

Effect of Zn dopant on the dielectric properties of $(\text{Ca}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ ceramics

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Zn doped $(\text{Ca}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ (CSTZ) ceramics were fabricated using the conventional solid state reaction method. Dopant (Zn), which plays the role of acceptor, substitutes the B-site in the perovskite structure and generates oxygen vacancies due to the charge compensation. With increasing concentration of Zn, the grain size and relative density of doped CSTZ was increased because oxygen vacancies assist in the migration of ion during sintering. As a result, the dielectric constant increased and the dielectric loss decreased. When the concentration of Zn is 0.25 mol%, the dielectric constant and loss of Zn doped CSTZ at 1,000Hz are 199 and 0.076, respectively. Therefore, Zn doped CSTZ has the possibility of being used as a microwave capacitor.

Key words: $(\text{Ca}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$, Zn Doping, Charge compensation, Dielectric properties.

Introduction

Recently lightness and ease of miniaturization have become important requirements in electronics such as tablets, personal computers, mobile phones, and laptops. However, recent electronics have many functions and require numerous components in order to use these functions [1, 2]. Consequently, in order to provide more components to electronics, research on these components is needed. Among these components, passive components occupy most of the surface of the printed circuit board (PCB). Therefore, to provide a greater number of passive components on the PCB, the size of the components should be reduced while maintaining their performance. Especially, because the proportion of the capacitor to the passive component is about 60%, research for the capacitor is an effective approach [3]. The important criteria of performance for the capacitor are dielectric constant and loss [4]. A promising material satisfying these requirements is the ABO_3 type ceramics with a perovskite structure. Particularly, among the perovskite structures, superior dielectric properties of $(\text{Ca}_{1-x}\text{Sr}_x)(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics with a change in the x value has been observed [3, 5-7]. The $(\text{Ca}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ (CSTZ) ceramics show high dielectric constant, low dielectric loss, and stable coefficient of capacitance. Also, the doping method in ABO_3 type ceramics has been extensively used to improve dielectric properties [8, 9]. Among the dopant types, the acceptor dopant generates an oxygen vacancy called a point defect. In the CSTZ, the Zn dopant substitutes Ti^{4+} or Zr^{4+} because the radii of Zn^{2+} (0.74 Å) are similar to those of

Ti^{4+} (0.605 Å) and Zr^{4+} (0.72 Å). The Zn^{2+} dopant thus plays an important role in CSTZ.

In this paper, we reported Zn doped CSTZ fabricated by the conventional solid state reaction method. The dielectric properties were investigated based on Zn amounts. To confirm the dielectric properties of Zn doped CSTZ, all the samples were measured by impedance analysis.

Experiments

The ZnO-doped $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2}$ samples were prepared using the conventional solid state reaction method. CaCO_3 (Aldrich, 99%), SrCO_3 (Aldrich, 99.93%), TiO_2 (Aldrich, 99.76%), ZrO_2 (Aldrich, 99.8%), and ZnO (Duksan, 99%) were used as starting powders. Based on the composition of $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2}$ and doped ZnO (0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 mol%), the starting powders were mixed using a ball mill for 24 hrs with ethyl alcohol and a zirconia ball. The mixed powder was dried at 100 °C, and calcined at 1,100 °C for 4 hrs in air in order to remove the impurities. The calcined powders were then pressed into 12 mm diameter discs. The fabricated Zn-doped CSTZ samples were sintered at 1,400 °C for 4 hrs and the resulting samples were polished. Silver paste was used as the electrode and then fired at 400 °C for 10 minutes. The crystallinity of Zn-doped CSTZ was confirmed by X-ray diffraction (XRD). A scanning electron microscope (SEM) was used to observe the microstructures of CSTZ according to the concentration of Zn. The relative density of CSTZ with doping concentration was measured using the Archimedes method. The dielectric properties of Zn-doped CSTZ were measured using an impedance analyzer.

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Results and Discussion

The X-ray diffraction patterns of CSTZ with Zn content ranging from 0 to 0.3 mol% are shown in Fig. 1(a). All samples, regardless of doping concentration, show a perovskite ABO_3 . However, the secondary phase was observed at 0.3 mol% because of the excessive amount of Zn. Fig. 1(b) shows the shifted peak associated with the doping concentration of Zn. When the Zn dopant in CSTZ increased, the peak close to 32° was slightly shifted toward a lower angle. This phenomenon can be explained by the difference of ionic radius located at the B site. The ion radius of Zn^{2+} (0.74 Å with 6 coordination number) was larger than that of Zr^{4+} and Ti^{4+} (0.72 and 0.605 Å with 6 coordination numbers, respectively). As a result, the lattice parameter of Zn doped CSTZ was increased.

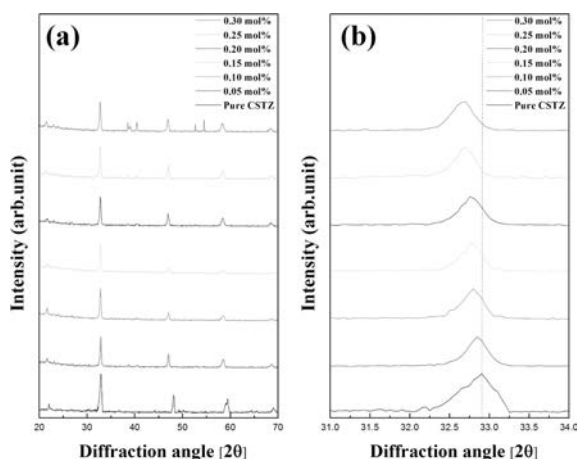


Fig. 1. XRD patterns of CSTZ ceramics doped with different contents of Zn: full spectrum of all samples; (b) evolution of all samples at 2θ from 31° to 34° .

The coordination numbers of the A and B sites in an ideal cubic perovskite ABO_3 are 12 and 6, respectively. In this experimental, A site: $\text{Ca}^{2+} = 1.34$ Å, $\text{Sr}^{2+} = 1.44$ Å; B site: $\text{Zr}^{4+} = 0.72$ Å, $\text{Ti}^{4+} = 0.605$ Å, $\text{Zn}^{2+} = 0.74$ Å, $\text{O}^{2-} = 1.4$ Å. Accordingly, Zn^{2+} substitutes the B site because the radius of Zn^{2+} is similar to the radius of the B site ion. As Zn^{2+} substitutes the B site, the incorporation reactions are as follows:



in perovskite unit cells, the oxygen vacancies arising from the doping of Zn ion give rise to local deformation. Therefore, these vacancies will affect the grain size and relative density of Zn doped CSTZ.

Fig. 2 shows the SEM images of x mol% Zn doped CSTZ sintered at $1,400^\circ\text{C}$ for 4 hrs. With increasing Zn doping content, the average grain size gradually increased. The primary factors of grain growth rate are boundary mobility (M_b) and interfacial energy (γ) [4]. The grain boundary mobility was obtained by $M_b = D_b \Omega / \delta k T$. In this equation, Ω , D_b , and δ are the atomic volume, boundary diffusion coefficient, and boundary thickness, respectively [10]. The diffusion coefficient was controlled by modifying the point defect concentrations generated by the additive [11]. The generated oxygen vacancies help the migration of the material during the sintering. Therefore, the increase of concentration for Zn leads to a high boundary diffusion coefficient and grain growth rate because the Zn dopant generated a high concentration of point defects. Compared with the SEM images, the grain size of CSTZ with 0.25 and 0.3 mol% is greater than that of pure CSTZ. Also, as the concentration of doping was increased, the reduction of

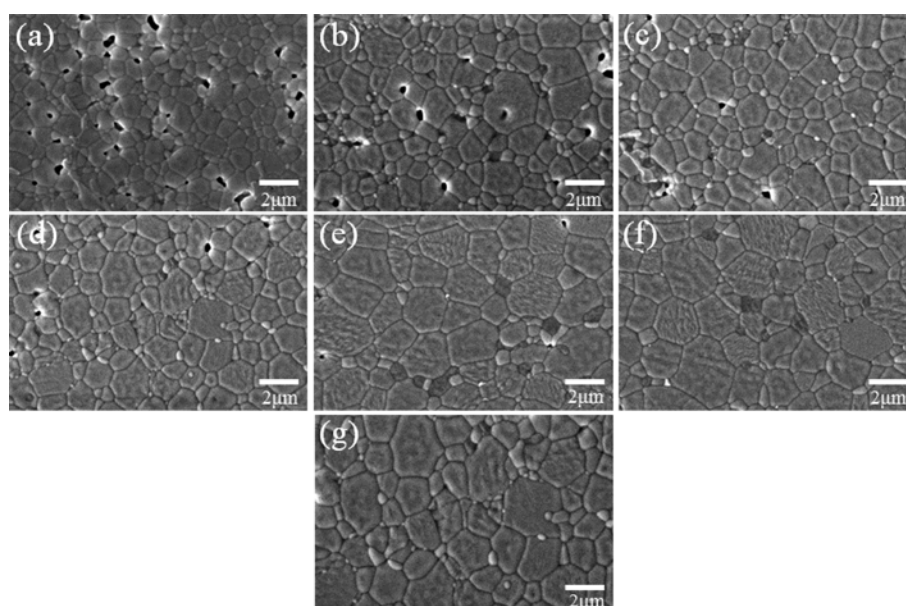


Fig. 2. SEM images of x mol% Zn doped-CSTZ ceramics (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.15$, (e) $x = 0.2$, (f) $x = 0.25$, and (g) $x = 0.3$.

porosities was observed until 0.3 mol%. The decreased number of porosities was related to the high relative density. Therefore, increased grain size and decreased number of porosities is associated with dielectric properties.

The relative densities of CSTZ with various Zn^{2+} doping concentrations are shown in Fig. 3. The relative density of Zn doped CSTZ initially increases to a maximum at 0.25 mol%. At 0.3 mol%, the relative density was not increased because Zn^{2+} in CSTZ was saturated. The high relative density will also affect the dielectric constant.

The dielectric constants of CSTZ with various Zn dopings at room temperature are shown in Fig. 4(a). When the amount of Zn in CSTZ was increased, the dielectric constant increased. Also, all samples regardless of applied frequency have a stable dielectric constant. At 1,000 Hz, the dielectric constant of 0.25 mol% Zn doped CSTZ, which is 1.7 times higher than that of pure CSTZ (122), was 199. This is explained by the increased grain size induced by point defects. It is well known that the grain size and densification affect the dielectric constant [9]. The dielectric constant Zn doped CSTZ initially increases to a maximum at 0.25 mol%, then decreases at 0.3 mol%. The cause of the decreased dielectric constant may be because Zn in CSTZ was saturated at 0.3 mol% [9, 12]. The substitution of

dopant Zn^{2+} also affects the dielectric loss because the oxygen vacancies will generate a higher dielectric loss [9]. When the doping concentration was increased, dielectric loss increased, as shown in Fig. 4(b). The dielectric loss of CSTZ with 0.25 and 0.3 mol% was high. This result shows that Zn doped CSTZ has better dielectric properties than those of pure CSTZ.

Conclusions

Zn doped CSTZ was fabricated by conventional solid state. The effect of Zn doping in CSTZ was investigated. The acceptor dopant Zn which generated the oxygen vacancies leads to increased grain size and decreased number of porosities. As a result, good dielectric properties were observed. The optimized concentration of doping was 0.25 mol% ($\epsilon = 199$ and $\tan\delta = 0.076$). Therefore, Zn doped CSTZ can be used for various applications.

Acknowledgments

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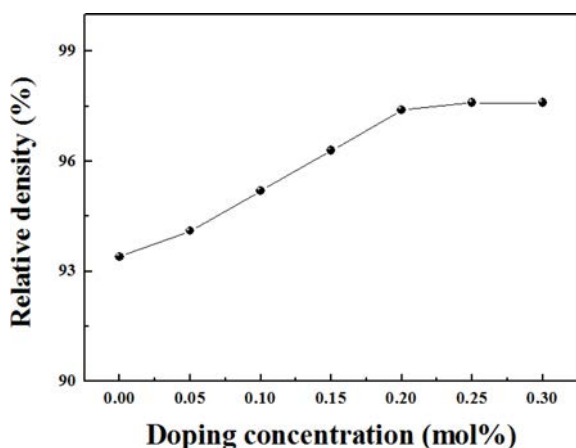


Fig. 3. Density of the Zn-doped CSTZ ceramics with various doping content.

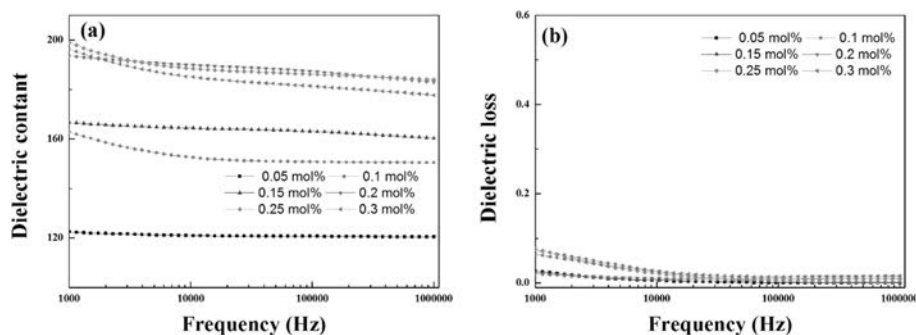


Fig. 4. Frequency dependences of the (a) dielectric constant and (b) dielectric loss of the x mol% Zn-doped CSTZ.

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