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Dielectric and microwave properties of ZrO_2 doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites

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ABSTRACT

The behavior of dielectric and microwave properties against sintering temperature has been carried out on $CaO–SiO_2–B_2O_3$ ceramic matrix composites with ZrO_2 addition. The results indicated that ZrO_2 addition was advantageous to improve the dielectric and microwave properties. X-ray diffraction (XRD) patterns show that the major crystalline β-$CaSiO_3$ and a little SiO_2 phase existed at the temperature ranging from 950 °C to 1050 °C. At 0.5 wt% ZrO_2, $CaO–SiO_2–B_2O_3$ ceramic matrix composites sintered at 1000 °C possess good dielectric properties: $\varepsilon_r = 5.85$, $\tan\delta = 1.59 \times 10^{-4}$ (1 MHz) and excellent microwave properties: $\varepsilon_r = 5.52$, $Q \cdot f = 28{,}487$ GHz (11.11 GHz). The permittivity of Zr-doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites exhibited very little temperature dependence, which was less than ±2% over the temperature range of −50 to 150 °C. Moreover, the ZrO_2-doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites have low permittivity below 5.5 over a wide frequency range from 20 Hz to 1 MHz.

1. Introduction

$CaO–SiO_2–B_2O_3$ ceramic matrix composites possessing good dielectric and microwave properties have recently been widely investigated [1–4]. With crystalline wollastonite (β-$CaSiO_3$) the major phase, $CaO–SiO_2–B_2O_3$ ceramic matrix composites are sintered at temperature of about 1000 °C [5,6]. On heating to above 1200 °C, β-$CaSiO_3$ (low-temperature phase) will undergo an irreversible transformation into the α-$CaSiO_3$ [7]. As a high-temperature and metastable phase, α-$CaSiO_3$ in the $CaO–SiO_2–B_2O_3$ ceramic matrix composites is unsuitable for microwave dielectric applications [8].

In order to achieve excellent properties, the effects of doping on dielectric properties for $CaO–SiO_2–B_2O_3$ ceramic matrix composites have been widely investigated [4,9–11]. Wang et al. found that doping B_2O_3 or H_3BO_3 can improve the sintering and dielectric properties [12]. In addition, Cai et al. reported that the excessive SiO_2 and clay can reduce the sintering temperature (1170–1230 °C) of β-$CaSiO_3$, and the dielectric properties are: $\varepsilon_r = 7.0–9.0$, $\tan\delta = (1.0–5.0) \times 10^{-4}$ at 1 MHz [13].

ZrO_2 addition to $CaO–B_2O_3–SiO_2$ ceramic matrix composites can maintain a low permittivity and low dielectric loss has been reported [14,15]. However, the effect of ZrO_2 on microwave properties of $CaO–SiO_2–B_2O_3$ dielectric ceramics was not widely investigated. In view of this point, the effect of ZrO_2 doping on the dielectric and microwave properties of $CaO–SiO_2–B_2O_3$ ceramic matrix composites was carried out in this work. Also, the resultant dielectric and microwave properties were evaluated at different sintering temperatures and frequencies. The synthesis of $CaO–SiO_2–B_2O_3$ ceramics was by solid-phase process using ($Ca(OH)_2$), silicic acid (H_2SiO_3) and H_3BO_3 as source materials with 0, 0.3, 0.5, and 1.0 wt% ZrO_2 added.

2. Experimental

The starting materials used for preparation of $CaO–SiO_2–B_2O_3$ ceramic matrix composites were analytical reagent $Ca(OH)_2$, H_2SiO_3, H_3BO_3 and $Zr(OH)_4$. According to a desired composition of $CaSiO_3$, a mixture with 0–1.0 wt% $Zr(OH)_4$ additions was placed in a barreled mill and milled for 24 h, then dried at 80 °C. Prepared powders were calcined at 700 °C for 3 h in air. The fine powder with organic binder (5 wt% acrylic emulsion) was carefully ground, and pressed at 20 MPa to make tablets of 18 mm in diameter and 1 mm in height. The tablets were then baked at a heating rate of 2 °C/min from room temperature to 950 °C (975 °C, 1000 °C and 1050 °C) for 3 h at the normal atmospheric pressure.

The dielectric properties (1 MHz) of sintered samples were tested with an Agilent 4284A LCR meter utilizing an environmental chamber for the temperature measurements. An X-ray powder diffractometer X'Pert PRO MPD (Philips) with Cu Kα radiation was used to estimate the crystalline phases. Thermogravimetry and differential thermal analysis (TG–DTA) curves were recorded on a Beifen PCT-IA instrument from room temperature to 1200 °C at a heating rate of 10 °C/min in air. Microwave dielectric permittivity (ε_r at f_0) and the quality values ($Q \cdot f$) at microwave

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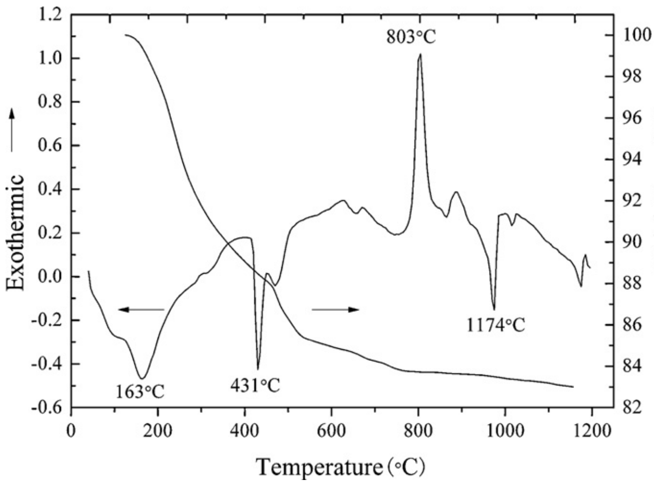

Fig. 1. TG and DTA curves for $CaO–SiO_2–B_2O_3$ powders with 0.5 wt% ZrO_2 addition.

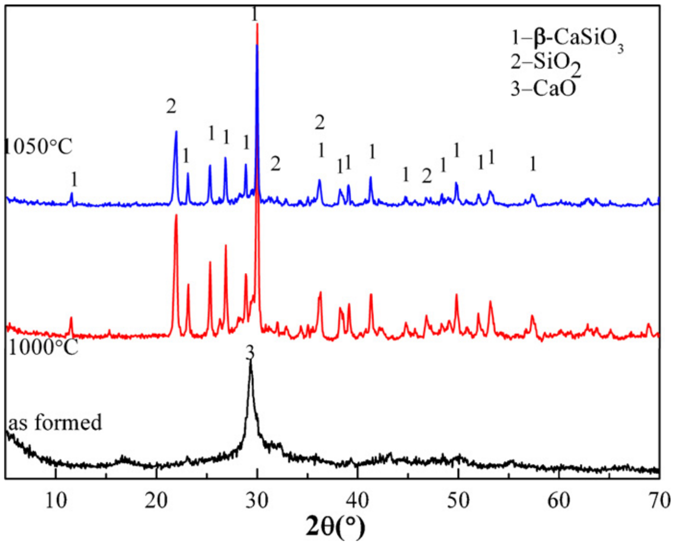

Fig. 2. XRD patterns of as made powder and ceramics with 0.5 wt% ZrO_2 sintered at 1000 °C and 1050 °C.

frequencies were measured by Hakki–Coleman dielectric resonator method [16] using an Agilent E8363A (45 MHz to 40 GHz) network analyzer.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the differential thermal analysis (DTA) and thermogravimetric (TG) analysis for typical $CaO–SiO_2–B_2O_3$ powders with 0.5 wt% ZrO_2 added. The DTA curves reveal that the first endothermic peak at 142 °C, corresponding to the weight loss 12%, which can be attributed to the vaporization of hydrated and coordinated water molecules and the decomposition of H_2SiO_3. The second endothermic peak in the DTA curve around 431 °C is due to the decomposition of the binder (acrylic acid), accompanied by another weight loss about 5 wt%. The exothermic peak around 803 °C in the DTA curve indicates the starting of crystallization of β-$CaSiO_3$.The third endothermic peak in the DTA curve around 1174 °C is due to the transition from β-$CaSiO_3$ to α-$CaSiO_3$.

3.2. X-ray diffraction

The phase evaluation of as formed and calcined (1000 and 1050 °C) $CaO–SiO_2–B_2O_3$ powders with 0.5 wt% ZrO_2 addition was examined by powder X-ray diffraction (XRD) and is shown in Fig. 2. The XRD patterns of as made $CaO–SiO_2–B_2O_3$ powders exhibit weak crystallinity with CaO peak at $2\theta = 29.5°$. On calcinations from 1000 °C to 1050 °C, the CaO peak disappears and becomes crystalline β-$CaSiO_3$ (PDF 84-0654). For the sample calcined at 1000 °C, the β-$CaSiO_3$ phase was predominant with a little SiO_2 (PDF 71-0785) phase. As the sintering temperature was raised to 1050 °C, the diffraction peaks weakened, which might be attributed to the emergence of amorphous phases.

Fig. 3(a) shows the volume density of 0, 0.3, 0.5, and 1.0 wt% ZrO_2 doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites at the sintering temperatures ranging from 950 °C to 1025 °C. With increasing sintering temperature, the volume density was found to increase and to a maximum value at 1000 °C. As a result, for Zr-doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites, the sintering temperature of 1000 °C is a reasonable temperature. The X-ray diffraction spectra of the $CaO–SiO_2–B_2O_3$ ceramic matrix composites calcined at 1000 °C with 0, 0.3, 0.5, and 1.0 wt% ZrO_2 additions is shown in Fig. 3(b). At 0 wt% ZrO_2, the single crystal phase of β-$CaSiO_3$ was obtained, and no second phase was observed. When ZrO_2 addition is over the range of 0.3–1.0 wt%, SiO_2 phase as a second phase was observed in addition to β-$CaSiO_3$ phase. It indicated that the addi-

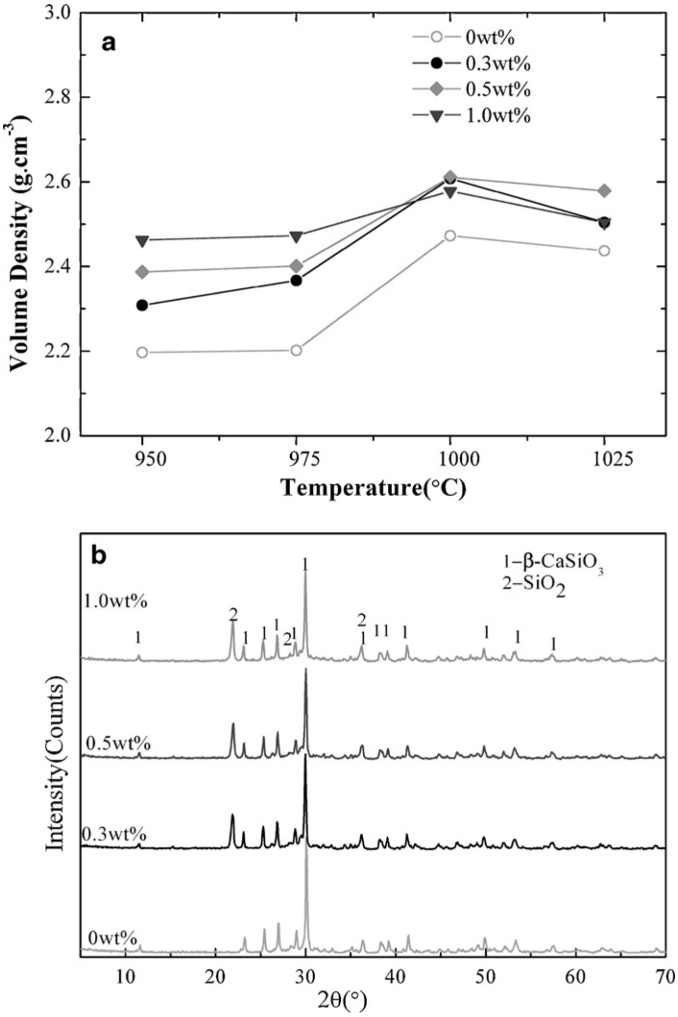

Fig. 3. With 0, 0.3, 0.5, and 1.0 wt% ZrO_2 additions, (a) volume density vs sintering temperature and (b) X-ray diffraction patterns of $CaO–SiO_2–B_2O_3$ ceramic matrix composites sintered at 1000 °C.

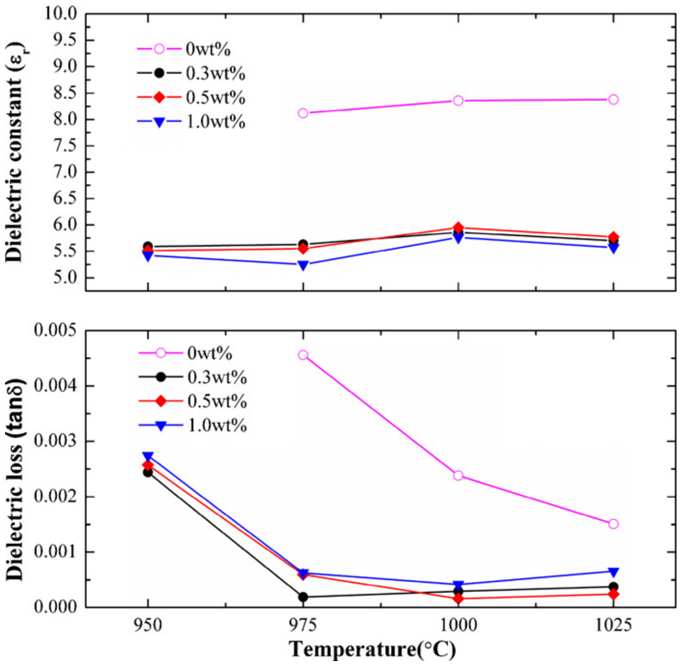

Fig. 4. Dielectric properties (1 MHz) measured at room temperature vs sintering temperature for sample with 0, 0.3, 0.5, and 1.0 wt% ZrO_2.

tion of ZrO_2, a little Si^{4+} ions were squeezed out by Zr^{4+} ions, which makes it difficult to form β-$CaSiO_3$ during Si–Ca reaction, however, easy to form SiO_2 phase.

3.3. Dielectric properties

The dielectric properties (1 MHz) at room temperature of Zr-doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites as a function of the sintering temperature are shown in Fig. 4. The results show that for no addition ZrO_2, the permittivity (ε_r) and loss ($\tan\delta$) of $CaO–SiO_2–B_2O_3$ matrix composites are obviously bigger than those Zr-doped composites, due to a fact that ZrO_2 addition resulting in the augment of glass phase, which would transform into liquid phase and promote the formation of β-$CaSiO_3$ crystalline phase. With increasing sintering temperature, the permittivity of $CaO–SiO_2–B_2O_3$ ceramic matrix composites with 0–1.0 wt% ZrO_2 addition was found to increase and obtain a maximum value at 1000 °C. The reason is that the increase of sintering temperature could result in the enhanced crystalline peaks (β-$CaSiO_3$ and SiO_2), which would increase the permittivity. With further increasing sintering temperature, the permittivity slightly decreases because of the emergence of glass phases. In addition, the permittivity decreases with the increase of doping ZrO_2 level and the sample with 1.0 wt% ZrO_2 addition has a minimum value, which indicates that the SiO_2 phase has a lower permittivity (about 4.5 [17]) than β-$CaSiO_3$ phase (about 8.6 [18]). The dielectric losses against sintering temperature for different doping levels of ZrO_2 show that the all the ZrO_2-doped samples exhibit very low dielectric loss and the lowest value of dielectric loss was 1.59×10^{-4} for 0.5 wt% ZrO_2 at 1000 °C. Moreover, the 0.5 wt% ZrO_2-doped composition exhibited dielectric loss below 4.15×10^{-4} over a wide temperature range from 975 to 1025 °C. The dielectric properties of $CaO–SiO_2–B_2O_3$ ceramic matrix composites at 1000 °C with 0.5 wt% ZrO_2 addition were: $\varepsilon_r = 5.95$, $\tan\delta = 1.59 \times 10^{-4}$ (1 MHz).

In Fig. 5, the dielectric properties at room temperature vs frequency are plotted for sample sintered at 1000 °C with 0.3, 0.5, and 1.0 wt% ZrO_2 added. It shows that the permittivity decreases when the frequency increases. The permittivity of ZrO_2-doped $CaO–SiO_2–B_2O_3$ ceramic matrix composites is mainly from the electronic and the ionic polarizations, and the electronic polarizability would not change but the ionic polarizability decreases with the increase of frequency. Over the frequency range of 1 kHz to 1 MHz, the permittivity of samples decreases with the increase of ZrO_2 doped concentration. The curves of dielectric loss against frequency show that and dielectric losses decrease with the increase of frequency and the 0.5 wt% ZrO_2-doped ceramics have the lowest dielectric loss and the lowest value was 1.46×10^{-4} at 100 kHz. Moreover, the 0.5 wt% ZrO_2-doped composition exhibited dielectric loss below 7×10^{-4} over a wide frequency range from 1 kHz to 1 MHz.

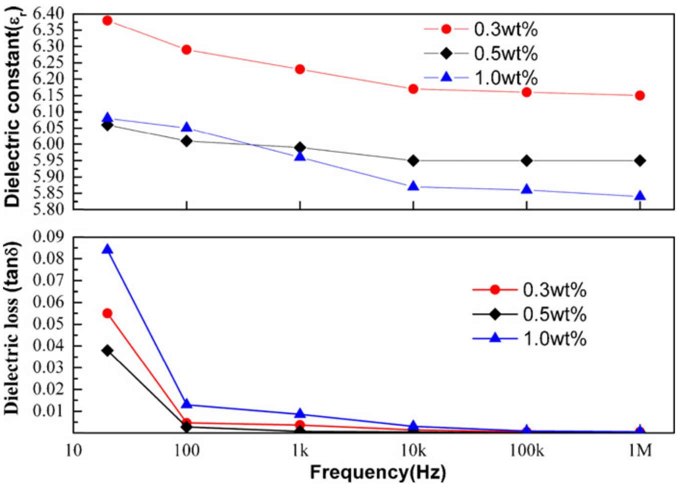

Fig. 5. Dielectric properties at room temperature vs frequency for sample sintered at 1000 °C with 0.3, 0.5, and 1.0 wt% ZrO_2.

The temperature dependence of the permittivity at 1 MHz for 0.5 wt% ZrO_2-doped sample sintered at 1000 °C is plotted in Fig. 6. Over the temperature range of −50 to 150 °C, the changes in permittivity were less than ±2%. Therefore, the ZrO_2 doping effectively can stable the permittivity over a wide range of temperature. $CaO–SiO_2–B_2O_3$ ceramic matrix composites with ZrO_2 addition exhibit excellent dielectric properties below 150 °C. Provided that these dielectric properties are largely independent of temperature, ZrO_2 doped $CaO–SiO_2–B_2O_3$ dielectric ceramic is a promising material system for high temperature applications.

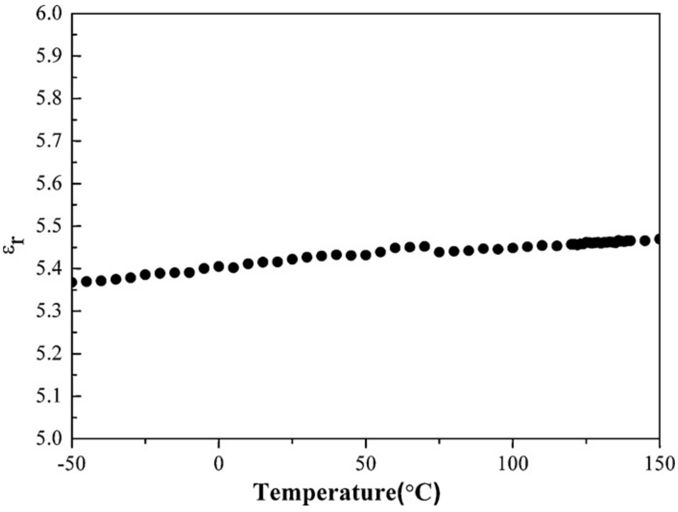

Fig. 6. Temperature dependence of the permittivity at 1 MHz for $CaO–SiO_2–B_2O_3$ ceramic matrix composites with 0.5 wt% Zr added at 1000 °C.

Table 1
Microwave properties of CaO–SiO_2–B_2O_3 ceramics.

Reference	Samples	Sintered temperature (°C)	Resonant frequency f_0 (GHz)	Permittivity at f_0	$Q \cdot f$ (GHz)
This work	0 wt% Zr	1000	10.36	5.07	24,434
	0.3 wt% Zr	1000	11.11	5.63	28,487
	0.5 wt% Zr	1000	10.57	5.66	29,199
	1.0 wt% Zr	1000	10.80	5.52	26,277
Wang et al. [4]	Solid phase	1340	–	6.59	13,109
Wang et al. [4]	Sol–gel	1320	–	6.69	25,398

3.4. Microwave properties

Table 1 illustrates the resonant frequency (f_0), the permittivity at f_0 and the microwave properties ($Q \cdot f$ value) of the samples sintered at 1000 °C. It is noticed that with the increase of ZrO_2-doped level, the $Q \cdot f$ values of the samples increase, and then decrease. The reason can be attributed that low melting glass can be formed with ZrO_2 addition during the sintering process, and the glass promotes the composition of β-$CaSiO_3$ crystalline phase, which leads to the increase of $Q \cdot f$ values. However, the diffraction peaks of β-$CaSiO_3$ are weakened and the glass phase is increased with the ZrO_2 content up to 1.0 wt% (Fig. 3). It is shown that the excessive ZrO_2 addition results in the emergence of too much glass phase, which causes to the decrease of $Q \cdot f$ values. Also, the results indicate that the $Q \cdot f$ values of glass are lower than which of β-$CaSiO_3$. The maximum $Q \cdot f$ value (29,199 GHz) is observed with the addition of ZrO_2 up to a concentration of 0.5 wt%. Comparing with the previous works, the dielectric constant at f_0 is slightly lower than that of Wang but the $Q \cdot f$ value is higher than that of Wang et al. [12]. However, the sintered temperature of Wang is higher than this work. This can be explained by the fact that ZrO_2 doped is helpful to lower sintering temperature and improve the microwave properties.

4. Conclusions

ZrO_2 doped CaO–SiO_2–B_2O_3 ceramic matrix composites have been synthesized by the solid-phase reaction method from 950 °C to 1050 °C. After 950 °C, the major crystalline phase was β-$CaSiO_3$ with a little SiO_2.The dielectric properties of ZrO_2-doped CaO–SiO_2–B_2O_3 ceramic matrix composites against sintering temperature and frequency were also investigated. B_2O_3 and ZrO_2 are not observed by XRD patterns, which were residual as glass phase. Sintered at 1000 °C, the 0.5 wt% ZrO_2-doped CaO–SiO_2–B_2O_3 ceramic matrix composites possess good dielectric properties: $\varepsilon_r = 5.95$ and $\tan\delta = 1.59 \times 10^{-4}$ (1 MHz). The 0.5 wt% ZrO_2-doped composition exhibited dielectric loss below 7×10^{-4} over a wide frequency range from 1 kHz to 1 MHz. Over the temperature range of −50 to 150 °C the change in permittivity is less than ±2%. At the sintering temperature of 1000 °C, the 0.5 wt% ZrO_2-doped CaO–SiO_2–B_2O_3 ceramic matrix composites also achieve excellent microwave properties: $\varepsilon_r = 5.52$, $Q \cdot f = 28487$ GHz (11.11 GHz).

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