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Effects of $CaSiO_3$ addition on sintering behavior and microwave dielectric properties of Al_2O_3 ceramics

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Abstract

The effects of $CaSiO_3$ addition on the sintering behavior and microwave dielectric properties of Al_2O_3 ceramics have been investigated. The addition of $CaSiO_3$ into Al_2O_3 ceramics resulted in the emergence of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$, which acting as liquid sintering aids can effectively lower the sintering temperature of Al_2O_3 ceramic. The $Q \times f$ value of Al_2O_3–$CaSiO_3$ ceramics decreased with the $CaSiO_3$ addition increasing because of the lower $Q \times f$ value of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$. Compared with the pure $CaSiO_3$ ceramic, the Al_2O_3–$CaSiO_3$ ceramic with 20 wt% $CaSiO_3$ addition possessed good dielectric properties of $\varepsilon_r = 9.36$ and $Q \times f = 13{,}678$ GHz at the similar sintering temperature.

Keywords: Microwave dielectric properties; Al_2O_3 ceramic; $CaSiO_3$ addition

1. Introduction

Development of microwave dielectric materials for applications in communication systems such as cellular phones, direct broadcasting satellites, wireless local area networks, global positioning systems and intelligent transport systems has been rapidly progressing in the past decades [1–3]. Utilized frequency has also increased from microwave to millimeter-wave range because large quantity of information must be transported with high speed. Dielectric resonator materials for millimeter-wave use are required to have high quality values ($Q \times f$) and relatively low dielectric constant (ε_r) [4].

Al_2O_3 ceramic with low ε_r (9.8) and high $Q \times f$ (360,000 GHz) is a promising materials for millimeter-wave applications [5,6], and commercially available alumina normally has a $Q \times f$ value around 10,000–20,000 GHz [7]. However, the high melting point of Al_2O_3 necessitates a high sintering temperature of around 1700 °C [8,9]. In order to lower the sintering temperature of Al_2O_3 ceramic, nanoparticles and sintering aids such as TiO_2, MnO, ZnO–B_2O_3–SiO_2 (ZBS) glass and MgO–CaO–Al_2O_3–SiO_2 (MCAS) glass have been used [4,10–14]. With TiO_2 addition, alumina ceramics possesses a quality factor of 333,000 GHz sintered at 1500 °C [10]. Using nano-particle-sized starting material, α-Al_2O_3 ceramics can be sintered at 1500 °C and promotes its $Q \times f$ value to 500,000 GHz [11]. The Al_2O_3 ceramics added with TiO_2 and MCAS glass have been sintered at the temperature of 1350 °C, and possess good dielectric properties: $\varepsilon_r = 11.6$, $Q \times f = 11{,}456$ GHz [14].

$CaSiO_3$ ceramic is also an important low dielectric constant material, and possesses good dielectric properties of $\varepsilon_r = 6.59$ and $Q \times f = 13{,}109$ GHz at the sintering temperature of 1340 °C [15]. In this work, $CaSiO_3$ was used as the sintering aid to lower the sintering temperature of Al_2O_3 ceramic. The sintering behavior, microstructures and microwave dielectric properties of Al_2O_3–$CaSiO_3$ ceramics were investigated.

2. Experimental procedure

Commercial oxide powders (>99.5%): $CaCO_3$, SiO_2 and Al_2O_3 were used as raw materials, and the specimens were prepared by a conventional solid-state method. Initially, $CaCO_3$ and SiO_2 powders were weighed according to the composition of $CaSiO_3$, and ground in ethanol for 24 h in a balling mill with ZrO_2 balls. Prepared powders were dried and calcined at 1100–1200 °C for 2 h

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in air. The $CaCO_3$–SiO_2 powders calcined at 1200 °C were mixed with Al_2O_3 powders, and the content of $CaSiO_3$ was 2, 5, 10, 20, 30 and 40 in wt%. The mixed powders were remilled for 24 h with 8 wt% polyvinyl alcohol (PVA) solution as a binder, and then pressed into pellets with 15 mm in diameter and 8 mm in thickness. These pellets were sintered at the temperatures of 1275–1575 °C for 2 h in air with the heating rate of 5 °C/min.

The bulk densities of the sintered pellets were measured by the Archimedes method. The crystalline phases of sintered ceramics were performed by X-ray diffraction pattern (XRD, ARL XTRA, Cu K_α). The microstructure observation of the sintered ceramics was identified by means of scanning electron microscopy (SEM, JSM-5601). Microwave dielectric constants ε_r and the quality values $Q \times f$ at microwave frequencies were measured by Hakki–Coleman dielectric resonator method using an Agilent 8719ET (50 MHz–13.5 GHz) Network Analyzer.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of alumina powders and $CaCO_3$–SiO_2 powders calcined at different temperatures. It can be seen clearly that both SiO_2 phase and $CaSiO_3$ phase were present in almost the same amount at the calcination temperature of 1100 °C. When the calcination temperature increased to 1200 °C, the presence of $CaSiO_3$ phase was observed as the main crystalline phase, compared with a little SiO_2. The α-Al_2O_3 phase can also be observed in Fig. 1(c).

Fig. 2 shows the bulk densities of Al_2O_3–$CaSiO_3$ ceramics sintered at different temperatures with different $CaSiO_3$ additions. It is clear that with increasing the sintering temperature, the densities of all bulks increase to a maximum value and then decrease. The optimal sintering temperature of Al_2O_3 ceramics with 2 wt%, 5 wt%, 10 wt%, 20 wt% and 30–40 wt% $CaSiO_3$ addition were 1550 °C, 1475 °C, 1400 °C, 1325 °C and 1300 °C, and the maximum bulk densities at these temperatures were 3.82 g/cm^3, 3.74 g/cm^3, 3.65 g/cm^3, 3.49 g/cm^3, 3.31 g/cm^3 and 3.17 g/cm^3, respectively. These results indicated that both the sintering temperature and the maximum density of Al_2O_3–$CaSiO_3$ ceramics were decreasing with the increasing of $CaSiO_3$ addition. However, because of the sintering temperature of pure $CaSiO_3$ ceramic was higher than 1300 °C [15], the sintering temperature could not be lowered down any more when the $CaSiO_3$ addition exceeded 30 wt%. The theoretical density of Al_2O_3 ceramic and $CaSiO_3$ ceramic was 3.98 g/cm^3 and 2.91 g/cm^3, respectively, which resulted in the decreasing of bulk density with the higher $CaSiO_3$ addition.

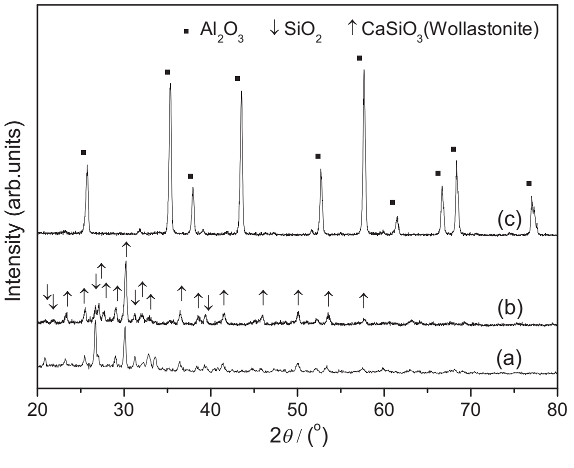

Fig. 1. XRD patterns of (c) Al_2O_3 powders and $CaCO_3$–SiO_2 powders calcined at (a) 1100 °C and (b) 1200 °C.

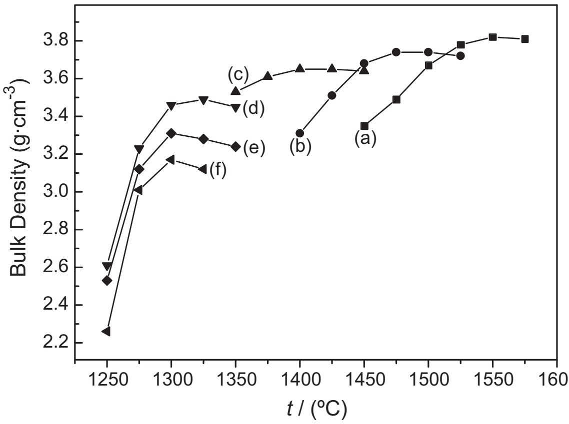

Fig. 2. Bulk densities of Al_2O_3–$CaSiO_3$ ceramics sintered at different temperatures with (a) 2 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, (e) 30 wt% and (f) 40 wt% $CaSiO_3$ additions.

Fig. 3 shows the X-ray diffraction patterns of Al_2O_3–$CaSiO_3$ ceramics with different $CaSiO_3$ additions sintered at different temperatures. With 2 wt% $CaSiO_3$ addition, the primary crystal phase of Al_2O_3 was obtained, and a little SiO_2, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ were observed, which suggested that the reaction between Al_2O_3 and $CaSiO_3$ resulted in the emergence of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$. With the $CaSiO_3$ addition increasing, the diffraction peaks of Al_2O_3 were weakened, and the peaks of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ were enhanced. When the addition of $CaSiO_3$ was up to 40 wt%, the $Ca_2Al_2SiO_7$ was the main phase, and the Al_2O_3 was the minor phase. Combining with the results of Fig. 2, it is obvious that the decrease of sintering temperatures with the increase of $CaSiO_3$ addition was due to the increase of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ phases, which promoted the sintering process of Al_2O_3 ceramic as liquid sintering aids.

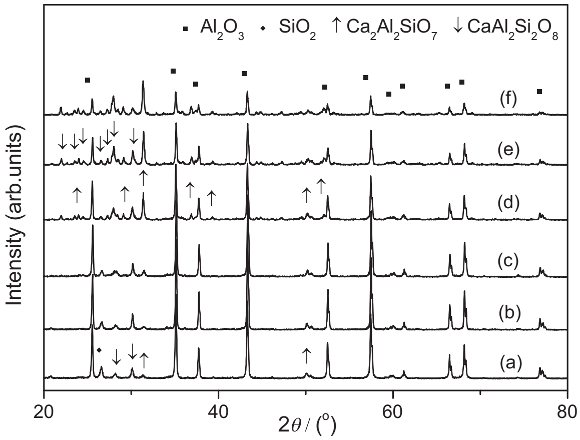

Fig. 3. XRD patterns of Al_2O_3–$CaSiO_3$ ceramics with different $CaSiO_3$ additions sintered at different temperatures (a) 2 wt% × 1550 °C, (b) 5 wt% × 1475 °C, (c) 10 wt% × 1400 °C, (d) 20 wt% × 1325 °C, (e) 30 wt% × 1300 °C and (f) 40 wt% × 1300 °C.

The microstructures of Al_2O_3–$CaSiO_3$ ceramics with different $CaSiO_3$ additions sintered at the optimal temperature are presented in Fig. 4. From picture (a), dense bodies with few pores are obtained, and the average grain is about 2–3 μm with 2 wt% $CaSiO_3$ addition. Picture (b) and picture (c) show that the grains become smaller with the increase of $CaSiO_3$ additions from 2 wt% to 10 wt%, due to the new phases of $CaAl_2Si_2O_8$ and $Ca_2Al_2SiO_7$ which stopped the growing of Al_2O_3 grains by surrounding the boundaries. Upon increasing $CaSiO_3$ from 20 wt% to 40 wt%, picture (d), picture (e) and picture (f) present the grains grow with the augment of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$, and there are many pores in these bulks. These results indicated that $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ melted and improved the sintering process as liquid sintering aids.

Fig. 5 demonstrates the dielectric constant (ε_r) of Al_2O_3–$CaSiO_3$ ceramics with different amount of $CaSiO_3$ additions as a function of their sintering temperatures. From the figure, it can be clearly seen that the dielectric constants increase to a maximum value and then decrease with the sintering temperature rising, and the maximum ε_r of Al_2O_3–$CaSiO_3$ ceramics with 2 wt%, 5 wt%, 10 wt%, 20 wt% and 30–40 wt% $CaSiO_3$ additions were 9.88, 9.85, 9.52, 9.36, 8.93 and 8.57, respectively. The relationships between ε_r and sintering temperatures revealed the same trend with those between densities and sintering temperatures, due to a fact that a higher density signified a lower porosity and the dielectric constant of $CaSiO_3$ ceramic was lower than that of Al_2O_3 ceramic.

The quality values ($Q \times f$) of Al_2O_3–$CaSiO_3$ ceramics with different amount of $CaSiO_3$ additions sintered at different

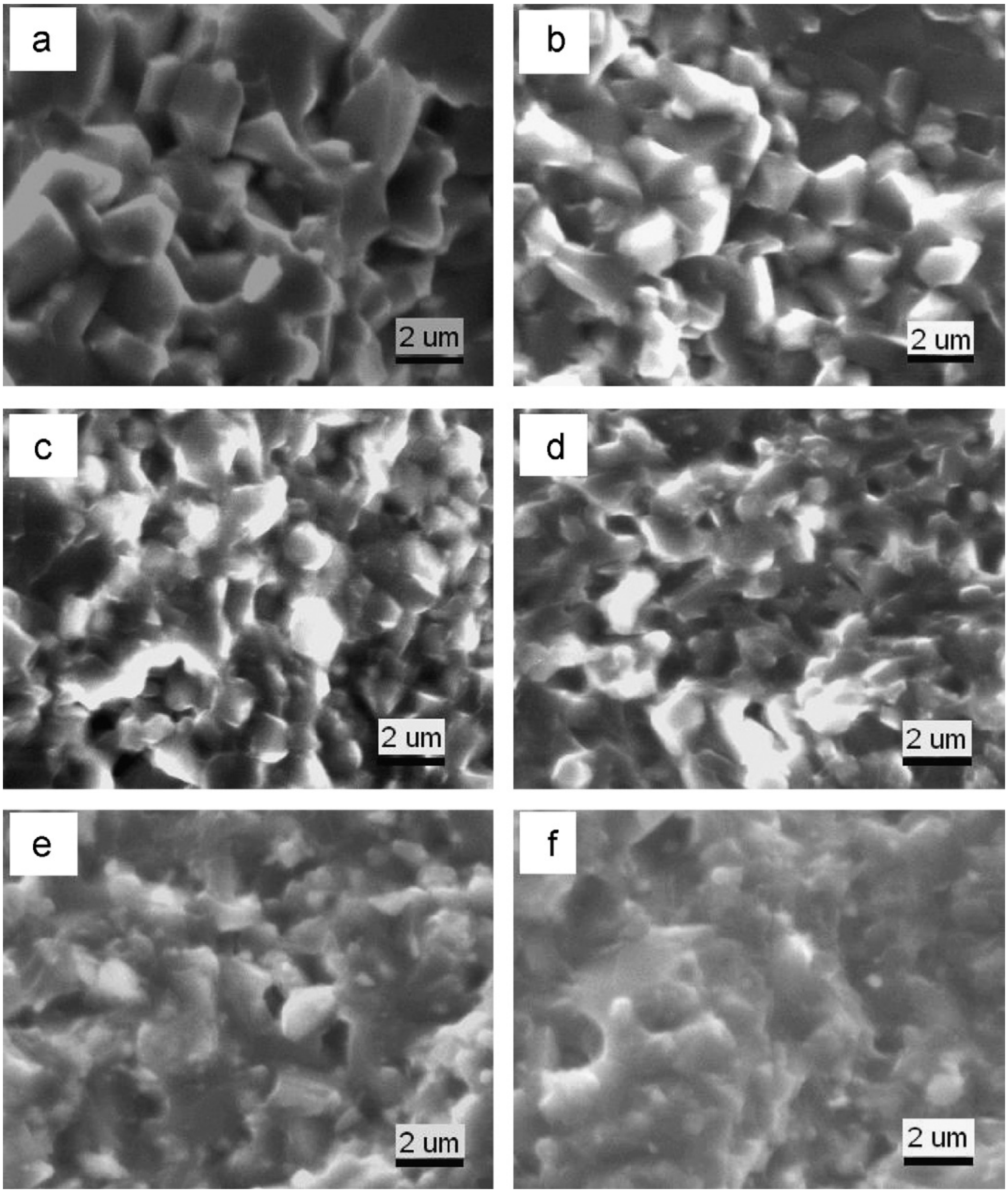

Fig. 4. SEM micrographs of Al_2O_3–$CaSiO_3$ ceramics with different $CaSiO_3$ additions sintered at different temperatures (a) 2 wt% × 1550 °C, (b) 5 wt% × 1475 °C, (c) 10 wt% × 1400 °C, (d) 20 wt% × 1325 °C, (e) 30 wt% × 1300 °C and (f) 40 wt% × 1300 °C.

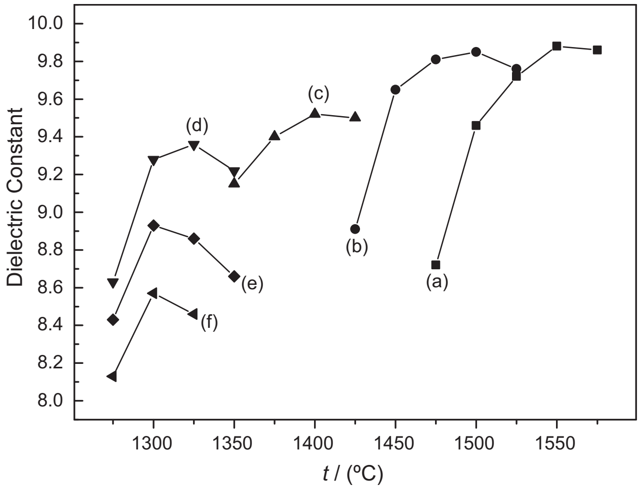

Fig. 5. Dielectric constants of Al_2O_3–$CaSiO_3$ ceramics sintered at different temperatures with (a) 2 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, (e) 30 wt% and (d) 40 wt% $CaSiO_3$ additions.

temperatures are illustrated in Fig. 6. The optimal $Q \times f$ value of Al_2O_3–$CaSiO_3$ ceramics with 2 wt%, 5 wt%, 10 wt%, 20 wt% and 30–40 wt% $CaSiO_3$ additions were 28,923 GHz, 20,146 GHz, 16,782 GHz, 13,678 GHz, 9914 GHz and 8712 GHz, separately, which indicated that the addition of $CaSiO_3$ was harmful to increasing the quality value of Al_2O_3–$CaSiO_3$ ceramics. Compared with the report that the $Q \times f$ value of $CaSiO_3$ ceramic sintered at 1340 °C was 13,109 GHz [15], the Al_2O_3–$CaSiO_3$ ceramics with 30–40 wt% $CaSiO_3$ additions have lower quality values. These results suggested that the $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ phases have lower quality values than $CaSiO_3$ phase, although it was advantageous to lower the sintering temperature of Al_2O_3 ceramic. The Al_2O_3–$CaSiO_3$ ceramic with 20 wt% $CaSiO_3$ addition possessed dielectric properties: $\varepsilon_r = 9.36$ and $Q \times f = 13{,}678$ GHz, which was a better result than that of pure $CaSiO_3$ ceramic at the similar sintering temperature.

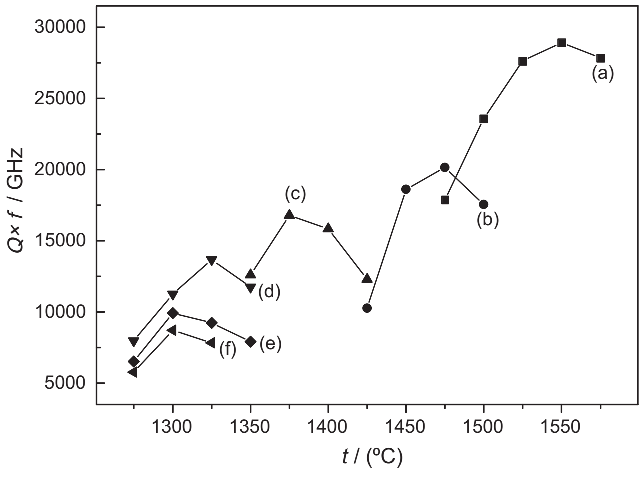

Fig. 6. $Q \times f$ values of Al_2O_3–$CaSiO_3$ ceramics sintered at different temperatures with (a) 2 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, (e) 30 wt% and (d) 40 wt% $CaSiO_3$ additions.

4. Conclusion

Added 2–40 wt% $CaSiO_3$ into Al_2O_3, the $CaSiO_3$ phase was not detected in the ceramics sintered at 1300–1550 °C, but existed as $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ phases, which acting as liquid sintering aids can effectively lower the sintering temperature of Al_2O_3 ceramic. However, the $CaSiO_3$ addition damaged the dielectric properties of Al_2O_3–$CaSiO_3$ ceramics, and the $Q \times f$ value decreased from 28,923 GHz to 8712 GHz with the addition of $CaSiO_3$ increased from 2 wt% to 40 wt%. Compared with the pure $CaSiO_3$ ceramic, the Al_2O_3–$CaSiO_3$ ceramics with 2–20 wt% $CaSiO_3$ additions have better microwave dielectric properties, although the $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ phases have lower quality values. Sintered at 1325 °C, The Al_2O_3–$CaSiO_3$ ceramic with 20 wt% $CaSiO_3$ addition possessed dielectric properties: $\varepsilon_r = 9.36$ and $Q \times f = 13{,}678$ GHz, which was a better result than that of pure $CaSiO_3$ ceramic at the similar sintering temperature.

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