EFFECT OF SINTERING TEMPERATURE ON DIELECTRIC PROPERTIES OF SiO_2 DOPED $BATiO_3$ CERAMICS

Kerim Emre Öksüz[1]*, Merve Torman[2], Şaduman Şen[2], Uğur Şen[2]

[1]Cumhuriyet University, Department of Metallurgical & Materials Engineering, 58140, Sivas, Turkey

[2]Sakarya University, Department of Metallurgical & Materials Engineering, 54187, Sakarya, Turkey

Abstract

SiO_2-doped $BaTiO_3$ ceramics were prepared by solid state mixed oxide technique. The effect of small amounts (0.3 mol %) of SiO_2 additive on the microstructure, sintering behavior and dielectric properties of $BaTiO_3$-based ceramics have been investigated. SiO_2-doped $BaTiO_3$ ceramics sintered at 1175°C, 1200°C and 1225°C for 4h in air atmosphere have been found to exhibit high density and a uniform grain size. A scanning electron microscopy, X-ray diffraction analysis and LCR meters have been used to determine the microstructure, phase analysis and dielectric properties of the SiO_2 doped $BaTiO_3$ ceramics. The SiO_2 can form a liquid phase belonging to the ternary system BaO-TiO_2-SiO_2, leading to the formation of $BaTiO_3$ ceramics with high density at the lower sintering temperature, and improves the sintering and dielectric properties of $BaTiO_3$-based ceramics.

Key words: *Barium titanate, Dielectric properties, Microstructure, Sintering, SiO_2*

1. INTRODUCTION

Donor doped barium titanate ($BaTiO_3$) ceramics, which has a positive temperature coefficient of resistance, is a great candidate of components for self-regulating heaters, overcurrent or overload protectors and thermal sensors (He 2000; Huang 2002). Usually, the microstructure of such ceramics is a result of liquid phase sintering. The required liquid phase is formed by a reaction between a suitable additive and the $BaTiO_3$ matrix powder (Felgner 2001; Shen 2009). Some glass-based flux additions are especially effective for these purposes and they are generally adopted as sintering aids for barium titanate-based ceramic components and devices, among which SiO_2 is one of the most important components. It was reported that there exists a ternary eutectic in the system of BaO–TiO_2–SiO_2, and SiO_2 addition promotes grain growth and lowers the sintering temperature of $BaTiO_3$ ceramics through liquid phase sintering (Felgner 2001), though the nature of the working liquid phase is still under investigation. Thus, its effects on the ceramic properties are so important that many researches have been done on this aspect (Lee 2009; Belous 1987; Koppen 1976; Chung 2010; Senz 1998; Hesse 2002). Yoo et al. (Yoo 1997) found that SiO_2 could trigger exaggerated grain growth of $BaTiO_3$ ceramics with Ba/Ti ratio of 0.999. Moreover, SiO_2 could not only promote anomalous grain growth, but also lowers the sintering temperature (Felgner 2001). Wang et al. have pointed out that glass-based flux additions not only result in liquid phases at high temperatures, some of their components can also be incorporated into $BaTiO_3$ lattice and modify the dielectric properties, such as the curie temperature and the sharpness of the ferroelectric transition as usual dopants (Shen 2009). In another aspect, the segregation of SiO_2 into grain boundaries was found to deteriorate the electrical properties (Nakano 1993). In this paper, SiO_2-doped $BaTiO_3$ ceramics are prepared via the solid state mixed oxide technique. The influence of the sintering temperature on the microstructure and dielectric properties of ceramics has also been investigated.

2. EXPERIMENTAL PROCEDURE

SiO_2-doped $BaTiO_3$ ceramics used in this study were prepared by the conventional ceramic processing techniques. Commercially available powders of $BaCO_3$, SiO_2 and TiO_2 (Alfa Aesar A1319, 98.9 % purity) were used as starting materials. $BaCO_3$, TiO_2 and SiO_2 powders were mixed as to be 0.7/1.0/0.3 molar ratio. The stoichiometrically weighed amounts of these powders were milled by ball milling technique in isopropyl alcohol using ZrO_2 balls at 200 cycles/min for 24 h. and then dried in a

pyrex pan. The dried powders were calcined at 800 ˚C for 2 h. The calcined powders were crushed using the planetary ball mill for a short duration, and compacted by cold uniaxial pressing at 200 MPa and then sintered at 1175, 1200 and 1225°C for 4 h (at a ramp of 5°C/min.). Then, the samples were polished and etched metallographically. The microstructures, surface morphology and elemental analysis of the ceramics were observed by scanning electron microscopy (SEM, Model JEOL-JSM 6060-LV, Japan) and energy-dispersive X-ray spectroscopy (EDX). XRD analysis was conducted with a Rigaku D/MAX-2200/PC type diffractometer (Tokyo, Japan) with Cu-K_α radiation, which has a wavelength of 1.5418 Å over a 2θ range of 10°–90° with of 0.033° increments per second to analyze phases formed in the ceramic materials. For dielectric measurements, Ag paste was printed on both sides of the sintered pellet and then heat treated at 600 °C for 30 min. The frequency dependence of dielectric properties was characterized using a precision LCR Meter (Hioki 3532-50 LCR, Japan) at 1 kHz-1MHz at room temperature. The densities were obtained by Archimedes' method.

3. RESULT AND DISCUSSION

The X-ray diffraction spectra of the SiO_2-doped $BaTiO_3$ ceramics sintered at 1175°-1200°C and 1225°C for 4h was given in Figure 1. In all cases, the diffractograms have predominantly registered the phase of barium titanate - ($BaTiO_3$), matched for every sample (ICSD card no. 79-2265). X-ray diffraction patterns of SiO_2 doped BaO-TiO_2 powders show that the peaks correspond to $BaTiO_3$ crystalline phase, confirming that SiO_2 is effectively incorporated into the $BaTiO_3$ matrix. The figure proves that the barium titanate ceramics are successfully produced without noticeable undesirable phases.

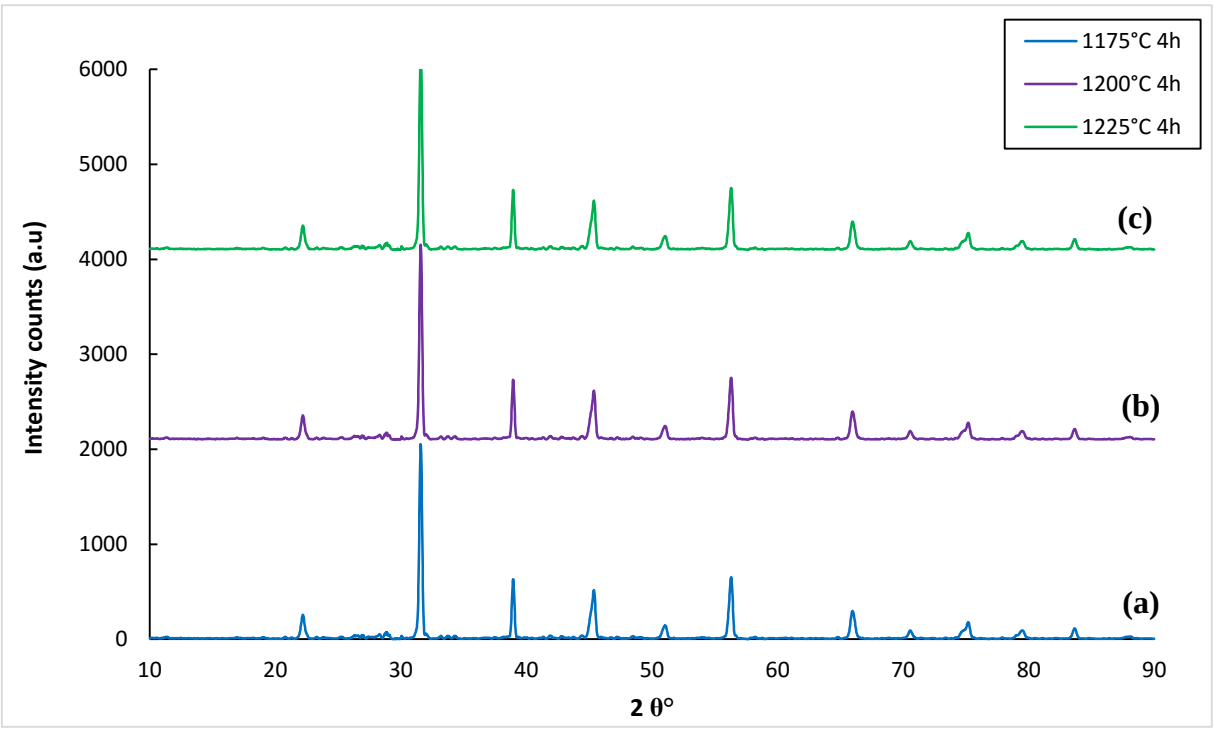


Figure 1. X-ray diffraction patterns of SiO_2-doped $BaTiO_3$ sintered at different temperatures for 4 h. (a) 1175°C, (b) 1200°C, and (c) 1225°C.

Yan et al. (Yan 2016) reported, when SiO_2 was 0.5 wt%, no second phase was detected in $BaTiO_3$ ceramics. With further increase of SiO_2 content, $Ba_2TiSi_2O_8$ was detected as the second phase. When SiO_2 addition reached 1 wt%, the Curie point of SiO_2 added BT ceramics increased slightly, but the dielectric constant decreased. That is because the amount of $Ba_2TiSi_2O_8$ phase increased with the

addition of SiO_2 from 0.5 to 1.0wt%, directly leading to smaller dielectric constant. When the addition of SiO_2 reached 2 wt%, more $Ba_2TiSi_2O_8$ phase appeared and induced the formation of the chemically in homogeneous structure, finally resulting in diffused phase transition and much smaller dielectric constant. The microstructures of SiO_2-doped $BaTiO_3$ ceramic with different sintering temperatures are shown in Figure 2. According to the reference (Felgner 2001), the surface morphologies of barium titanate based ceramics are also strongly dependent on sintering temperature. From Figure 2, we can obviously see that a dense microstructure consisting of essentially large grains compared to other samples was observed when *T*= 1225°C (Fig 2c). SEM images (a), (b) and (c) in Figure 2 reveal that homogeneous morphology with different grain size distribution were obtained for all compositions depending on sintering temperatures. Figure 2 reveals that the increasing sintering temperature (1175°C to 1225°C) increases the bulk density of the composites due to the higher amount of glassy phase. Figure 2 (from a, b to c) also represents the surface morphology of samples become more smooth by increasing temperature due to increasing glassy phase as can be seen in SEM images (Fig. 2c′). Density measurements showed that the density of SiO_2 doped barium titanate ceramics increased from 3.98 to 5.69 g•cm^{-3} with increase in sintering temperatures of 1175° to 1225°C. As observed, especially in Figure (2c and 2c′), the increasing glassy phase and SiO_2 may contribute to the smoothness of the surface and more particles seem to be embedded to the matrix structure. Also, in this specimen, the fine-grained structure has completely appeared.

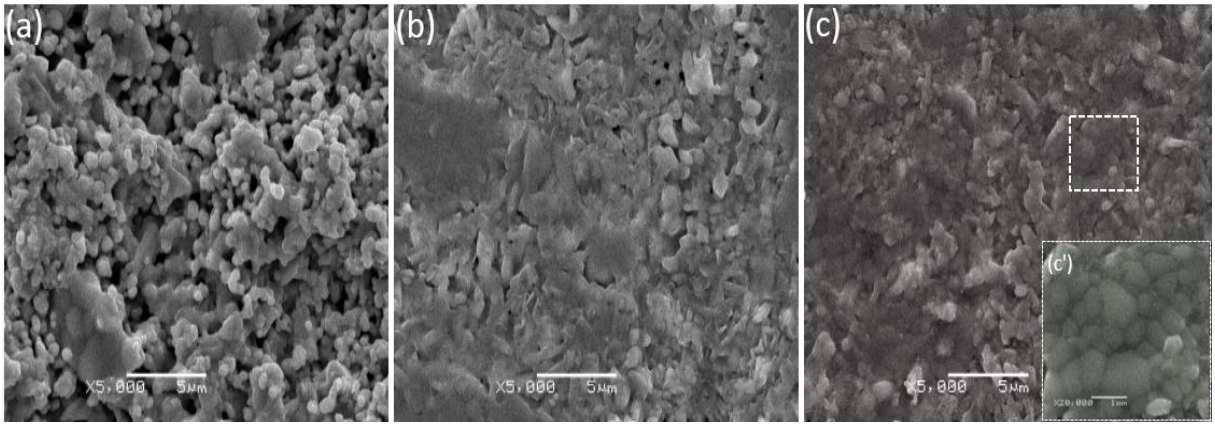


Figure 2. SEM photos of the microstructure of the SiO_2 doped BT ceramics: (a)1175°C, (b)1200°C and (c-c′) 1225°C.

The dielectric constant of the $BaTiO_3$-based ceramics was measured at 1 KHz - 1 MHz, and the results are shown in Figure 3. The dielectric constant of the $BaTiO_3$-based ceramics increases with increasing sintering temperature. The results agree with ref (Lee 2009b). ε_r value of the $BaTiO_3$-based ceramic with 0.3 mol %, SiO_2 addition spans from 2850 (1175ºC) to 5350 (1225ºC). For this class of ceramics, it is possible to obtain high dielectric constant, *e.g.* ε_r>12000, only by raising the sintering temperature above 1300ºC. 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 (Lee 2009a,2009b). In this case, the sintering temperature can be lowered down to 1300ºC by an addition of 0.3 mol % of SiO_2 glass to the ceramics. From the graph, the dielectric constant is seen to decrease with increase in frequency. The largest value of dielectric constant at low frequency is due to the presence of space charge polarization (Bhat 2002). The decrease in the value of dielectric constant with increase in frequency is due to the fact that the frequency of electric charge carriers cannot follow the alternation of the AC electric field applied beyond a certain critical frequency (Ponpandian 2002). The loss tangent of the $BaTiO_3$-based ceramics is shown in Figure 4. The dielectric loss of $BaTiO_3$-based ceramics is apparently reduced by enhancing sintering temperatures. It clearly shows the dielectric loss (tanδ) value of SiO_2 doped $BaTiO_3$ ceramic sintered at 1225°C has much lower when compare to other ceramics sintered at 1175°C and 1200°C. In both sintering temperature, dielectric loss decreases with increase in the frequency.

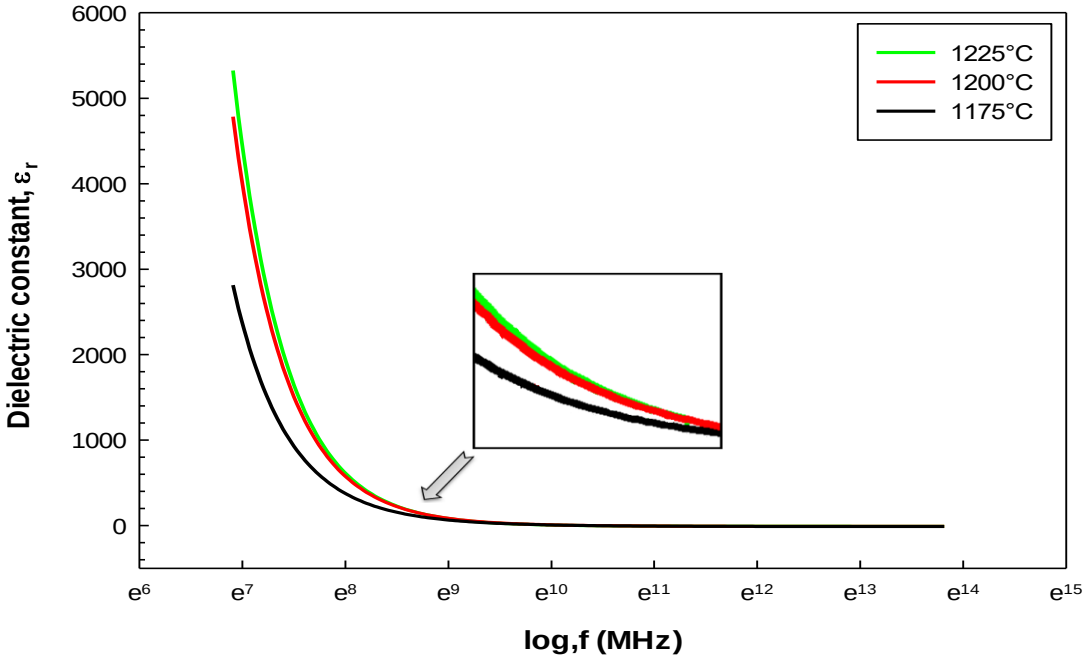


Figure 3. Dielectric constants of the SiO_2 doped BT ceramics as a function of the frequency.

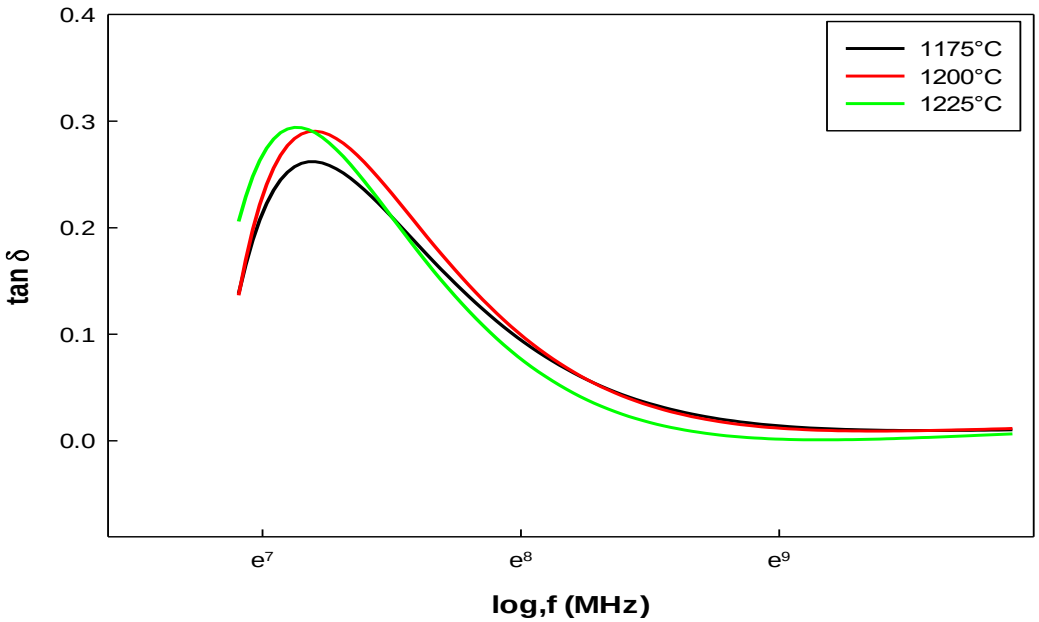


Figure 4. Dielectric loss of SiO_2 doped BT ceramics as a function of the frequency.

4. CONCLUSIONS

SiO_2-doped $BaTiO_3$ solid solutions were prepared by the solid state reaction method. All the ceramics examined showed that there was a single-phased perovskite crystal structure after sintering at 1175, 1200 and 1225ºC for 4 hours. The influence of sintering temperature, sintering behavior, the microstructural evolution and the electrical properties of SiO_2-doped $BaTiO_3$ ceramics has been investigated. 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 by increasing the sintering temperature due to the improvement of densification.

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