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Original Research

Effect of CuO addition on the sintering temperature and microwave dielectric properties of CaSiO₃–Al₂O₃ ceramics

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Abstract

CuO-doped CaSiO₃–1 wt% Al₂O₃ ceramics were synthesized via a traditional solid-state reaction method, and their sintering behavior, microstructure and microwave dielectric properties were investigated. The results showed that appropriate CuO addition could accelerate the sintering process and assist the densification of CaSiO₃–1 wt% Al₂O₃ ceramics, which could effectively lower the densification temperature from 1250 °C to 1050 °C. However, the addition of CuO undermined the microwave dielectric properties. The optimal amount of CuO addition was found to be 0.8 wt%, and the derived CaSiO₃–Al₂O₃ ceramic sintered at 1100 °C presented good microwave dielectric properties of $\epsilon_r=7.27$, $Q \times f=16,850$ GHz and $\tau_f=-39.53$ ppm/°C, which is much better than those of pure CaSiO₃ ceramic sintered at 1340 °C ($Q \times f=13,109$ GHz). The chemical compatibility of the above ceramic with 30 Pd/70 Ag during the cofiring process has also been investigated, and the result showed that there was no chemical reaction between palladium–silver alloys and ceramics.

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Keywords: Microwave dielectric properties; CaSiO₃ ceramic; Al₂O₃ ceramic; CuO addition

1. Introduction

Low temperature co-fired ceramic (LTCC) multilayer device, which consists of alternating dielectric ceramics and internal metallic electrode layers, has been extensively investigated for the miniaturization of microwave dielectric components [1–4]. 30 Pd/70 Ag has been widely used as a metallic electrode because of its high conductivity and temperature stability. Since the melting temperature of 30 Pd/70 Ag is 1167 °C, the microwave dielectric ceramics which can be

sintered at about 1100 °C are required to synthesize the LTCC multilayer devices. Particularly, with the need of various RF ranges, great effects have been devoted to the synthesis of the microwave dielectric materials with different dielectric constants [5–7].

CaSiO₃ ceramic has been proven to be an excellent dielectric material with a low dielectric constant and a low dielectric loss, and it might be regarded as a suitable candidate for microwave dielectric resonators. However, the sintering temperature range of neat CaSiO₃ ceramic is very narrow. Chakradhar et al. pointed out that it was difficult to obtain dense CaSiO₃ ceramic since its grains grew exceptionally and the bulk CaSiO₃ ceramic became more porous with the increase of the calcination temperature [8]. In our previous work, the sintering behavior and microwave dielectric properties of CaSiO₃ ceramics have been investigated by a traditional solid-state process and a sol–gel method, respectively [9]. The maximum bulk density of CaSiO₃ ceramic sintered at 1340 °C prepared by the conventional solid-state process was 2.439 g/cm³,

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and the microwave dielectric properties were $\epsilon_r=6.59$ and $Q \times f=13,109$ GHz, whereas for CaSiO_3 ceramic obtained by the sol–gel method, the maximum bulk density was 2.505 g/cm^3 . 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 et al. have used Mg^{2+} to substitute Ca^{2+} in the CaSiO_3 host to prepare the CaO-MgO-SiO_2 ceramics for LTCC applications [10–12]. Moreover, in our previous work, we have found that the addition of Al_2O_3 can restrict the growth of CaSiO_3 grains by surrounding their boundaries and also improve the bulk density of $\text{CaSiO}_3\text{-Al}_2\text{O}_3$ ceramics. The optimum amount of Al_2O_3 addition was found to be 1 wt%, and the derived $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramic presented improved microwave dielectric properties of $\epsilon_r=6.66$ and $Q \times f=24,626$ GHz. However, the sintering temperature is still high, which is about 1250°C [13]. For practical manufacturing process, it is desired to reduce the densification temperature of $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramics.

Since CuO is commonly used as a liquid-phase flux and has been shown to accomplish a substantial sintering temperature reduction [14–18], it was selected as a sintering aid in the present study. The objective of this study is to develop $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramics with a low sintering temperature and a high quality factor by incorporating with different amounts of CuO . The sintering behavior, microstructure, microwave dielectric properties, green tape and co-firing with 30 Pd/70 Ag electrode of the CuO -doped $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramics were investigated.

2. Experimental procedure

Specimen powders were prepared by a conventional solid-state method using commercial oxide powders ($> 99.5\%$) of CaCO_3 , SiO_2 , Al_2O_3 , and CuO as raw materials. Stoichiometric CaCO_3 and SiO_2 powders were weighed and milled in a plastic jar with zirconium balls under ethanol for 24 h. Prepared powders were dried and calcined at 1200°C for 2 h in air to obtain CaSiO_3 . The calcined powders were mixed as desired for the composition of CaSiO_3 with 1 wt% Al_2O_3 and different amounts of CuO additions as sintering aids, and the contents of CuO were 0.5, 0.8, 1, 1.2, 1.5 and 2 in weight percent. The mixed powders were re-milled for 24 h with 8 wt% polyvinyl alcohol (PVA) solution as a binder, and then pressed into pellets with dimensions of 15 mm in diameter and 8 mm in thickness by applying a pressure of 135 MPa. These pellets were sintered at $1025\text{--}1125^\circ\text{C}$ for 2 h in air with a heating rate of 5°C/min .

In order to investigate ceramics' slurry for tape casting, the CuO -doped $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramic powders were first mixed with solvent and dispersant in a ball mill for 12 h. Then the binder and plasticizer were added, and mixed for another 12 h to obtain the slurry. The solvent was the mixture of toluene and ethanol, and the dispersant was menhaden fish oil.

The binder itself was polyvinyl butyral (PVB), and the compatible plasticizer was butyl benzyl phthalate (S160). After homogenizing, the slurries were degassed under vacuum to remove air bubbles. Finally, the tape casting was performed on membrane belt-scraper style ceramic film with membrane belt width of 150 mm at a speed of 0.5 m/min. After drying freely in open air at ambient temperature for 4–5 h, the co-fired samples were prepared with the green tapes and 30 Pd/70 Ag paste.

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 (XRD, ARL XTRA) with $\text{Cu K}\alpha$ radiation (36 kV, 30 mA, $2\theta=10^\circ\text{--}80^\circ$). The polished surfaces of the ceramics were investigated by scanning electron microscopy (SEM, TM3000) after thermal etching. The microstructures of the green tapes and co-fired interface were also investigated by scanning electron microscopy. The dielectric constant 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 to 13.5 GHz) Network Analyzer. The temperature coefficient of the resonant frequency τ_f was also measured by the same method in the temperature range of $25\text{--}80^\circ\text{C}$ and calculated by the following equation:

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \times 55} \times 10^6 (\text{ppm}/^\circ\text{C})$$

where f_{80} and f_{25} represent the resonant frequency at 80°C and 25°C , respectively.

3. Results and discussion

Fig. 1 shows the bulk densities of $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramics sintered at different temperatures with different amounts of CuO addition. It is obvious that with the increase of CuO addition, the densification temperature of the bulks

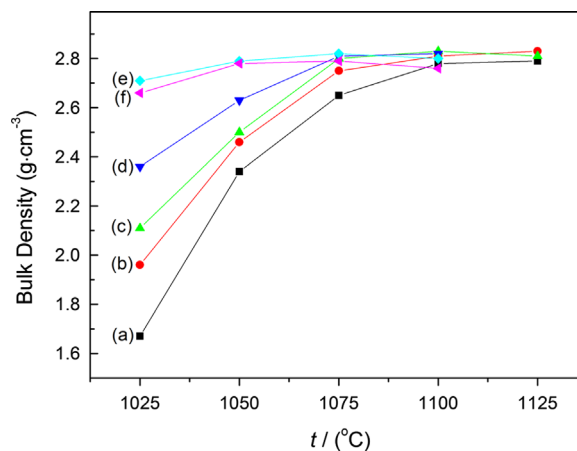


Fig. 1. Bulk densities of $\text{CaSiO}_3\text{-1 wt% Al}_2\text{O}_3$ ceramics sintered at different temperatures with (a) 0.5 wt%, (b) 0.8 wt%, (c) 1 wt%, (d) 1.2 wt%, (e) 1.5 wt%, and (f) 2 wt% CuO additions.

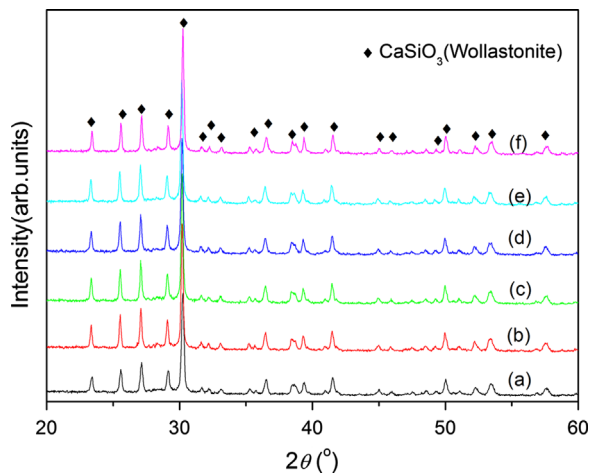


Fig. 2. XRD patterns of CaSiO_3 -1 wt% Al_2O_3 ceramics sintered at 1075 °C incorporated with (a) 0.5 wt%, (b) 0.8 wt%, (c) 1 wt%, (d) 1.2 wt%, (e) 1.5 wt%, and (f) 2 wt% CuO.

decreases from 1100 °C to 1050 °C. The optimal sintering temperatures of CaSiO_3 -1 wt% Al_2O_3 ceramics with 0.5 wt%, 0.8 wt%, 1 wt%, 1.2 wt%, 1.5 wt% and 2 wt% CuO additions are 1100 °C, 1100 °C, 1075 °C, 1075 °C, 1050 °C and 1050 °C, and the bulk densities at these temperatures are 2.78 g cm^{-3} , 2.81 g cm^{-3} , 2.80 g cm^{-3} , 2.81 g cm^{-3} , 2.79 g cm^{-3} and 2.78 g cm^{-3} , respectively. In our previous work, the densification temperature of CaSiO_3 -1 wt% Al_2O_3 ceramic without CuO addition is 1250 °C, and the maximum bulk density is 2.79 g cm^{-3} [13]. The melting point of CuO is 1026 °C. Therefore, it is considered that the CuO phase exists as a liquid phase during the sintering process and assists the densification of the CaSiO_3 -1 wt% Al_2O_3 ceramic. It is also evident that the bulk density of CaSiO_3 -1 wt% Al_2O_3 ceramics sintered at 1075 °C increases from 2.65 g cm^{-3} to 2.82 g cm^{-3} as the CuO addition increases from 0.5 wt% to 1.5 wt%. However, when the CuO addition reaches 2 wt%, the bulk density of the sample decreases to 2.79 g cm^{-3} , indicating that the volatilization of CuO happens and results in the decrease of the bulk density.

Fig. 2 shows the X-ray diffraction patterns of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with different amounts of CuO sintered at 1075 °C. It is clear that all the diffraction peaks can be indexed as the CaSiO_3 ceramic. No other phase caused by CuO additions is observed, since the detection of a minor phase by the X-ray diffraction is extremely difficult. However, the intensity of the CaSiO_3 diffraction peaks strengthens with the increase of CuO content, which may be due to the liquid phase originated from the CuO addition.

The SEM images of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with different amounts of CuO sintered at 1075 °C for 2 h are illustrated in Fig. 3. Fig. 3(a) shows that the average grain size is about 1 μm and there are many pores in the bulks, which indicates that the CaSiO_3 -1 wt% Al_2O_3 ceramic with 0.5 wt% CuO addition could be hardly sintered at 1075 °C. With the addition of 0.8 wt% CuO, the grains grow and the porosity decreases, as shown in Fig. 3(b). As the CuO content increases gradually, Fig. 3(c)–(e) shows that the grain grows fast and

specimens become well-densified. In the case of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with 0.8–1.5 wt% CuO, the volume fraction of the liquid increases with the CuO addition. The grains may dissolve into the liquid phase and rapidly rearrange, in which contact points among agglomerates will be dissolved and re-crystallized into grains. Based on this approach, the grains will grow and the pores will disappear. However, the surface of the ceramics seems to be porous as the CuO addition reaches 2 wt%, which may be caused by the volatilization of the excessive CuO.

Fig. 4 shows the dielectric constant of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with different amounts of CuO sintered at different temperatures. With the fixed CuO addition, it is evident that the dielectric constants increase to a maximum value and then become saturated with the increase of the sintering temperature from 1025 °C to 1125 °C. The relationship between dielectric constant and sintering temperature follows approximately the same trend as that between bulk density and sintering temperature because a higher density is associated with a lower porosity and results in a higher dielectric constant, which implies that the presence of the CuO content is not expected to bring much deviation to the constant of the specimen. It is also observed that with the increase of CuO content, the dielectric constant of the CaSiO_3 -1 wt% Al_2O_3 ceramics sintered at optimum temperatures shows a slightly rising trend, which may be caused by the high bulk density and large grain size with CuO addition.

The $Q \times f$ values of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with different amounts of CuO sintered at various temperatures are illustrated in Fig. 5. Among all the cases considered, increasing temperature caused the $Q \times f$ value to increase to a maximum, and then decrease thereafter. When the CuO additions are 0.5 wt%, 0.8 wt%, 1 wt%, 1.2 wt%, 1.5 wt% and 2 wt%, the $Q \times f$ values of the ceramics sintered at the optimum temperatures are 17,620 GHz, 16,850 GHz, 13,238 GHz, 12,821 GHz, 11,931 GHz and 10,962 GHz, respectively. Generally, the microwave dielectric loss is affected not only by the lattice vibrational modes, but also by the secondary phases and grain morphologies of specimens. It can be seen that the $Q \times f$ values of the specimens doped with a small amount of CuO (0.5–1 wt%) are higher than others when the sintering temperature is above 1075 °C, so we conclude that CuO addition deteriorates the microwave dielectric properties. In addition, the grains of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with 0.8–1 wt% CuO are more uniform than those doped with CuO with high content, which indicates that the abnormal grain growth as well as the CuO second phase could be responsible for the decrease in $Q \times f$ values. Combined with the cofiring with 30 Pd/70 Ag paste, good microwave dielectric properties of $\epsilon_r = 7.27$, $Q \times f = 16,850 \text{ GHz}$ and $\tau_f = -39.53 \text{ ppm}/^\circ\text{C}$ were obtained for the ceramics with 0.8 wt% CuO addition sintered at 1100 °C. The $Q \times f$ value of pure CaSiO_3 ceramic sintered at 1340 °C is 13,109 GHz [9]. So the CaSiO_3 ceramic incorporated with 1 wt% Al_2O_3 and 0.8 wt% CuO shows improved microwave dielectric properties at a lower sintering temperature.

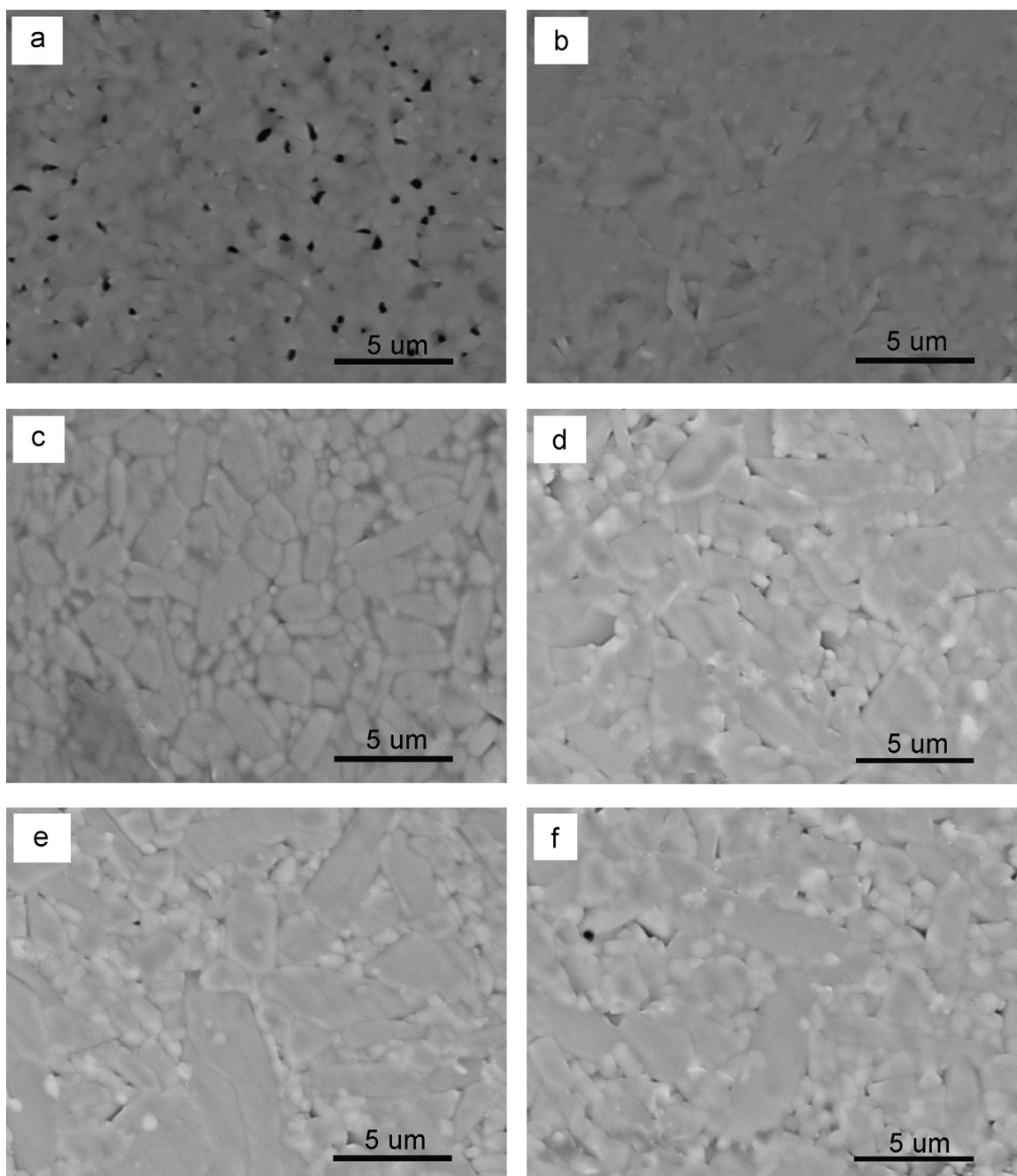


Fig. 3. SEM photographs of CaSiO_3 -1 wt% Al_2O_3 ceramics sintered at 1075 °C with (a) 0.5 wt%, (b) 0.8 wt%, (c) 1 wt%, (d) 1.2 wt%, (e) 1.5 wt%, and (f) 2 wt% CuO additions.

Fig. 6 shows the microstructure of CaSiO_3 -1 wt% Al_2O_3 green tapes with 0.8 wt% CuO addition. It is clear that the average particle size of the ceramic powders is around 1 μm , and the microstructures of the green tapes are uniform and there is no agglomeration. Furthermore, the surface of the green tape is glabrous. The green tape has very high density and tensile strength. The image of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with 0.8 wt% CuO co-fired with 30 Pd/70 Ag in air at 1100 °C is presented in Fig. 7. It is obvious that the ceramic materials do not react with palladium-silver alloys' electrodes, indicating that the as-prepared composite

ceramics are suitable for low-temperature co-fired ceramics applications.

4. Conclusions

In summary, the addition of CuO has a significant effect on the sintering process, microstructures and microwave dielectric properties of CaSiO_3 -1 wt% Al_2O_3 ceramics. The CuO addition could accelerate the sintering process and lower the densification temperature of CaSiO_3 -1 wt% Al_2O_3 ceramics from 1250 °C to 1050 °C. A dense microstructure developed

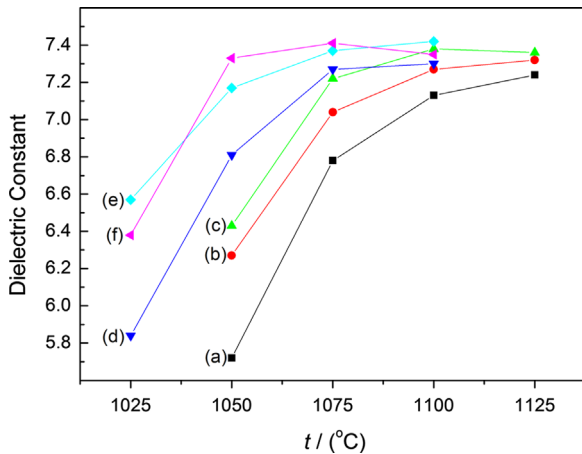


Fig. 4. Dielectric constants of CaSiO_3 -1 wt% Al_2O_3 ceramics sintered at different temperatures with (a) 0.5 wt%, (b) 0.8 wt%, (c) 1 wt%, (d) 1.2 wt%, (e) 1.5 wt%, and (f) 2 wt% CuO additions.

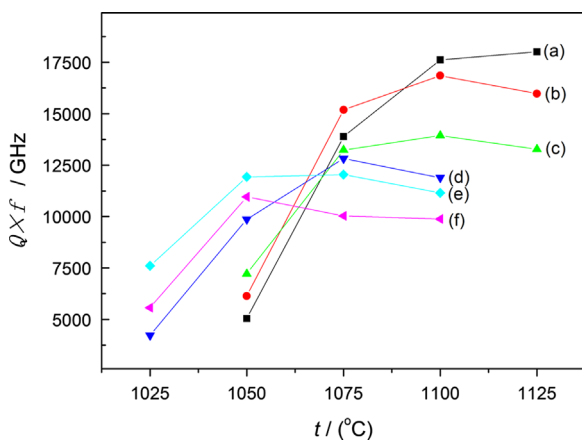


Fig. 5. $Q \times f$ values of CaSiO_3 -1 wt% Al_2O_3 ceramics sintered at different temperatures with (a) 0.5 wt%, (b) 0.8 wt%, (c) 1 wt%, (d) 1.2 wt%, (e) 1.5 wt%, and (f) 2 wt% CuO additions.

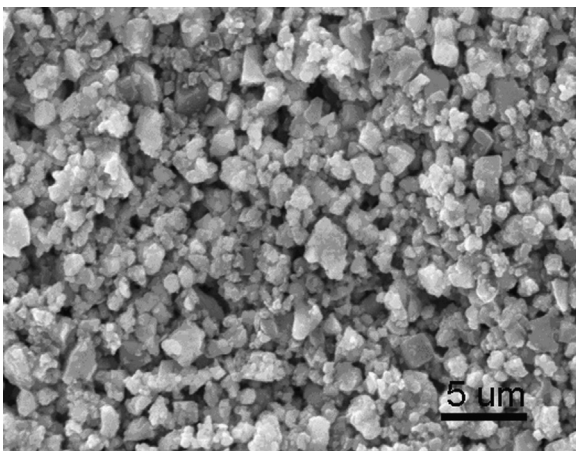


Fig. 6. SEM micrograph of CaSiO_3 -1 wt% Al_2O_3 green tapes with 0.8 wt% CuO addition.

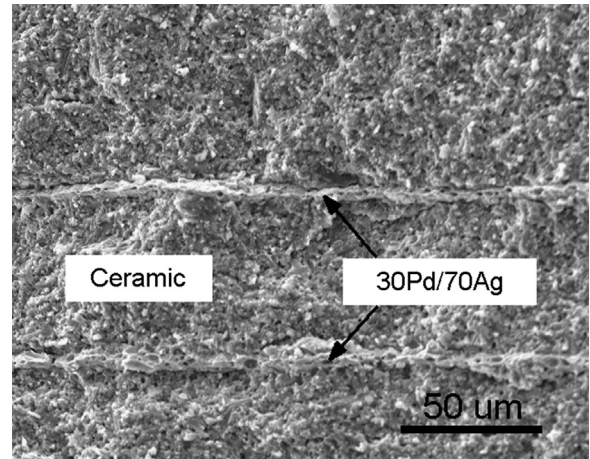


Fig. 7. SEM micrograph of CaSiO_3 -1 wt% Al_2O_3 ceramics incorporated with 0.8 wt% CuO co-fired with 30 Pd/70 Ag in air at 1100 °C for 2 h.

with a limited CuO (0.8–1.2 wt%) content but a porous microstructure was formed when a large amount of CuO (2.0 wt%) was added. However, the addition of CuO undermined the microwave dielectric properties. The optimal amount of CuO addition was found to be 0.8 wt%, and the derived CaSiO_3 - Al_2O_3 ceramic sintered at 1100 °C presented good microwave dielectric properties of $\epsilon_r = 7.27$, $Q \times f = 16,850$ GHz and $\tau_f = -39.53$ ppm/°C. The as-prepared low-temperature sintering ceramics powders were suitable for the tape casting process, and these ceramics were good candidates for LTCC applications with 30 Pd/70 Ag electrode.

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