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Characteristics of Ag-doped $BaTiO_3$ nanopowders prepared by spray pyrolysis

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Abstract

Pure and Ag-doped $BaTiO_3$ nanopowders were prepared by spray pyrolysis. Precursor powders, prepared from a spray solution with citric acid and ethylenediaminetetraacetic acid (EDTA) as chelating agents, had large, hollow particles irrespective of Ag doping. Both pure and Ag-doped powders had partially aggregated particles after post-treatment at 900 °C that could be easily milled to nanoparticles. The mean sizes of the pure and Ag-doped $BaTiO_3$ particles were 75 and 91 nm, respectively. The Ag-doped particles were mainly of cubic $BaTiO_3$ crystal structure, with small Ag phases observed. High-density $BaTiO_3$ pellets were formed by sintering the powders at the low temperature of 1000 °C. The silver was uniformly distributed in a tetragonal $BaTiO_3$ phase without phase separation in the doped pellet. The dielectric constants of the pellets formed from the pure and Ag-doped $BaTiO_3$ powders were 1826 and 2400, respectively.

Keywords: Barium titanate; Spray pyrolysis; Dielectric material; Nano powder

1. Introduction

Barium titanate ($BaTiO_3$) is a common dielectric material in multilayer ceramic capacitors (MLCCs) due to its high dielectric constant [1–6]. An MLCC's performance can be enhanced by improving this material's dielectric constant, mechanical properties and sintering temperature [7]. Multilayer capacitors have reported dielectric constants 15–20% higher than those in disk form [1,2,8]. Dielectric properties can also be improved significantly by metallic doping [1–9]. Incorporation of ductile metallic species has an added benefit of improving the mechanical properties of the brittle dielectric ceramic [5–7,10–12].

Metal–$BaTiO_3$ composite powders, such as Ni–$BaTiO_3$ and Ag–$BaTiO_3$, are promising high-performance dielectric materials [2,4,13,14]. Sanchez-Jimenez et al. prepared Ni-$BaTiO_3$ composites by dry grinding conventional powders [5]. Kojima et al. prepared Ag–$BaTiO_3$ composite powders by reducing Ag complex-coated $BaTiO_3$ powders obtained by a gel–sol method [7]. The dielectric constants of the Ni–$BaTiO_3$ and Ag–$BaTiO_3$ composites were much higher than that of sintered pure $BaTiO_3$. However, the metal–$BaTiO_3$ composite required two-step processing and would be more costly to produce. The direct synthesis of fine Ag–$BaTiO_3$ powders has not been well studied.

Reducing particle size can decrease the required sintering temperature of the $BaTiO_3$ and so can avoid mismatched shrinkages due to the different sintering behaviors of the metal and ceramic layers. Fine $BaTiO_3$ also allowed reduced dielectric layer thickness and increased the capacitance of MLCCs [15–17]. Therefore, various $BaTiO_3$ nanoparticle powders have been made using liquid-solution and gas-phase processes [16–19]. Recently, spray pyrolysis has synthesized $BaTiO_3$ nanoparticle powders [20–22]. Precursor powders prepared from spray solutions with organic additives had hollow and porous particles. Heat treatment and milling resulted in non-aggregated $BaTiO_3$ nanoparticle powders.

Spray pyrolysis has the advantage of allowing the direct preparation of metal-ceramic composite powders [23–25]. However, such powders have not been studied as dielectric materials. This work reports the preparation by spray pyrolysis of $BaTiO_3$ nanoparticle powders with low-level Ag doping. The effects of silver doping on the sintering and the dielectric constant of the $BaTiO_3$ were investigated.

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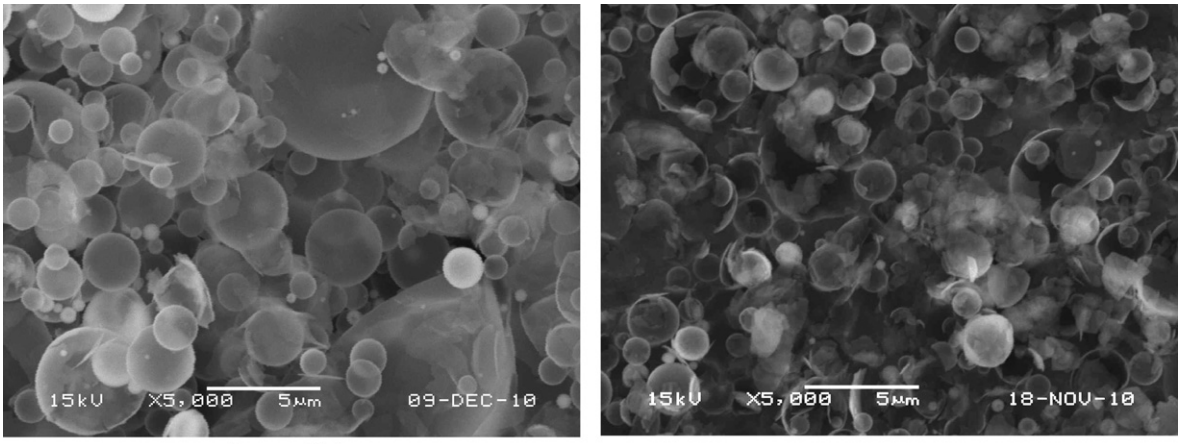
2. Experimental procedure

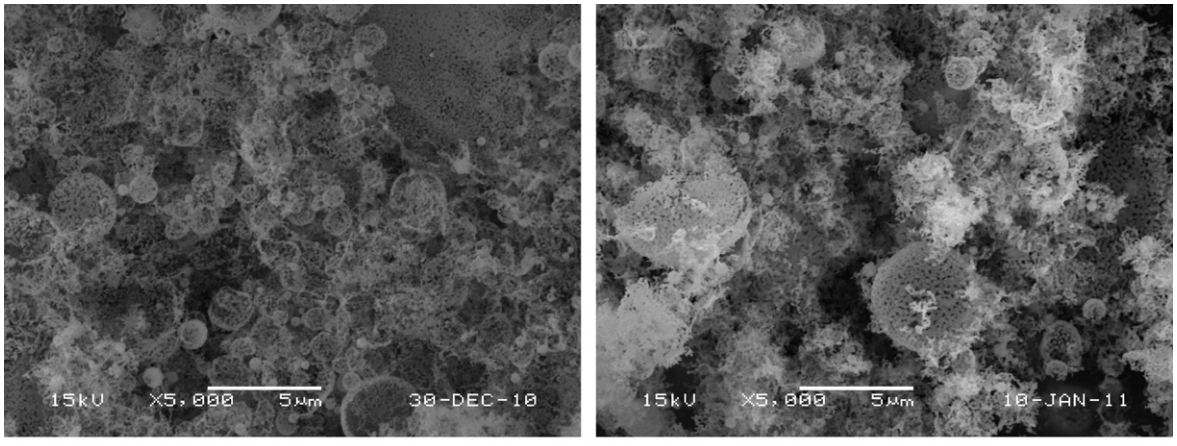
The pure and Ag-doped $BaTiO_3$ powders were prepared by spray pyrolysis. The equipment for this consisted of six ultrasonic spray generators operating at 1.7 MHz, a tubular alumina reactor (length: 1000 mm; ID: 50 mm), and a bag filter. The starting materials for the syntheses were barium nitrate, titanium tetra-iso-propoxide (TTIP) and silver nitrate solution. 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 and the content of Ag in the powder was 2 mol% of the $BaTiO_3$ concentration. 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 of the air carrier gas was fixed at 40 L min^{-1}. The precursor powders prepared by spray pyrolysis were post-treated at 900 °C for 2 h under air. The powders were pelletized at 250 kgf cm^{-2} to 10 mm diameter, sintered at 900 and 1000 °C for 2 h, and then allowed to cool to room temperature. Dielectric properties were measured by applying silver paste to the surfaces of the pellets as an electrode.

The crystal structures of the pure and Ag-doped $BaTiO_3$ powders and the sintered pellets were investigated by X-ray diffraction (XRD, PANalytical, X'Pert PRO MPD) using Cu Kα radiation (λ = 1.5418 Å, step size = 0.0167, time per step = 20 s) in the scan range of 10–80°. The morphologies of the powders were investigated by scanning electron microscopy (SEM, JEOL, JSM-6060) and transmission electron microscopy (TEM, JEOL, JEM-2010). For preparing the TEM sample, the collected powders were dispersed in ethanol. The dispersed powders were then placed on a carbon-coated copper grid for TEM examination. The composition of the Ag-doped $BaTiO_3$ powders was investigated by energy-dispersive X-ray spectroscopy (EDX). Dielectric constants were investigated with an LCR meter.



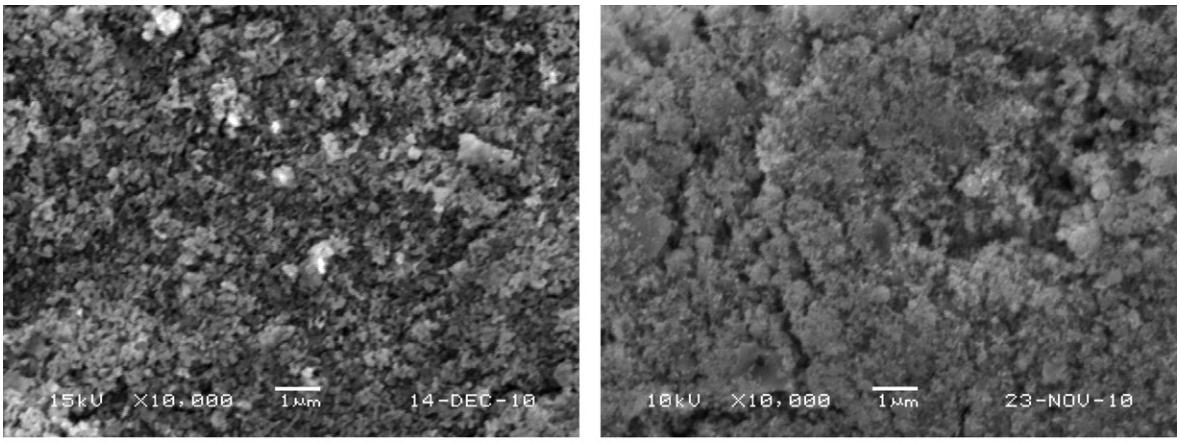
(a) no additive (b) 2 mol% Ag

Fig. 1. SEM images of the precursor powders prepared by spray pyrolysis.



(a) no additive (b) 2 mol% Ag

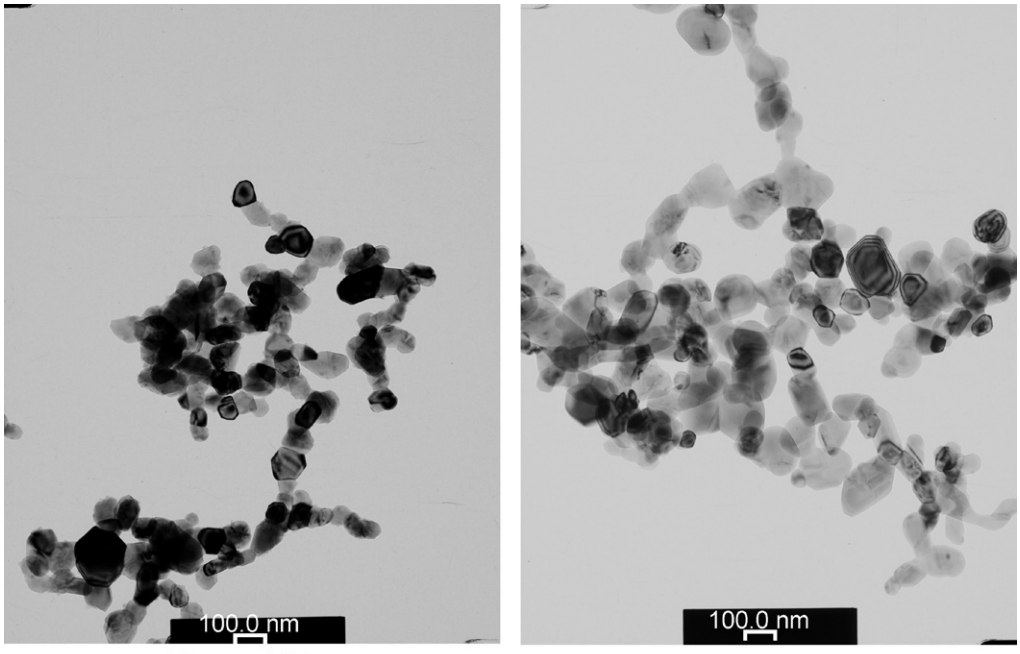
Fig. 2. SEM images of the pure and Ag-doped $BaTiO_3$ powders post-treated at 900 °C.



(a) no additive (b) 2 mol% Ag

(c) 2 mol% Ag

Fig. 3. SEM images of the pure and Ag-doped $BaTiO_3$ powders obtained after milling process.



(a) no additive (b) 2 mol% Ag

Fig. 4. TEM images of the pure and Ag-doped $BaTiO_3$ powders obtained after milling process.

3. Results and discussion

Pure and Ag-doped $BaTiO_3$ powders were prepared by spray pyrolysis from spray solutions containing citric acid and EDTA additives. The additives acted as chelating agents to improve the hollowness of the precursor particles (Fig. 1). They were large and hollow, irrespective of Ag doping. The drying and decomposition of the metal precursors during pyrolysis affected the powders' morphologies. The EDTA and citric acid in the metal chelates decomposed and released gases that aided the formation of precursor powders with hollow, thin-walled structures. The Ag doping did not affect the morphology of the precursor powder.

The precursor powders were post-treated at of 900 °C for 2 h under air to form crystalline $BaTiO_3$ phases. Fig. 2 shows SEM images of the post-treated powders. The hollow, thin-walled structures of the precursor powders were maintained after post-treatment. Both powders showed slight aggregation of the primary nanoparticles, though the connections between

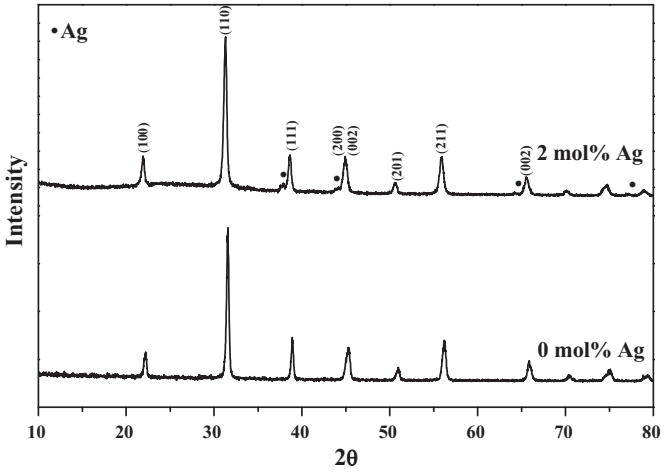


Fig. 5. XRD patterns of the pure and Ag-doped $BaTiO_3$ powders post-treated at 900 °C.

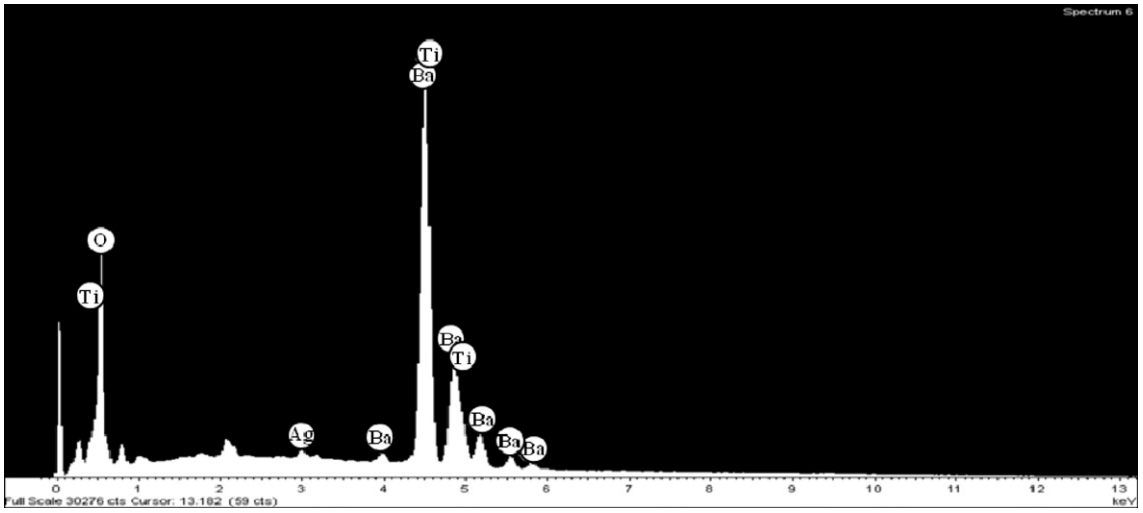
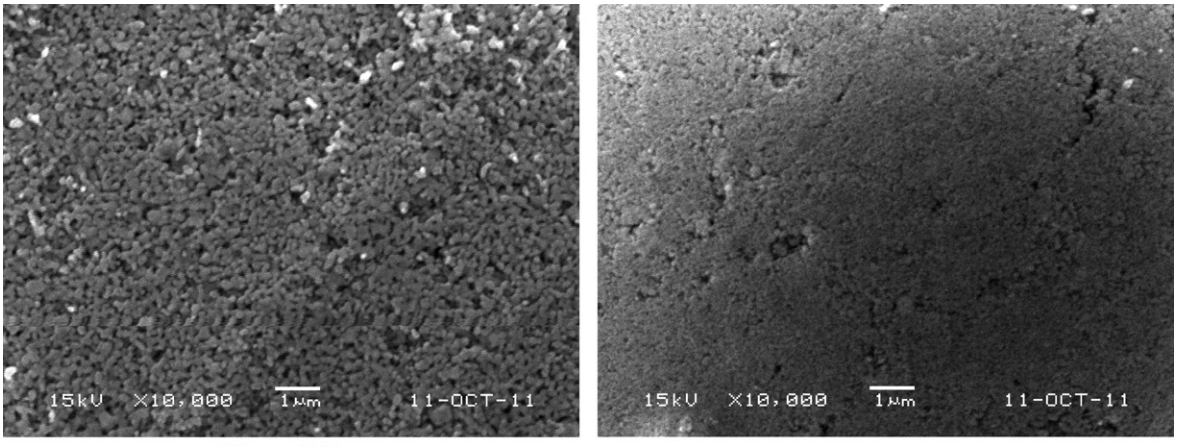
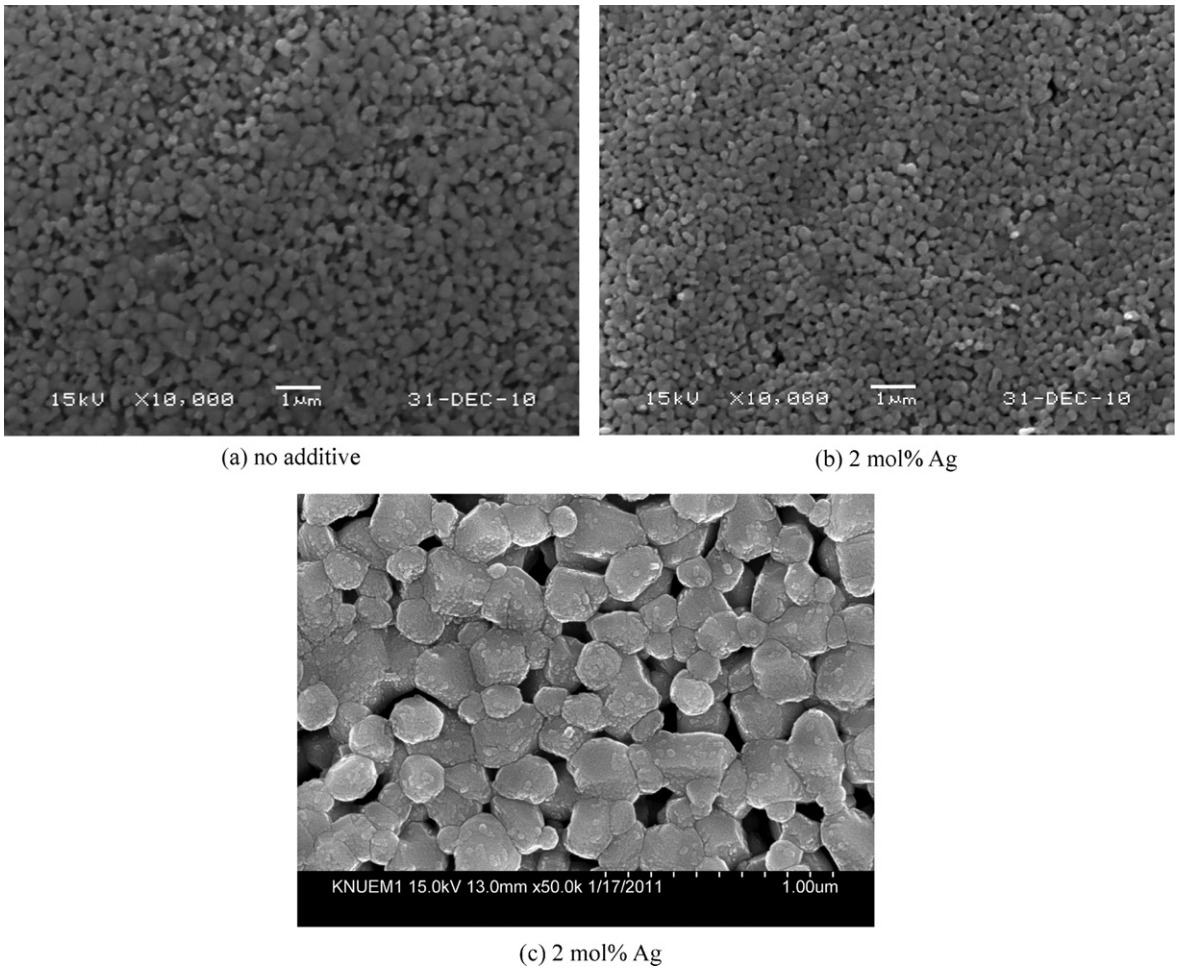


Fig. 6. EDX spectrum of the 2 mol% Ag-doped $BaTiO_3$ powders.



(a) no additive (b) 2 mol% Ag

Fig. 7. SEM images of the surfaces of the pellets sintered at 900 °C.



(a) no additive

(b) 2 mol% Ag

(c) 2 mol% Ag

Fig. 8. SEM images of the surfaces of the pellets sintered at 1000 °C.

particles were weak. Therefore, the aggregated particles could be easily milled to nanometer size. Figs. 3 and 4 show the powders' morphologies after milling by hand using an agate mortar. Both powders comprised nanoparticles with slight aggregation. The mean sizes and geometric standard deviations of the powders were determined from TEM images by counting more than 500 powders in each sample in order to minimize errors. The mean size and geometric standard deviation of the pure Ag powders measured from the TEM images were 75 nm and 1.36, respectively. However, the mean size and geometric standard deviation of the Ag-doped $BaTiO_3$ powders 91 nm and 1.45, respectively. The low-level Ag doping did not affect the morphology of the milled, post-treated $BaTiO_3$ powder.

The XRD patterns of the powders post-treated at 900 °C are shown in Fig. 5. Pure $BaTiO_3$ showed only cubic $BaTiO_3$, as the (2 0 0) and (0 0 2) peaks at $2\theta = 44.95^\circ$ were not split. The Ag-doped $BaTiO_3$ powder showed mainly cubic $BaTiO_3$, though with small peaks in the XRD spectrum attributable to Ag. The mean crystallite sizes of the pure and Ag-doped $BaTiO_3$ powders calculated from the full-width at half maximum (FWHM) of the (1 1 0) peaks of the XRD patterns using the Scherrer equation were 24 and 22 nm, respectively.

Fig. 6 shows the powders' EDX spectrum, which was used to derive the powders' compositions. The amount of Ag in the Ag-doped $BaTiO_3$ powders was 2.1 mol%. The composition of the spray solution was well maintained in the resulting Ag-doped $BaTiO_3$ powder.

The powders' sintering characteristics were investigated through examination of the surfaces of pellets sintered at 900 and 1000 °C for 2 h (Figs. 7 and 8). The pellet of Ag-doped $BaTiO_3$ had more fine grain size than that of pure $BaTiO_3$ at a sintering temperature of 900 °C. High content Ag dopant prohibited the coarsening of $BaTiO_3$ [4]. However, both powders sintered well, forming dense $BaTiO_3$ pellets, even at the low sintering temperature of 1000 °C. Fig. 9 shows dot mapping results of the sintered, doped pellet. Silver was uniformly distributed in the pellet without phase separation because the Ag was well distributed in the original $BaTiO_3$ powder.

The XRD patterns (Fig. 10) of the pellets sintered at 1000 °C showed single phase $BaTiO_3$ in the pure and doped pellets. The Ag dopant increased the tetragonality of the pellet. The doped pellet had distinct, split (2 0 0) and (0 0 2) peaks at $2\theta = 44.95^\circ$.

The dielectric constants at room temperature of the pure and doped pellets sintered at 1000 °C were 1826 and 2400, respectively (Fig. 11). The metal dopant was distributed

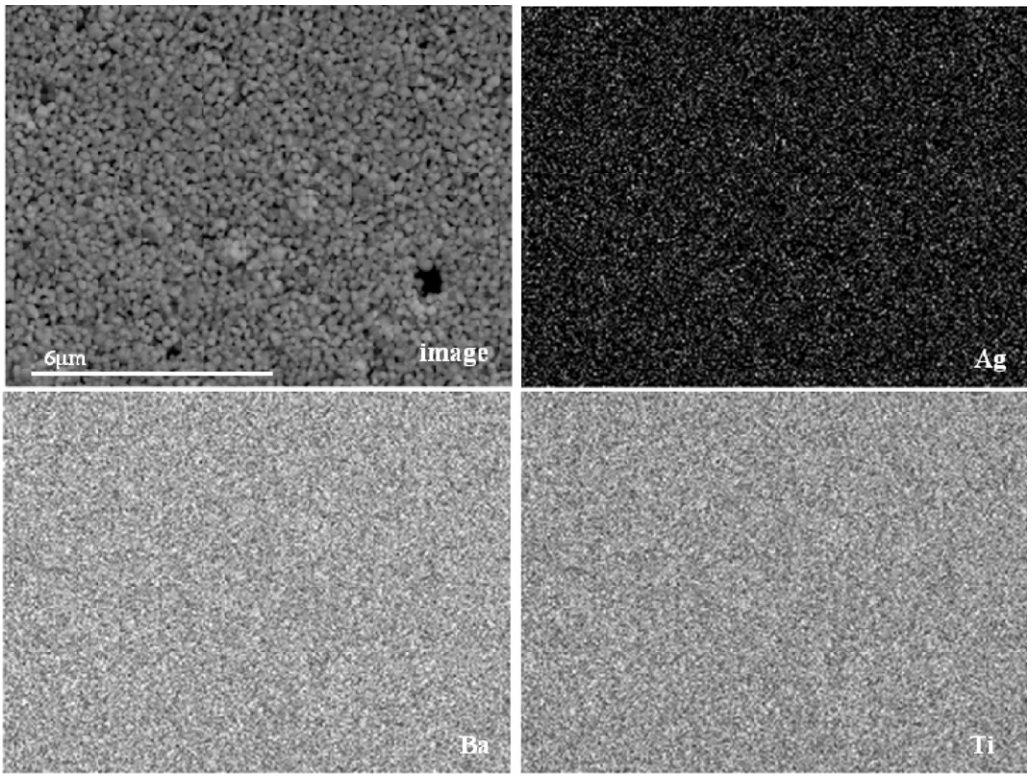


Fig. 9. Results of dot mapping of the pellet formed from the 2 mol% Ag-doped $BaTiO_3$ powders.

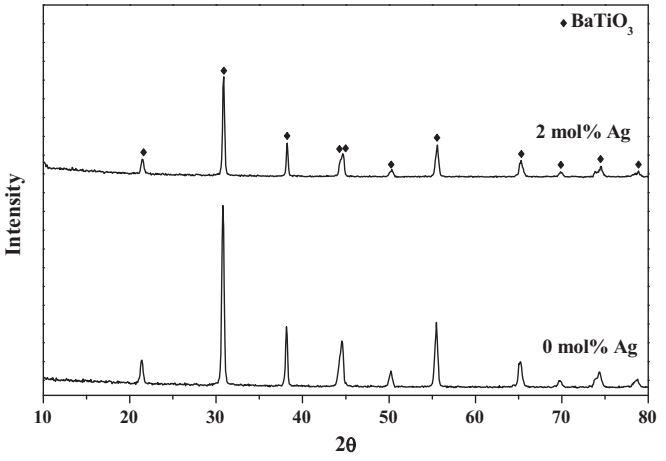


Fig. 10. XRD patterns of the pellets formed from the pure and Ag-doped $BaTiO_3$ powders.

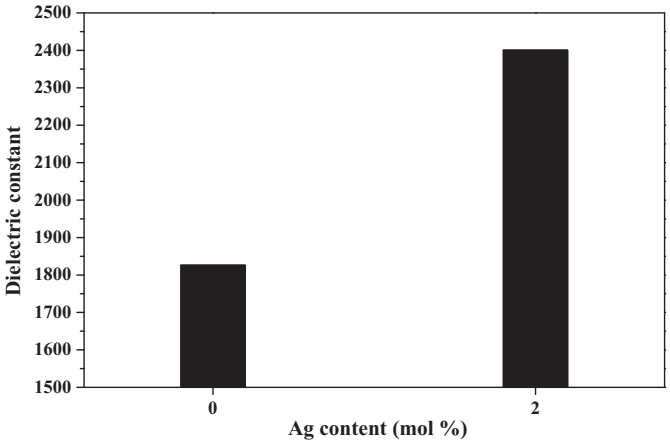


Fig. 11. Dielectric constants of the pure and Ag-doped $BaTiO_3$ ceramics sintered at 1000 °C.

uniformly in the $BaTiO_3$ matrix because Ag is insoluble in $BaTiO_3$ [6]. Therefore, the dopant was present in the form of second-phase inclusions in the $BaTiO_3$ matrix. Silver enhanced the effective electric area, acting as an inner electrode in the ceramic capacitor, increasing the dielectric constant the pellet [2].

4. Conclusions

The direct synthesis by spray pyrolysis of Ag-doped $BaTiO_3$ nanoparticle powder was studied. Citric acid and ethylenediaminetetraacetic acid (EDTA) were used as chelating agents in the powder's preparation. The hollow, thin-walled structures of the precursor powders allowed the formation of Ag-doped $BaTiO_3$ nanoparticle powder after heat treatment and hand milling. The nanoparticle powder sintered well, forming a pellet with uniformly distributed Ag because of the good distribution of Ag in the original powder. The Ag-doped $BaTiO_3$ pellet sintered at 1000 °C was of tetragonal $BaTiO_3$. Doping increased the pellet's tetragonality, and the Ag dopant, present as second-phase inclusions in the $BaTiO_3$ matrix, enhancing its dielectric constant.

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