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

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Abstract

The effects of Al_2O_3 addition on the densification, structure and microwave dielectric properties of $CaSiO_3$ ceramics have been investigated. The Al_2O_3 addition results in the presence of two distinct phases, e.g. $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$, which can restrict the growth of $CaSiO_3$ grains by surrounding their boundaries and also improve the bulk density of $CaSiO_3$–Al_2O_3 ceramics. However, excessive addition (≥2 wt%) of Al_2O_3 undermines the microwave dielectric properties of the title ceramics since the derived phases of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ have poor quality factor. The optimum amount of Al_2O_3 addition is found to be 1 wt%, and the derived $CaSiO_3$–Al_2O_3 ceramic sintered at 1250 °C presents improved microwave dielectric properties of $\varepsilon_r = 6.66$ and $Q \times f = 24{,}626$ GHz, which is much better than those of pure $CaSiO_3$ ceramic sintered at 1340 °C ($Q \times f = 13{,}109$ GHz).

Keywords: Sintering; Electron microscopy; Dielectric properties; $CaSiO_3$ ceramic; Al_2O_3 addition

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1. Introduction

Remarkable progress has been made in microwave related advanced wireless communication systems such as cellular phones, direct broadcasting satellites, wireless local area networks, global positioning systems and intelligent transport systems.[1–3] The available frequencies have therefore been extended from microwave to millimeter-wave ranges because large quantity of information must be transported with high speed in the later range. High operating frequency in these microwave applications requires dielectric materials with low dielectric constant (ε_r), high quality factor ($Q \times f$) and stable temperature coefficient of the resonant frequency ($\tau_f \leq \pm 10$ ppm/°C).[4,5]

$CaSiO_3$ ceramic has been proved to be an excellent dielectric material with low dielectric constant ($\varepsilon_r = 5$) and low dielectric loss ($\tan\delta = (1.0–3.0) \times 10^{-4}$).[6] However, the sintering temperature range of pure $CaSiO_3$ ceramic is very narrow. Chakradhar et al. pointed out that it was difficult to obtain dense $CaSiO_3$ ceramic since its grains grew exceptionally and the bulk $CaSiO_3$ ceramic became more porous with the increase of the calcination temperature.[7] In our previous work, the sintering behavior and microwave dielectric properties of $CaSiO_3$ ceramics have been investigated by the traditional solid-state process and a sol–gel method, respectively.[8] The maximum bulk density of $CaSiO_3$ ceramic sintered at 1340 °C prepared by the conventional solid-state process is 2.439 g/cm^3, and the microwave dielectric properties are $\varepsilon_r = 6.59$ and $Q \times f = 13{,}109$ GHz. Whereas for $CaSiO_3$ ceramic obtained by the sol–gel method, the maximum bulk density is 2.505 g/cm^3 and the microwave dielectric properties are $\varepsilon_r = 6.69$ and $Q \times f = 25{,}398$ GHz. The density value of the above two samples synthesized either by the traditional solid-state method or by the sol–gel method is much smaller than that of the theoretical density of the $CaSiO_3$ ceramic, which is 2.91 g/cm^3, indicating that it is difficult to obtain dense $CaSiO_3$ ceramic.

In order to improve the sintering characteristic and microwave dielectric properties, Sun and co-workers have used Mg^{2+} to substitute Ca^{2+} in the $CaSiO_3$ host.[9,10] When the substitution is 0.1 in molar ratio, the bulk density of $(Ca_{0.9}Mg_{0.1})SiO_3$

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ceramic is 2.75 g/cm^3, which exhibits excellent dielectric properties of $\varepsilon_r = 6.49$, $Q \times f = 62{,}420$ GHz and $\tau_f = -43.3$ ppm/°C.[9] In addition, the synthesis of CaO–B_2O_3–SiO_2 (CBS) glass–ceramics has been investigated and B_2O_3 has been added into $CaSiO_3$ ceramics to decrease its sintering temperature.[11–14] The B_2O_3 addition results in the presence of a CaO–B_2O_3–SiO_2 glass phase, which is supposed to lower the densification temperature of $CaSiO_3$ ceramic. With 6 wt% B_2O_3 addition, the $CaSiO_3$ ceramic sintered at 1100 °C has good dielectric properties of $\varepsilon_r = 6.84$ and $\tan\delta = 6.9 \times 10^{-4}$ (1 MHz).[11] Zhu et al. found that the optimal sintering temperature of CBS glass–ceramic is 820 °C, and the glass–ceramic with the major phases of $CaSiO_3$, CaB_2O_4 and SiO_2 possesses dielectric properties of $\varepsilon_r = 6.5$ and $\tan\delta = 2 \times 10^{-3}$ (10 MHz).[12] Chang and co-workers demonstrated that the dielectric properties of the CBS system consisting of $CaSiO_3$, $Ca_6Si_4O_3$ and CaB_2O_4 are $\varepsilon_r = 5.1$ and $\tan\delta = 1.3 \times 10^{-3}$ (1 GHz).[13,14]

Al_2O_3 ceramic with low ε_r (9.8) and high $Q \times f$ (360,000 GHz) is also a promising material for millimeter-wave applications,[15,16] and commercially available alumina normally has a $Q \times f$ value around 10,000–20,000 GHz.[17] In this work, the addition of Al_2O_3 was used to improve the sintering characteristic of $CaSiO_3$ ceramic, and the effects of Al_2O_3 addition on the microstructure and microwave dielectric properties of $CaSiO_3$–Al_2O_3 ceramics were investigated and discussed.

2. Experimental procedure

$CaSiO_3$ powders were prepared by a conventional solid-state method using commercial oxide powders (>99.5%) of $CaCO_3$ and SiO_2 as raw materials. Stoichiometric $CaCO_3$ and SiO_2 powders were weighed and ground in ethanol for 24 h in a balling mill with ZrO_2 balls. Then the mixture was calcined at 1200 °C for 2 h in air and $CaSiO_3$ powders were obtained. The $CaCO_3$–SiO_2 powders calcined at 1200 °C were mixed with commercial Al_2O_3 powders (>99.95%), and the content of Al_2O_3 was 0.1, 0.3, 0.6, 1, 2 and 5 in weight percent. The mixed powders were remilled for 24 h with 8 wt% polyvinyl alcohol (PVA) solution as a binder, and then pressed into pellets with the sizes of 15 mm in diameter and 8 mm in thickness. These pellets were sintered at 1200–1275 °C for 2 h in air with a heating rate of 5 °C/min.

The bulk densities of the sintered pellets were measured by the Archimedes method using distilled water as medium. The sintered bulks were broken up and ground to powders using an agate mortar. Crystal structures of the powders were performed by X-ray diffraction pattern (XRD, ARL XTRA) with Cu K$_\alpha$ radiation (36 kV, 30 mA, $2\theta = 10$–$80°$). The polished surfaces of the ceramics were investigated by scanning electron microscopy (SEM, TM3000) after thermal etching. The dielectric constants ε_r and the quality values $Q \times f$ were measured by Hakki–Coleman dielectric resonator method using an Agilent 8719ET (50 MHz to 13.5 GHz) Network Analyzer. The center frequencies of the sintered bulks were 10–11 GHz.

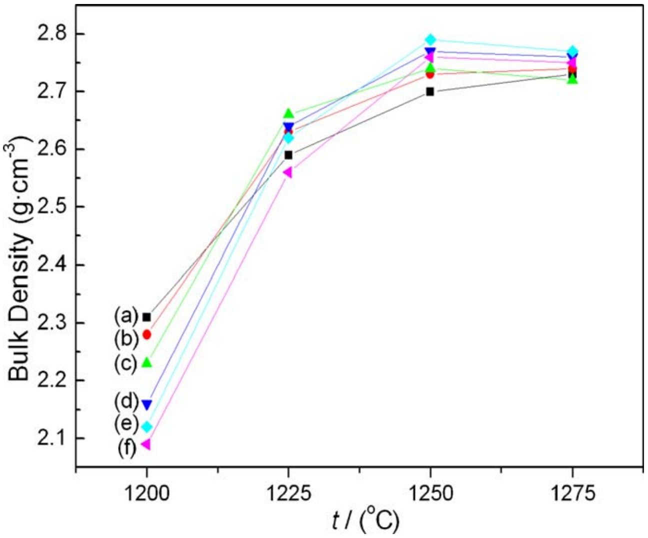

Fig. 1. Bulk densities of $CaSiO_3$–Al_2O_3 ceramics sintered at different temperatures with (a) 0.1 wt%, (b) 0.3 wt%, (c) 0.6 wt%, (d) 1 wt%, (e) 2 wt% and (f) 5 wt% Al_2O_3 additions.

3. Results and discussion

Fig. 1 shows the bulk densities of $CaSiO_3$–Al_2O_3 ceramics sintered at different temperatures with different amounts of Al_2O_3 addition. It is obvious that with the increase of the sintering temperature, the densities of all bulks increase to a maximum value and then they are saturated. The optimal sintering temperature of $CaSiO_3$ ceramics with 0.1–0.3 wt% and 0.6–5 wt% Al_2O_3 additions are 1275 °C and 1250 °C, respectively. Sintered at 1250 °C, the bulk densities of $CaSiO_3$ ceramics with 0.1 wt%, 0.3 wt%, 0.6 wt%, 1 wt%, 2 wt% and 5 wt% Al_2O_3 additions are 2.70 g/cm^3, 2.73 g/cm^3, 2.74 g/cm^3, 2.77 g/cm^3, 2.79 g/cm^3 and 2.76 g/cm^3, respectively. In our previous work, the maximum bulk density of $CaSiO_3$ ceramics prepared by the conventional solid-state process was 2.439 g/cm^3, which is 84% of the

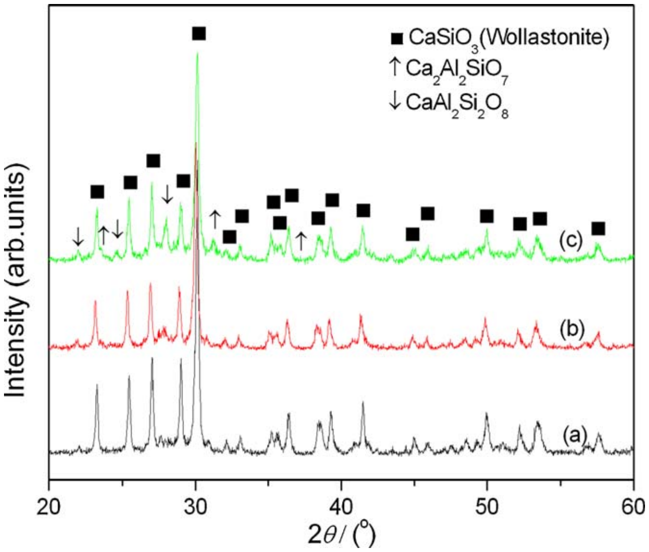

Fig. 2. XRD patterns of $CaSiO_3$–Al_2O_3 ceramics sintered at 1250 °C with (a) 1 wt%, (b) 2 wt% and (c) 5 wt% Al_2O_3 additions.

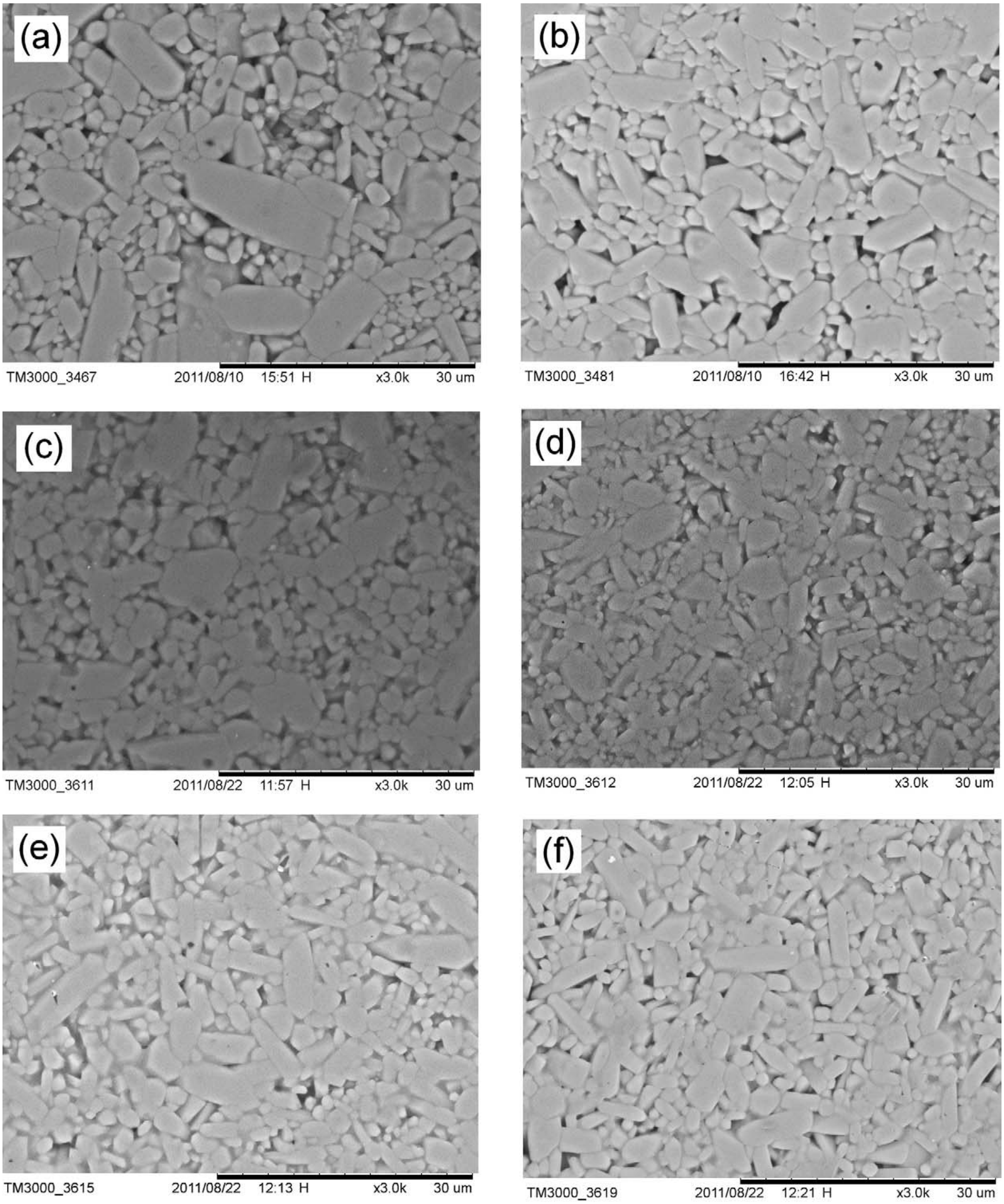

Fig. 3. SEM micrographs of $CaSiO_3$–Al_2O_3 ceramics sintered at 1250 °C with (a) 0.1 wt%, (b) 0.3 wt%, (c) 0.6 wt%, (d) 1 wt%, (e) 2 wt% and (f) 5 wt% Al_2O_3 additions.

theoretical density.[8] These results in the present work indicate that appropriate Al_2O_3 addition benefits the sintering process of $CaSiO_3$ ceramic and a density of $CaSiO_3$ ceramic as high as 96% of the theoretical value can be achieved with 1–2 wt% Al_2O_3 addition. It is well known that the high melting point of Al_2O_3 requires a high sintering temperature around 1700 °C so that excessive Al_2O_3 addition will result in the increase of sintering temperature of $CaSiO_3$–Al_2O_3 ceramic.

Fig. 2 shows the X-ray diffraction patterns of $CaSiO_3$–Al_2O_3 ceramics sintered at 1250 °C with different amounts of Al_2O_3 addition. When the Al_2O_3 additions are 1–5 wt%, the primary crystal phase of $CaSiO_3$–Al_2O_3 ceramics is wollastonite–$CaSiO_3$, and trace amounts of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ are observed, which suggests that the reaction between Al_2O_3 and $CaSiO_3$ results in the presence of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$. Moreover, sequential addition of

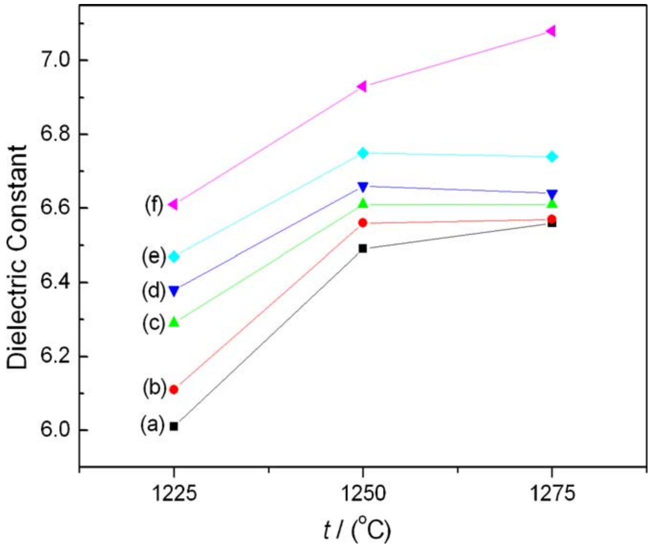

Fig. 4. Dielectric constants of $CaSiO_3$–Al_2O_3 ceramics sintered at different temperatures with (a) 0.1 wt%, (b) 0.3 wt%, (c) 0.6 wt%, (d) 1 wt%, (e) 2 wt% and (f) 5 wt% Al_2O_3 additions.

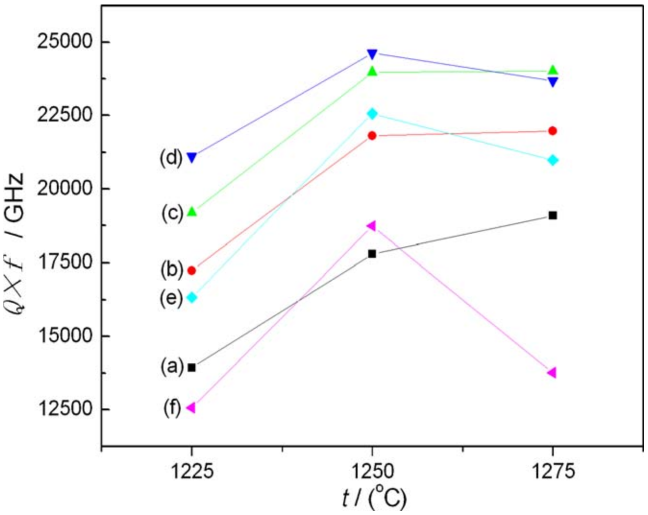

Fig. 5. $Q \times f$ values of $CaSiO_3$–Al_2O_3 ceramics sintered at different temperatures with (a) 0.1 wt%, (b) 0.3 wt%, (c) 0.6 wt%, (d) 1 wt%, (e) 2 wt% and (f) 5 wt% Al_2O_3 additions.

Al_2O_3 weakens the intensities of diffraction peaks of $CaSiO_3$ but strengthens those of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$.

The microstructures of $CaSiO_3$–Al_2O_3 ceramics sintered at 1250 °C with different amounts of Al_2O_3 addition are presented in Fig. 3. It can be intuitively seen that the grain structure is uniformed distributed throughout the samples, e.g. the coarse grains are surrounded by the fine grains. As the Al_2O_3 content increases from 0.1 wt% to 0.6 wt%, the average size of the coarse grains decreases from 10 μm to 6 μm. In our previous work, the grains grows exceptionally and results in the pores in the pure $CaSiO_3$ ceramics.[8] Therefore the incorporation of Al_2O_3 effectively restricts the abnormal grain growth of $CaSiO_3$. With Al_2O_3 addition, the sintering process of $CaSiO_3$ ceramic can be improved due to the presence of the new phases of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$, which restricts the growth of $CaSiO_3$ grains by surrounding their boundaries. It indicates that appropriate Al_2O_3 addition (0.6–5 wt%) benefits the sintering process of $CaSiO_3$ ceramics, which is consistent with the results of bulk densities sintered at different temperatures, as shown in Fig. 1.

Fig. 4 illustrates the dielectric constant (ε_r) of $CaSiO_3$–Al_2O_3 ceramics sintered at different temperatures with different amounts of Al_2O_3 addition. It is evident that the dielectric constants increase to a maximum value and then they are saturated. With the fixed $CaSiO_3$–Al_2O_3 component, the relationship between dielectric constant and sintering temperature follows the same trend as that between density and sintering temperature because a higher density is associated with a lower porosity and results in a higher dielectric constant. However, the dielectric constant increases with Al_2O_3 addition, and the maximum ε_r of $CaSiO_3$–Al_2O_3 ceramics with 0.1 wt%, 0.3 wt%, 0.6 wt%, 1 wt%, 2 wt% and 5 wt% Al_2O_3 additions are 6.56, 6.57, 6.61, 6.66, 6.75 and 7.08, respectively. The gradual increase of the value of dielectric constant with Al_2O_3 addition is attributed to the higher dielectric constant of Al_2O_3 (9.8) compared with that of $CaSiO_3$ (6.59), which results in the larger dielectric constants of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ with respect to that of $CaSiO_3$.

The quality values ($Q \times f$) of $CaSiO_3$–Al_2O_3 ceramics sintered at different temperatures with different amounts of Al_2O_3 addition are demonstrated in Fig. 5. The optimal $Q \times f$ values of $CaSiO_3$–Al_2O_3 ceramics with 0.1 wt%, 0.3 wt%, 0.6 wt%, 1 wt%, 2 wt% and 5 wt% Al_2O_3 additions are 19,087 GHz, 21,974 GHz, 24,018 GHz, 24,626 GHz, 22,566 GHz and 18,738 GHz, respectively. These results indicate that the appropriate Al_2O_3 addition (0.6–1 wt%) benefits the microwave dielectric properties. However, excessive Al_2O_3 addition (≥2 wt%) degrades the quality factor, although Al_2O_3 ceramics have been proved to be an excellent dielectric material with high $Q \times f$ value (360,000 GHz).[15,16] Since the $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ restrict the growth of $CaSiO_3$ grains by surrounding their boundaries, the appropriate Al_2O_3 addition improves the densities of $CaSiO_3$–Al_2O_3 ceramics, and therefore improves the microwave dielectric properties. Due to the poor quality factor of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$,[18] the excessive addition of Al_2O_3 undermines the microwave dielectric properties. With 1 wt% Al_2O_3 addition, the $CaSiO_3$–Al_2O_3 ceramic sintered at 1250 °C possesses good microwave dielectric properties: $\varepsilon_r = 6.66$ and $Q \times f = 24{,}626$ GHz, which shows much preferable properties compared with those of pure $CaSiO_3$ ceramic sintered at 1340 °C ($Q \times f = 13{,}109$ GHz).[8]

4. Conclusion

The sintering behavior and microwave dielectric properties of $CaSiO_3$ ceramics with Al_2O_3 addition were investigated. The phase of Al_2O_3 was not detected in the $CaSiO_3$–Al_2O_3 ceramics and Al_2O_3 had reacted with $CaSiO_3$ to form $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$. Since the new phases of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ restrict the growth of $CaSiO_3$ grains by surrounding their boundaries, the appropriate Al_2O_3 addition (0.6–1 wt%) improves the densities of $CaSiO_3$–Al_2O_3 ceramics, and therefore improves the microwave dielectric properties. The excessive Al_2O_3 addition ($\geq$2 wt%) undermines the microwave dielectric properties because of the poor quality factor of the new phases of $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$. With 1 wt% Al_2O_3 addition, the $CaSiO_3$–Al_2O_3 ceramic sintered at 1250 °C possesses much better microwave dielectric properties: $\varepsilon_r = 6.66$ and $Q \times f = 24{,}626$ GHz, compared with those of pure $CaSiO_3$ ceramic sintered at 1340 °C.

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