Effects of BaO–B₂O₃–SiO₂ glass additive on densification and dielectric properties of BaTiO₃ ceramics

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Abstract

Effects of BaO–B₂O₃–SiO₂ glass additive on densification and dielectric properties of BaTiO₃ ceramics started from hydrothermally synthesized nano-sized BaTiO₃ powders (∼60 nm) were investigated. Addition of an optimal amount of the BaO–B₂O₃–SiO₂ glass to BaTiO₃ compacts accelerated densification with a limited grain growth. The sintering temperature of the BaTiO₃ ceramics was lowered to 900 °C with high density above 93%. Furthermore, there was no formation of secondary phases in the sintered bodies at the optimal amount of the glass. Higher dielectric constant was obtained from the BaTiO₃ ceramics with 1 wt% BaO–B₂O₃–SiO₂ glass, sintered at 900 °C, than those observed for the pure BaTiO₃ sintered at 1350 °C.

Keywords: BaTiO₃; Hydrothermal synthesis; Glass additive; Densification; Electrical properties

1. Introduction

Barium titanate (BaTiO₃) is one of the most widely used materials in electric ceramics. It has been utilized in primary materials for multi layer ceramic capacitor (MLCCs), electro-optic devices and thermistor because of its highly dielectric characteristics [1]. The current demand for device miniaturization in the electronic industry needs fabrication of MLCCs with uniform, ultra thin ceramic layers having excellent microstructure and electrical characteristics.

In conventional process of MLCC, the green dielectric BaTiO₃ layer and silver–palladium electrodes have been co-sintered at high temperature, above 1000 °C. The silver–palladium alloys have been widely used as an electrode material of which the firing temperature is limited by the amount of palladium required [2]. Since the noble metal electrodes are so expensive and the firing temperature is also high, the production cost of the multilayer ceramics is highly increased. For the low production cost, usage of cheaper electrodes and low temperature firing are required. To lower the sintering temperature of BaTiO₃ enables for us to use relatively inexpensive internal electrodes. Especially, to sinter at below 1000 °C is necessary in the low-temperature co-fired ceramics (LTCC) multilayer circuits with Cu internal electrodes [3]. Therefore, lowering the sintering temperature of the multilayered ceramics with a high dielectric constant should be studied.

The addition of glasses to BaTiO₃ green bodies promotes sinterability of the bodies, enabling us to fabricate high density BaTiO₃ ceramics at low temperature [4–10]. It has been reported that the glass materials form particle–particle bridges and disintegrate the solid particles into smaller grains by the liquid penetration [4]. Though the interaction and resultant liquid–solid interface properties are known to be strongly dependent upon chemical composition of the liquid phase, it is still difficult to make precise predictions about the liquid phase sintering behavior. The desirable characteristics of the liquid phase used as a sintering aid for the densification of BaTiO₃ ceramics are a low melting point,
unreactivity with BaTiO₃, a low viscosity at the sintering temperature and a high dielectric constant of the crystalline or the glassy secondary phase [5]. Wang et al. studied the effect of PbO-B₂O₃, PbO-SiO₂ and B₂O₃-B₂O₃ glass addition on the BaTiO₃ sintering [6]. The substitution of Pb into BaTiO₃ led to a noticeable grain growth of BaTiO₃ while the addition of the Bi glass deteriorated the density of the sintered body [5,6]. Sarkar and Sharma sintered micrometer-sized BaTiO₃ with B₂O₃ and PbB₂O₄ glasses from the temperature of 850–1000 °C [7]. Dielectric constants of the co-sintered BaTiO₃ were, however, below 900 because an excess amount of glass phases was used to densify micrometer-sized BaTiO₃ powder compacts.

The glass additive, though reducing the sintering temperature, may also introduce certain undesirable effects, such as decrease in dielectric constant, introduction of pores and formation of undesirable secondary phases, etc. [10]. The present study focuses on obtaining high-density dielectrics by low temperature sintering in the presence of an optimal amount of liquid phase without any undesirable phase formation. In order to obtain high dielectric ceramics, the most important step is to control the amount of glass additive for obtaining a high densification with a limited grain growth and to reduce the volume fraction of low dielectric secondary phases and porosity. For the study, grain size, relative density and dielectric properties of sintered samples at various temperatures were measured to investigate the effects of the BaO-B₂O₃-SiO₂ glass additive on BaTiO₃ ceramics.

2. Experiments

2.1. Preparation of BaTiO₃ powders

We prepared high-purity and nano-sized BaTiO₃ powders by the hydrothermal method using acylated titanium(IV) isopropoxide and barium acetate in KOH solution (pH 13.7, starting Ba/Ti = 1.8) [11]. As shown in Fig. 1(a), the BaTiO₃ particle size was approximately 60 nm with the narrow particle size distribution. Those raw powders were stabilized in the metastable cubic form at room temperature. The Ba/Ti ratio of raw powders is 0.974. Calcination was carried out to eliminate the organic compounds and hydroxide derivatives at 800 °C for 2 h.

2.2. Preparation of BaO-B₂O₃-SiO₂ glass

The glass of composition, 30 wt% BaO-60 wt% B₂O₃-10 wt% SiO₂, was prepared by mixing the raw materials BaCO₃, H₃BO₃ and SiO₂ (laboratory grade, Aldrich) as starting materials and melting them in a platinum crucible at 1300 °C [9]. The BaO-B₂O₃-SiO₂ glass exhibited density of 4.02 g cm⁻³ and melting temperature of below 850 °C. The glass was powdered homogeneously and then was mixed with pure BaTiO₃ powders in 1, 5 and 10 wt% proportion. Glass and BaTiO₃ powders were thoroughly wet-mixed with the addition of ethyl alcohol as a dispersion medium and the obtained slurry was dried in an oven. The dry mixture was pressed into pellets at the pressure of 3000 kgf cm⁻² (thickness: 2 mm, diameter: 10 mm). Green pellets were sintered at various temperatures for 3 h in air. The optimum sintering temperature was determined by the analysis of sintered densities and dielectric properties.

The sintered BaTiO₃ ceramics were studied by X-ray diffractometer (Rigaku, Miniflex, λ = 1.5406 Å, 30 kV, 15 mA, measured area: 44°–47°, 0.01°/step, 1/6 step/s) to analyze [0 0 2]/[2 0 0] peak splits and tetragonality. Scanning electron microscopy (SEM, Hitachi, S-4200) was employed to determine grain shape and size. Bulk density was measured on sintered pellets of pure and glass-added BaTiO₃ by the liquid displacement method. Capacitance was measured with the impedance analyzer (HP 4194) at the frequency of 1 kHz at 25 °C.

3. Results and discussion

Fig. 1 shows SEM micrographs of (a) the raw BaTiO₃ powders synthesized by hydrothermal method and (b)
BaTiO$_3$ ceramics sintered at 1350 °C for 3 h. Exact composition, particle size and distribution of BaTiO$_3$ powders make a direct influence on the microstructure of sintered BaTiO$_3$. The average particle size of the raw BaTiO$_3$ powders was about 60 nm and their size distribution was narrow. Even with nano-sized BaTiO$_3$ powders (∼60 nm), the grain size distribution of the sintered body became broad when sintering was performed at such a high temperature, as shown in Fig. 1(b). The relative density of pure BaTiO$_3$ sintered at 1350 °C for 3 h was found to be slightly smaller (94.5%, 5.69 g cm$^{-3}$) than that of theoretical density (6.02 g cm$^{-3}$). The sintering density for the nano-sized BaTiO$_3$ powders in this study is nearly similar with the density for the sub-micron sized powders (Cabot BT10, 400 nm) sintered at between 1300 and 1400 °C [12].

Fig. 2 shows the change of relative density of the BaTiO$_3$ ceramics with the amount of glass additive and sintering temperature. The effect of the glass additive became noticeable at a concentration of 1 wt% fraction by a substantial increase of the relative density in the interval from 850 to 900 °C. Their relative densities were 59.5 and 93.0%, respectively. We can see that the uniformly melted glass phase accelerates the densification of sintered bodies and lowers the sintering temperature. The lower density shown by all samples sintered at 850 °C might be due to the fact that the glass phase of these compositions was too viscous to penetrate the voids between BaTiO$_3$ particles. The addition of 1 wt% BaO–B$_2$O$_3$–SiO$_2$ glass was enough to densify the nano-sized BaTiO$_3$ particles at 900 °C. At above 900 °C all the samples did not show increase in sintering density with further addition of glass. The desintering phenomenon is very close related to a rapid grain growth with pore entrapment [13]. Excess liquid phase makes the growth rate of grain faster than the removal rate of entrapped gas in the inside pores. It leads an increase in entrapped gas pressure in the closed pores and bloats the pores. As a result the final density decreased.

Fig. 3 shows SEM micrographs of the BaTiO$_3$ ceramics sintered at temperature of 900 °C for 3 h with amount of glass. It is considered that the distribution of glass is so uniform in the green compact that a consistently small grain size (<0.6 µm) is achieved at 1 wt% glass (Fig. 3(a)). Since Ba$^{2+}$ is donor dopant, it seems to inhibit grain growth during liquid phase sintering at optimum amount of glass, 1 wt% BaO–B$_2$O$_3$–SiO$_2$ glass. It can be explained that the presence of 1 wt% liquid phase is enough to cause mobility of the BaTiO$_3$ particles and to result in the rearrangement of particles. Excess addition of glass phase, however, led to
the formation of heterogeneous size distribution of grains even at 900°C as shown in Fig. 3(b) and (c). It has been reported that abnormal grain growth is caused by heterogeneous distribution of liquid phase and broad size distribution of raw particles [14]. Since the size distribution of raw BaTiO₃ particles in this study is narrow, it is thought that abnormal grain growth is attributed to heterogeneous distribution of liquid phase. Fig. 4 is an EPMA analysis of the sintered bodies at temperature of 900°C for 3 h with different amount of glass additive. The sintered body with 1 wt% glass showed homogeneous composition in the entire area of the body. There were little variations in Ba/Ti ratio of the sintered body with 1 wt% glass. The compositional variation between normal grain and abnormal grain, however, was observed on the surface of the sintered body with 5 wt% glass. It is apparent that the variation of composition causes abnormal grain growth as observed in the SEM micrographs of Fig. 4(b). The abnormal grains showed compositions with an excess of Ba cations (Ba/Ti > 1.08), while the normal grains showed stoichiometric composition (Ba/Ti ≈ 1.01). It is well reported that BaO-rich BaTiO₃ (Ba/Ti > 1) undergoes normal grain growth [15,16]. We did not observed Ti-excess BaTiO₃ in the sintered body with 5 wt% glass. The inconsistency shows that the variation of composition is not caused by inhomogeneous composition of the Ba-excess grains but by heterogeneous distribution of glass phase.

Fig. 5 is XRD patterns of BaTiO₃ sintered at 900°C for 3 h with 1 wt% glass. The peak intensity ratio between them is 1:2 [17]. A substantial peak split in the XRD pattern was not observed until the raw BaTiO₃ particles were calcined at 1200°C [5]. The sintered sample at 900°C with 1 wt% glass, however, shows a clear peak split at 2θ = 45°. Li and Shih reported that the critical crystal size of BaTiO₃ was about 0.27 μm to show the tetragonal phase [18]. Combining SEM and XRD results, we came to a conclusion that the optimum amount of glass accelerated a fine grain growth of BaTiO₃. Hence,
tetragonality was well developed as well. Additional impurity peaks were not shown in the XRD patterns.

Changes of dielectric constant (at room temperature) for the BaTiO$_3$ ceramics with glass additives sintered at various temperatures for 3 h are shown in Fig. 6. The dielectric constant of pure BaTiO$_3$ sintered at 1350 $^\circ$C for 3 h is about 2,211. Dielectric constants of the BaO–B$_2$O$_3$–SiO$_2$ glass-added BaTiO$_3$ sintered at various temperatures for 3 h were found to be higher than that of the pure BaTiO$_3$ sintered at 1350 $^\circ$C for the same time. The maximum density and dielectric constants were obtained from the BaTiO$_3$ ceramics with 1 wt% glass (density = 5.62, dielectric constant = 2,781). Decrease in dielectric constants with further addition of BaO–B$_2$O$_3$–SiO$_2$ glass was again attributed to the decrease in density, which might be the result of the presence of excess vitreous phase and entrapped pores.

4. Conclusions

The sintering temperature of BaTiO$_3$ was lowered to 900 $^\circ$C with high density above 93% without formation of secondary phases when an optimal amount of the glass phase was added. Density and dielectric constants of BaTiO$_3$ ceramics with 1 wt% BaO–B$_2$O$_3$–SiO$_2$ glass sintered at 900 $^\circ$C were the maximum among all the glass-added BaTiO$_3$ ceramics examined in this study (density = 5.62 g cm$^{-3}$, dielectric constant = 2,781). Since the raw BaTiO$_3$ powders consisted of nano-particles ($\sim$60 nm), 1 wt% BaO–B$_2$O$_3$–SiO$_2$ glass addition caused to enhance densification with a fine grain size by low temperature firing. Regularly grown grains brought about tetragonal phase transition of the BaTiO$_3$ ceramics and achieved high performance dielectrics by low temperature firing.

References