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# Nano-sized barium titanate powders with tetragonal crystal structure prepared by flame spray pyrolysis

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## Abstract

Nano-sized $BaTiO_3$ powders with regular morphology and tetragonal crystal structure were prepared by flame spray pyrolysis from a spray solution with citric acid. The precursor powders prepared at the low flow rates of fuel gas at 2 and 2.5 L/min had large, hollow, thin wall structures. On the other hand, the precursor powders prepared at a high flow rate of fuel gas at 4 L/min had a dense submicronic structure. Those precursor powders with a hollow, thin wall structure formed a slightly aggregated $BaTiO_3$ of nanometer-sized primary powders after post-treatment. The slightly aggregated $BaTiO_3$ became nano-sized powders via a simple milling process. The mean sizes of the powders changed from several tens to 200 nm when post-treatment temperatures changed from 700 to 1000 °C. The $BaTiO_3$ powders obtained from the citric acid spray solution had tetragonal crystal structure at post-treatment temperature of 1000 °C. Conversely, those $BaTiO_3$ powders prepared from a spray solution that did not contain citric acid had cubic crystal structures at this same post-treatment temperature.

*Keywords:* Powders–gas phase reaction; $BaTiO_3$ and titanates; Capacitors

## 1. Introduction

Multilayer ceramic capacitors (MLCCs) with a high capacitance of 1–100 μF can be engineered into passive components in circuits for LSI, replacing the widely used tantalum capacitors and aluminum electrolytic capacitors. To meet the growing requirements for miniaturization, higher performance, and lower electric power consumption, the number and the dielectric constant of the dielectric active layers are expected to increase, the layer thickness reach less than 2 μm, and the grain size of the dielectric layers become smaller in consideration of reliability factors.[1] For this reason, current MLCC industries prefer to use $BaTiO_3$ powders that are nano-sized, have a narrow size distributions, and are structured with regular morphologies.

It is well known that the shape and size of a powder size are important components in material properties. Nano-sized $BaTiO_3$ powders have been synthesized by wet-chemistry synthesis techniques, including sol–gel, sol-precipitation, combustion synthesis, chemical co-precipitation, and hydrothermal synthesis.[2–6] Nano-sized $BaTiO_3$ powders prepared by wet-chemistry synthesis techniques, however, have a low crystallinity. A post-treatment process performed to improve the crystallinity of the powders causes a growth in size and aggregation between the powders.[7,8]

The aerosol process of spray pyrolysis has been successfully applied to synthesize ceramic powders because it is a simple, continuous process, and produces powders with a spherical shape, a narrow size distribution, and high phase purity.[9–12] Lee et al. prepared nano-sized $BaTiO_3$ powders by spray pyrolysis from a spray solution containing an organic additive.[11] Xia et al. developed a new preparation strategy for spray pyrolysis – called ‘salt-assisted’ spray pyrolysis – to efficiently produce nano-sized $BaTiO_3$ powders.[12] Submicronic powders prepared by salt-assisted spray pyrolysis formed nano-sized $BaTiO_3$ powders with non-agglomeration characteristics after repeated washings with distilled water.

Flame spray pyrolysis, which has the merits of spray pyrolysis, has been adapted for the preparation of nano-sized powders since it is not only economical but it also amends the defects found in spray pyrolysis. In this study, nano-sized $BaTiO_3$ powders with regular morphology and high

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crystallinity were prepared by flame spray pyrolysis. $BaTiO_3$ powders with large, hollow, thin wall structures were prepared by flame spray pyrolysis from a spray solution containing citric acid. Precursor powders with large, hollow, thin wall structures became coarse aggregates of nano-sized primary powders through the post-treatment process. In flame spray pyrolysis, the effects of the preparation conditions on the characteristics of the $BaTiO_3$ powders were investigated. These conditions included the flow rates of fuel, the oxidizer and the carrier gases.

## 2. Experimental procedure

Fig. 1 shows the schematic diagram of the flame spray pyrolysis apparatus. The flame spray pyrolysis system is composed of a droplet generator, a flame nozzle, a quartz reactor, a powder collector and a blower. A 1.7 MHz ultrasonic spray generator with six resonators is used to generate droplets, which are then carried into the high-temperature diffusion flame with oxygen as the carrier gas. Droplets or powders were dried, decomposed, and crystallized inside the diffusion flame. Propane and oxygen were used as the fuel and oxidizer gas, respectively, to create a diffusion flame.

The flame nozzle has five concentric pipes. Droplets generated from the precursor solution are supplied to the diffusion flame through the center pipe by different flow rates of the carrier gas. The temperatures of the diffusion flame and the residence time for the powders inside the diffusion flame are controlled by changing the flow rates of fuel, oxidizer, and carrier gases.

The materials used in the synthesis of the $BaTiO_3$ powders were barium carbonate and titanium tetra-*iso*-propoxide (TTIP). A small amount of nitric acid was used to peptize the hydrolyzed TTIP and form a clear solution. The concentration of barium carbonate and TTIP was fixed at 0.1 M and citric acid monohydrate was used as an organic additive. All as-prepared powders in the flame spray pyrolysis were post-treated from 700 to 1000 °C for 2 h in air atmosphere. The milling of the calcinated powders was performed by a simple milling system.

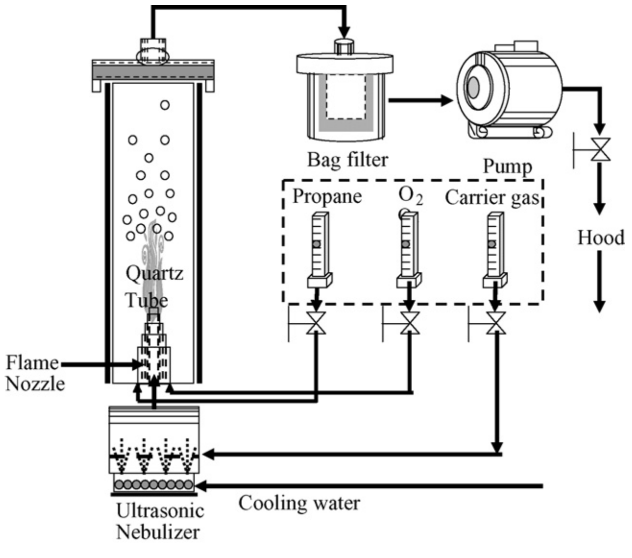

Fig. 1. Schematic diagram of flame spray pyrolysis.

The crystal structures of the as-prepared and post-treated $BaTiO_3$ powders were investigated by using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal structures of the $BaTiO_3$ powders were estimated from the splitting of the (200) peak in the XRD spectra. The mean crystallite sizes of the $BaTiO_3$ powders were calculated using Scherrer's equation while the morphological characteristics of the powders were investigated by using scanning electron microscopy (SEM) and transmission electron microscope (TEM).

## 3. Results and discussion

In flame spray pyrolysis, the flow rates of the fuel and carrier gas affect the morphologies of the prepared powders by changing the temperature of the diffusion flame and the residence time of the powders inside the high temperature flame. The key idea in this study for preparing nano-sized $BaTiO_3$ powders was to create precursor powders with hollow, thin wall structures and the control of the flow rates of the fuel, oxidizer, and carrier gases in the flame spray pyrolysis is critical to this preparation.

This study investigated the effects of the flow rates of the fuel, oxidizer and carrier gases on the morphologies of barium titanate powders prepared by flame spray pyrolysis. The morphologies of the barium titanate powders prepared by flame spray pyrolysis were strongly affected by the flow rates of the fuel and carrier gases. Therefore, the flow rate of the oxidizer gas was fixed at 35 L/min, through which a complete decomposition of the precursors occurred. The flow rates of the carrier gas were changed from 10 to 40 L/min at a constant flow rate of the fuel and oxidizer gases. However, the barium titanate powders prepared at a low flow rate of carrier gas displayed aggregated morphologies because of the long residence time of the powders inside the high temperature diffusion flame. Therefore, the flow rate of the carrier gas was fixed at 40 L/min. The flow rates of the propane used as the fuel gas were critical at the constant flow rates of the oxidizer and carrier gases to the preparation of the nano-sized barium titanate powders in the flame spray pyrolysis. A description of the effect of the flow rates of fuel gas on the morphology of the barium titanate powders has therefore been focused on in the text. The flow rates of the propane used as the fuel gas were changed from 2 t 4 L/min.

Fig. 2 shows the SEM photographs of the precursor powders obtained by flame spray pyrolysis at different flow rates of fuel gas. The concentration of citric acid dissolved in the spray solution was 0.4 M. The precursor powders had different morphology and mean size according to the flow rates of fuel gas. The precursor powders prepared at the low flow rates of fuel gas of 2 and 2.5 L/min had a large mean size above 5 μm. The high evaporation and decomposition rates of droplets or powders inside a low temperature diffusion flame formed precursor powders with a large size and hollow structure.[13] On the other hand, the precursor powders prepared at the high flow rate of fuel gas of 4 L/min were submicronic

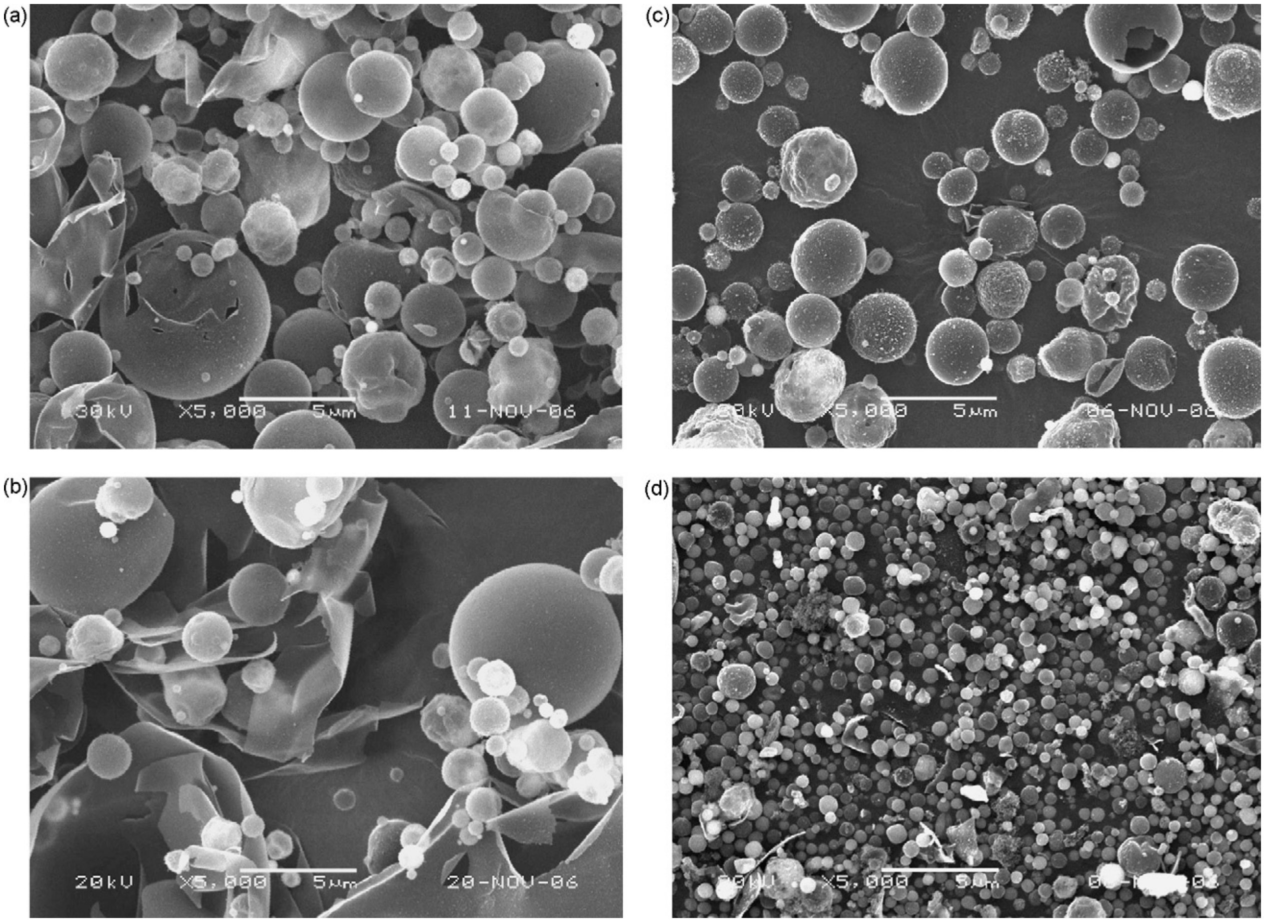

Fig. 2. SEM photographs of the precursor powders prepared by flame spray pyrolysis (fuel–oxidizer–carrier gas, (a) 2–35–40; (b) 2.5–35–40; (c) 3–35–40; (d) 4–35–40).

in size. The melting of the intermediate powders inside the high temperature diffusion flame formed fine-sized precursor powders.

In this study, precursor powders were prepared from spray solutions with the same concentrations of barium and titanium components. The precursor powders prepared at low flow rates of fuel gas had thinner wall thickness than those prepared at high flow rates of carrier gas. The number of nano-sized powders formed by a chemical vapor deposition (CVD) process for evaporated components increased with the increasing flow rates of the fuel gas.[14] Conversely, some of the powders prepared at the low flow rate of fuel gas of 2 L/min had an irregular morphology through the incomplete decomposition of the precursors. In this study, therefore, the optimum flow rate of fuel gas was 2.5 L/min for the preparation of precursor powders with hollow, thin wall structures.

In spray pyrolysis, polymeric precursors such as citric acid and ethylene glycol are used to control the morphology of the powders. A viscous gel promoted volume precipitation and resulted in the formation of spherical-shaped particles with filled morphology and non-aggregation characteristics.[15] Recently, however, the polymeric additives have also been used to prepare nano-sized powders. The formation mechanism of these nano-sized powders in spray pyrolysis from a spray solution with organic additives has been described in a previous paper.[11] Thus, the effect of the concentration of citric acid added to the spray solution on the morphology of the precursor and post-treated $BaTiO_3$ powders was investigated.

Fig. 3 shows the SEM photographs of the precursor powders obtained from the spray solutions at different concentrations of citric acid. The precursor powders obtained from the spray solution that did not contain citric acid had an irregular and distorted shape. Conversely, powders prepared from the citric acid spray solutions had a different morphology, according to the concentration of citric acid. The precursor powders obtained from the spray solution with a low concentration of citric acid (0.2 M) had several micron sizes, a spherical shape and a filled morphology. Precursor powders obtained from the spray solutions with high concentrations of citric acid (above 0.4 M), on the other hand, had large, hollow, thin wall structures (Figs. 2 and 3). The thickness of the wall of the precursor powders (Fig. 2(b)) obtained from the SEM photograph was about 50 nm. The high evolving rate of gas by the decomposition of the citric acid formed precursor powders with hollow, thin wall structures.

Fig. 4 shows the XRD spectra of the precursor powders obtained by flame spray pyrolysis from spray solutions with

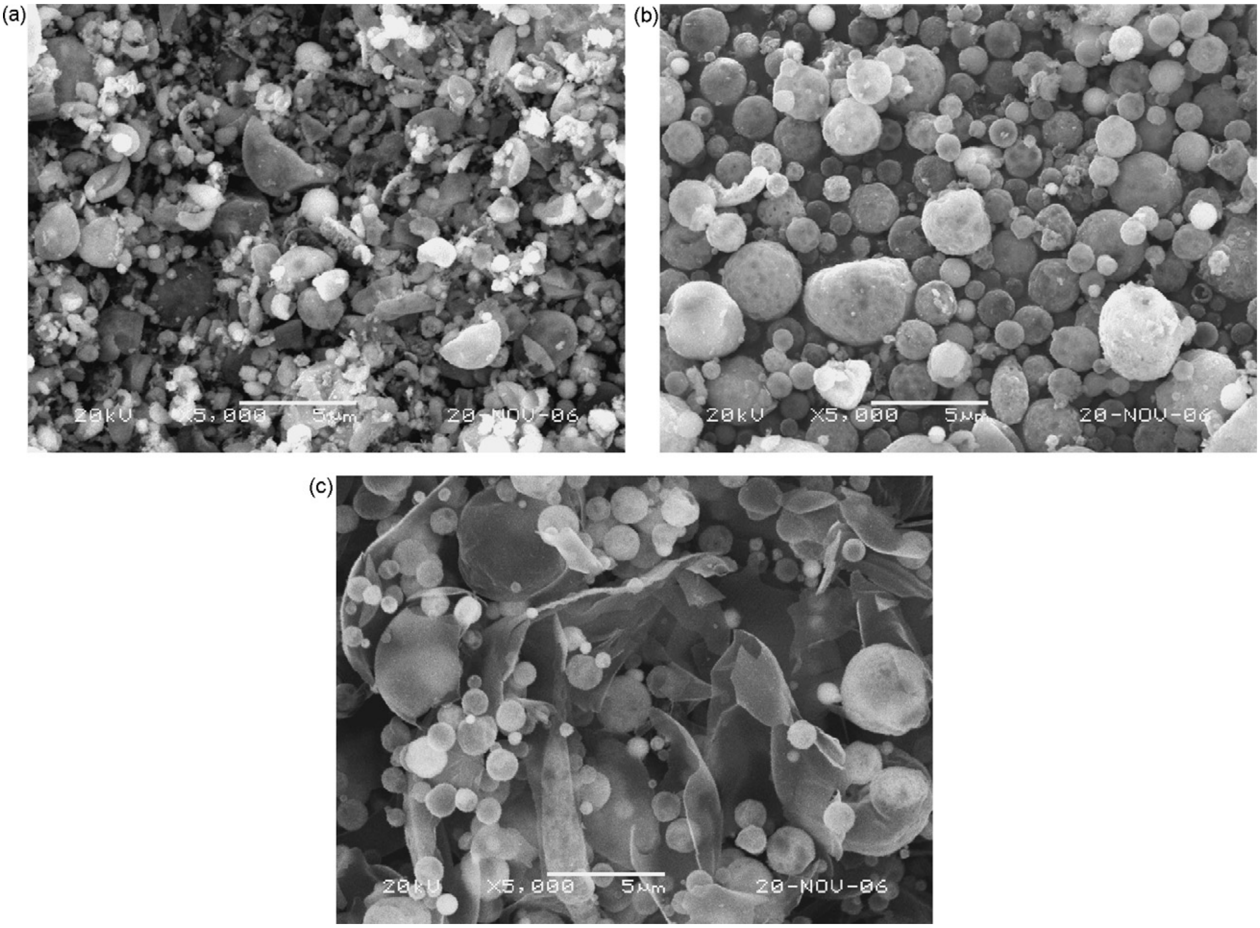

Fig. 3. SEM photographs of the precursor powders prepared by flame spray pyrolysis from different concentrations of citric acid. (a) No additive; (b) 0.2 M CA; (c) 0.6 M CA.

different concentrations of citric acid. The crystal structures of the precursor powders were affected by the concentrations of the citric acid dissolved in the spray solutions. The precursor powders obtained from the spray solution without citric acid had mixed crystal structures of cubic $BaTiO_3$ and $Ba(NO_3)_2$. In the XRD spectra, the peaks of barium nitrate disappeared upon the increase of the citric acid concentration. Phase pure $BaTiO_3$ particles were obtained from spray solutions with citric acid above 0.4 M. The short residence time of the powders inside the diffusion flame formed precursor powders with mixed crystal structures of cubic $BaTiO_3$ and $Ba(NO_3)_2$. The decomposition heat of citric acid, however, affected the crystal structures of the precursor powders obtained by flame spray pyrolysis. The heat generated by the decomposition of the citric acid increased the temperature of the powders inside the diffusion flame. The precursor powders obtained from the spray solutions with citric acid above 0.4 M, therefore, had a pure $BaTiO_3$ crystal structure.

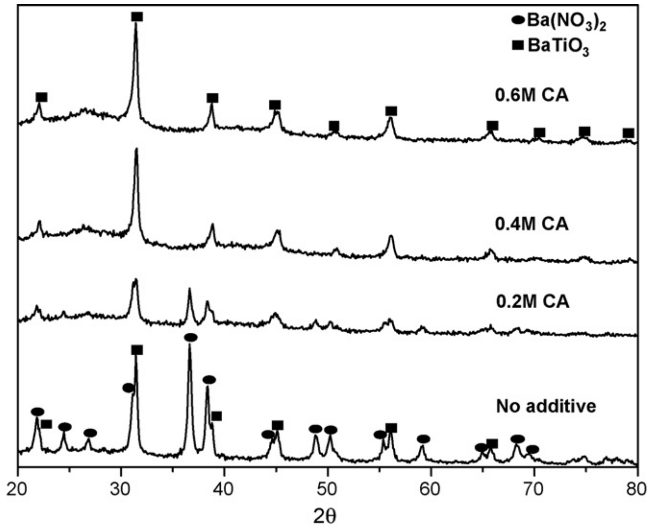

Fig. 4. X-ray diffraction spectra of the precursor powders prepared by flame spray pyrolysis.

The precursor powders obtained by flame spray pyrolysis from the spray solutions with different concentrations of citric acid were post-treated at a temperature of 900 °C. Fig. 5 shows the SEM photographs of the post-treated $BaTiO_3$ powders. The $BaTiO_3$ powders obtained from the spray solution without citric acid had the irregular shape and aggregated morphology of the submicronic primary powders. The addition of citric acid to the spray solution changed the morphologies of the post-treated $BaTiO_3$ powders. The $BaTiO_3$ powders obtained from the 0.2 M citric acid spray solution had a micronic size, spherical shape

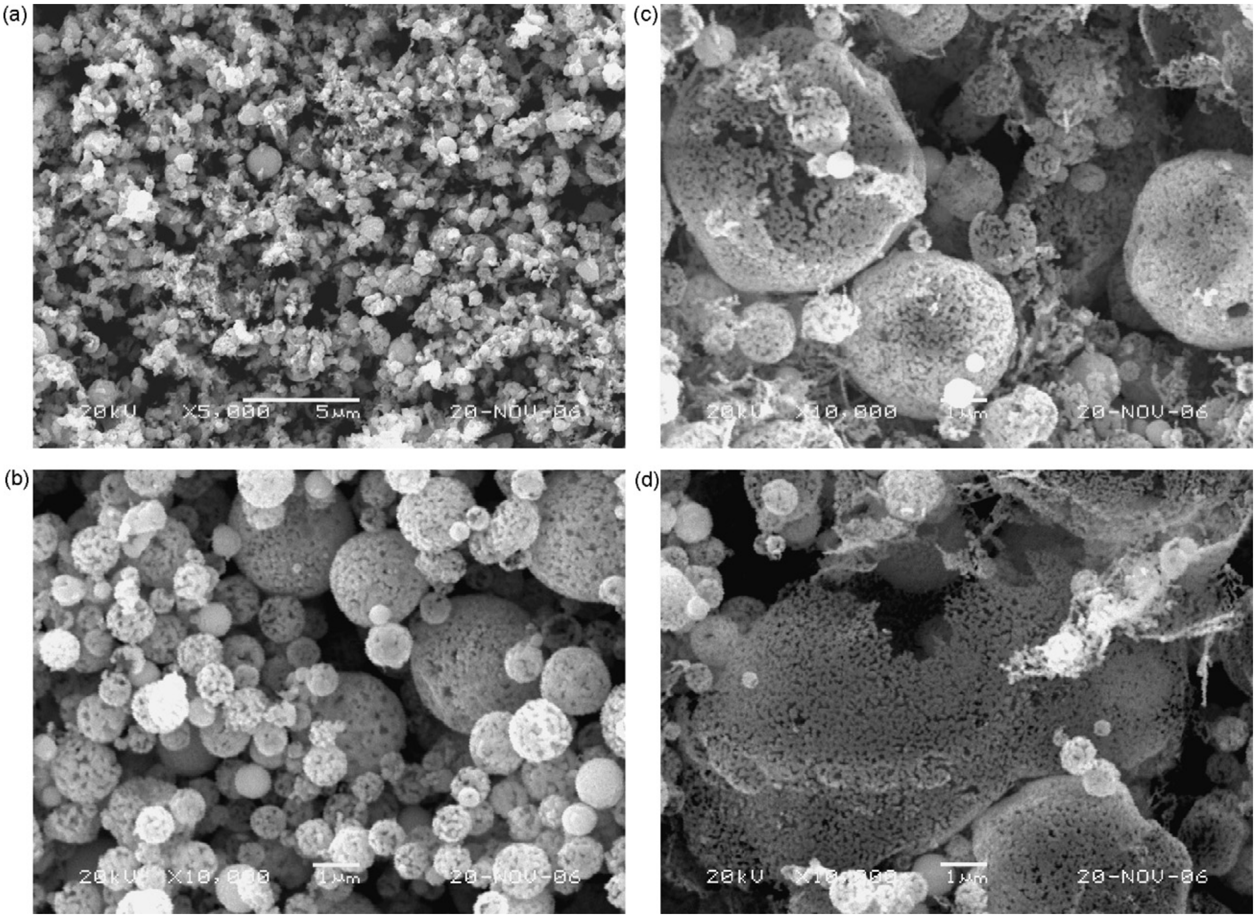

Fig. 5. SEM photographs of the $BaTiO_3$ powders post-treated at 900 °C for 2 h. (a) No additive; (b) 0.2 M CA; (c) 0.4 M CA; (d) 0.6 M CA.

and porous structure. On the other hand, the $BaTiO_3$ powders obtained from highly concentrated citric acid spray solutions had a slightly aggregated morphology of primary powders with a nanometer size. Precursor powders with a hollow, thin wall structure formed the nano-structured $BaTiO_3$ powders after post-treatment. However, the neck strength between the nano-sized primary powders was weak. Therefore, it was easy to disintegrate the nano-structured $BaTiO_3$ powders into nanometer-sized non-aggregated powders by a simple milling process. Fig. 6 shows the TEM and high magnification SEM photographs of the $BaTiO_3$ powders milled by hand with an agate mortar. The post-treated powders obtained from the 0.4 M citric acid spray solution became nano-sized powders through a simple milling process. The mean size of the powders measured from the TEM photograph was 70 nm. Fig. 7 shows the schematic diagram of the mechanism by which the nano-sized $BaTiO_3$ powders were formed during flame spray pyrolysis. In the flame spray pyrolysis, precursor powders with hollow, thin wall structures were prepared from the citric acid spray solutions. The precursor powders became slightly aggregated $BaTiO_3$ powders of nanometer-sized primary powders after post-treatment. The nano-sized $BaTiO_3$ powders with a regular morphology were obtained by a simple milling process of the post-treated $BaTiO_3$ powders.

The mean size of the $BaTiO_3$ powders obtained by flame spray pyrolysis could be controlled by changing the post-treatment temperatures. The precursor powders obtained from the 0.4 M citric acid spray solution were post-treated at various temperatures. Fig. 8 shows the SEM photographs of the $BaTiO_3$ powders post-treated at temperatures of 700 and 1000 °C. The $BaTiO_3$ powders post-treated at temperature of 700 °C were of a fine size, below 50 nm. On the other hand, the mean size of the $BaTiO_3$ powders post-treated at a temperature of 1000 °C was 200 nm.

Fig. 9 shows the XRD spectra of the $BaTiO_3$ powders post-treated at various temperatures. The precursor powders obtained from spray solutions with and without citric acid were post-treated between 700 and 1000 °C for 2 h. The post-treated powders had a pure $BaTiO_3$ phase irrespective of the post-treatment temperatures. However, the addition of citric acid to the spray solution affected the crystal structures of the post-treated $BaTiO_3$ powders. As the post-treatment temperature increased, the crystal structure of the $BaTiO_3$ powders obtained from the citric acid spray solution changed from metastable cubic to tetragonal, which can be identified by the peak splitting at $2\theta = 45.5°$. A clear peak splitting for the $BaTiO_3$ powders prepared from the citric acid spray solution was observed at the post-treatment temperature of 1000 °C. Conversely, the $BaTiO_3$

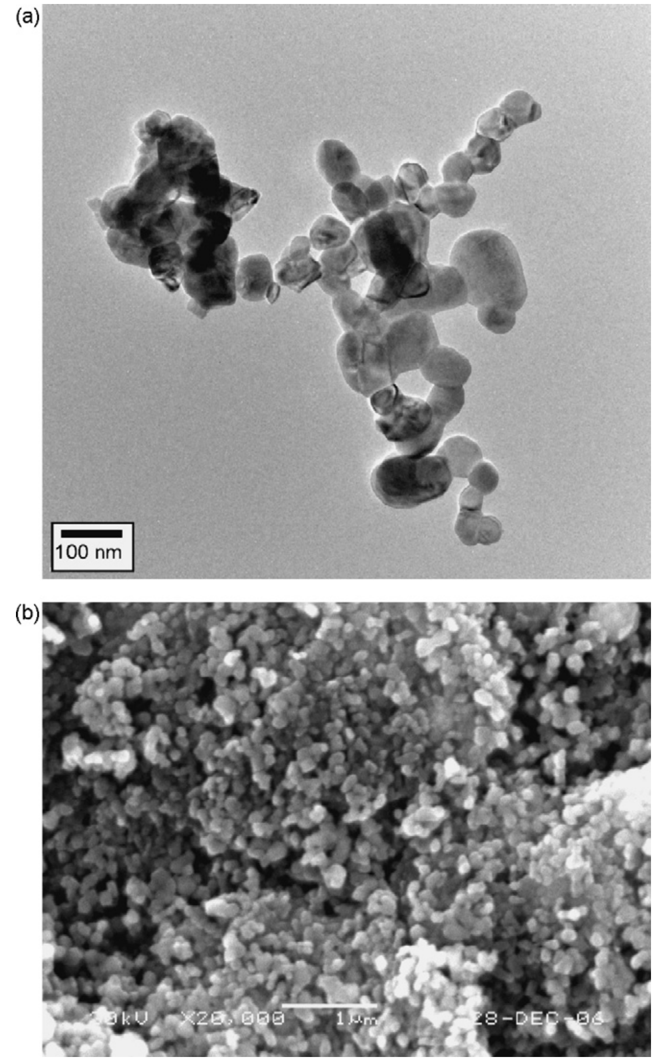

Fig. 6. TEM and SEM photographs of the $BaTiO_3$ powders. (a) TEM and (b) SEM.

powders prepared from the spray solution not containing citric acid had no peak splitting at post-treatment temperatures between 700 and 1000 °C.

The addition of citric acid to the spray solutions decreased the mean crystallite sizes of the post-treated $BaTiO_3$ powders. The mean crystallite sizes of the $BaTiO_3$ powders obtained from the spray solutions without citric acid were changed from 23 to 42 nm when the post-treatment temperatures were changed from 700 to 1000 °C. At the same post-treatment temperature ranges, however, the mean crystallite sizes of the $BaTiO_3$ powders obtained from the citric acid spray solutions were changed from 20 to 32 nm.

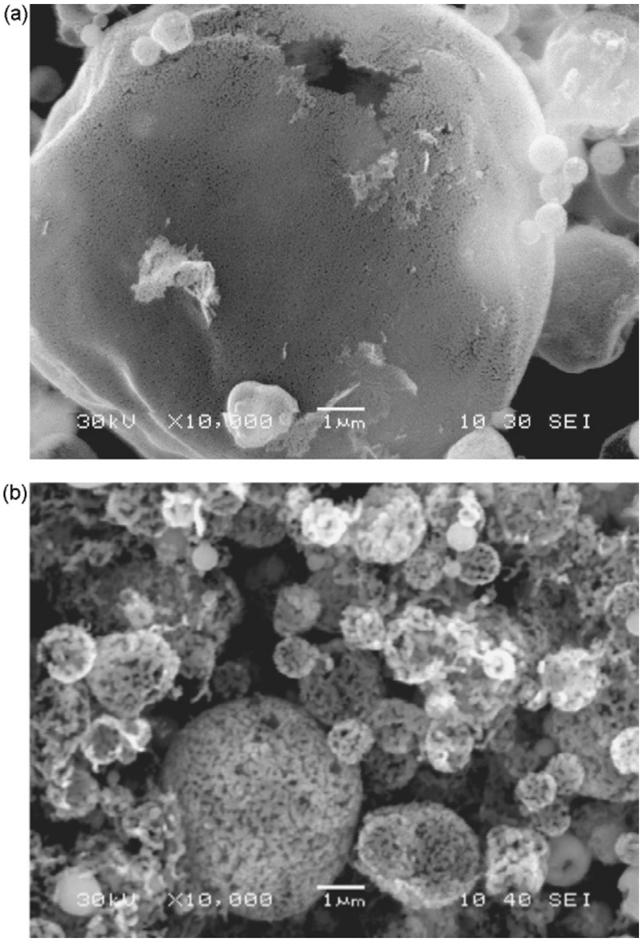

Fig. 8. SEM photographs of the $BaTiO_3$ powders post-treated at different temperatures: (a) 700 °C and (b) 1000 °C.

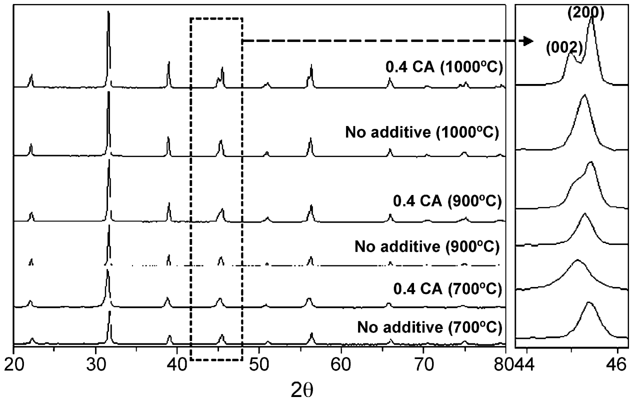

Fig. 9. X-ray diffraction spectra of the $BaTiO_3$ powders at different post-treatment temperatures.

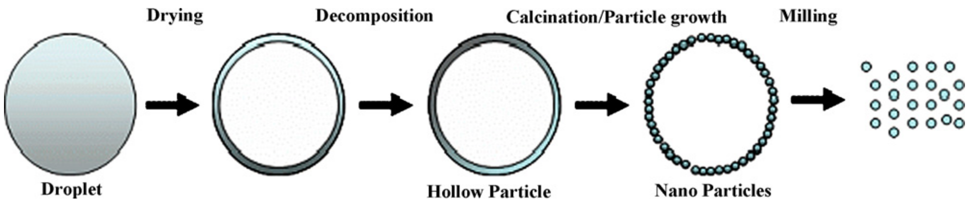

Fig. 7. Formation mechanism of the nano-sized $BaTiO_3$ powders by flame spray pyrolysis.

## 4. Conclusion

Nano-sized $BaTiO_3$ powders were prepared by flame spray pyrolysis from spray solutions containing citric acid. The effects of the preparation conditions and organic additives on the characteristics of the $BaTiO_3$ powders obtained by flame spray pyrolysis were investigated. The key idea in this study preparing nano-sized $BaTiO_3$ powders was to create precursor powders with hollow, thin wall structures. In this study, the flow rates of the fuel, the oxidizer and the carrier gases were optimized to prepare these kinds of precursor powders. Citric acid dissolved in a spray solution improved the hollowness of the precursor powders obtained by flame spray pyrolysis. The addition of citric acid to the spray solution changed the morphologies of the post-treated $BaTiO_3$ powders. The $BaTiO_3$ powders obtained from highly concentrated citric acid spray solutions had the slightly aggregated morphology of the primary powders with a nanometer size. Precursor powders with hollow, thin wall structures formed nano-structured $BaTiO_3$ powders after post-treatment. The post-treatment of powders obtained from the 0.4 M citric acid spray solution became nano-sized powders via a simple milling process. The mean size of the powders at the post-treatment temperature of 900 °C was 70 nm. The addition of citric acid to the spray solution also affected the crystal structures and mean crystal sizes of the post-treated $BaTiO_3$ powders.

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