Sintering behavior and dielectric properties of Al$_2$O$_3$ ceramics with CaMgSi$_2$O$_6$ addition

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Al$_2$O$_3$–CaMgSi$_2$O$_6$ ceramics with different amount of CaMgSi$_2$O$_6$ additions were prepared by a conventional solid-state method, and the effects of CaMgSi$_2$O$_6$ addition on the sintering behavior and dielectric properties of Al$_2$O$_3$ ceramics have been investigated. CaMgSi$_2$O$_6$ was used as a liquid sintering aid to effectively lower the sintering temperature of Al$_2$O$_3$ ceramics and its addition resulted in the presence of CaAl$_2$Si$_2$O$_6$ and MgAl$_2$O$_4$ phases. However, the CaMgSi$_2$O$_6$ addition deteriorated the dielectric properties of Al$_2$O$_3$–CaMgSi$_2$O$_6$ ceramics because of the higher dielectric loss of the derived CaAl$_2$Si$_2$O$_6$ and MgAl$_2$O$_4$ compared with that of Al$_2$O$_3$ ceramics. After sintered at 1450°C, the Al$_2$O$_3$–CaMgSi$_2$O$_6$ ceramic with 10 wt% CaMgSi$_2$O$_6$ addition possessed dielectric properties of $\varepsilon_r = 9.83$, tan $\delta = 1.5 \times 10^{-4}$ (1 MHz) and $Q \times f = 20,425$ GHz ($f_0 = 12$ GHz).

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1. Introduction

Modern communication systems have moved to the microwave frequency region, where advanced dielectric ceramics are frequently used in resonators and filters.\(^3\) This requires the dielectric ceramics to have a low dielectric constant ($\varepsilon_r$), a low dielectric loss (high quality factor) and a near-zero temperature coefficient of resonant frequency ($\alpha$).\(^4\) Al$_2$O$_3$ has been one of the most widely used dielectric ceramics which not only finds application in microwave and millimeter-wave communication fields from 10 to 300 GHz frequency band but also has been used as resonators for ultrafast oscillators in clocks and as substrates because of the low dielectric constants ($\varepsilon_r \approx 9.8$) and ultra-low dielectric loss ($\tan \delta < 10^{-5}$).\(^5\) However, the high melting point of Al$_2$O$_3$ necessitates a high sintering temperature of around 1700°C.\(^11\)\(^,\)\(^12\) In order to lower the sintering temperature of Al$_2$O$_3$ ceramic, sintering aids such as TiO$_2$, MnO, ZnO–B$_2$O$_3$–SiO$_2$ (ZBS) glass and MgO–CaO–Al$_2$O$_3$–SiO$_2$ (MCAS) glass have been used.\(^13\)\(^\)–\(^17\) For example, with TiO$_2$ addition, Al$_2$O$_3$ ceramic sintered at 1500°C possesses a quality factor of 333,000 GHz.\(^13\)\(^\)\(^,\)\(^14\) Dai et al. added TiO$_2$ and MCAS glass into Al$_2$O$_3$ ceramics and the derived samples sintered at 1350°C had good dielectric properties of $\varepsilon_r = 11.6$ and $Q \times f = 11,456$ GHz.\(^15\) Huang and co-workers found that nanoparticles can also reduce the sintering temperature significantly and also promote the $Q \times f$ value of $\alpha$-Al$_2$O$_3$ ceramics to 500,000 GHz.\(^18\)

CaMgSi$_2$O$_6$ ceramic is an important material with good dielectric properties ($\varepsilon_r = 7.46$, $Q \times f = 59,638$ GHz) and low dielectric loss ($\kappa_{11} = 9.69$, $\tan \delta = 1.6 \times 10^{-4}$, $\kappa_{22} = 7.31$, $\tan \delta = 7 \times 10^{-4}$, $\kappa_{33} = 7.29$ and $\tan \delta = 1.9 \times 10^{-3}$), and low densification temperature (about 1290°C).\(^19\)\(^\)\(^20\) In this paper, CaMgSi$_2$O$_6$ was used as a sintering aid to lower the sintering temperature of Al$_2$O$_3$ ceramic, and the sintering phases, phase composition, microstructure analysis and dielectric properties of the Al$_2$O$_3$–CaMgSi$_2$O$_6$ ceramic have been investigated.

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2. Experimental procedure

Samples were prepared by a conventional solid-state method. Commercial oxide powders (>99.5%) of CaCO$_3$, MgO, SiO$_2$ and Al$_2$O$_3$ were used as the raw materials. Firstly, CaCO$_3$, MgO and SiO$_2$ powders were weighed according to the stoichiometry (CaMgSi$_2$O$_6$) and ground in ethanol for 24 h in a ball mill with zirconia balls. The CaCO$_3$–MgO–SiO$_2$ powders were dried and calcined at 1100–1200°C for 2 h. Then the CaCO$_3$–MgO–SiO$_2$ powders calcined at 1200°C were mixed with Al$_2$O$_3$ powders, and the content of CaMgSi$_2$O$_6$ was 1, 3, 5, 10, 15, 20, 25 and 30 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 at 150 MPa. These pellets were sintered at 1300–1600°C for 2 h in air with a heating rate of 300°C/h.

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 were examined by X-ray diffraction pattern (XRD, ARL XTRA) with CuK$_\alpha$ radiation (36 kV, 30 mA, $2\theta = 10–80^\circ$). The fracture surfaces of the sintered bulks were coated with gold and the morphology was identified by scanning electron microscopy (SEM, JSM-5601). The dielectric constant ($\varepsilon_r$) 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., $\varepsilon_r = Cd/\varepsilon_0$, where $C$ was the capacitance of the specimens, $d$ and $A$ were the thickness and the area of the electrode, respectively, and $\varepsilon_0$ was the dielectric permittivity of vacuum ($8.854 \times 10^{-12}$ F/m). A silver paste was used for the electrode. The quality values $Q \times f$ at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using an Agilent 8719ET (50 MHz to 13.5 GHz) Network Analyzer.
3. Results and discussion

3.1 Raw powders phase composition

Figure 1 shows the X-ray diffraction patterns of alumina powders and CaCO3–MgO–2SiO2 powders calcined at different temperatures. All diffraction peaks in Fig. 1(a) correspond to the diffraction patterns of Al2O3. The CaCO3–MgO–2SiO2 powders calcined at 1100°C lead to two dominant phases Ca2MgSi2O7 and SiO2 with poor crystallinity and trace amount of MgO, as evidenced by the broad diffraction peaks in Fig. 1(b). A higher temperature sintering at 1200°C not only improves the crystallinity of the powders but also enables a phase transition from Ca2MgSi2O7 to CaMgSi2O6. No diffraction peaks associated with SiO2 and MgO are observed.

3.2 Sintering behaviors of Al2O3–CaMgSi2O6 ceramics

Figure 2 shows the bulk densities of Al2O3–CaMgSi2O6 ceramics sintered at different temperatures with different amount CaMgSi2O6 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 temperatures of Al2O3 ceramics with 1, 3, 5, 10, 15, 20, 25 and 30 wt% CaMgSi2O6 additions are 1575, 1550, 1525, 1450, 1425, 1375, 1375 and 1375°C, and the maximum bulk densities at these temperatures are 3.83, 3.74, 3.72, 3.59, 3.54, 3.48, 3.38 and 3.33 g/cm3, respectively. These results indicate that both the sintering temperature and the maximum density of Al2O3–CaMgSi2O6 ceramics decrease with the CaMgSi2O6 addition. The sintering temperature of CaMgSi2O6 (1290°C) is lower than that of Al2O3 (1700°C)11),12),20) therefore the optimal sintering temperatures of Al2O3 ceramics decrease from 1575 to 1375°C with the CaMgSi2O6 additions from 1 to 20 wt%. On the other hand, the theoretical density of CaMgSi2O6 ceramic (2.91 g/cm3) is lower than that of Al2O3 ceramic (3.98 g/cm3), which results in the smaller bulk density with the larger amount addition of CaMgSi2O6.

3.3 Phase composition and microstructure of Al2O3–CaMgSi2O6 ceramics

Figure 3 shows the X-ray diffraction patterns of Al2O3–CaMgSi2O6 ceramics with different amount CaMgSi2O6 additions sintered at different temperatures. With 5 wt% CaMgSi2O6 addition, a dominant Al2O3 phase together with trace amount of CaAl2Si2O8 and MgAl2O4 phase are obtained, which suggests that the reaction between Al2O3 and CaMgSi2O6 results in the presence of CaAl2Si2O8 and MgAl2O4. Gradually increase the addition amount of CaMgSi2O6 weakens the intensity of Al2O3 diffraction peaks while strengthens those of CaAl2Si2O8 and MgAl2O4. Combining with the results in Fig. 2, it is supposed that the decrease of sintering temperatures with the increase of CaMgSi2O6 addition can be attributed to the presence of CaAl2Si2O8 and MgAl2O4 phases, which promotes the sintering process of Al2O3 ceramic as liquid sintering aids.21) Figure 4 shows the microstructures of Al2O3–CaMgSi2O6 ceramics with different amount CaMgSi2O6 additions sintered at their corresponding optimum temperatures. As can be seen from picture (a), dense bodies with few pores are obtained, and the average grain size is about 3–5 μm with 1 wt% CaMgSi2O6 addition. The increase of CaMgSi2O6 addition from 3 to 20 wt% leads to smaller grains of the derived ceramics, as shown in Figs. 4(b)–4(f). The new phases of CaAl2Si2O8 and MgAl2O4 distribute along grain boundaries of alumina major phase, which can restrict grain growth of Al2O3 ceramics during the sintering process.
process. When the amount of CaMgSi2O6 is increased to 25–30 wt %, Figs. 4(g) and 4(h) show the grains growing even larger with the augment of CaAl2Si2O8 and MgAl2O4, indicating that CaAl2Si2O8 and MgAl2O4 acting as liquid sintering aids melt and can improve the sintering process.

3.4 Dielectric properties of Al2O3–CaMgSi2O6 ceramics

Figure 5 demonstrates the dielectric constant ($\varepsilon_r$) of Al2O3–CaMgSi2O6 ceramics with different amount of CaMgSi2O6 additions as a function of their corresponding sintering temperatures. As shown in Fig. 5, the dielectric constant increases to a maximum and then decreases with the increase of sintering temperature, and the maximum $\varepsilon_r$ of Al2O3–CaMgSi2O6 ceramics with 1, 3, 5, 10, 15, 20, 25 and 30 wt % CaMgSi2O6 additions are 10.38, 10.20, 10.09, 9.83, 9.73, 9.59, 9.39 and 9.22, respectively. The relationships between $\varepsilon_r$ and sintering temperatures reveal the same trend with those between densities and sintering temperatures since that a higher density signifies a lower porosity and results in higher dielectric constant. Because the dielectric constants of CaAl2Si2O6 and MgAl2O4 are lower than that of Al2O3,21) the values of $\varepsilon_r$ decrease from 10.38 to 9.22 when the CaMgSi2O6 addition is increased from 1 to 30 wt %.

The dielectric loss of Al2O3–CaMgSi2O6 ceramics with different amount of CaMgSi2O6 additions sintered at different temperatures is illustrated in Fig. 6. The least dielectric loss of Al2O3–CaMgSi2O6 ceramics with 1, 3, 5, 10, 15, 20 and 30 wt % CaMgSi2O6 additions are $0.8 \times 10^{-4}$, $1.1 \times 10^{-4}$, $1.4 \times 10^{-4}$, $1.5 \times 10^{-4}$, $3.2 \times 10^{-4}$, $9.8 \times 10^{-4}$, $11.5 \times 10^{-4}$ and $12.2 \times 10^{-4}$, respectively. It's evident that the addition of CaMgSi2O6 can lower the sintering temperature of Al2O3 ceramic. However, excess addition may lead to a larger dielectric loss, suggesting that the CaAl2Si2O6 and MgAl2O4 secondary phases have higher dielectric loss than Al2O3 phase. The Al2O3–CaMgSi2O6 ceramic with 10 wt % CaMgSi2O6 addition possesses dielectric properties of $\varepsilon_r = 9.83$ and $\tan \delta = 1.5 \times 10^{-4}$ at 1450°C, which shows better performance compared with those of pure CaMgSi2O6 ceramic.

Figure 7 shows the quality values ($Q \times f$) at microwave frequencies of Al2O3–CaMgSi2O6 ceramics with different amount of CaMgSi2O6 additions sintered at different temperatures. The optimal $Q \times f$ value of Al2O3–CaMgSi2O6 ceramics...
Fig. 7. (Color online) $Q \times f$ values of $\text{Al}_2\text{O}_3$–$\text{CaMgSi}_2\text{O}_6$ ceramics sintered at different temperatures with (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt% and (f) 20 wt% $\text{CaMgSi}_2\text{O}_6$ additions.

with 1, 3, 5, 10, 15 and 20 wt% $\text{CaMgSi}_2\text{O}_6$ additions are 36,362, 29,239, 24,315, 20,425, 14,946 and 12,921 GHz, separately, which indicates that the addition of $\text{CaMgSi}_2\text{O}_6$ is harmful to increasing the quality value of $\text{Al}_2\text{O}_3$–$\text{CaMgSi}_2\text{O}_6$ ceramics. Compared with the report that the $Q \times f$ value of $\text{CaMgSi}_2\text{O}_6$ ceramic is 59,638 GHz,19) the $\text{Al}_2\text{O}_3$–$\text{CaMgSi}_2\text{O}_6$ ceramics with different amount of $\text{CaMgSi}_2\text{O}_6$ additions have lower quality values at microwave frequencies. These results suggest that the $\text{CaAl}_2\text{Si}_2\text{O}_8$ and MgAl$_2$O$_4$ phases have lower quality values at microwave frequencies. These results suggest that the $\text{CaAl}_2\text{Si}_2\text{O}_8$ and MgAl$_2$O$_4$ phases have lower quality values at microwave frequencies.

4. Conclusions

The addition of $\text{CaMgSi}_2\text{O}_6$ into $\text{Al}_2\text{O}_3$ ceramics results in the presence of CaAl$_2$Si$_2$O$_8$ and MgAl$_2$O$_4$, which are acting as liquid sintering aids to effectively lower the sintering temperature of $\text{Al}_2\text{O}_3$ ceramic. With amount of 1, 3, 5, 10, 15 and 20 wt% $\text{CaMgSi}_2\text{O}_6$ addition, the densification temperature of $\text{Al}_2\text{O}_3$–$\text{CaMgSi}_2\text{O}_6$ ceramics are 1575, 1550, 1525, 1450, 1425 and 1375°C, respectively. However, the $\text{CaMgSi}_2\text{O}_6$ addition deteriorates the dielectric properties of $\text{Al}_2\text{O}_3$–$\text{CaMgSi}_2\text{O}_6$ ceramics since the derived CaAl$_2$Si$_2$O$_8$ and MgAl$_2$O$_4$ phases have higher dielectric loss than $\text{Al}_2\text{O}_3$ phase, and the dielectric loss increases from $1 \times 10^{-4}$ to $12.2 \times 10^{-4}$ when the addition of $\text{CaMgSi}_2\text{O}_6$ is increased from 1 to 30 wt%. Sintered at 1450°C, the $\text{Al}_2\text{O}_3$–$\text{CaMgSi}_2\text{O}_6$ ceramic with 10 wt% $\text{CaMgSi}_2\text{O}_6$ addition possesses dielectric properties of $\varepsilon_r = 9.83$, tan $\delta = 1.5 \times 10^{-4}$ (1 MHz) and $Q \times f = 20,425$ GHz ($f_0 = 12$ GHz).

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