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Characteristics of $BaO–B_2O_3–SiO_2$ nano glass powders prepared by flame spray pyrolysis as the sintering agent of $BaTiO_3$ ceramics

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ABSTRACT

Nanosized $BaO–B_2O_3–SiO_2$ glass powders are directly prepared by flame spray pyrolysis. The mean size of the $BaO–B_2O_3–SiO_2$ glass powders with amorphous phase and spherical shape is 30 nm. The effects of glass powders on the sintering characteristics of the $BaTiO_3$ pellet formed from the nanosized $BaTiO_3$ powders are investigated. The mean size and BET surface area of the $BaTiO_3$ powders prepared by spray pyrolysis are 110 nm and 9.1 m^2/g. The $BaTiO_3$ pellet with glass additive has large grain size with several microns, dense structure and pure tetragonal crystal structure at a sintering temperature of 1000 °C. The XRD pattern of the pellet has distinct split of (2 0 0) and (0 0 2) peaks at $2\theta \approx 44.95^\circ$. The dielectric constant of the pellet without glass additive is 2180. However, the dielectric constants of the pellets with 1, 3, 5 and 7 wt% glass additive with respect to $BaTiO_3$ are 2496, 2514, 2700 and 2225, respectively.

1. Introduction

Barium titanate ($BaTiO_3$)-based ceramics are widely used in multilayer ceramic capacitors (MLCCs) owing to their good dielectric properties [1–4]. However, in order to achieve $BaTiO_3$ with a high density and high dielectric constant, high sintering temperatures above 1300 °C is required. At present, adding glass with a low melting point is an effective and inexpensive way to reduce the sintering temperature of $BaTiO_3$-based ceramics [3–9]. Jeon et al. showed the effects of $BaO–B_2O_3–SiO_2$ glass additive on densification and dielectric properties of $BaTiO_3$ ceramics started from hydrothermally synthesized nano-sized $BaTiO_3$ powders (~60 nm) [5]. Addition of an optimal amount of the $BaO–B_2O_3–SiO_2$ glass to $BaTiO_3$ compacts accelerated densification with a limited grain growth. Hsiang et al. investigated the effects of various glasses ($BaO–B_2O_3–SiO_2$, $PbO–B_2O_3–SiO_2$, and $ZnO–B_2O_3–SiO_2$) addition on both the sintering behavior and dielectric properties of $BaTiO_3$ [6]. The results indicated that $ZnO–B_2O_3–SiO_2$ glass could be used as a sintering aid to reduce the sintering temperature of $BaTiO_3$ from 1300 °C to 900 °C without the formation of secondary phase.

To fabricate miniature MLCCs with high performance and low electric power consumption, the number of active dielectric layers is increased, while the thickness of these layers is decreased. Thus, the mean sizes of the dielectric and glass powders are decreased [10]. Nanosized $BaTiO_3$ powders have been widely studied in various liquid-solution and gas phase preparation processes for ceramic powders [11–14]. In recent, spray pyrolysis has been successfully applied to synthesize the nano-sized $BaTiO_3$ powders [15–17]. The precursor powders prepared from the spray solutions with organic additives by spray pyrolysis had hollow and porous morphology. After milling process followed the post-treatment process, nano-sized $BaTiO_3$ powders with non-aggregation characteristics could be obtained [15,16]. However, micron or submicron size glass powders with irregular morphology prepared by conventional melting process have been mainly used to decrease the sintering temperature of $BaTiO_3$ ceramic [3–9]. Nanosized glass powders have not been applied as the sintering agent for $BaTiO_3$ ceramics.

In recent, nanosized glass powders with various compositions were prepared by high-temperature flame spray pyrolysis [18–21]. Nanosized glass powders were formed from the evaporated vapors by chemical vapor deposition (CVD) process. The mean size of the Bi-based glass powders prepared by flame spray pyrolysis increased from 37 to 52 nm as the concentration of spray solution was changed from 0.05 to 1 mol/L [21].

In this study, nanosized $BaO–B_2O_3–SiO_2$ glass powders were directly prepared by flame spray pyrolysis. The effects of nanosized $BaO–B_2O_3–SiO_2$ glass powders on the sintering characteristics of the nanosized $BaTiO_3$ powders, which are prepared by spray pyrolysis, are investigated.

2. Experimental procedure

Glass powders with a 30 wt% BaO-60 wt% B_2O_3-10 wt% SiO_2 composition were directly prepared by high-temperature flame spray pyrolysis. The system of flame

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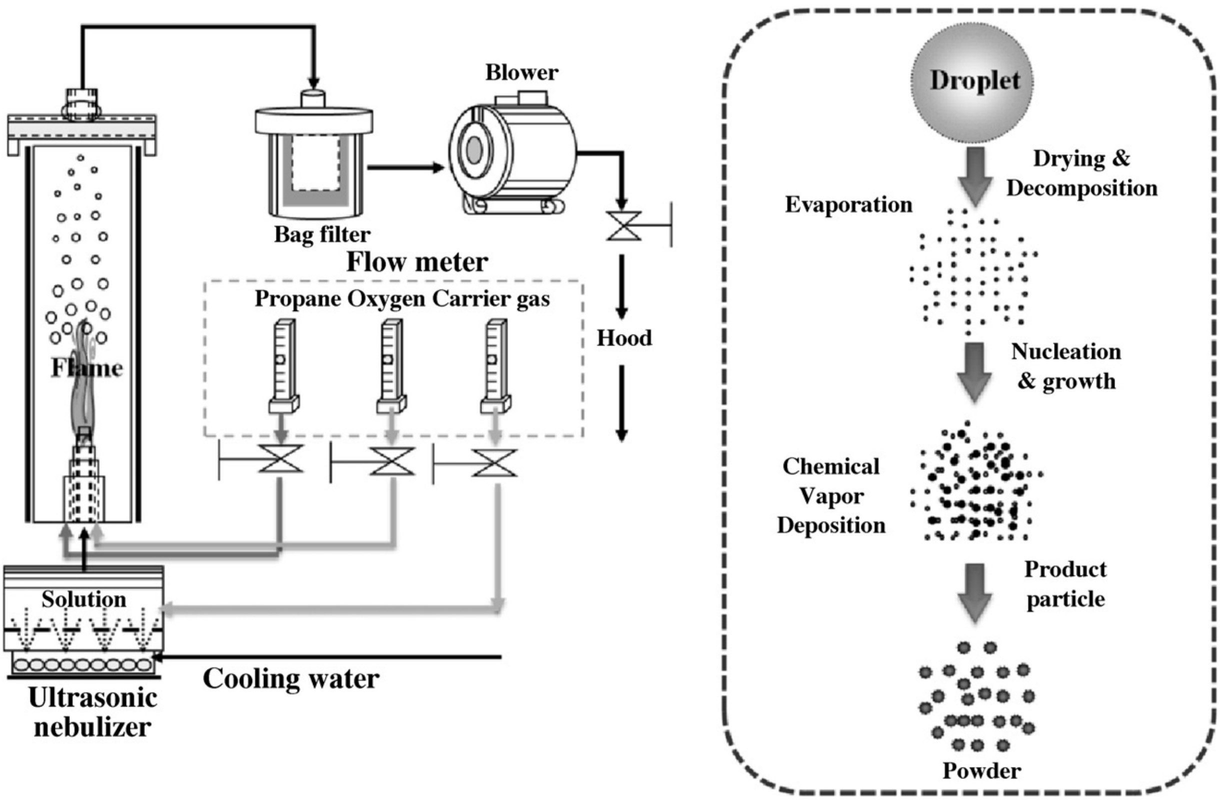


Fig. 1. Schematic diagram of flame spray pyrolysis and formation mechanism of nanosized glass powders.

spray pyrolysis has a droplet generator, flame nozzle, quartz reactor, powder collector, and blower as shown in Fig. 1. A 1.7 MHz ultrasonic spray generator with 6 resonators is used to generate droplets, which are carried into the high-temperature diffusion flame by oxygen, as the carrier gas. Droplets or powders evaporate, decompose, and melt inside the diffusion flame. Propane as the fuel and oxygen as the oxidizer create the diffusion flame. The flow rates of fuel, oxidizer and carrier gases were each 5, 40, and 10 L min^{-1}. The spray solutions were obtained by adding $Ba(NO_3)_2$, H_3BO_3, tetraethyl orthosilicate (TEOS) and nitric acid to the mixed solvent of distilled water and ethyl alcohol. Ethyl alcohol was added to the spray solution to increase the temperature of diffusion flame. Volume ratio of ethyl alcohol to distilled water was 30:70. The total concentration of Ba, B and Si components was 0.25 M.

Nanosized $BaTiO_3$ powders were prepared by spray pyrolysis [15,16]. Barium carbonate and titanium tetra-iso-propoxide (TTIP) were used as starting materials to prepare $BaTiO_3$ powders. The starting materials were added into a mixed solution of water and nitric acid to form a clear solution. The concentration of Ba and Ti was fixed at 0.1 M. The concentration of citric acid used as an organic additive was 0.4 M. The preparation temperature of $BaTiO_3$ powders was 900 °C. The flow rate of the carrier gas was 40 L min^{-1}, in which the residence time of the powders inside the hot wall reactor was 0.45 s. The as-prepared powders obtained by spray pyrolysis were post-treated at 900 °C for 2 h in air atmosphere.

The $BaTiO_3$ and glass powders were thoroughly wet-mixed with the addition of ethanol in an agate bowl and then small amount of PVA solution was added for granulation. The amount of glass powders were changed from 1 wt% to 7 wt% of $BaTiO_3$ powders. The mixed powders were pelletized at 250 kg cm^{-2} pressure into a 10 mm diameter. The pellets were then sintered at 1000 °C for 3 h and cooled naturally to room temperature while furnace power was off.

The crystal structures of the $BaTiO_3$ and glass powders and sintered pellets were investigated by using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu K α radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The morphological characteristics of the $BaTiO_3$ and glass powders were investigated by using field emission scanning electron microscopy (FE-SEM, HITACHI, S-4300) and transmission electron microscopy (TEM, FEI, TECHNAI 300 K). The composition of the glass powders and morphological characteristics of the pellets were investigated by using scanning electron microscopy (SEM, JEOL, JSM-6060) with energy dispersive spectroscopy (EDS). Dielectric measurements of the samples were performed by using a LCR meter at 1 kHz.

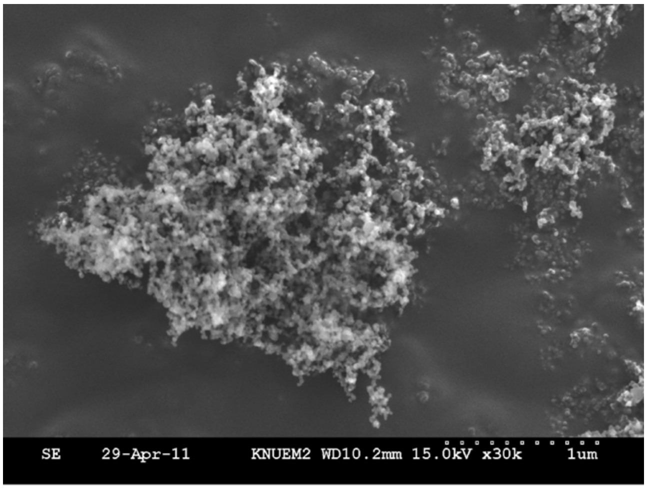
3. Results and discussion

The morphologies of the $BaO–B_2O_3–SiO_2$ glass powders prepared by flame spray pyrolysis are shown in Fig. 2. The glass powders had nanometer size and spherical shape. The mean size of the glass powders measured from the TEM image was 30 nm. Submicron size glass powders were not observed from the SEM and TEM images. Complete evaporation of glass components occurred inside the high temperature diffusion flame. Nanosized $BaO–B_2O_3–SiO_2$ glass powders were formed by chemical vapor deposition process from the evaporated vapors. The formation mechanism of the nanosized glass powders is shown in Fig. 1.

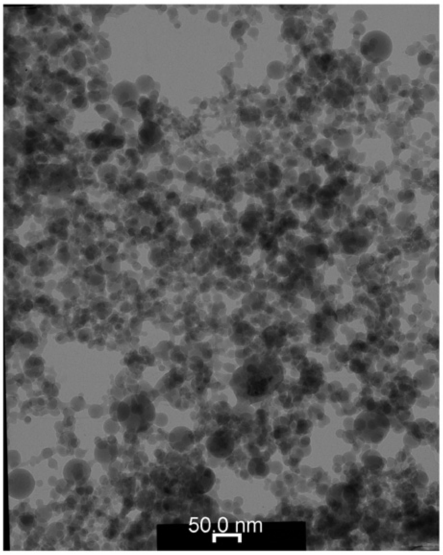
Fig. 3 shows the XRD pattern of the $BaO–B_2O_3–SiO_2$ glass powders prepared by flame spray pyrolysis. The XRD pattern reveals the amorphous nature of these prepared glass powders. However, small peaks of crystals are observed from the XRD pattern. Fig. 4 shows the EDS spectrum of the glass powders. The molar ratios of Ba to Si components in the spray solution and the glass powders were each 100:85 and 100:92. The molar ratio of Ba to Si components in the spray solution was well maintained in the glass powders.

The morphological characteristics of the $BaTiO_3$ powders are shown in Fig. 5. The $BaTiO_3$ powders used in this work were prepared by citric acid assisted spray pyrolysis [15]. The precursor powders prepared by spray pyrolysis from the spray solution with citric acid had hollow and porous structure [15]. The precursor powders prepared by spray pyrolysis were converted to nanosized $BaTiO_3$ powders after post-treatment at 900 °C. The mean size of the $BaTiO_3$ powders measured from the TEM image was 110 nm. The BET surface area of the $BaTiO_3$ powders was 9.1 m^2/g.

The effects of glass powders on the sintering characteristics of the $BaTiO_3$ pellets are investigated. Fig. 6 shows the surface morphologies of the sintered pellets containing various amounts of glass, ranging from 0 to 7 wt% with respect to $BaTiO_3$. The pellets were sintered at a temperature of 1000 °C. The $BaTiO_3$ pellet without glass powders had fine grain size and porous structure. The relative densities of the $BaTiO_3$ pellets with 0, 1, 3, 5 and 7 wt% glass measured by Archimedes' principle were 74, 91, 97, 98, and 95%. Addition of glass powders improved the sintering



(a) SEM



(b) TEM

Fig. 2. SEM and TEM images of the BaO–B_2O_3–SiO_2 glass powders prepared by flame spray pyrolysis.

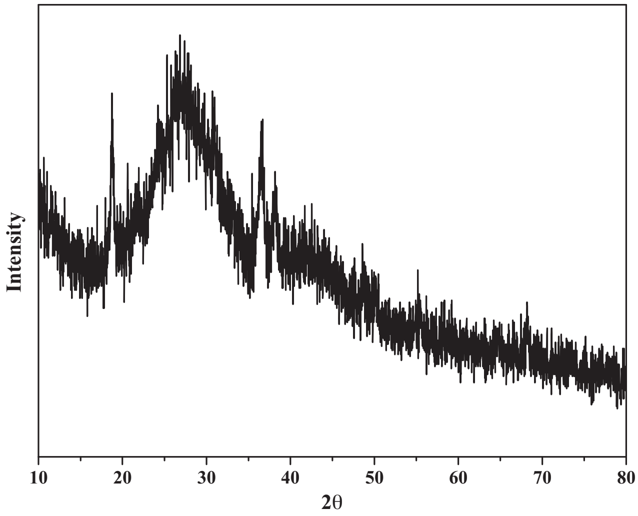


Fig. 3. XRD pattern of the BaO–B_2O_3–SiO_2 glass powders prepared by flame spray pyrolysis.

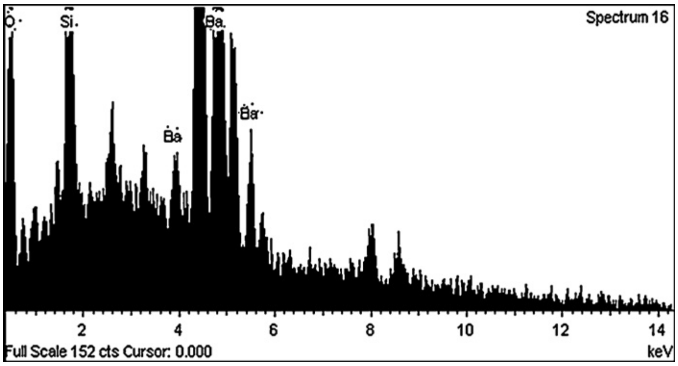
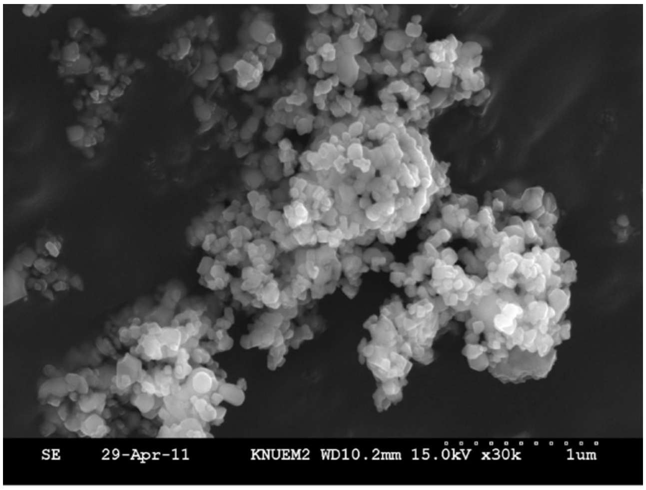
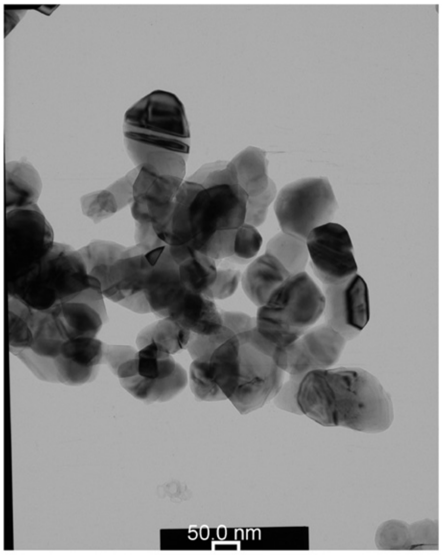


Fig. 4. EDS spectrum of the BaO–B_2O_3–SiO_2 glass powders prepared by flame spray pyrolysis.

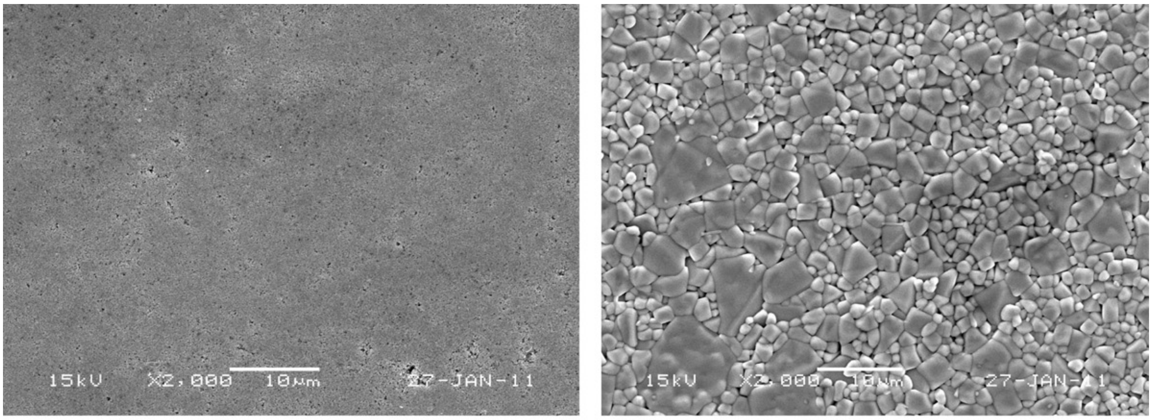


(a) SEM image

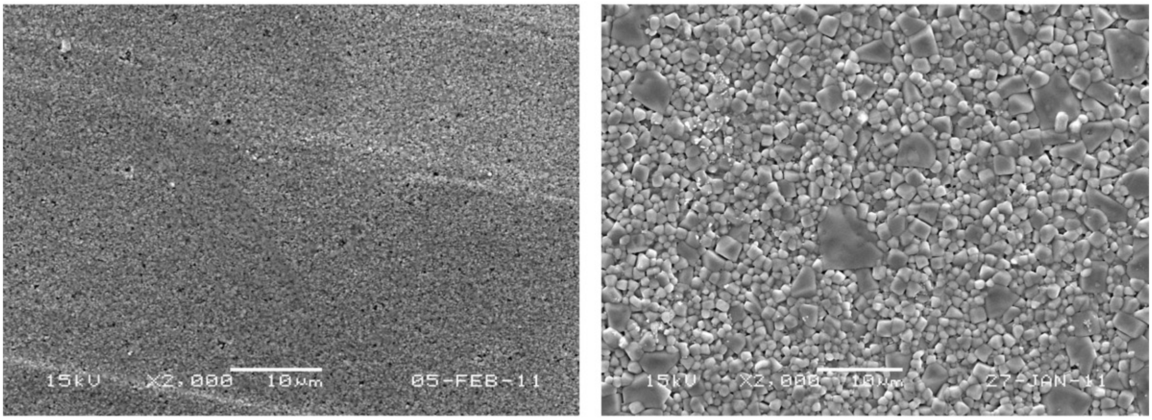


(b) TEM image

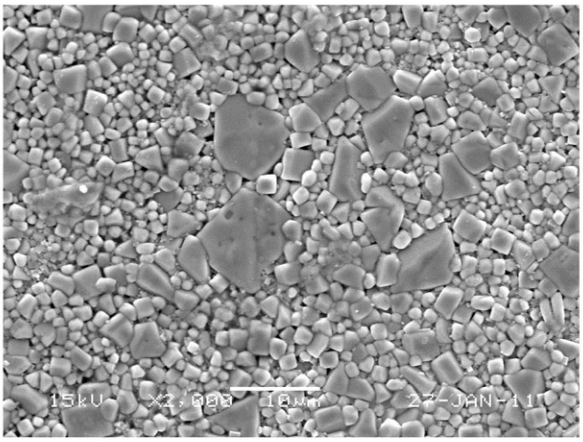
Fig. 5. SEM and TEM images of the $BaTiO_3$ powders prepared by spray pyrolysis.



(a) No glass (c) 3 wt% glass



(b) 1 wt% glass (d) 5 wt% glass

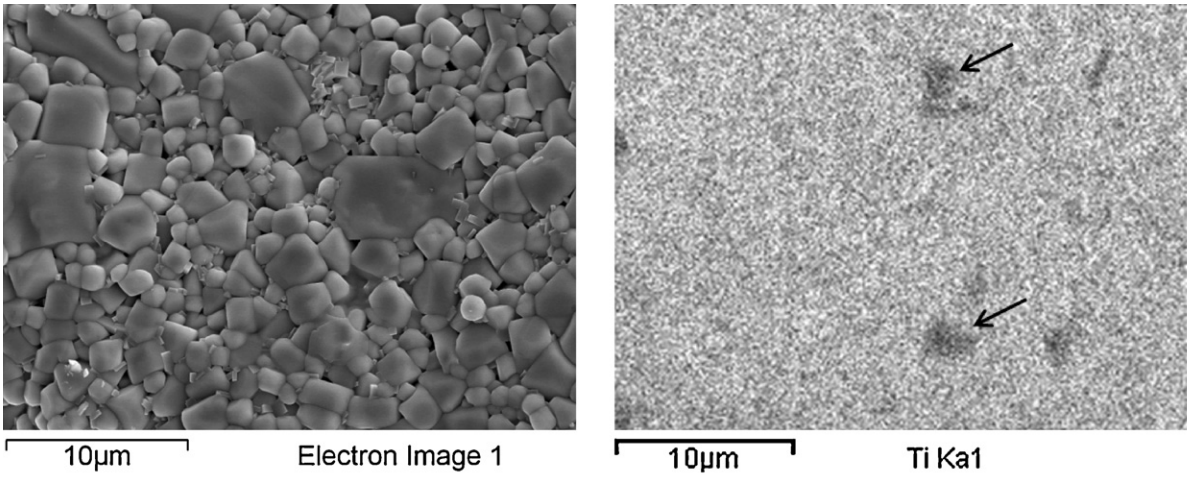


(e) 7 wt% glass

Fig. 6. SEM images of the $BaTiO_3$ pellets with different amounts of glass content.

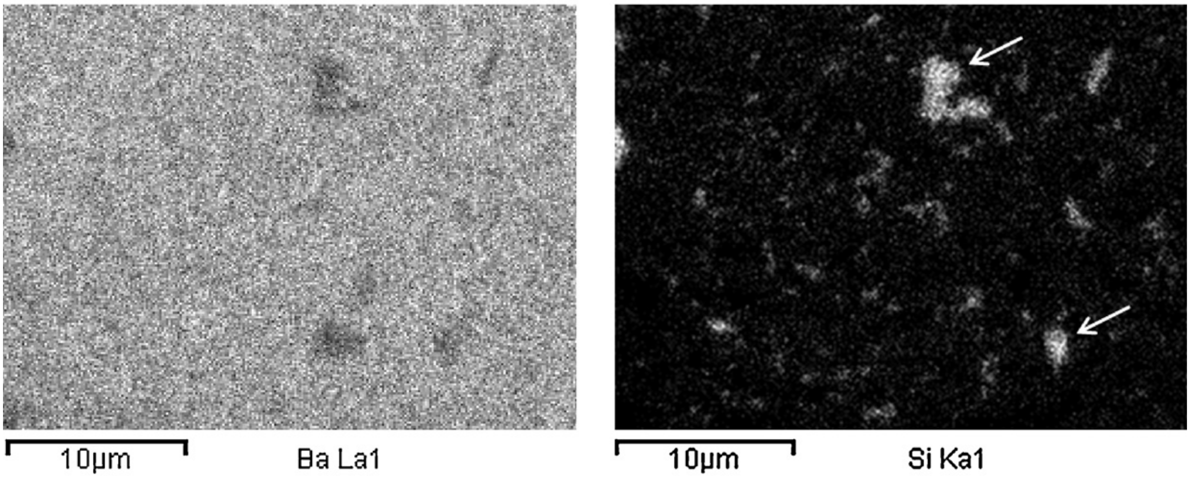
characteristics of the powders. The $BaTiO_3$ pellet with 1 wt% glass had fine grain size with several hundreds nanometers. On the other hand, the $BaTiO_3$ pellets with 3, 5 and 7 wt% glass had large grain sizes with several microns and dense structure. Fig. 7 shows the results of dot mapping of the $BaTiO_3$ pellet with 5 wt% glass. Some of glass material was segregated between the $BaTiO_3$ grains as shown by arrows in Fig. 7. However, the Si component of glass material was uniformly distributed between the $BaTiO_3$ grains. Well distribution of the glass powders in the pellet improved the sintering characteristics of $BaTiO_3$ even at a low sintering temperature.

Fig. 8 shows the XRD patterns of the sintered pellets with and without glass additive. The glass content was 5 wt% with respect to $BaTiO_3$. The pellet with glass additive had pure tetragonal crystal structure. The XRD pattern of the pellet with glass additive had distinct split of (2 0 0) and (0 0 2) peaks at $2\theta \approx 44.95^\circ$. The impurity peaks originated from the glass powders were not observed from the XRD pattern of the pellet. On the other hand, the split of (2 0 0) and (0 0 2) peaks at $2\theta \approx 44.95^\circ$ did not occur in the XRD pattern of the pellet without glass additive.



(a) 5 wt% glass

(c) Ti component



(b) Ba component

(d) Si component

Fig. 7. Results of dot mapping of the $BaTiO_3$ pellet with 5 wt% glass content.

Fig. 9 shows the dielectric constants of the $BaTiO_3$ pellets with various amounts of the glass additive. The sintering temperature was 1000 °C. The dielectric constant of the pellet without glass additive was 2180. However, the dielectric constants of the pellets with 1, 3, 5 and 7 wt% glass additive with respect to $BaTiO_3$ were 2496, 2514, 2700 and 2225, respectively. The high densities and improved tetragonality of the $BaTiO_3$ pellets containing glass additive resulted in an increase in the dielectric constants of the pellets.

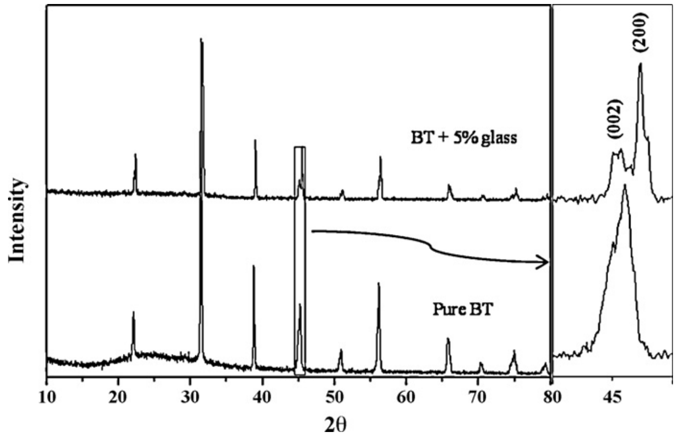


Fig. 8. XRD patterns of the $BaTiO_3$ pellets with and without glass.

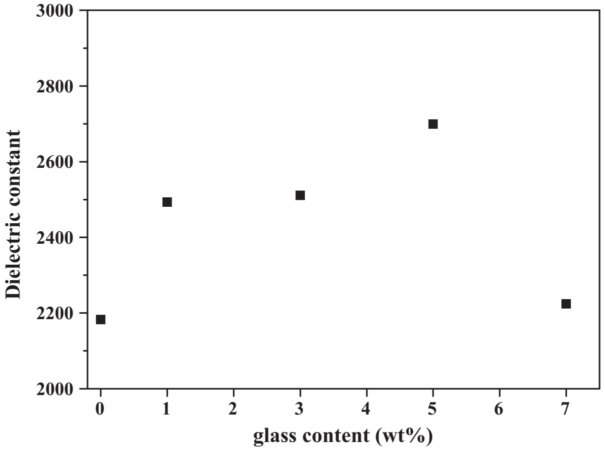


Fig. 9. Dielectric constants of the $BaTiO_3$ pellets with different amounts of glass content.

4. Conclusion

The effects of nanosized BaO–B_2O_3–SiO_2 glass powders on the sintering characteristics of the nanosized $BaTiO_3$ powders are investigated. Nano-sized glass powders prepared by flame spray pyrolysis had good characteristics as the sintering additive to obtain the $BaTiO_3$ pellet with dense structure and high dielectric constant. Well distribution of the glass powders in the pellet improved the sintering characteristics of $BaTiO_3$ even at a low sintering temperature. The high densities and improved tetragonality of the $BaTiO_3$ pellets containing glass additive resulted in an increase in the dielectric constants of the pellets.

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