

Dielectric and structural properties of $(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ ceramics

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$(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ ceramics were fabricated on conventional mixed oxides method. The experimental results show that sintering temperature strongly affects the microstructure and dielectric properties of CSZT ceramics. The optimum sintering temperature was 1450 °C, exhibiting relatively high dielectric constants and quality factors in wide frequency ranges (51.7 and 1379) (at 1 MHz), (50.1 and 1328) (at 3.5 GHz). Also, CSZT ceramics sintered at 1450 °C meets C0G characteristic (± 30 ppm/°C, $-55^\circ\text{C} \sim 125^\circ\text{C}$). These results indicated that CSZT ceramics can be applied to materials for microwave ceramics.

Key words: $(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$, Dielectric properties, Sintering temperature, C0G characteristic

Introduction

With the ever increasing functionality, portability, and switching frequencies of consumer electronics, multilayered ceramic capacitors (MLCCs) classified as passive components have been intensively studied to improve the dielectric properties of ceramic materials such as high dielectric constant (ϵ_r) to reduce the size of components, low dielectric loss, and a small temperature coefficient of dielectric constant (TCK) (τ_ϵ). Generally, the MLCCs can be divided into two categories regarding to the capacitance variation as a function of temperature. One is based on ferroelectric materials with a high dielectric constant and a high δ_a (Class 2 dielectrics), and the other is based on paraelectric materials such as MgTiO_3 , CaTiO_3 , and CaZrO_3 (Class 1 dielectrics) [1, 2, 3]. The Class 1 dielectrics have most stable temperature characteristics which are small τ_ϵ , thus these dielectrics can be used at a high frequency applications [4].

CaTiO_3 ceramics have been normally used in Class 1 dielectric materials because of their acceptable dielectric properties ($\epsilon_r = 170$, $Q = 3600$ at 7 GHz, and $\tau_\epsilon = -1800$ ppm/°C) [5, 6]. However, the τ_ϵ of CaTiO_3 ceramics is still large negative value for high frequency applications. Thus, in order to obtain compensated value of τ_ϵ , two compatible compounds with τ_ϵ of opposite sign have been combined. CaTiO_3 ceramics have perovskite structure with orthorhombic symmetry at room temperature. Therefore, to combine compatible compounds, ceramic materials which have same or similar

crystal structure with CaTiO_3 ceramics should be used.

In this study, for high ϵ_r and small τ_ϵ to be as close to 0 ppm/°C called as C0G characteristic, SrTiO_3 ceramics with cubic perovskite structure and CaZrO_3 ceramics with orthorhombic perovskite structure are simultaneously used as substitutions. Because, SrTiO_3 ceramics possess high ϵ_r around 250 and large τ_ϵ (-3600 ppm/°C) [7] and, CaZrO_3 ceramics show ϵ_r around 30 and positive τ_ϵ (40 ppm/°C) [8]. These substitution may be performed at the A site and the B site in the perovskite structure, and a combined ratio is $(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$. Furthermore, in this work, dielectric and structural properties of the $(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ (CSZT) ceramics are investigated with various sintering temperatures to obtain optimized condition of sintering temperature.

Experiments

The $(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ (CSZT) ceramics were fabricated by the conventional mixed oxide method. The starting materials were CaCO_3 (Aldrich, 99%), SrCO_3 (Aldrich, 99.93%), TiO_2 (Aldrich, 99.76%), ZrO_2 (Aldrich, 99.8%) and weighed according to the composition of the $(\text{Ca}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.8}\text{Ti}_{0.2})$. The weight ratio of zirconia ball to powder in the mill was 1 : 1 and ethyl alcohol was used as a process control agent. The slurry was dried at 100 °C for 24 h. and calcined at 1200 °C for 6 h. The calcined powders were screened by mesh (#325) and then pressed to cylindrical pellets in steel die ($\Phi = 2$ inch). The CSZT samples were sintered ranged from 1300 ~ 1500 °C for 4 h. After the samples were polished to 1 mm thickness, silver paste was used as electrodes and then fired at 400 °C for 10 minutes. We used x-ray diffraction (XRD) and scanning electron microscope (SEM) to analyze the crystallinity and microstructures. The dielectric properties were

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measured using an LCR meter (PM6306, Pluke). In addition, the dielectric properties in microwave frequency were measured using a network analyzer (E5071C ENA, Agilent) with the Hakki-Coleman dielectric resonator method. The temperature stability of CSZT ceramics were measured by precision LCR meter (4284A, Agilent). The relative densities were measured by the Archimedes method.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the $(\text{Ca}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.8}\text{Ti}_{0.2})$ (CSZT) ceramics with various sintering temperatures ranged from 1300 °C to 1500 °C. All samples indexed orthorhombic structures and observed no secondary phases. The shapes of all samples with various sintering temperatures exhibit similar; however, peak intensity of all samples slightly but not significantly different. It is indicated that crystallization of CSZT ceramics were affected by sintering temperatures.

The relative density and microstructure of CSZT ceramics are shown in figure 2 and figure 3, respectively. The relative densities of samples were measured by Archimedes method and all samples show higher than 94%. It can be inferred that higher relative densities cause superior electrical properties because relative density is the most important factor to represent permittivity. The grain size of CSZT ceramics was shown in figure 3. Generally, the grain sizes slightly increase with increasing sintering temperatures until 1450 °C. At this time, the range of grain sizes were distributed from 0.5 μm to 5 μm and shape of all CSZT

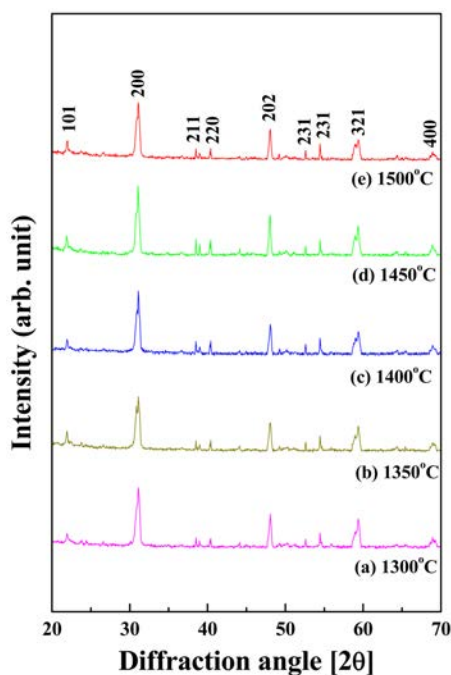


Fig. 1. X-ray diffraction patterns of the CSZT ceramics with various sintering temperatures (a) 1300 °C (b) 1350 °C (c) 1400 °C (d) 1450 °C (e) 1500 °C.

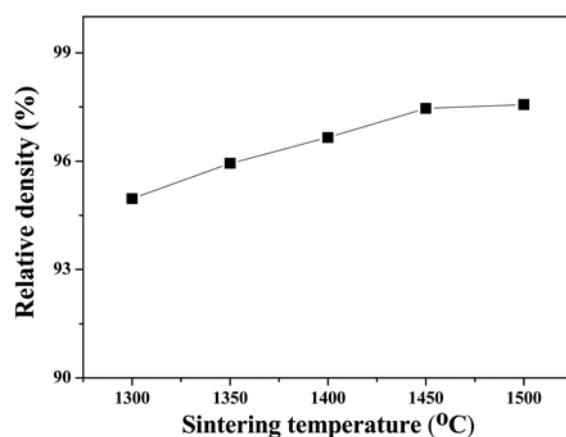


Fig. 2. Relative density of CSZT ceramics with various sintering temperature.

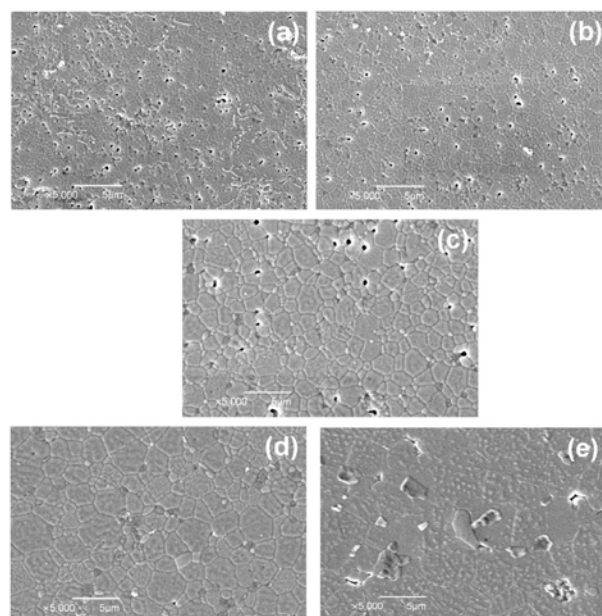


Fig. 3. SEM images of CSZT ceramics with various sintering temperature (a) 1300 °C (b) 1350 °C (c) 1400 °C (d) 1450 °C (e) 1500 °C.

ceramics show almost round. The CSZT ceramics show dense structure sintered at 1450 °C. However, when the sintering temperature exceeded 1450 °C, the grain of CSZT ceramics grow abnormally because of liquid phase. At the same time, the shapes of grain boundaries are ambiguous. These microstructures directly affect on dielectric properties of CSZT ceramics.

The dielectric properties of the CSZT ceramics versus the sintering temperatures were shown in figure 4. All dielectric constants of CSZT ceramics regardless of sintering temperatures show slightly decrease with increasing frequency. The dielectric constants of CSZT ceramics increase with increasing sintering temperatures up to 1450 °C. These trends were related to microstructure of CSZT ceramics by figure 3. The dielectric properties improve with increasing relative density due to increase of grain size. However, the abnormal grain

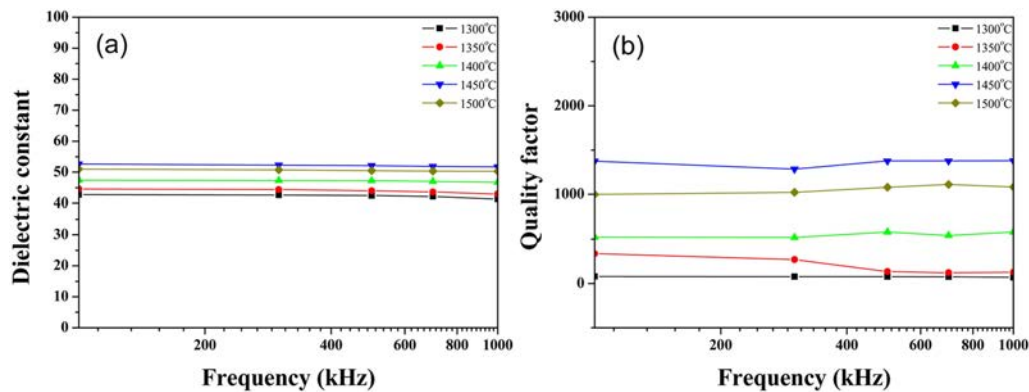


Fig. 4. (a) dielectric constants and (b) quality factors of CSZT ceramics.

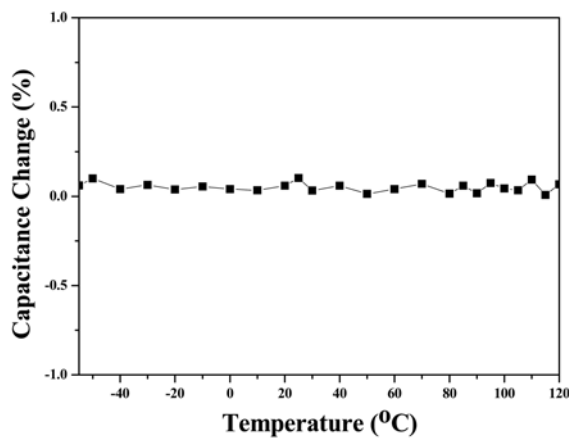


Fig. 5. The temperature stability of CSZT ceramics.

size of CSZT ceramics sintered at over 1450 °C lead to a decrease in dielectric properties. Among various sintering temperatures, the CSZT ceramics sintered at 1450 °C show maximum dielectric properties. The dielectric constants and quality factors of CSZT ceramics sintered at 1450 °C were 51.7 and 1379 at 1 MHz, respectively. The quality factor was also affected by grain morphology owing to non-uniform and abnormal grain size. In the case of microwave frequency ranges, dielectric properties of CSZT ceramics were 50.1 and 1328 at 3.5 GHz. No significant change in various frequency ranges indicated that CSZT ceramics can be applied to high-frequency dielectric materials. The temperature stability of CSZT ceramics was shown in figure 5. The temperature stability of CSZT ceramics was measured at 1 kHz, temperature range of -55 °C to 125 °C. The amount of capacitances variation of CSZT ceramics were satisfied C0G characteristics (± 30 ppm/°C, -55 °C ~ 125 °C) in the temperature range shown above. These C0G characteristics can be applied to temperature compensation requiring stable dielectric properties.

Conclusions

In summary, CSZT ceramics were manufactured by conventional mixed oxide method. The structural and dielectric properties of CSZT ceramics were investigated. The sintering temperatures lead to changes in the microstructure as well as dielectric properties of CSZT ceramics. It was observed that the CSZT ceramics was sintered 1450 °C has maximum dielectric constants and quality factors (51.7 and 1379) (at 1 MHz), (50.1 and 1328) (at 3.5 GHz). These stable frequency-dependent dielectric properties and stable temperature characteristics which are small τ_e indicated that CSZT ceramics can be applied to a wide range of frequency dielectric materials.

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