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Improved microwave dielectric properties of CaMgSi₂O₆ ceramics through CuO doping

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High-performance dielectric materials for microwave communication requires low dielectric constants ($\epsilon_r < 10$), high quality factor (Qf) and near-zero temperature coefficient of resonance frequency (t_f). However, CaMgSi₂O₆ ceramics typically exhibit low Qf and largely negative t_f , despite its low ϵ_r . In this study, nominal composition CaMg_{1-x}Cu_xSi₂O₆ (0 $\leq x \leq 0.16$) ceramics were synthesized via a solid-state reaction. Enhanced microwave dielectric properties were achieved in the $x = 0.04$ ceramic sintered at 1250 °C with $\epsilon_r = 7.41$, $Qf = 160$ GHz (two times better than the previously reported values), and $t_f = -42$ ppm/°C. Benefited from the optimal CuO doping, this enhancement in microwave dielectric property was realized by the contribution of order structure and the densification. Excess CuO doping, which can lead to a phase transition (from C2/c to P2₁/c), could degenerate the microwave dielectric properties of the CaMgSi₂O₆ ceramics. Considering the excellent microwave dielectric properties, the CuO-doped CaMgSi₂O₆ ceramic is a promising candidate material for microwave communication applications.

1. Introduction

The recent rapid growth in wireless communication has led to an increasing demand for high-performance microwave dielectric materials [1,2]. In order to be applied in the wireless communications, these materials should have the low dielectric constants ($\epsilon_r < 10$), high quality factor (Qf) and near-zero temperature coefficient of resonance frequency (t_f) value, because the low ϵ_r values can shorten the delay time of signal transmission and minimize cross coupling with electrodes, high Qf values can decrease signal loss, and near-zero t_f values can ensure the frequency stability as temperature changes [3e5].

CaMgSi₂O₆ ceramic typically exhibits a low ϵ_r value (~ 7.5) and is considered as an important candidate material for wireless communication devices [6e9]. However, CaMgSi₂O₆ ceramics possess a low Qf (~ 60 GHz) and largely negative t_f (~ -46 ppm/°C), and require a high sintering temperature (1290 °C) [6]. These drawbacks directly limit the practical use of the CaMgSi₂O₆ ceramics. In order to improve the microwave dielectric properties, Al₂O₃, CoO and ZnO were used to dope/substitute CaMgSi₂O₆ ceramics [8,10,11]. However, the CaMgSi₂O₆:Al₂O₃, Ca(Mg_{0.92-x}Co_xAl_{0.08}) and CaMg_{1-x}Zn_xSi₂O₆ ceramics exhibited the low Qf values of ~ 60132 , 60125 and 76100 GHz, respectively. Recently, Kuei-Chih Feng et al. [12] further investigated that Al₂O₃-doped CaMgSi₂O₆ glass-ceramic improved the microwave dielectric properties. The samples were sintered at low temperature of 950 °C in nitrogen atmospheres, but unfortunately the Qf value (~ 8312 GHz) was seriously deteriorated, which limits its practical application. Therefore, its relatively low Qf values should be improved in future studies. CuO is a promising dopant owing to its ability in improving the densification and reducing the sintering temperature [13,14]. However, there has been little study on the influence of CuO doping on the microwave dielectric properties of CaMgSi₂O₆ ceramic.

In this work, the nominal composition of CaMg_{1-x}Cu_xSi₂O₆ (0 $\leq x \leq 0.16$) ceramics was fabricated via a conventional solid-state process. Benefited from the low melting point of CuO, enhanced microwave properties were achieved in the CuO-doped CaMgSi₂O₆ ceramics. Furthermore, the influences of their structure on the microwave dielectric properties were comprehensively investigated by varying the CuO doping concentration and sintering temperature.

2. Experimental procedure

Analytically pure CaCO₃, MgO, CuO, and SiO₂ were used as raw materials for the nominal composition CaMg_{1-x}Cu_xSi₂O₆ ceramics. The raw materials were wet-mixed in a plastic container using distilled water and ZrO₂ balls. Then, the CaMg_{1-x}Cu_xSi₂O₆ slurries were dried and the drying mixed-powders were calcined at 1150 °C for 4 h. The calcined CaMg_{1-x}Cu_xSi₂O₆ powders were further milled. The mixed powders were pressed into cylindrical pellets with 12 mm in diameter and 6 mm in height and then sintered at 1100 °C–1250 °C for 4 h.

The phase composition and microstructure were analyzed through XRD (Miniflex600, Rigaku, Japan) with Cu K α radiation, Raman scattering spectroscopy (InVia, Renishaw, UK) with an argon ion laser (I 514.5 nm) as the excitation light (The spectra in the range of 100e1200 cm⁻¹ with a precision of ~ 0.3 cm⁻¹ and a resolution ~ 1 cm⁻¹) and SEM (JSM-6490; JEOL, Japan). The microwave dielectric properties of these samples were measured through a HakkeColeman dielectric resonator cavity method. The changes in the resonant frequencies were obtained with a temperature of 25 and 85 °C. The t_f (ppm/°C) values were calculated based on the following formula:

$$t_f = \frac{f_{85^\circ\text{C}} - f_{25^\circ\text{C}}}{f_{25^\circ\text{C}}} \times 10^6 \quad (1)$$

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the CaMg_{1-x}Cu_xSi₂O₆ ceramics sintered at 1200 °C. The main phase, the monoclinic CaMgSi₂O₆ (ICDD no. #86-0932), was observed with increasing x . The secondary phases, Ca₂MgSi₂O₇ (ICDD no. #79-2425) and SiO₂ (ICDD no. #79-1906), were detected at $x = 0$. The Ca₂MgSi₂O₇ and SiO₂ phases disappeared, whereas the Cu₂O phase presented as the minor phase with 0.04 $\leq x \leq 0.16$. The Cu₂O can be derived from CuO decomposition under high temperature as follows: $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$ (2)

The presence of Cu₂O phase could indicate that Cu²⁺ ions did not form a solid solution with CaMgSi₂O₆, which led to the formation of Mg-deficient CaMgSi₂O₆. Cu²⁺ ions can incorporate into the Mg₂SiO₄ lattice and occupy the M1 site because of the different structures between Mg₂SiO₄ and CaMgSi₂O₆ [15]. The Mg₂SiO₄ crystal exhibits an orthorhombic Pbnm structure that consists of M1O₆, M2O₆ octahedra, and isolated SiO₄ tetrahedra. In the current study, the Ca²⁺ ions in the CaMgSi₂O₆ crystal occupy a distorted eightfold-coordinated M2 polyhedron (Fig. 2(a) and (b)). In addition, the Al³⁺ and Co²⁺ ions were also used to substitute Mg²⁺ ions and to form the solid solution [11,16-18]. It shall be noted that ionic substitution is related to an ionic radius and electronegativity [19,20]. In comparison to Al³⁺ (*r* = 0.535 Å) and Co²⁺ ions (*r* = 0.745 Å), the ionic radius of Cu²⁺ ions (*r* = 0.73 Å) is closer to

that of Mg²⁺ (*r* = 0.72 Å). Therefore, we can conclude that the difference in the electronegativity can be more important in the formation of solid solutions of CaMgSi₂O₆. The back-scattering electron diffraction (BSED) and energy dispersive spectrum (EDS) of the x = 0.08 ceramics sintered at 1200 °C are presented in Fig. 1(b). Two different kinds of black grains and white liquid morphology were observed. According to the EDS analysis, the regions of black and white contrast could correspond to CaMgSi₂O₆ phase and Cu₂O-rich eutectic liquid phase, respectively, which is consistent with our XRD phase evaluations and previous studies [14,21]. The parallel reactions with the x = 0 were as follows [11]:

Therefore, the CaMgSi₂O₆, Ca₂MgSi₂O₇ and SiO₂ phases were observed at x = 0 sintered at 1200 °C. With increasing x, the reaction could occur as follows [11]:

Therefore, the XRD patterns of the Ca₂MgSi₂O₇ and SiO₂ phases disappeared, whereas those of the CaMgSi₂O₆ and Cu₂O-rich eutectic liquid phase could present 0.04 < x < 0.16. In contrast to the CuO-free CaMgSi₂O₆, the CuO-doping could reduce the reaction temperature (Eq. (5)) [11]. Furthermore, a new diffraction peak at 22.04° emerged as the 0.08 < x < 0.16 (Fig. 1(a)). The appearance of the new peak indicates a phase transition from C2/c into P2₁/c in the CaMgSi₂O₆ crystal due to the Mg-deficiency [22-25]. From the structure point of view, CaMgSi₂O₆ is a pyroxene group of minerals with a general formula of pyroxenes (M₂M₁Si₂O₆). In the holotypic structure of pyroxene diopside, Ca occupies an eightfold-coordinated M2 polyhedron (Fig. 2(b)), and Mg occupies a small and regular M1 octahedron. Both the M2 and M1 polyhedra are linked to a SiO₄ tetrahedron [26,27]. Structurally, phase transition from C2/c into P2₁/c is driven by the arrangement of the SiO₄ tetrahedral chain. For the CaMgSi₂O₆ crystal, symmetrically Table 1

The reliability factors from Rietveld refinement for CaMg_{1-x}Cu_xSi₂O₆ ceramics.

equivalent SiO₄ tetrahedral chains exist in C2/c structure, whereas

two symmetrically independent SiO₄ tetrahedral chains, which have different Si-O bond lengths and deformation angles, are observed in P2₁/c structure (Fig. 2(a) and (c)) [24,28]. The impact of the structure change on the microwave dielectric properties of these samples will be evaluated later in this study.

To study the structures of the Mg-deficient CaMgSi₂O₆ crystal, the XRD patterns were refined by the FullProf program [29]. The monoclinic CaMgSi₂O₆ with the C2/c space group (*a* = 9.7397 Å, *b* = 8.9174 Å, *c* = 5.2503 Å and β = 105.8660°) and the P2₁/c space group (*a* = 9.7730 Å, *b* = 8.9620 Å, *c* = 5.2710 Å and β = 108.9900°)

served as structure model. The refined XRD patterns with x = 0 and

0.08 and the reliability factors are presented in Fig. 3 and Table 1, respectively. The fitted patterns were consistent with the experimental data.

The *c*² factors were reasonably small. These results suggested that the refinement parameters used in the simulations were reasonable.

Fig. 4 summarizes the lattice parameters of CaMg_{1-x}Cu_xSi₂O₆ sintered at 1200 °C. The refinement results showed that the lattice constant *a* values increased, and the *b* values exhibited a peak at x = 0.08 as the increasing of x value. Note that the *c* values decreased and *b* values drastic increased for x values within the range 0 < x < 0.08, and then almost constant (Fig. 4). This could be due to phase transitions from C2/c into P2₁/c at x = 0.08 [30]. The unit cell volumes firstly increased and then decreased. It is concluded that the lattice distortion induced by phase transitions. The microstructures and morphologies of the sintered surface for CaMg_{1-x}Cu_xSi₂O₆ ceramics were investigated through SEM (Fig. 5(a-h)). The pores decreased and grain size increased with x increasing sintered at 1200 °C (see Fig. 5(a-e) and Fig. 6(a-e)). At x = 0.04, pores and small grain (0.5-2.5 μm) were observed (see Fig. 6(a, b)). At 0.08 < x < 0.16, dense microstructures were obtained because of Cu₂O-rich eutectic liquid phase, which contributed to the densification, as shown in Fig. 5(c, d) [14,31]. When sintered at 1150 °C, pores (see Fig. 5(e, g)) and small grains (see Fig. 6(e, g)) were observed at both x = 0.04 and 0.08, because these ceramics did not reach the optimized sintering temperatures. However, Fig. 5(h) shows that a porous microstructure was observed at the surfaces of x = 0.08 samples sintered at a high temperature (1250 °C), owing to the over-sintering [32]. The dense microstructure, which enhanced the microwave dielectric properties, were achieved in the 0.08 < x < 0.16 samples sintered at 1200 °C and x = 0.04 sample sintered at 1250 °C.

Raman scattering spectroscopy has been widely applied to give an insight into the crystal structure and phase transitions. Fig. 7(a) displays the Raman scattering spectroscopy of CaMg_{1-x}Cu_xSi₂O₆ ceramics sintered at 1200 °C. According to the symmetry analysis of space group and Bilbao Crystallographic Server [33], their irreducible representation of optical modes for CaMgSi₂O₆ crystal (C2/c space group) could be given as follow:

$$G_{\text{opt}} = 14A_g + 8B_g + 16B_g + 13A_u + 8B_u + 14B_u \quad (6)$$

The theoretical numbers of Raman and IR vibrational modes were 30 and 27, respectively. A strong Raman peak at 1011 cm⁻¹ could be ascribed to the Si-O stretching modes [24,28,34,35].

The strong asymmetric single or double peak near 664 cm⁻¹ was caused by the bending/stretching modes of the Si-O-Si bonds. The peaks at 450-600 cm⁻¹ could be assigned to the Si-O vibrations, and the peaks at 300-450 cm⁻¹ were attributed to vibration of the cations in the M1 and M2 sites that were related to tilting and chain motion of the SiO₄ tetrahedron. The Raman peaks at <

300 cm⁻¹ could be assigned to the translations of the SiO₄ tetrahedron. A new peak appears at approximately 214 cm⁻¹ at x = 0.08, and its intensity increases with the x increasing. This band could be due to the characteristic Raman peak of Cu₂O [36], which further verifies the Cu₂O-rich eutectic liquid phase. This finding is consistent with our XRD and EDS results. The Raman peak at ~323 cm⁻¹

(A_g) shifted toward a low frequency with increasing x. This result ε_r values were in line with the densification (Fig. 5). In addition, the Raman

shift increased because of the change in polarizability in the molecule. Therefore, the relationship of the ϵ_r values and Raman shift could be expressed as follows [40,41]:

$$U^2 \exp \left(\frac{h}{kT} \right) \propto E^0 - x$$

reveals the change in the short-range order of the SiO_4 tetrahedron due to the Mg-deficiency [37]. Moreover, splitting of the 664 cm^{-1} mode at $x = 0.08$ was observed (Fig. 7(b)). Such splitting correlated with the structural changes that involved the silicate chains [24]. The splitting of 664 cm^{-1} peak was interpreted as the phase transition from the $C2/c$ to $P2_1/c$ space group because the 664 cm^{-1} peak correlated with the bending vibration of the SiO_4 tetrahedral chain. Fig. 7(c) shows that the Raman intensities of the peak at 640 cm^{-1} increase with increasing x sintered at 1200°C , which indicates that the $\text{CaMgSi}_2\text{O}_6$ phase of $P2_1/c$ space group increases. This finding is consistent with the XRD results. With regard to the 320 and 664 cm^{-1} modes (Fig. 7(d)), the full width at half maximum (FWHM) values barely changed at $x < 0.08$, but the FWHM increased as x further increased. Since FWHM values reflected the order degree [38], this result suggested that the order degree of the $\text{CaMgSi}_2\text{O}_6$ crystal gradually reduced because of the phase transition from $C2/c$ to $P2_1/c$.

The ϵ_r values of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics with varying sintering temperatures are shown in Fig. 8(a). With the x increasing, the ϵ_r values increased after sintering at 1100 and 1150°C (Fig. 8(a)). The ϵ_r values initially increased and then decreased when sintered at 1200 and 1250°C . In general, the ϵ_r values of the microwave ceramics depend on the secondary phase, densification and ionic polarizability [39]. In the current study, the

where U_P is the plasma frequency and ϵ_r and u are the dielectric constant and phonon frequency, respectively. Based on Eq. (7), the dielectric constant is inversely proportional to the Raman shift. The ϵ_r values of the sintered at 1200°C samples and Raman shift of the phonon mode (at $\sim 320 \text{ cm}^{-1}$) are shown in Fig. 8(b). When changing x , the opposite trend of the ϵ_r values and Raman shift of the phonon mode was observed. This agrees with Eq. (7).

Fig. 9(a) shows the Qf values of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics as a function of x and sintering temperature. When fixing a sintering temperature or an x value, the Qf values increased initially reached the maximum and then declined with increasing x or sintering temperature. The Qf values are related to extrinsic losses, such as the secondary phases and densification, and also to intrinsic losses, such as the order degree and lattice vibration [42e45]. As already shown in Fig. 5, the dense microstructures were obtained with $0.08 \leq x \leq 0.16$ at 1200°C sintering and $x = 0.04$ at 1250°C sintering. However, the order degree gradually reduced with the x increasing because of the phase transition from $C2/c$ to $P2_1/c$. Therefore, the Qf values of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics were in accordance with the densification and order degree. A maximum Qf value of 160 GHz was obtained for $x = 0.04$ specimens sintered at 1250°C . Even at increased CuO content ($x = 0.08$ sintered at

1200°C), the sample presented a relatively high Qf value (see Fig. 9(a and b)). Comparisons of the microwave dielectric properties of $\text{CaMgSi}_2\text{O}_6$ -based materials are presented in Fig. 9(b) [6,8,10,11,46e48]. The high Qf value could be attributed to the order structure and dense microstructure due to moderate CuO doping in this work. It can be concluded the CuO doping is an effective approach to improve the Qf values because it could promote the densification and do not change the structure. Fig. 9(c) shows the t_f values as a function of x in the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics. The negative t_f values could derive from in/anti-phase tilting of the octahedra [49]. The reverse variation trend between the t_f values and the FWHM of the Raman band is presented in Fig. 9(d), which indicated that the order structure was responsible for the stable t_f values. The FWHM values increased with increasing x , which suggested the conversion of the structure from ordered to disordered because of the phase transition from $C2/c$ to $P2_1/c$. The disordered structure can be responsible for the degeneration of the t_f values [40].

4. Conclusions

In this work, nominal composition $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ($0 \leq x \leq 0.16$) ceramics were synthesized via a solid-state route. The XRD, SEM, and EDS indicated that the Cu^{2+} ions did not form a solid solution with $\text{CaMgSi}_2\text{O}_6$. The Cu_2O -rich eutectic liquid phase located at the grain boundaries. The phase transition from $C2/c$ to $P2_1/c$ was detected at $x = 0.08$ through XRD and Raman scattering spectroscopy. The dense microstructures were obtained with 200°C sintering and $x = 0.04$ at 1250°C sintering. Most importantly, at $x = 0.04$ sintered at 1250°C , markedly improved Qf value of $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ was observed owing to order structure and densification. However, excess CuO doping, which led to phase transition because Cu^{2+} ions did not form into a solid solution with $\text{CaMgSi}_2\text{O}_6$, could degenerate the microwave dielectric properties of the $\text{CaMgSi}_2\text{O}_6$ ceramics. For the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ at $x = 0.04$ sintered at 1250°C for 4 h with $\epsilon_r = 7.41$ and $t_f = 42 \text{ ppm}^\circ\text{C}$, the Qf value is 160 GHz , about two times higher than that reported in other literature.

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Fig. 1. XRD and BSED results of $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics. (a) The XRD patterns of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics sintered at 1200°C ; (b) BSED of the $x = 0.08$ ceramics sintered at 1200°C (The associated energy dispersive spectrum is inserted).

Fig. 2. $\text{CaMgSi}_2\text{O}_6$ crystal structure with different phase and Ca-cluster (a) The $C2/c$ structure patterns, (b) The cluster of eightfold coordinated Ca polyhedron, (c) The $P2_1/c$ structure patterns.

Fig. 3. Refined XRD pattern for $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ sintered at 1200°C , (a) $x = 0$, (b) $x = 0.08$, showing the calculated and experimental profile.

Fig. 5. SEM images of $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics.

Fig. 6. The grain size distribution of $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics.

Fig. 7. (a) Raman scattering spectroscopy of $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics sintered at 1200°C ; (b) Raman fit of $x \approx 0.04$ and $x \approx 0.08$ sample; (c) Raman intensity of 640 cm^{-1} ; (d) FWHM of Raman peaks at 320 and 664 cm^{-1} .

Fig. 8. (a) The ϵ_r values of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics with different sintering temperature; (b) The ϵ_r values of the ceramics sintered at 1200°C versus Raman shift.

Fig. 9. Microwave properties of $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics. (a) The Qf values of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics; (b) Summary of Qf and τ_f values of various $\text{CaMgSi}_2\text{O}_6$ from different works; (c) τ_f values of the $\text{CaMg}_{1-x}\text{Cu}_x\text{Si}_2\text{O}_6$ ceramics; (d) The τ_f values of the ceramics sintered at 1200 °C versus FWHM.