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Materials

Effect of SiO_2 addition on the dielectric properties and microstructure of $BaTiO_3$-based ceramics in reducing sintering

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Abstract: The effect of SiO_2 doping on the sintering behavior, microstructure, and dielectric properties of $BaTiO_3$-based ceramics has been investigated. Silica was added to the $BaTiO_3$-based powder prepared by the solid state method with 0.075mol%, 0.15mol%, and 0.3mol%, respectively. The SiO_2-doped $BaTiO_3$-based ceramic with high density and uniform grain size were obtained, which were sintered in reducing atmosphere. A scanning electron microscope, X-ray diffraction, and LCR meter were used to determine the microstructure as well as the dielectric properties. SiO_2 can form a liquid phase belonging to the ternary system of BaO-TiO_2-SiO_2, leading to the formation of $BaTiO_3$ ceramics with high density at a lower sintering temperature. The SiO_2-doped $BaTiO_3$-based ceramics can be sintered to a theoretical density higher than 95% at 1220°C with a soaking time of 2 h. The dielectric constants of the sample with 0.15mol% SiO_2 addition sintered at 1220°C is about 9000. Doping with a small amount of silica can improve the sintering and dielectric properties of $BaTiO_3$-based ceramics.

Key words: barium titanate; multilayer ceramic capacitor (MLCC); reducing atmosphere; dielectric properties

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1. Introduction

Barium titanate ($BaTiO_3$, BT), a perovskite structure, has been widely investigated because of its dielectric and ferroelectric properties [1-2]. It is obvious that replacing the noble metal with base metal in multilayer ceramic capacitors (MLCC) can significantly reduce the production costs. The best candidate for such a replacement is Ni. Dielectric formulation and process technology for MLCC has been extensively investigated in the electronics industry [3]. Recently, MLCC with base-metal internal electrodes such as nickel have been developed to reduce the material cost [4-5]. In this case, dielectric should be sintered in a reducing atmosphere to prevent the oxidation of internal electrode. However, barium titanate ceramic becomes semiconducting and loses their high insulation resistance due to the unlocalized electrons produced by the formation of oxygen vacancies in a reducing atmosphere [6]. For the fabrication of MLCC with base metal electrodes, Mn is often added to maintain high insulation resistance even after sintering in a reducing atmosphere [7].

The Ni electrode is easily oxidized during the firing process. Consequently, low oxygen partial pressure during firing is indispensable. A reducing atmosphere may cause the formulation of oxygen vacancies in the ceramic body of a capacitor. For that reason, annealing as the sequential process of sintering was carried out in order to oxidize the ceramic bodies. The oxygen partial pressure was controlled by the equilibrium of H_2/H_2O, *i.e.* the water vapor pressure was adjusted by bubbling a hydrogen/nitrogen mixture through water at a controlled temperature. On the other hand, the reduction of the sintering temperature of $BaTiO_3$-based ceramics is very necessary to enable it to co-fire with Ni or Cu electrodes and for better electrical performance. The addition of some glass components is sometimes useful in decreasing the ceramic sintering temperature [8]. In the conventional method, glass was prepared in advance and then mixed with the other starting materials [9-10].

The purpose of this study is to investigate the ef-

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fects of the SiO_2 addition on the dielectric properties of $BaTiO_3$-based ceramics. The influence of sintering temperature on the microstructure was investigated using scanning electron microscopy (SEM) examination.

2. Experiment

The samples were prepared from high purity $BaCO_3$, TiO_2, $CaCO_3$, ZrO_2, and MnO_2 raw materials by using the conventional solid state reaction method. The raw materials are shown in Table 1. The average particle sizes for all raw materials are listed in Table 2. The SiO_2-doped powder was pressed into disk form (10 mm in diameter, 1 mm in thickness) using the 3wt% PVA binder. The specimens were sintered at the temperatures ranging from 1220 to 1300°C for 2 h in reducing atmosphere (o_2: 50 ppm). The densities of the sintered compacts were measured by the Archimedes' method using water as the liquid medium. The microstructures of the polished samples were examined by SEM (model S2500, Hitachi, Tokyo, Japan). Using an automatic capacitance bridge (HP4278A), the capacitance and dissipation factor of the samples were measured at 1 kHz/1 V, and the temperature dependence of relative capacitance was studied in the range of –30 to 85°C. Insulation resistance was measured using HP 4140A after applying 50 V D.C.

Table 1. Brand of the chemical agents

Reagent	Molecular weight	Brand
$BaCO_3$	197.35	Nippon-chemical
$CaCO_3$	100.08	Merck
TiO_2	79.9	Fuji-titanium
ZrO_2	123.22	Merck
MnO_2	86.94	Merck

Table 2. Average particle size distribution of raw materials

Raw powder	Average particle size, D_{50} / μm
$BaCO_3$	1.75
$CaCO_3$	0.46
TiO_2	0.29
ZrO_2	0.27
MnO_2	1.50

3. Results and discussion

3.1. Effect of sintering temperature and SiO_2 on the physical characteristic and microstructure

The particle size of the starting powder was controlled at 0.4±0.1 μm. The curves of the bulk density of $BaTiO_3$-based ceramic pellets *vs.* sintering temperature with different SiO_2 additions are shown in Fig. 1. It can be seen that the density of the sintered ceramics without SiO_2 addition increases approximately linearly with sintering temperature ranging from 1220 to 1300°C. The bulk density of $BaTiO_3$-based ceramics sintered at 1300°C for 2 h is 5.5 g/cm^3. The bulk density can be increased significantly at 1220°C by 0.15mol% and 0.3mol% SiO_2 addition. It is well known that the addition of some glass components is sometimes useful in decreasing the ceramic sintering temperature [8].

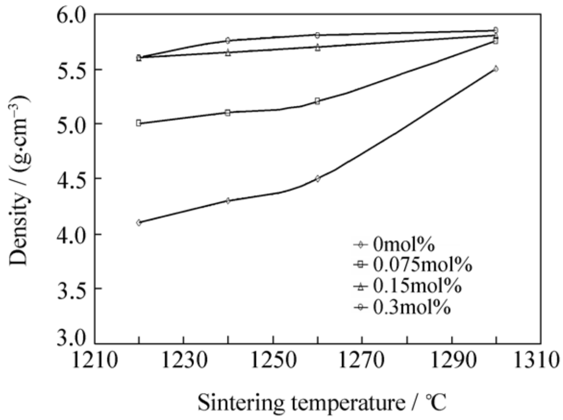

Fig. 1. Bulk density *vs.* sintering temperature of the $BaTiO_3$-based ceramics with different SiO_2 additions.

The X-ray diffraction spectra of the as-sintered ceramic are given in Fig. 2. The XRD pattern of the sintered sample mainly consists of the $BaTiO_3$ crystalline phase without minority phases in the ceramic. Fig. 3 shows the SEM photographs of the $BaTiO_3$ samples sintered at 1220°C for various SiO_2 additions. Many pores in the sample can be observed in Fig. 3(a), which was sintered at 1220°C without SiO_2 addition. Significant densification and grain growth progress as the SiO_2 content increases. Fig. 4 shows the grain size of the $BaTiO_3$-based specimen as a function of the SiO_2 content. The sintered specimen with 0.15mol% SiO_2 addition exhibits the average grain size of about 2.5 μm, where the bulk density is 5.7 g/cm^3 (> 95% of the theoretical density). However, the sintered specimen with 0.075mol% SiO_2 addition shows smaller grain sizes with poor sintering densities (83% of the theoretical density). This result represents the normal densification process of ceramic bodies, indicating that there is no densification without grain growth. It was reported that the driving forces for densification and grain growth are comparable in magnitude, both being proportional to the reciprocal grain size in this final-stage sintering [11-12]. Thus, this has greatly hampered the efforts to produce dense materials with a nano-size grain structure. For the SiO_2 addition from 0.15mol% to 0.3mol% and sintered at 1220°C, a slight grain growth was observed, whereas the density insignificantly increased still keeps at 5.7 g/cm^3.

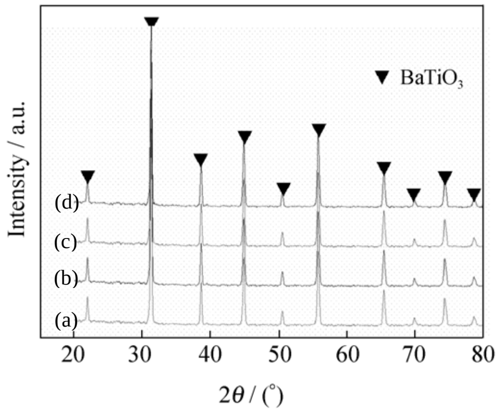

Fig. 2. X-ray diffraction spectra of the $BaTiO_3$-based ceramics at 1220°C with different SiO_2 additions: (a) 0; (b) 0.075mol%; (c) 0.15mol%; (d) 0.3mol%.

3.2. Effects of sintering temperature and SiO_2 on dielectric properties

The dielectric constant of the $BaTiO_3$-based ceramics was measured at 1 kHz, and the result is shown in Fig. 5. Similar to the bulk density *vs*. sintering temperature curve of the sample without SiO_2 addition in Fig. 1, the dielectric constant of the $BaTiO_3$-based ceramics increases with increasing sintering temperature. The ε_r value of the $BaTiO_3$-based ceramic without SiO_2 addition spans from 5600 (1220ºC) to 15000 (1300ºC). For this class of ceramics, it is possible to obtain high dielectric constant, *e.g.* $\varepsilon_r > 12000$, only by raising the sintering temperature above 1300ºC. The sintering temperature can be lowered down to 1220ºC by an addition of 0.15mol% or 0.3mol% of SiO_2 glass to the ceramics. Therefore, it can be concluded that the SiO_2 glass phase is effective in lowering the sintering temperature of the $BaTiO_3$-based ceramics having high dielectric constant. The loss tangent of the $BaTiO_3$-based ceramics is shown in Fig. 6. The dielectric loss of $BaTiO_3$-based ceramics is apparently reduced by enhancing the sintering temperature, and it also depends on the addition of SiO_2. For the $BaTiO_3$-based ceramics without SiO_2 addition, it is closely related to the sintering temperature only, *e.g.*, the dielectric losses of the ceramic are 5.44%, 3.62%, 2.43%, and 2.33% for sintering at 1220, 1240, 1260, and 1300ºC, respectively.

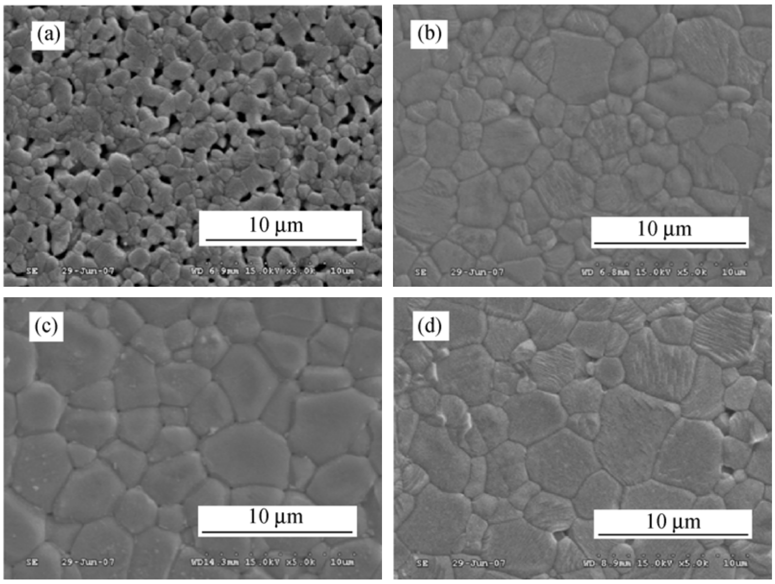

Fig. 3. SEM images of the samples of the $BaTiO_3$-based ceramics sintered at 1220°C with different SiO_2 additions: (a) 0; (b) 0.075mol%; (c) 0.15mol%; (d) 0.3mol%.

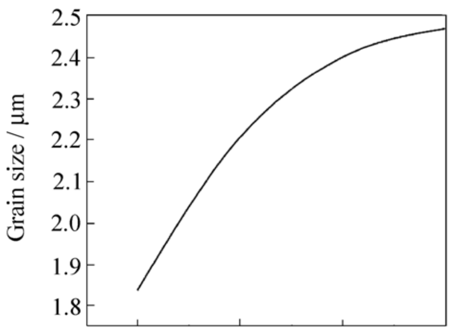

Fig. 4. Relationship between the mean grain size and SiO_2 addition for the $BaTiO_3$-based ceramics sintered at 1220°C.

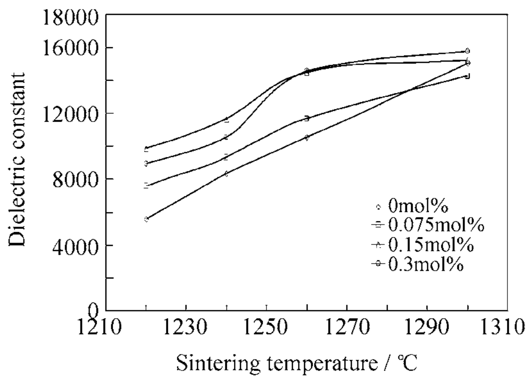

Fig. 5. Curves of the dielectric constant *vs.* sintering temperature of $BaTiO_3$-based ceramics with different SiO_2 contents.

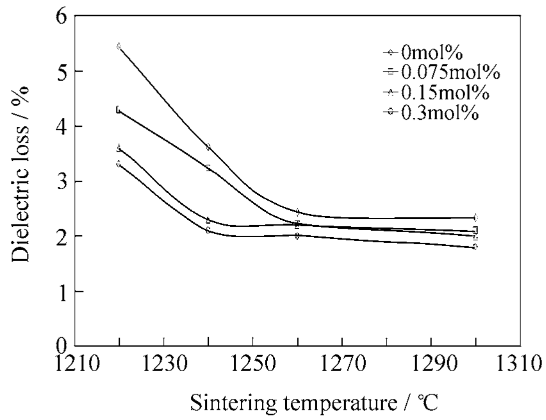

Fig. 6. Curves of the dielectric loss *vs.* sintering temperature of $BaTiO_3$-based ceramics with different SiO_2 contents.

Fig. 7 shows the insulation resistance of $BaTiO_3$-based ceramics sintered at 1220°C as a function of SiO_2 content. It can be seen that the insulation resistance of $BaTiO_3$-based ceramics increases with increasing SiO_2 content. The reason for this can be explained by the density of ceramics. Fig. 8 shows the temperature coefficient of the capacitance (TCC) of $BaTiO_3$-based ceramics at the temperature ranging from –30 to 85°C. All the samples can satisfy the Y5V TCC specification ($\Delta C/C$: +20% ~ –80%).

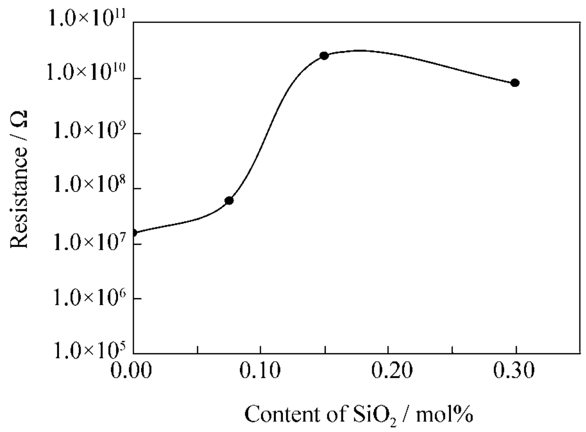

Fig. 7. Insulation resistance of $BaTiO_3$-based ceramics sintered at 1220°C as a function of SiO_2 content.

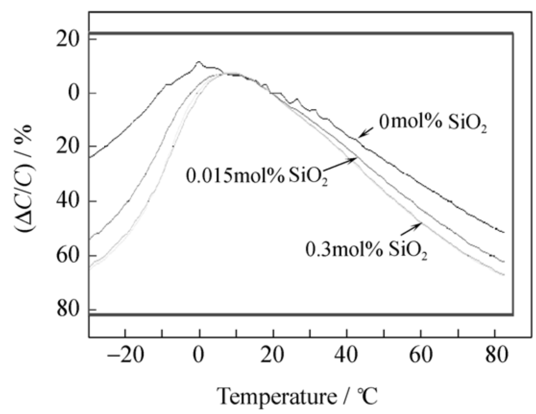

Fig. 8. TCC curves of the $BaTiO_3$-based ceramics with different SiO_2 additions.

4. Conclusions

(1) The grain size is enhanced by increasing the SiO_2 content for the $BaTiO_3$-based ceramics sintered at 1220ºC in reducing atmosphere.

(2) Sintering temperatures can be lowered from 1300 to 1220ºC when SiO_2 is added at 0.15mol% and 0.3mol%, respectively.

(3) The SiO_2 dopant plays the role of sintering in aiding to enhance the densification of $BaTiO_3$-based ceramics without change in the stoichiometry. Better electrical properties are obtained with increasing SiO_2 content due to the improvement of densification.

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