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Dielectric properties of nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders prepared by spray pyrolysis

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Abstract

Nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders are prepared by post-treatment of the precursor powders with hollow and thin wall structure at temperatures between 900 and 1100 °C. Ethylenediaminetetraacetic acid and citric acid improve the hollowness of the precursor powders prepared by spray pyrolysis. The mean sizes of the powders post-treated at temperatures of 900, 1000 and 1100 °C are 42, 51 and 66 nm, respectively. The densities of the $Ba_{0.7}Sr_{0.3}TiO_3$ pellets obtained from the powders post-treated at 900, 1000 and 1100 °C are each 5.36, 5.55 and 5.38 g cm^{-3} at a sintering temperature of 1300 °C. The pellet obtained from the powders post-treated at 1000 °C has higher maximum dielectric constant than those obtained from the powders post-treated at 900 and 1100 °C.

Keywords: C. Dielectric properties; Barium strontium titanate; Spray pyrolysis; Nano powders

1. Introduction

Barium strontium titanate (BST) [$Ba_{1-x}Sr_xTiO_3$, $0 < x < 1$] are widely used in the thick film forms in various fields because of their high dielectric constant and composition-dependent Curie temperature [1–7]. Pure BST thick films has to be sintered at high temperatures above 1300 °C, and therefore only platinum or refractory metals can be used as conductors [8,9]. In recent, nickel, copper and silver conductors with low sintering temperatures are mainly applied to reduce the production cost. Therefore, the sintering characteristics of BST thick films should be improved at low temperatures. One method of decreasing the sintering temperature of BST is to decrease the mean size of the powders. The performance of BST thick films is also highly dependent on the characteristics of powders, such as stoichiometry, phase homogeneity, powders size and its distribution [10].

Fine size BST powders with various compositions were widely prepared by liquid solution methods such as sol–gel, co-precipitation and hydrothermal [11–18]. However, the characteristics of BST powders prepared by gas phase reaction methods are scarcely studied. Jung et al. investigated the mean sizes, morphologies, and crystal structures of the $Ba_{0.5}Sr_{0.5}TiO_3$ powders prepared by flame spray pyrolysis using "CA-assisted" spray solution [19]. The mean size of the $Ba_{0.5}Sr_{0.5}TiO_3$ powders was 32 nm at a post-treatment temperature of 1000 °C. Branković et al. prepared the submicron-sized $Ba_{0.8}Sr_{0.2}TiO_3$ powders by ultrasonic spray pyrolysis from the polymeric precursors [20], in which one particle was formed from the one droplet. The sintering characteristics and dielectric properties of the nano-sized BST powders are strongly affected by the composition as well as the preparation process.

In this study, nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders were prepared by spray pyrolysis from the spray solution with ethylenediaminetetraacetic acid (EDTA) and citric acid. The sintering characteristics and dielectric properties of the $Ba_{0.7}Sr_{0.3}TiO_3$ powders prepared by spray pyrolysis were investigated.

2. Experimental

The schematic diagram of the equipment and the formation mechanism of the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders in the spray pyrolysis are shown in Fig. 1. The precursor powders with hollow and thin wall structure were prepared by spray pyrolysis

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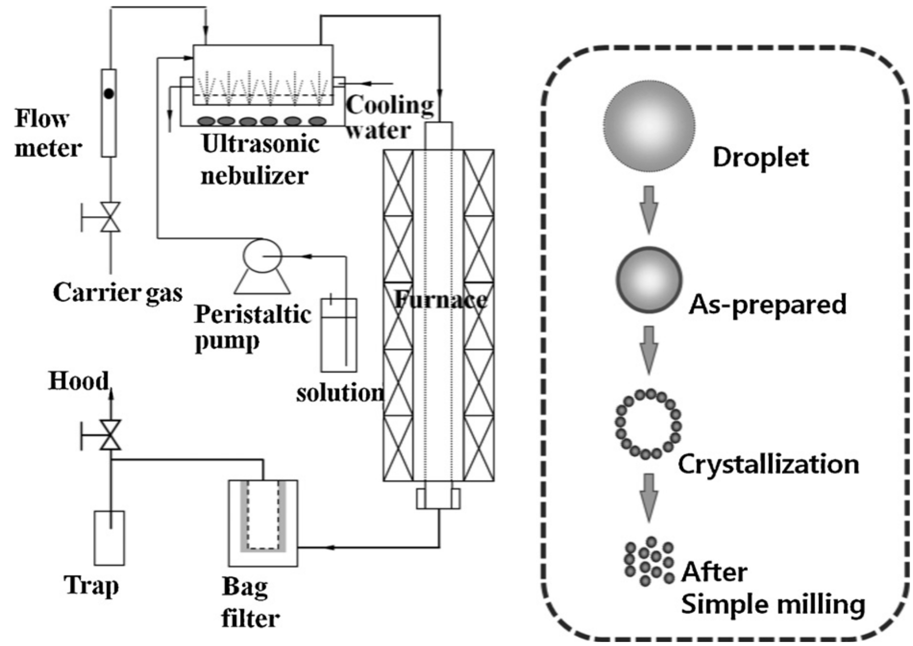
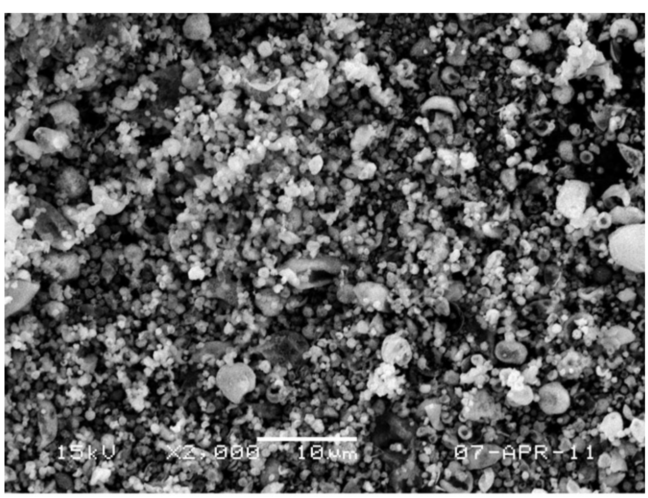
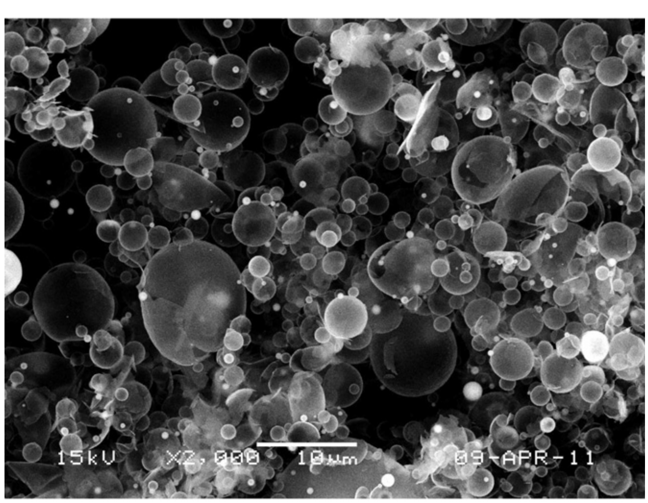


Fig. 1. Schematic diagram of spray pyrolysis process and formation mechanism of nano-sized ceramic powders.



(a) no additive



(b) 0.1 M EDTA+0.1 M CA

Fig. 2. SEM images of the precursor powders prepared by spray pyrolysis.

to obtain the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders. The equipment consisted of six ultrasonic spray generators operating at 1.7 MHz, a tubular quartz reactor (length: 1200 mm; ID: 50 mm), and a bag filter. The starting materials for the synthesis were barium nitrate, strontium nitrate 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 concentrations of metal components were fixed at 0.1 M. Citric acid and ethylenediaminetetraacetic acid (EDTA) were used as chelating agents to improve the hollowness of the precursor particles. The concentrations of citric acid and EDTA were each 0.1 M. The spray pyrolysis temperature of the precursor powders was fixed at 900 °C. The flow rate the air carrier gas was fixed at 40 L min^{-1}. The precursor powders prepared by spray pyrolysis were post-treated at temperatures of 900, 1000 and

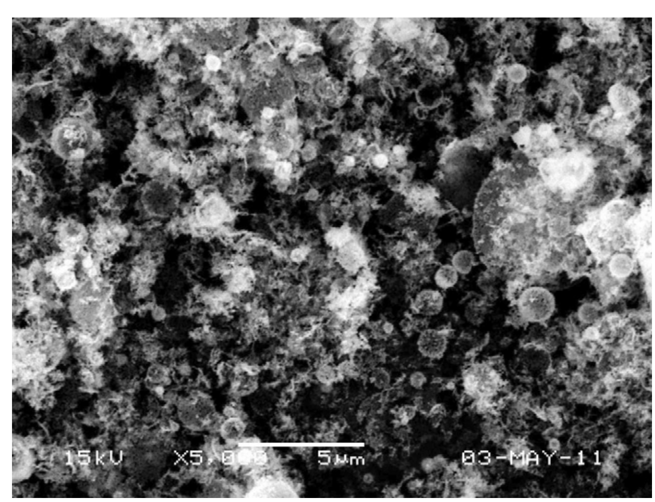


Fig. 3. SEM image of the BST powders post-treated at 1000 °C prepared from the spray solution with organic additive.

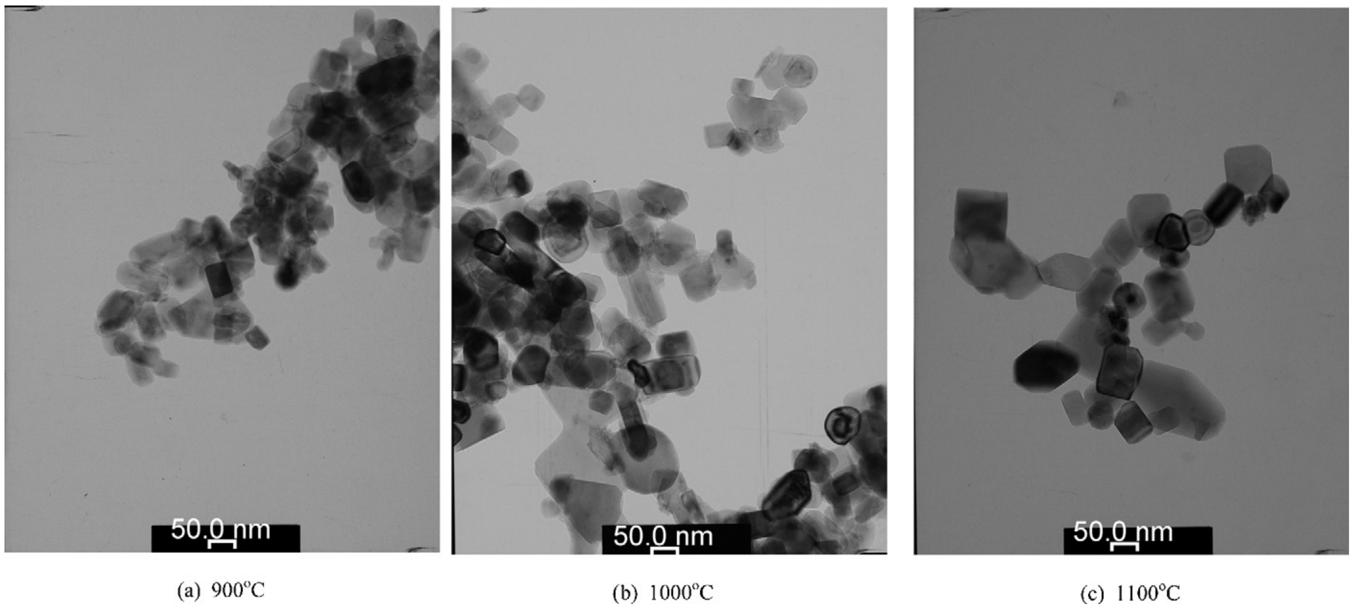


Fig. 4. TEM images of the BST powders post-treated at various temperatures.

1100 °C for 2 h under air atmosphere. The powders were pelletized at 250 kgf cm^{-2} to 10 mm diameter and then sintered at 1300 °C for 2 h. Dielectric properties were measured by applying silver paste to the surfaces of the pellets as an electrode.

The crystal structures of the precursor and post-treated $Ba_{0.7}Sr_{0.3}TiO_3$ powders were investigated by using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu-Kα radiation (λ = 1.5418 Å). The mean crystallite sizes of the $Ba_{0.7}Sr_{0.3}TiO_3$ powders were calculated using Scherrer's equation. The morphological characteristics of the powders were investigated by using scanning electron microscopy (SEM, JEOL, JSM 6060) and transmission electron microscope (TEM, JEOL, JEM-2010). The post-treated powders were milled by hand using agate mortar for the preparation of TEM sample.

3. Results and discussion

The ceramic powders prepared by spray pyrolysis at high drying and decomposition conditions of droplets had hollow and thick wall structure [21]. The precursor powders with hollow and thick wall structure could not be well crushed to the nano-sized powders by a simple milling process. Therefore, in this study, the precursor powders with hollow and thin wall structure for nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders were prepared by spray pyrolysis. Fig. 2 shows the SEM images of the precursor powders prepared from the spray solution with and without organic additives. The precursor powders prepared from the spray solution without organic additive had fine size, hollow shape and thick wall structure. On the other hand, the precursor powders prepared from the spray solution with organic additive had large size, hollow shape and thin wall structure. The hollowness of the powders increased the mean size of the precursor powders. EDTA and citric acid improved the hollowness of the precursor powders by acting as the chelating agent as well as the gas evolution additives.

The precursor powders prepared from the spray solution with organic additive were post-treated at various temperatures. Fig. 3 shows the SEM image of the $Ba_{0.7}Sr_{0.3}TiO_3$ powders post-treated at 1000 °C. The $Ba_{0.7}Sr_{0.3}TiO_3$ powders had slightly aggregated morphology of primary particles with nanometer size. The $Ba_{0.7}Sr_{0.3}TiO_3$ powders post-treated at temperatures of 900, 1000 and 1100 °C were milled by hand using an agate mortar. Fig. 4 shows the TEM images of the milled $Ba_{0.7}Sr_{0.3}TiO_3$ powders. The powders had well-crystallized structure irrespective of the post-treatment temperatures. The mean sizes of the milled powders increased with increasing

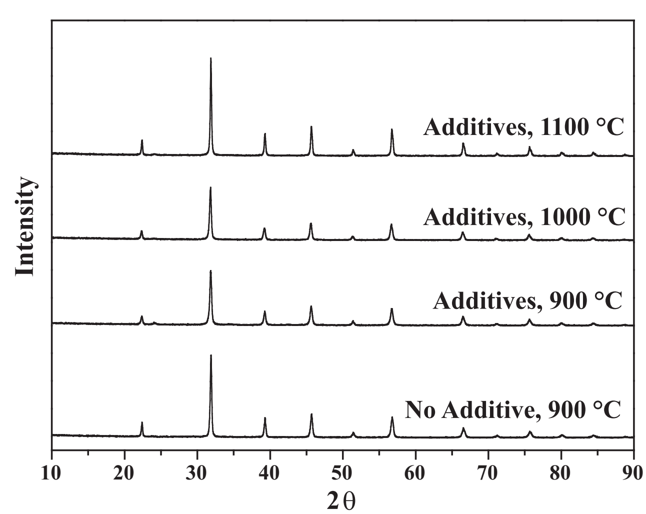
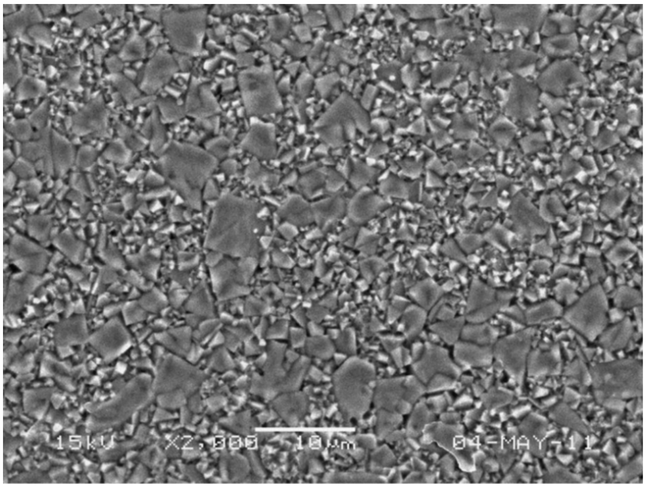
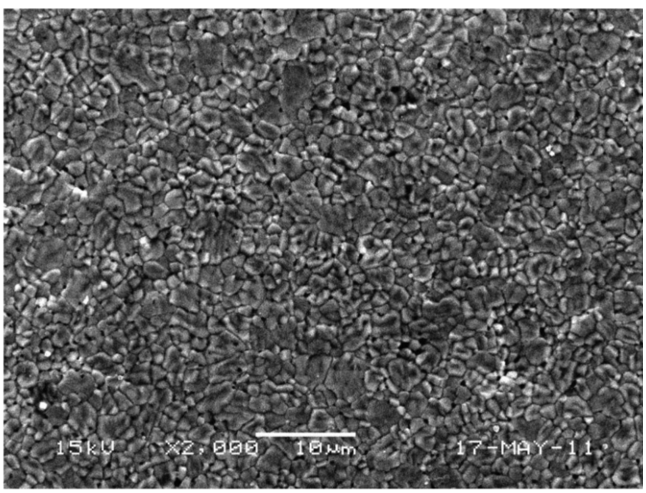


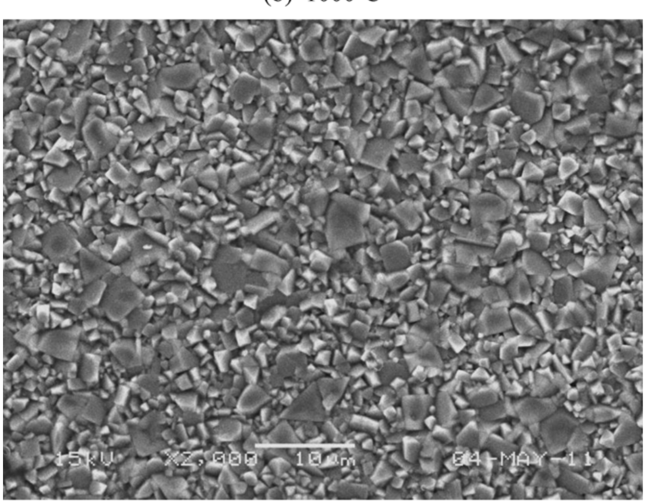
Fig. 5. XRD patterns of the BST powders prepared from the spray solutions with and without organic additives.



(a) 900°C



(b) 1000°C



(c) 1100°C

Fig. 6. SEM images of the pellets obtained from the BST powders post-treated at various temperatures.

the post-treatment temperatures. The mean sizes of the powders post-treated at temperatures of 900, 1000 and 1100 °C measured from the TEM images were 42, 51 and 66 nm, respectively.

Fig. 5 shows the XRD patterns of the $Ba_{0.7}Sr_{0.3}TiO_3$ powders post-treated at temperatures of 900, 1000 and 1100 °C. The powders prepared from the spray solution with and without organic additives had single BST perovskite phase at post-treatment temperature of 900 °C. The mean crystallite sizes of the $Ba_{0.7}Sr_{0.3}TiO_3$ powders prepared from the spray solution with and without organic additives were each 29 and 34 nm. The thin wall structure of the precursor powders prepared from the spray solution with organic additive minimized the crystal growth of the powders. The mean crystallite sizes of the powders post-treated at temperatures of 1000 and 1100 °C were each 33 and 44 nm. The crystal growth of the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powder was occurred according to the post-treatment temperatures.

The sintering characteristics of the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders prepared by spray pyrolysis are investigated. The SEM images of the surface of the $Ba_{0.7}Sr_{0.3}TiO_3$ pellets obtained from the powders post-treated at 900, 1000 and 1100 °C are shown in Fig. 6. The pellets were sintered at a temperature of 1300 °C for 2 h. The pellets had dense structure irrespective of the post-treatment temperatures of the $Ba_{0.7}Sr_{0.3}TiO_3$ powders. The densities of the pellets obtained from the powders post-treated at 900, 1000 and 1100 °C were each 5.36, 5.55 and 5.38 g cm^{-3}. The theoretical density of $Ba_{0.7}Sr_{0.3}TiO_3$ is 5.75 g cm^{-3}. Therefore, the densities of the pellets obtained from the powders post-treated at 900, 1000 and 1100 °C were each 93.2, 96.5 and 93.6% of the theoretical density. The nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders prepared by spray pyrolysis had good sintering characteristics.

The temperature dependence of the dielectric constant at 1 kHz for the $Ba_{0.7}Sr_{0.3}TiO_3$ pellets is shown in Fig. 7. The pellet obtained from the powders post-treated at 1000 °C had larger ε_{max} than those obtained from the powders post-treated at 900 and 1100 °C. The high density of the pellet obtained from the powders post-treated at 1000 °C resulted in the high dielectric constant.

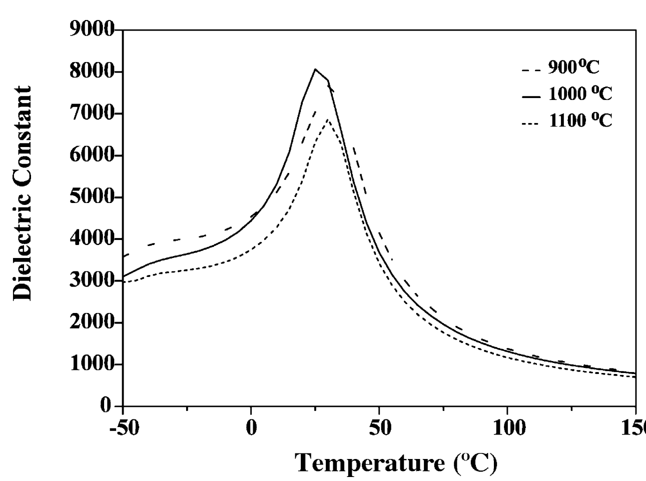


Fig. 7. Dielectric constants of the BST pellets measured at various temperatures.

4. Conclusions

The sintering characteristics and dielectric properties of the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders prepared by spray pyrolysis are investigated. Ethylenediaminetetraacetic acid (EDTA) and citric acid dissolved into the spray solution enable the formation of the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders even at a high post-treatment temperature of 1100 °C. The post-treatment temperature of the powders affects the dielectric properties of the pellet as well as the mean size of the powders. The $Ba_{0.7}Sr_{0.3}TiO_3$ pellet obtained from the powders post-treated 1000 °C has high density and high dielectric constant at a sintering temperature of 1300 °C.

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