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Dielectric properties and microstructures of $CaSiO_3$ ceramics with B_2O_3 addition

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Abstract

The effects of B_2O_3 additives on the sintering behavior, microstructure and dielectric properties of $CaSiO_3$ ceramics have been investigated. The B_2O_3 addition resulted in the emergence of CaO–B_2O_3–SiO_2 glass phase, which was advantageous to lower the synthesis temperature of $CaSiO_3$ crystal phase, and could effectively lower the densification temperature of $CaSiO_3$ ceramic to as low as 1100 °C. The 6 wt% B_2O_3-doped $CaSiO_3$ ceramic sintered at 1100 °C possessed good dielectric properties: $\varepsilon_r = 6.84$ and $\tan\delta = 6.9 \times 10^{-4}$ (1 MHz).

Keywords: C. Dielectric properties; Microstructure; $CaSiO_3$ ceramic; B_2O_3 addition

1. Introduction

Low temperature co-fired ceramic (LTCC) technology has been playing an important role in modern wireless communication systems. In order to process ceramic with electrode material, such as 30 Pd/70 Ag (mp 1167 °C) and silver (mp 961 °C), it is required to sinter the dielectrics at temperatures lower than the melting temperature of the co-fired electrode material. Research on the development of co-fired dielectrics with different dielectric constants ε_r has been going for years to fill the need for various RF ranges [1–6]. However, low ε_r material is still the most popularly used one, such as DuPont 951 (ε_r 7.8, $Q \times f$ 700 GHz at 3 GHz, τ_f 8 ppm/ °C), since it provides fast transmission in communication systems [7,8].

$CaSiO_3$ ceramic was proved as a low-permittivity dielectric ceramic system and possessing good dielectric properties: $\varepsilon_r = 5$, $\tan\delta = (1.0–3.0) \times 10^{-4}$ [9]. However, the sintering temperature range of pure $CaSiO_3$ was very narrow and it was difficult to obtain dense $CaSiO_3$ ceramics materials by the traditional solid-state preparation process [10]. The synthesis and microwave dielectric properties of $CaSiO_3$ nanopowder prepared by sol–gel method have been investigated, and it was also difficult to obtain dense $CaSiO_3$ ceramics by sintering the $CaSiO_3$ nanopowders at 1280–1320 °C [11].

In order to improve the sintering characteristic, the study on the synthesis of CaO–B_2O_3–SiO_2 (CBS) glass-ceramics and decreasing sintering temperature with aids have been investigated. Zhu et al. found that the optimal sintering temperature for CaO–B_2O_3–SiO_2 glass-ceramic is 820 °C for 15 min, and the glass-ceramic possesses excellent dielectric properties: $\varepsilon_r = 6.5$, $\tan\delta < 2 \times 10^{-3}$ at 10 MHz with the major phases are $CaSiO_3$, CaB_2O_4 and SiO_2 [12]. Chang and co-workers demonstrated that the dielectric properties of the CBS system which comprised of $CaSiO_3$, $Ca_6Si_4O_3$ and CaB_2O_4 are: $\varepsilon_r = 5.1$, $\tan\delta = 0.0013$ (1 GHz) [13,14]. Cai et al. reported that the excessive SiO_2 and clay can reduce the sintering temperature (1170–1230 °C) of $CaSiO_3$, and the dielectric properties are: $\varepsilon_r = 7.0–9.0$, $\tan\delta = (1.0–5.0) \times 10^{-4}$ [9].

In this work, B_2O_3 was used as the sintering aid to lower the sintering temperature of $CaSiO_3$ ceramic. The resultant dielectric properties were analyzed based upon the densification, the X-ray diffraction patterns and the microstructures of the ceramics.

2. Experimental procedure

Specimen powders were prepared by a conventional solid-state method. High-purity oxide powders (>99.5%): $CaCO_3$,

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SiO_2 and B_2O_3 were used as raw materials. The powders were weighed according to the composition of $CaSiO_3$, and ground in ethanol for 24 h in a balling mill with agate balls. Prepared powders were dried and calcined at 1100–1200 °C for 2 h in air. The powders calcined at 1200 °C were mixed as desired composition of $CaSiO_3$ with 0.5–8 wt% B_2O_3 additions and remilled for 24 h. The fine powder together with the organic binder (5 wt% PVA) was pressed into pellets with dimensions of 15 mm in diameter and 5 mm in thickness. These pellets were sintered at temperatures of 1000–1200 °C for 2 h in air with the heating rate of 5 °C/min.

The crystalline phases of calcined powders and sintered ceramics were identified by X-ray diffraction pattern (XRD, ARL XTRA, Cu K_α). The microstructure observation of the sintered ceramics was performed by means of scanning electron microscopy (SEM, JSM-5601). The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and dielectric loss ($\tan\delta$) at room temperature were determined from capacitance measurements by an LCR meter (HEWLETT PACKARD 4278A) at 1 MHz, and the electric voltage value was 1 V. The dielectric constant was calculated from a parallel-plate capacitor equation, e.g., $\varepsilon_r = Cd/\varepsilon_0 A$, where C was the capacitance of the specimens, d and A were, respectively, the thickness and the area of the electrode, and ε_0 was the dielectric permittivity of vacuum (8.854×10^{-12} F/m). Silver paste was used for the electrodes.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $CaCO_3$–SiO_2 powders calcined at different temperatures. For the sample calcined at 1100 °C, the SiO_2 phase was predominant with a great deal of $CaSiO_3$ phase. As the calcination temperature was raised to 1200 °C, the $CaSiO_3$ phase became the main phase accompanied with a little SiO_2 phase.

The X-ray diffraction patterns of $CaSiO_3$ ceramics sintered at 1100 °C with different B_2O_3 additions are shown in Fig. 2. With 0.5 wt% B_2O_3 addition, the single crystal phase of $CaSiO_3$ was obtained, and no second phase was observed, which indicated that the addition of B_2O_3 could lower the synthesis temperature of $CaSiO_3$ crystal phase. Moreover, it is clear that the diffraction peaks of $CaSiO_3$ were weakened and the amorphous phase was increased with the B_2O_3 content. The results showed that the B_2O_3 addition resulted in the emergence of CaO–B_2O_3–SiO_2 glass phase, which was advantageous to lower the synthesis temperature of $CaSiO_3$ crystal phase.

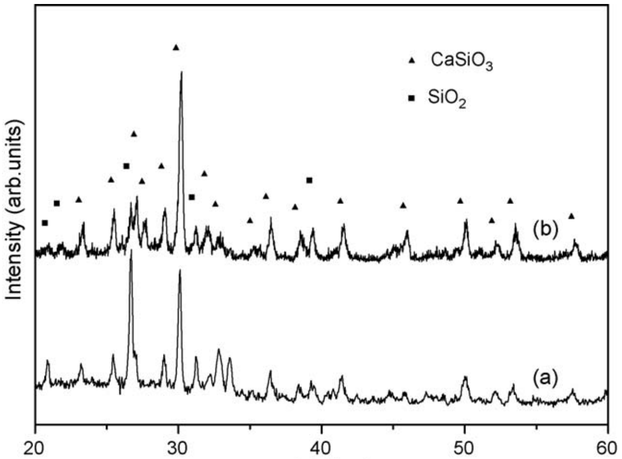

Fig. 1. X-ray diffraction patterns of $CaCO_3$–SiO_2 powders calcined at (a) 1100 °C and (b) 1200 °C.

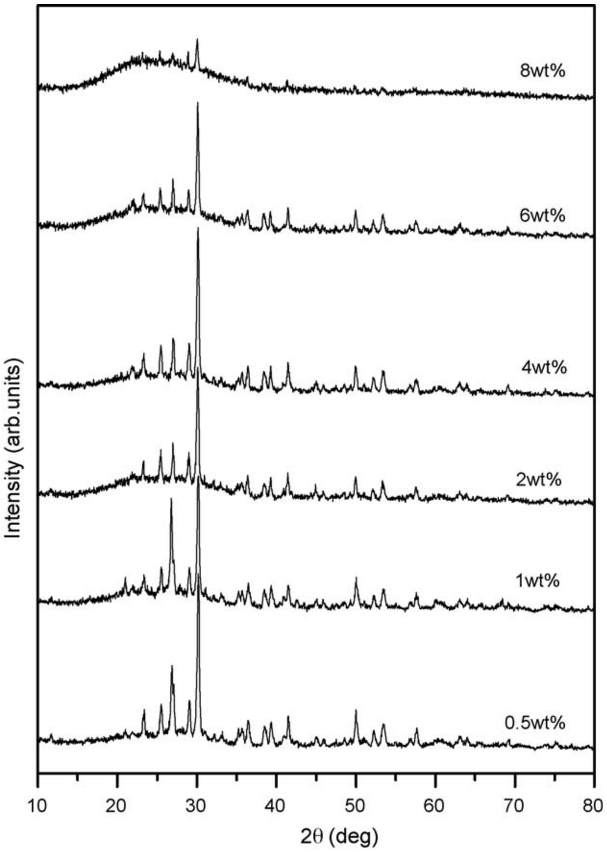

Fig. 2. X-ray diffraction patterns of $CaSiO_3$ ceramics sintered at 1100 °C with different B_2O_3 additions.

The density of B_2O_3-doped $CaSiO_3$ ceramics at different sintering temperatures is shown in Fig. 3. With increasing sintering temperature, the apparent density was found to increase to a maximum value, and higher B_2O_3 content shifts the obtainable maximum density to a lower temperature. The bulk densities of $CaSiO_3$ ceramics sintered at 1100 °C with 0.5 wt%, 1 wt%, 2 wt%, 4 wt%, 6 wt% and 8 wt% B_2O_3 additions were 2.22 g cm^{-3}, 2.51 g cm^{-3}, 2.69 g cm^{-3}, 2.78 g cm^{-3}, 2.85 g cm^{-3} and 2.82 g cm^{-3}, respectively. The optimal sintering temperatures of $CaSiO_3$ ceramics with 0.5 wt%, 1–2 wt%, 4 wt%, 6 wt% and 8 wt% B_2O_3 additions were 1200–1250 °C, 1150–1200 °C, 1150 °C, 1100 °C and 1100–1150 °C, separately. The decrease of sintering temperature with the increase of B_2O_3 addition was due to the augment of CaO–B_2O_3–SiO_2 glass phase, which would transform into liquid phase and promote the sintering process. As it is obvious, the $CaSiO_3$ ceramic sintered at 1100 °C with 6 wt% B_2O_3 addition reached above 98% of the theoretical density (the

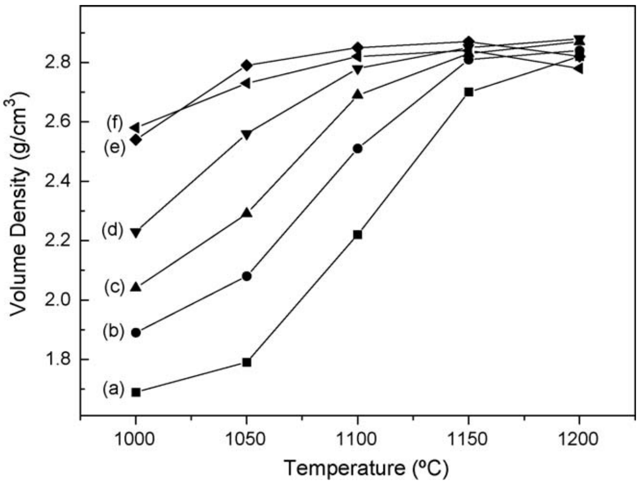

Fig. 3. Dependence of volume density on sintering temperature for $CaSiO_3$ ceramics with (a) 0.5 wt%, (b) 1 wt%, (c) 2 wt%, (d) 4 wt%, (e) 6 wt% and (f) 8 wt% B_2O_3 additions.

theoretical density of $CaSiO_3$ ceramic is 2.91 g cm^{-3}), which could be co-fired with 30 Pd/70 Ag electrode material.

The microstructures of $CaSiO_3$ ceramics sintered at 1100 °C with different B_2O_3 additions are presented in Fig. 4. From picture (a), it can be seen that the specimen was not dense and the grain did not grow with 0.5 wt% B_2O_3 addition. Picture (b), picture (c) and picture (d) show that the grain size increased with the increase of B_2O_3 addition due to the liquid phase effect resulted from the addition of B_2O_3, and there were many grains which grow up to 5 μm with 4 wt% B_2O_3 added in. However, the $CaSiO_3$ ceramics had many pores with 1–4 wt% B_2O_3 addition, which indicated that it is difficult to lower down the sintering temperature of $CaSiO_3$ ceramics to 1100 °C by adding 1–4 wt% B_2O_3. This was probably due to an insufficient amount of liquid phase ($CaO–B_2O_3–SiO_2$ glass phase). When the B_2O_3 content increased to 6 wt%, the grains of $CaSiO_3$ ceramic were in close contact and there was little porosity, which was consistent with the result of bulk densities. However, a low grain growth rate was observed by adding 8 wt% B_2O_3, which was due to the decreasing of $CaSiO_3$ phase and the augment of $CaO–B_2O_3–SiO_2$ glass phase.

The dielectric properties (dielectric constant ε_r and dielectric loss tan δ) of B_2O_3-doped $CaSiO_3$ ceramics sintered at different temperatures (1050–1200 °C) are illustrated in Figs. 5 and 6. The relationships between dielectric properties and sintering temperature followed similar trend to those between density and sintering temperature, due to a fact that a higher density signifying a lower porosity. The dielectric constant (ε_r) increased

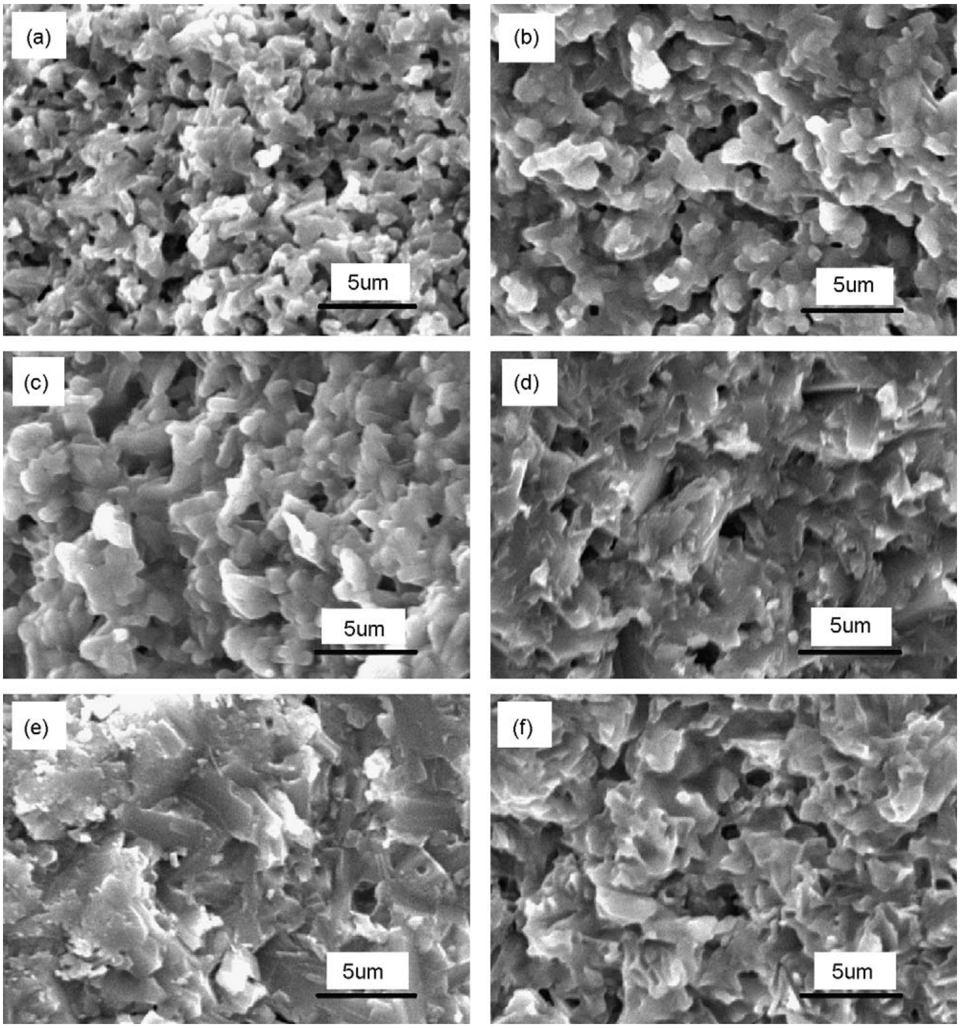

Fig. 4. SEM photographs of $CaSiO_3$ ceramics sintered at 1100 °C with (a) 0.5 wt%, (b) 1 wt%, (c) 2 wt%, (d) 4 wt%, (e) 6 wt% and (f) 8 wt% B_2O_3 additions.

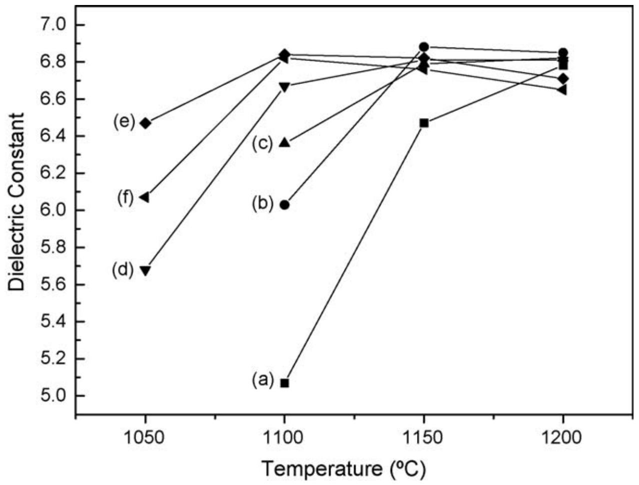

Fig. 5. Dependence of dielectric constant on sintering temperature for $CaSiO_3$ ceramics with (a) 0.5 wt%, (b) 1 wt%, (c) 2 wt%, (d) 4 wt%, (e) 6 wt% and (f) 8 wt% B_2O_3 additions.

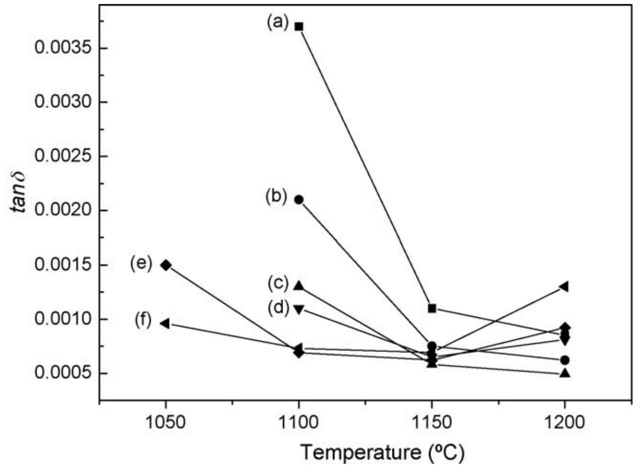

Fig. 6. Dependence of dielectric loss on sintering temperature for $CaSiO_3$ ceramics with (a) 0.5 wt%, (b) 1 wt%, (c) 2 wt%, (d) 4 wt%, (e) 6 wt% and (f) 8 wt% B_2O_3 additions.

and the dielectric loss (tan δ) decreased with the increasing sintering temperature. Sintered at 1100 °C, the $CaSiO_3$ ceramic with 6 wt% B_2O_3 addition possessed good dielectric properties: $\varepsilon_r = 6.84$ and tan $\delta = 6.9 \times 10^{-4}$ (1 MHz), which was a better result than the dielectric properties of $CaO–B_2O_3–SiO_2$ glass-ceramic [12–14]. The dielectric properties of $CaSiO_3$ ceramic with 8 wt% B_2O_3 addition were: $\varepsilon_r = 6.76$ and tan $\delta = 7.3 \times 10^{-4}$ (1 MHz). It suggested that the dielectric constant decreased and the dielectric loss increased with the increasing of B_2O_3 addition, although it was advantageous to lower the sintering temperature by adding sufficient B_2O_3. These results also indicated that the dielectric constant of $CaO–B_2O_3–SiO_2$ glass was lower than which of $CaSiO_3$ ceramic and the dielectric loss of $CaO–B_2O_3–SiO_2$ glass was higher than which of $CaSiO_3$ ceramic.

4. Conclusion

The dielectric properties and microstructures of B_2O_3-doped $CaSiO_3$ ceramics were investigated. B_2O_3 was not detected in the ceramics but residual as a $CaO–B_2O_3–SiO_2$ glass phase. The emergence of $CaO–B_2O_3–SiO_2$ glass phase, acting as a sintering aid, can effectively lower the synthesis temperature of $CaSiO_3$ crystal phase and the sintering temperature of $CaSiO_3$ ceramic. Sintered at 1100 °C, the 6 wt% B_2O_3-doped $CaSiO_3$ ceramic possesses good dielectric properties: $\varepsilon_r = 6.84$ and tan $\delta = 6.9 \times 10^{-4}$ (1 MHz), which can be co-fired with 30 Pd/70 Ag electrode material.

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