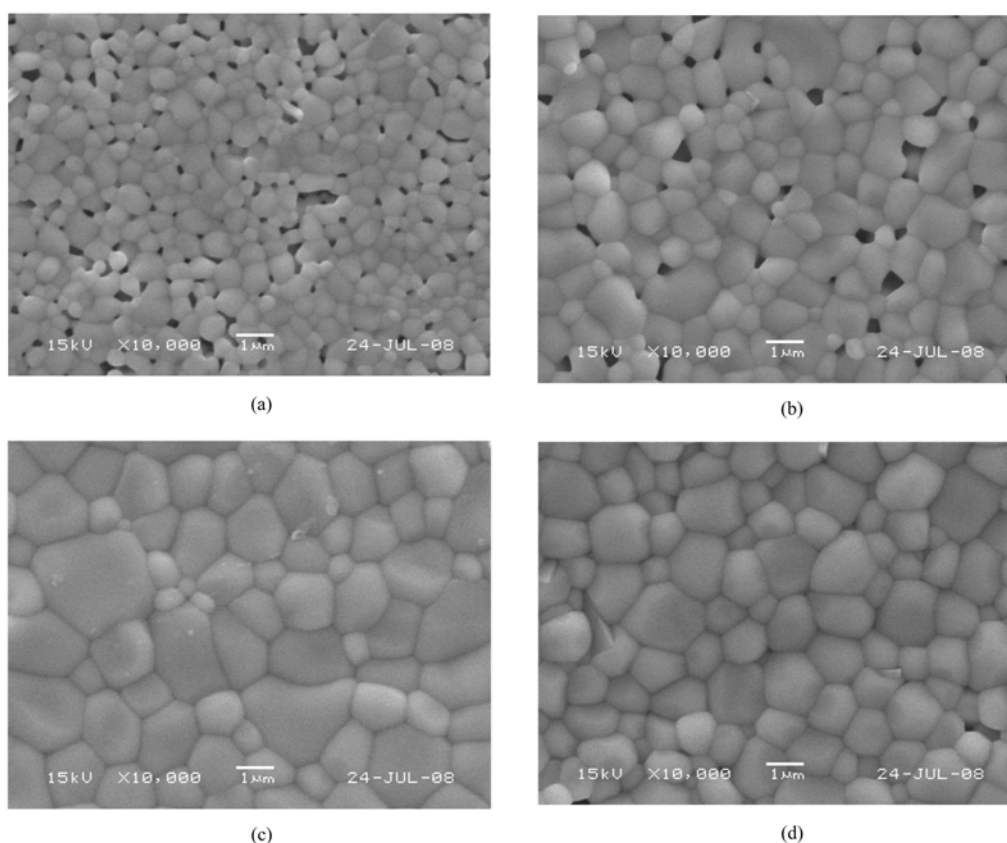
Figs. 8 and 9 show the SEM images of the BNT pellets sintered at various temperatures. The pellets obtained from the powders as shown in Fig. 4(a) and (c) were sintered



**Fig. 7.** SEM images of the BNT ceramics sintered at 800 °C. (a) No additive; (b) 0.1 M CA; (c) 0.4 M CA; (d) 0.8 M CA.



**Fig. 8.** SEM images of the BNT ceramics obtained from the micrometre-sized powders at different sintering temperatures. (a) 850 °C; (b) 900 °C; (c) 950 °C; (d) 1000 °C.



**Fig. 9.** SEM images of the BNT ceramics obtained from the nanometre-sized powders at different sintering temperatures. (a) 850 °C; (b) 900 °C; (c) 950 °C; (d) 1000 °C.

at temperatures between 850 and 1000 °C. The mean sizes of the BNT powders prepared by spray pyrolysis affected the sintering characteristics of the pellets. A remarkable sintering of the pellet obtained from the BNT powders with a micrometre size occurred at a temperature of 900 °C. On the other hand, sintering and grain growth of the pellet obtained from the BNT powders with a nanometre size occurred even at the low temperature of 850 °C. The pellet obtained from the BNT powders with a micrometre size had a porous structure even at a high sintering temperature of 1000 °C. However, pores inside the sintered pellets obtained from the BNT powders with a nanometre size were not observed at a sintering temperature of 950 °C. The relative densities and mean grain sizes of the pellets shown in Fig. 9 are shown in Table 1. The relative densities of the pellets increased

with an increase in the sintering temperatures. The pellets sintered at temperatures of 950 and 1000 °C were 95 and 96% of the theoretical density of BNT. The mean grain sizes of the pellets were also increased with an increase in the sintering temperature. However, the mean grain sizes of the pellets sintered at temperatures of 950 and 1000 °C were the same at 1.10 μm.

## Conclusions

The mean sizes and morphologies of the BNT powders prepared by ultrasonic spray pyrolysis were controlled by changing the concentrations of citric acid added into the spray solutions. The BNT powders obtained from the spray solution without citric acid had micrometre sizes, spherical shapes and dense inner structures before and after calcination. On the other hand, the precursor powders obtained from the spray solution with an optimum concentration of citric acid at 0.4 M had a large size, hollow and thin walled structure. The precursor powders with a hollow and thin walled structure turned into nanometre size BNT powders after calcination. The mean size of the BNT powders affected the sintering characteristics of the pellets. Sintering of the pellets obtained from the nanometre sized BNT powders occurred at low temperatures. The pellet obtained from the nanometre sized BNT powders had a high relative density at a low sintering temperature of 950 °C.

**Table 1.** Characteristics of BNT ceramics obtained from the nano-sized powders at different sintering temperatures.

Sintering temperature (°C)	Percentage of theoretical density (%)	Average grain size (μm)
800	76	0.18
850	86	0.48
900	90	0.77
950	95	1.10
1000	96	1.10

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