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Lai, Yuanming; Su, Hua; Wang, Gang; Tang, Xiaoli; Huang, Xin; Liang, Xiaofeng; Zhang, Huaiwu; Li, Yuanxun; Huang, Ke; Wang, Renshaw Xiao

2018

Lai, Y., Su, H., Wang, G., Tang, X., Huang, X., Liang, X., . . . Wang, R. X. (2018).
Low-temperature sintering of microwave ceramics with high Q values through LiF addition.
Journal of the American Ceramic Society, 102, 1893–1903. doi:10.1111/jace.16086

<https://hdl.handle.net/10356/144555>

<https://doi.org/10.1111/jace.16086>

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Low-temperature sintering of microwave ceramics with high Qf values through LiF addition

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Abstract: Microwave ceramic with low sintering temperature is one of the most important classes of material to realize the integration and miniaturization of microwave devices. In this work, in order to simultaneously realize low-temperature sintering and good microwave dielectric properties, $\text{CaMgSi}_2\text{O}_6$ was sintered at various sintering temperatures using LiF as a sintering aid ($\text{CaMgSi}_2\text{O}_6$ – $x\text{LiF}$). In comparison to $\text{CaMgSi}_2\text{O}_6$ ($x = 0$) sintered at 1250 °C, desirable microwave dielectric properties of $\epsilon_r = 7.45$, $Qf = 64\,800$ GHz, and $\tau_f = -34$ ppm/°C and good chemical compatibility with the Ag electrodes, were achieved sintered at 900 °C when adding 2 wt% LiF into $\text{CaMgSi}_2\text{O}_6$. Furthermore, a secondary phase, $\text{Li}_2\text{MgSiO}_4$, occurs at x at rwt%, and the densest microstructure was obtained at the x value of ~2 wt%. We propose that the high Qf value of 64 800 GHz and the low sintering temperature of 900 °C were obtained through moderate LiF addition, which promotes densification and provides Li as the acceptor dopant. By further verifying in Mg_2SiO_4 ceramic, our study demonstrates that the approach of adding LiF can realize low temperature sintering without

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jeopardizing the excellent microwave dielectric properties, and can potentially be applied in a wide range of low temperature sintering of electronic ceramic.

1. Introduction

In recent years, with rapid advances in wireless communication, the microwave devices require miniaturization and integration.¹ Low temperature co-fired ceramic (LTCC) is one of the most promising candidates to serve as a substrate of the miniaturized and integrated devices,²⁻⁴ owing to its low sintering temperature to realize co-firing with electrodes (such as Ag, melting point 961 °C).⁵ Furthermore, considering the transmission characters of an electromagnetic wave, the LTCC substrate shall also have good microwave properties, including low dielectric constant (ϵ_r), high quality factor (Qf) value and temperature-independent coefficient of resonance frequency (τ_f).

Benefiting from the low ϵ_r value (~ 7.5), $\text{CaMgSi}_2\text{O}_6$ can be a suitable LTCC substrate with a short delay time, if its conventional high sintering temperature (1250 °C to 1290 °C) is reduced to a temperature lower than 950 °C.⁶ Several methods have been adopted for this purpose. B_2O_3 was served for reducing the sintering temperature of the $\text{CaMgSi}_2\text{O}_6$ ceramics by Wang *et al.*⁷ However, the sintering temperature of the $\text{CaMgSi}_2\text{O}_6$ ceramics just reduced to 1100 °C. Moreover, the free- B_2O_3 has inferior chemical compatibility with the organics in the technological process of LTCC.⁸ A low melting glasses were also considered as sintering aids to reduce the sintering temperature of $\text{CaMgSi}_2\text{O}_6$ ceramics.⁹ But, these glasses greatly deteriorated the Qf values of $\text{CaMgSi}_2\text{O}_6$ ceramics, which restricted its LTCC application. In addition, $\text{CaMgSi}_2\text{O}_6$ glass-ceramics were also considered as a way to decrease the sintering temperature. But the preparation of the raw $\text{CaMgSi}_2\text{O}_6$ glass needs a high temperature (~ 1500 °C) and the final glass-ceramics generally yields low Qf values.¹⁰⁻

¹² LiF usually serve as develop low temperature fired dielectric ceramics, such as $\text{Li}_2\text{Mg}_3\text{SnO}_6$, BaTiO_3 , $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$, MgO and $\text{Ba}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3\text{-TiO}_2$ system, for LTCC applications.^{13–17} The low sintering temperature and excellent microwave dielectric properties were achieved simultaneously in these dielectric ceramics through moderate LiF addition. In our previous work, low temperature sintering (900 °C) of Mg_2SiO_4 ceramic was also realized through adding LiF, which has a low melting point (~848 °C).¹⁸ Note that the excellent microwave dielectric properties were obtained through moderate LiF addition ($\epsilon_r = 6.1$, $Qf = 109700$ GHz and $\tau_f = -61$ ppm/°C). However, thus far, there is little discussion about the working mechanism and LiF's impact on microwave dielectric properties of $\text{CaMgSi}_2\text{O}_6$ ceramic. Therefore, it is worthy of study about the structure and microwave dielectric properties of $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ceramic at low temperature sintering, which contributes to further understanding of the formation mechanism for high microwave dielectric properties at low temperature sintering, and better control of the microwave dielectric properties of ceramic to establish high-performance LTCC devices.

In this work, LiF was added to $\text{CaMgSi}_2\text{O}_6$ with a purpose of simultaneously realizing both low temperatures sintering and excellent dielectric properties. In order to determine the LiF's impact on microwave dielectric properties, the structures in the samples were further investigated through X-ray diffraction (XRD), relative density, scanning electron microscopy (SEM) and Raman spectroscopy. The microwave dielectric properties of these samples were measured through microwave resonant cavitation. Mg_2SiO_4 ceramic has excellent microwave dielectric properties ($\epsilon_r \sim 6\text{-}7$, $Qf \sim 240000$ GHz and $\tau_f \sim -67$ ppm/°C). But it also requires high temperature sintering (~1450 °C).¹⁹ Therefore, it was considered as a validation sample. In the combination of the $\text{Mg}_2\text{SiO}_4\text{-}x\text{LiF}$ results, a generic LiF-based approach to achieve high quality microwave ceramics with

reduced sintering temperature is proposed and validated.

2. Experimental Procedure

CaMgSi₂O₆ ceramics were synthesized through a conventional solid-state reaction method. Analytically pure CaCO₃, MgO, and SiO₂ were adopted as raw materials according to the stoichiometry of CaMgSi₂O₆ ceramics. The raw materials were mixed in a plastic container with distilled water and zirconia balls for 4 h. Then the slurries were dried and the drying raw materials were calcined at 1250 °C for 4 h. The CaMgSi₂O₆ powders were re-mixed with 0-6 wt% LiF. The mixed powders were pressed to form cylindrical disks and sintered at 850, 900 and 950 °C for 4 h, respectively. Additional LiF-free CaMgSi₂O₆ ceramic were sintered at 1250 °C for 4 h as a control sample. Serving as additional samples to validate our approach, Mg₂SiO₄-*x*LiF (*x* = 2, 4, 6, 8 and 10 wt%) were sintered at 850, 900 and 950 °C for 4 h, respectively. The *Qf* values were provided with low sintering temperature (*Supporting information*). In order to study the chemical compatibility between CaMgSi₂O₆ and electrode, the CaMgSi₂O₆-2 wt% LiF ceramic was mixed with 20 wt% Ag and then co-fired at 900 °C for 4 h.

The phase composition and microstructure were examined through XRD (Miniflex600, Rigaku, Japan) with Cu *K*_α radiation, Raman spectra (InVia, Renishaw, UK) and SEM (JSM-6490; JEOL, Japan). The density of these samples was measured using an Archimedes method with distilled water as the suspension medium at room temperature. The microwave dielectric properties (*ε*_r, *Qf*, and *τ_f* values) of these samples were measured through a Hakki–Coleman dielectric resonator method and a cavity method. The changes in the resonant frequency were obtained at temperatures of 25 and 85 °C. The *τ_f* (ppm/°C) values were calculated based on the following formula:

$$\tau_f = \frac{f(85\text{ }^{\circ}\text{C}) - f(25\text{ }^{\circ}\text{C})}{60(f(25\text{ }^{\circ}\text{C}))} \times 10^6 \quad (1)$$

3. Results and discussion

Figures 1(a) and (b) show the ϵ_r and Qf values of the $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ceramics as a function of LiF content, x . With the x increasing, the ϵ_r values initially increase and then decline. When sintered at 850 and 900 °C, the $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ceramics exhibit a maximum Qf value at $x = 2$ wt%. But the Qf value declines when sintering at 950 °C. Moreover, comparing with the LiF-free $\text{CaMgSi}_2\text{O}_6$ sintered at 1250 °C, moderate LiF additive is able to produce higher Qf values with lower sintering temperatures. Figure 1(d) and (e) show a comparison of the Qf values and sintering temperatures of $\text{CaMgSi}_2\text{O}_6$ -based and Mg_2SiO_4 -based materials.^{6, 9–12, 18, 20–38} With help of the LiF addition, high Qf values were successfully obtained in $\text{CaMgSi}_2\text{O}_6$ and Mg_2SiO_4 ceramics with a low sintering temperature. Therefore, we demonstrate that the adding LiF is an effective approach to simultaneously realize both low temperature sintering and excellent microwave dielectric properties in these ceramics. Figure 1(c) shows the τ_f values of the $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ceramics, exhibiting a nonlinear function of x . Overall, the negative τ_f values can derive from in/anti-phase tilting of the octahedra.³⁹ The difference in τ_f values among different sintering temperatures can be attributed to complicated factors, such as the contribution of electron and phonon, octahedral distortion, pore and secondary phase.⁴⁰ The XRD patterns can be used to confirm the phase composition and structure. Figure 2(a) presents the XRD patterns of the $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ($x > 0$) ceramics sintered at 900 °C and $\text{CaMgSi}_2\text{O}_6$ ($x = 0$) sintered at 1250 °C. The main phase, the monoclinic $\text{CaMgSi}_2\text{O}_6$ (ICDD No. #86-0932), was observed regardless of the x value. The small amount of the $\text{Li}_2\text{MgSiO}_4$ (ICDD No. #24-0636) secondary phase was detected when x when wt%. The result indicated that a chemical reaction occurred between LiF and $\text{CaMgSi}_2\text{O}_6$ at x at Swt%. The same phase was also detected in the $\text{Li}_2\text{O-MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ system.⁴¹ The secondary

phase can influence the microwave dielectric properties of these ceramics, and this will be discussed later. Additionally, no phase containing F^- ions was found, and this could be due to (i) the F^- ions substituted a partial O^{2-} ions and/or (ii) a liquid phase of LiF and volatilization of F^- ions due to LiF's low melting point ($\sim 848^\circ\text{C}$). This is in agreement with the previous reports on LiF-doped Li_2TiO_3 ceramics.⁴²

In order to further investigate the structure, the XRD data were refined through the Fullprof program.⁴³ The monoclinic structure, $\text{CaMgSi}_2\text{O}_6$ with a $C2/c$ space group ($a = 9.7397 \text{ \AA}$, $b = 8.9174 \text{ \AA}$, $c = 5.2503 \text{ \AA}$, and $\beta = 105.8660^\circ$) and $\text{Li}_2\text{MgSiO}_4$ with a $P121/n1$ space group ($a = 6.3000 \text{ \AA}$, $b = 10.6920 \text{ \AA}$, $c = 4.9950 \text{ \AA}$, and $\beta = 90.47^\circ$), were adopted as models. Figures 2(b) and (c) show the refined XRD patterns with $x = 0$ and $x = 2 \text{ wt\%}$, and Table 1 summarized their refined XRD results. The reasonable reliability factors indicate that a mixed-phase of $\text{CaMgSi}_2\text{O}_6$ and $\text{Li}_2\text{MgSiO}_4$ were obtained when x btaiwt%. While the secondary phase, $\text{Li}_2\text{MgSiO}_4$, increases with the x increasing, the cell parameters and unit cell volume present a non-linear variation with x increasing. We will discuss the change of secondary phase and cell volume further combining the relative density and microstructure. In addition, in the $\text{CaMgSi}_2\text{O}_6$ structure, Mg occupies a smaller and more regular $\text{M}(1)\text{O}_6$ octahedron than the Ca.^{44, 45} The MgO_6 octahedron closely correlates with the microwave dielectric properties.^{46, 47} Quantitatively, the MgO_6 octahedral distortions (δ) can be calculated according to the Mg-O bond length as shown in the following formula:

$$\delta = \frac{1}{6} \sum \left(\frac{R_i - \bar{R}}{\bar{R}} \right)^2 \quad (2)$$

Figure 2(d) shows that the τ_f values of all samples correlates with MgO_6 octahedral distortions.^{40, 48,}

⁴⁹ Overall, with the x increasing, the δ values decrease, due to the change in the Mg-O bond length derived from the substitution of Li^+ and F^- ions for a part of Mg^{2+} and O^{2-} ions.

The theoretical density and relative density of $\text{CaMgSi}_2\text{O}_6$ and $\text{Li}_2\text{MgSiO}_4$ composites were calculated based on the rule of mixtures.^{50–53} Figure 3(a) shows the relative densities of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics. With x increasing, the relative densities first increase, then reach a maximum value at $x = 2$ wt%, and finally decrease. Moreover, $x < 2$ wt%, the relative densities increase with increasing the sintering temperature. However, lower densification was observed due to a large amount of volatilization of LiF at x at awt% when sintered at 950 °C. It agrees with the previous studies, which indicate that LiF begin to evaporate when the temperature up to 900 °C.^{54,}
⁵⁵ In comparison with the $x = 0$ sintered at 1250 °C, the moderate LiF addition can obtain higher relative density sintered at 900 °C. Figures 3(b)-(e) show the microstructures of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics sintered at 900 °C were investigated through SEM. Compared with $x = 0$ sample, the morphology of grains becomes round and smooth at $x = 1$ wt%, indicating the presence of a small amount of liquid phase during the sintering process. But these liquid phases are not enough to make the densification of ceramics.⁵⁶ The crystalline boundaries become blurry at $x \geq 3$ wt% because of a large amount of LiF liquid phase. The dense microstructures were observed at $x = 2$ wt%. However, the pores, which can originate from the volatilization of LiF, appear in the $x \geq 3$ wt% samples. In particular, the LiF-free $\text{CaMgSi}_2\text{O}_6$ ceramic was sintered at high temperature (1250 °C), but the pores were also observed. Hence, the densification greatly impacts on the microwave dielectric properties, and moderate LiF additive could realize low temperature sintering and improve the densification of $\text{CaMgSi}_2\text{O}_6$ ceramics.

Previous studies have shown that volatilization of F⁻ ions are easier than that of Li⁺ ions in LiF at high temperature process.^{57, 58} Therefore, at low LiF content, a large amount of F⁻ ions may volatilize as gas, while Li⁺ ions can enter into the CaMgSi₂O₆ lattice. In this system, Li⁺ ions are more likely to occupy the Mg-sixfold coordination octahedra rather than Ca-eightfold coordination polyhedra. The oxygen vacancy can be produced in order to charge compensation because of the difference of between Li⁺ ion valence and Mg²⁺ ions valence. The process can be described as:

The Li serves as the acceptor dopant and substitutes for Mg site in CaMgSi₂O₆. In addition, the ionic radius of Li⁺ ions ($r = 0.76 \text{ \AA}$) is larger than that of Mg²⁺ ions ($r = 0.72 \text{ \AA}$), which results in increasing of unit cell volume. This agrees with the increasing of unit cell volume at x wt%. Furthermore, since Li⁺ ions substitute for Mg²⁺ ions, which could result that the Mg²⁺ ions are precipitated. This is consistent with the emergence of the secondary phase, Li₂MgSiO₄. The F⁻ ions ($r = 1.33 \text{ \AA}$) can be involved in the CaMgSi₂O₆ lattice and substituted the O²⁻ ($r = 1.40 \text{ \AA}$) with the increase of LiF content, which could lead to a decrease of unit cell volume. Meanwhile, a large amount of LiF liquid phase was also observed at $x \geq 2 \text{ wt\%}$ (Figs. 3(d) and (e)). In this case, there are no extra Li⁺ ions available for the formation of Li₂MgSiO₄, which leads to the no significant increase in Li₂MgSiO₄ content at $1 \text{ wt\%} \leq x \leq 3 \text{ wt\%}$. However, the secondary phase content significant increases with the further increase of LiF content. It can be concluded that the liquid phase reach saturation at $x = 3 \text{ wt\%}$. The extra Li⁺ ions further substitute for Mg²⁺ ions. Meanwhile, the liquid phase reaction sintering mechanism,⁵⁹ which shows that a chemical reaction between an additive and the matrix is accelerated by the liquid phase, may occur between LiF and CaMgSi₂O₆. This reaction between LiF and CaMgSi₂O₆ crystal can be accelerated by the LiF liquid phase. This may lead to a significant

increase in the $\text{Li}_2\text{MgSiO}_4$ content, which is consistent with the XRD refined results. Similar processes have also been reported in LiF doped MgAl_2O_4 spinel.^{60–62}

We employ Raman spectra to detect the local structures of $\text{CaMgSi}_2\text{O}_6\text{--}x\text{LiF}$ ceramics sintered at 900 °C, including short-range ordering, defects, and cation disorders (see Fig. 4(a)). According to the space group and Bilbao Crystallographic Server,⁶³ the irreducible representation of optical modes for $\text{CaMgSi}_2\text{O}_6$ crystal can be shown as follow:

$$\Gamma_{opt} = 14A_g(R) + 16B_g(R) + 13A_u(IR) + 14B_u(IR) \quad (4)$$

In theory, the $\text{CaMgSi}_2\text{O}_6$ crystal can have 30 Raman and 27 IR vibrational modes, respectively. Meanwhile, the irreducible representation of Raman modes for $\text{Li}_2\text{MgSiO}_4$ crystal should be 48 Raman vibrational modes: $\Gamma_{Raman} = 24A_g + 24B_g$. However, all samples exhibit almost exactly the same Raman shift (see Fig. 4(a)). This may be due to the fact that only one characteristic Raman peak of $\text{Li}_2\text{MgSiO}_4$ at 520 cm^{-1} due to the vibration of Si–O–Si bond was observed in the experiment.^{64, 65} Coincidentally, the Raman peak at 520 cm^{-1} can be also observed in the $\text{CaMgSi}_2\text{O}_6$ crystal because it includes the Si–O–Si bonds. Therefore, the Raman spectra are almost identical in all samples. According to previous studies,^{66–69} the Raman shift at < 300 cm^{-1} could be attributed to translations of SiO_4 tetrahedron, the peak at 300–450 cm^{-1} could be assigned to motions of the cations in the M(2) and M(1) sites that were related with tetrahedral chain motion and tilting tetrahedron. Moreover, the Raman shifts in the region of 225–303, 360, 450–600, 666, and 1011 cm^{-1} can be attributed to the O–Li–O bending and Li–O stretching vibrations,⁷⁰ the O–Si–O vibrations, the stretching/bending modes of the Si–O–Si bonds, and O–Si–O stretching modes, respectively. Raman shift is related to the short-range order, while the full width at half maximum (FWHM) is more sensitive to the defects and cation disorders.⁷¹ Fig. 4(b) presents the FWHM of

Raman peak at 666 cm^{-1} . In this study, the Raman shifts do not show any significant change, but the FWHM is different with the x increasing. These findings indicate that the short-range order of samples does not change significantly, but the defects and cation disorders occur with the x increasing. The defects and cation disorders could be due to Li^+ and F^- ions substitution for Mg^{2+} and O^{2-} ions in $\text{CaMgSi}_2\text{O}_6$, respectively. This is consistent with the XRD results. Fig. 4(b) shows that FWHM of Raman peak at 666 cm^{-1} has a similar varying tendency with cell volume, which indicates further that the variation of cell volume can be caused by ions substitution.

In general, the microwave dielectric properties, particularly ϵ_r and Qf , are both determined by both intrinsic and extrinsic factors.

The intrinsic factor of ϵ_r value is mainly ionic polarizability and structural characteristics, and the extrinsic factors of ϵ_r value is generally the secondary phase and relative density.⁴⁸ Most importantly, among all these factors, the most dominant one is the relative density. High relative density always leads to large ϵ_r values, and the ϵ_r values, presented in Fig. 1(a), and the relative density, presented in Fig. 3(a), exhibit the same trend when changing the x . At the same sintering temperature, the ϵ_r values climb up and then decline, and the maximum at $x = 4\text{ wt}\%$, $3\text{ wt}\%$ and $2\text{ wt}\%$ for sintering at $850\text{ }^\circ\text{C}$, $900\text{ }^\circ\text{C}$ and $950\text{ }^\circ\text{C}$, respectively. However, the relative densities reach a maximum value at $x = 2\text{ wt}\%$ with different sintering temperature. The difference between the ϵ_r values and relative densities may be due to structural changes and liquid phase at the different sintering temperatures. In addition, the secondary phase and ion substitution can affect the ϵ_r values because the secondary phase ($\text{Li}_2\text{MgSiO}_4$) has a smaller ϵ_r values (~ 5.1) than the $\text{CaMgSi}_2\text{O}_6$ and the ion substitution can lead to the lower dielectric polarizabilities ($\alpha(\text{Li}^+) = 1.20\text{ \AA}^3$, $\alpha(\text{F}^-) = 1.62\text{ \AA}^3$, $\alpha(\text{Mg}^{2+}) = 1.32\text{ \AA}^3$ and $\alpha(\text{O}^{2-}) = 2.01\text{ \AA}^3$). Because our XRD refinement results shows that the

secondary phase of $\text{Li}_2\text{MgSiO}_4$ increase as the x increases, low ϵ_r values are achieved, in well agreement with the Lichtenecker empirical logarithmic rule. At the same LiF content, the ϵ_r values increase with the increase of sintering temperature as $x \leq 2$ wt%, while the ϵ_r values increase firstly and then decrease as $x \geq 3$ wt%. It presented a similar trend to that of relative density with the x increasing (Figs.1(a) and 3(a)). For the $x = 2$ wt% sample, the ϵ_r value for sintering at 950 °C sample is larger than that of 900 °C. But relative density has the opposite trend. This may be due to structural differences induced by ions substitution at different sintering temperature. In conclusion, it can be concluded that the relative density is responsible for the ϵ_r values.

The Qf values are affected by two types of losses, namely (i) the intrinsic losses which are mainly dominated by the defects, cation disorders, and lattice vibration, and (ii) the extrinsic losses caused by the densification, secondary phases, and crystallinity.^{72, 73} The Qf values have a same trend with FWHM of Raman spectra sintered at 900 °C (see Figs. 1(b) and 4(b)), which is consistent with previous studies.^{74, 75} This indicates that the Qf value is closely related to the ions substitution. The large amounts of Li^+ ions substitution correspond to the high Qf value. This may be due to the inhibition of dielectric loss by Li as the acceptor dopant.^{58, 76} Moreover, the relative density and secondary phase can affect Qf values (see Fig. 5). The secondary phase, $\text{Li}_2\text{MgSiO}_4$, has inferior Qf value ($Qf \sim 15\ 385$ GHz) than those of the $\text{CaMgSi}_2\text{O}_6$ ceramics.³⁸ The low densification and high secondary phase level can also lead to the degeneration of Qf values at $x > 2$ wt% sintered at 850 and 900 °C. When sintered at 950 °C, the $x = 1$ wt% sample has a relative density higher than those of the samples sintered at 900 °C, whereas the relative density is lower at $x \geq 2$ wt%. Therefore, in consideration of both the relative density and secondary phase, the maximum Qf value can only be obtained at an optimized $x = 1$ wt% and sintering temperature of 950 °C. These results indicate

that the Li^+ ions substitution, high relative density and low secondary phase level, which are all caused by moderate LiF addition, are responsible for the excellent Qf value of $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics sintered at low temperature. In comparison with other sintering aids, the excellent Qf value can be achieved through moderate LiF addition in the $\text{CaMgSi}_2\text{O}_6$ system (see Fig. 1(d)), which due to the Li^+ ions as the acceptor dopant. In addition to the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$, Figs. S1(a) and (b) (Supporting information) demonstrates that high Qf values of $\text{Mg}_2\text{SiO}_4-x\text{LiF}$ ceramics can also be enhanced by introducing moderate LiF content at the low sintering temperature¹⁸, indicating that the introduction of moderate LiF be applied in a large variety of microwave ceramic systems to achieve low sintering temperature and excellent microwave dielectric properties. To evaluate the chemical compatibility, the Ag was added to $x = 2$ wt% sample and then co-fired at 900 °C. Fig. 6 shows the XRD, BSE image and EDS of the co-fired sample. The main phases, $\text{CaMgSi}_2\text{O}_6$ and Ag, were detected by XRD. The two significant phases are observed by BSE. The EDS indicate the black and white regions are mainly $\text{CaMgSi}_2\text{O}_6$ and Ag, respectively, which is consistent with the XRD results. This indicates that $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics have good chemical compatibility with the Ag electrode. This is beneficial to the $\text{CaMgSi}_2\text{O}_6$ ceramics in LTCC application.

4. Conclusions

$\text{CaMgSi}_2\text{O}_4-x\text{LiF}$ ceramics were sintered at low temperature (Sias added The chemical reaction occurred between LiF and $\text{CaMgSi}_2\text{O}_6$, and produced the secondary phase ($\text{Li}_2\text{MgSiO}_4$). The partial Li^+ and F^- ions were also incorporated into $\text{CaMgSi}_2\text{O}_6$ lattice and substituted Mg^{2+} and O^{2-} ions. In comparison with $x = 0$ sintered at 1250 °C, the excellent microwave dielectric properties were achieved in the $x = 2$ wt% ceramic sintered at 900 °C: $\epsilon_r = 7.45$, $Qf = 64\,800$ GHz, and $\tau_f = -34$

ppm/°C, which is dominated by dense microstructure and Li⁺ ions substitution through moderate LiF adding. Moreover, the sample has good chemical compatibility with the Ag electrode. Therefore, the CaMgSi₂O_{4-x}LiF material is one of a promising candidates for the LTCC substrate. The moderate LiF addition can realize low temperature sintering and achieve excellent microwave dielectric properties.

Acknowledgments

This work was supported by National Natural Science Foundation of China under Grant Nos. 61771104, 61471096 and 51772047, Science and Technology Department of Sichuan Province 2016JQ0016 and 2015JQ0031, Special Projects on Science and Technology of Guizhou Province [2016]3011, National Key Research and Development Plan No. 2016YFA0300801. X.R.W. acknowledges supports from the Nanyang Assistant Professorship grant from Nanyang Technological University and Academic Research Fund Tier 1 (RG108/17) from Singapore Ministry of Education.

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Figure captions:

Fig. 1. Microwave dielectric properties of $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ and $\text{Mg}_2\text{SiO}_4-x\text{LiF}$ ceramics. (a,b,c) The ϵ_r (a), Qf (b) and τ_f (c) values of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics. (d,e) Summary of Qf values and sintering temperature of various $\text{CaMgSi}_2\text{O}_6$ (d) and Mg_2SiO_4 (e) from different works.

Fig. 2. Structural analysis of samples. (a) XRD pattern of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ($x > 0$) ceramics sintered at 900 °C and $\text{CaMgSi}_2\text{O}_6$ ($x = 0$) sintered at 1250 °C. Rietveld refinements of XRD pattern of (b) $x = 0$ sintered at 1250 °C, (c) $x = 2$ wt% sintered at 900 °C, (d) The τ_f values versus the MgO_6 octahedral distortion for samples sintered at 1250 and 900 °C.

Fig. 3. Densification of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics, (a) The relative densities of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics. Different from other composition, the $x = 0$ (without LiF) was sintered at 1250 °C in order to achieve the adequate density in a ceramic phase. SEM images of (b) $x = 0$ wt% sintered at 1250 °C, sintered at 900 °C with (c) $x = 1$ wt%, (d) $x = 2$ wt% and (e) $x = 4$ wt%.

Fig. 4. Raman spectra analysis of samples. (a) The Raman spectra of the $\text{CaMgSi}_2\text{O}_6-x\text{LiF}$ ceramics sintered at 900 °C ($x = 0$ sintered at 1250 °C); (b) The cell volume versus the FWHM of Raman at 666 cm^{-1} .

Fig. 5. Qf values of $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ceramics versus the secondary phase and densification sintered at 900 °C ($x = 0$ sintered at 1250 °C).

Fig. 6. The chemical compatibility with Ag electrode. (a) The XRD of $x = 2$ wt% ceramics with 20 wt% Ag co-fired at 900 °C; (b) BSE image and EDS results of $x = 2$ wt% ceramics with 20 wt% Ag co-fired at 900 °C.

Table caption:

Table 1. Lattice and refinement parameters obtained from Rietveld refinement for $\text{CaMgSi}_2\text{O}_6\text{-}x\text{LiF}$ ceramics.