Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 2051–2058

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Low-temperature sintering and microwave dielectric properties of LiF-doped $CaMg_{1-x}Zn_xSi_2O_6$ ceramics

Jie Zhang, Yuanyuan Zhou, Zhenxing Yue*

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

Received 9 July 2012; received in revised form 18 August 2012; accepted 18 August 2012
Available online 23 August 2012

Abstract

The diopside ceramics, $CaMg_{1-x}Zn_xSi_2O_6$ ($x=0$–0.3), were synthesized via the solid-state reaction method. Zn^{2+} substitution for Mg^{2+} can markedly lower the densification temperature and improve the microwave dielectric properties of $CaMgSi_2O_6$ ceramics. For $x=0.1$, $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics, can be sintered at 1200 °C and exhibit good microwave dielectric properties of $\varepsilon_r=7.88$, $Qf=76{,}100$ GHz and $\tau_f=-22.5$ ppm/°C. LiF addition was proved to be effective to lower the sintering temperature to ~900 °C without degrading the dielectric properties apparently. The $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics doped with 0.6 wt% LiF can be sintered in the temperature range of 900–975 °C and have excellent dielectric properties of $\varepsilon r\sim7.7$, $Qf\sim70{,}000$ GHz and $\tau_f\sim-25$ ppm/°C. With low sintering temperature and good dielectric properties, these LiF-doped diopside ceramics are promising materials for LTCC integration applications.

Keywords: C. Microwave dielectric properties; D. Low-temperature co-fired ceramics; D. Silicates

1. Introduction

With the rapid development of miniaturized and multi-functional microwave devices, low-temperature co-fired ceramic (LTCC) technology has been playing an increasingly important role in the wireless communication systems and electronic industries. In LTCC devices fabrication, the ceramics are co-fired with highly conductive electrode materials, such as silver (melting point 961 °C) and copper (melting point 1083 °C), to form three-dimensional ceramic modules [1]. Therefore, the ceramics are required to have low sintering temperature which can be co-sinterable with Ag or Cu metal electrodes. Additionally, the low dielectric constant is preferred for dielectric ceramics which can promote the signal propagation speed in ceramic-metal modules. The low dielectric loss (i.e. high quality factor, Qf) and small temperature coefficient of resonant frequency (τ_f) are also indispensable properties for LTCCs to ensure low insertion loss and good stability against temperature change [2–4]. Thus, dielectric microwave components with these attributes mentioned above are identified as one of the best candidates for integrated circuit applications used at a higher frequency.

Recently, a large number of strategies have been reported to lower the densification temperature of ceramics: (a) addition of low melting point materials, such as B_2O_3, Li_2CO_3 and glass [5–7]; (b) chemical processing for smaller particle sizes of starting materials [8]; (c) searching for novel glass-free low-sintering dielectric ceramics [9,10]; and (d) forming solid solutions through ionic substitution [11–13]. The first approach is widely used to lower the densification temperature of commercially available dielectric ceramics because it is the least expensive. However, these low melting point compounds may also have a detrimental effect on the microwave dielectric properties due to the appearance of unexpected secondary phases, which is a major contribution to dielectric loss. It is hence necessary to minimize these phases [14]. As for the last method, the formation of solid solutions can generally modify the dielectric properties of microwave materials, not just lowering the sintering temperature [11,13].

*Corresponding author. Tel.: +86 10 62784579; fax: +86 10 62771160.
E-mail address: yuezhx@mail.tsinghua.edu.cn (Z. Yue).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.08.058

For example, Pei et al. [11] investigated the substitution of Sr^{2+} for Ba^{2+} in the $(Ba_{1-x}A_x)La_4Ti_4O_{15}$ (A=Sr, Ca) system, which could lower about 100–150 °C and significantly promote the *Qf* values with increasing Sr content. Thirumal et al. [13] reported that τ_f could be tuned to a near zero value by suitable substitution in the $Sr_3Zn_{1-x}Mg_xNb_2O_9$ ceramics.

$CaMgSi_2O_6$ is a type of inosilicate belonging to the group of clinopyroxenes. Ca^{2+} occupies the distorted eight-fold-coordinated M_2 polyhedra, while Mg^{2+} occupies the regular six fold-coordinated M_1 octahedral sites [15]. More recently, $CaMgSi_2O_6$ ceramics have been demonstrated as a potential candidate material for high-frequency devices fabrication [16–19]. The pure $CaMgSi_2O_6$ ceramic sintered at 1290 °C possessed good microwave dielectric properties, namely ε_r, *Qf* and τ_f were 7.46, 59,638 GHz and −46 ppm/°C, respectively [16]. Several low melting point additions, such as B_2O_3, Li_2O–B_2O_3–SiO_2 and Li_2O–MgO–ZnO–B_2O_3–SiO_2 glasses, have been considered to lower the sintering temperature of $CaMgSi_2O_6$ [17,18]. However, the relatively high sintering temperature together with low quality factor limited the applications for LTCC-based devices. So, the more effective sintering additives should be searched to obtain the low-fired diopside ceramics with good dielectric properties. Some low melting oxides and fluorides, such as ZnO and LiF, were reported to be effective as flux in several microwave ceramic systems [20–23].

In the present study, we utilized two steps to obtain the low-temperature co-fired ceramics with excellent dielectric properties in the diopside material system. Firstly, Zn^{2+} substituted for Mg^{2+} to lower the densification temperature and improve the dielectric properties of $CaMgSi_2O_6$. Then, a small amount of LiF was considered to further lower the sintering temperature to ~900 °C. The as-prepared diopside materials exhibited good microwave dielectric properties. In this paper, the effects of Zn^{2+} substitution for Mg^{2+} and LiF addition on the sintering behaviors, microstructure and dielectric properties of $CaMgSi_2O_6$ will be investigated.

2. Experimental procedure

The ceramics were prepared using the conventional solid-state method. MgO (98.5%), $CaCO_3$ (99%), ZnO (99.5%), SiO_2 (99%) and LiF (99%) were used as the starting materials. Stoichiometric proportions of the above powders according to the composition of $CaMg_{1-x}Zn_xSi_2O_6$ (x=0, 0.05, 0.1, 0.15, 0.2, and 0.3) were mixed in ethanol for 4 h with zirconia balls as milling media. The wet mixtures were dried and calcined at 1100 °C for 4 h in air. The calcined powders were re-milled. After drying and sieving, the as-prepared powders together with the organic binder (5 wt% polyvinyl alcohol) were uniaxially pressed under a pressure of 200 MPa into cylinders of 10 mm in diameter and 4–6 mm in thickness. These samples were sintered in the temperature range of 1100–1300 °C for 4 h in air with the heating rate of 5 °C/min.

Different weight percentages (0.3–3 wt%) of LiF powders were considered to further achieve the low-fired $CaMg_{1-x}Zn_xSi_2O_6$ ceramics. The LiF-containing samples were sintered in the temperature range of 775–1000 °C.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The relative densities were obtained from the bulk and theoretical densities which were calculated from lattice parameters. The crystal phases of the ceramics were characterized by X-ray diffraction (XRD) analysis with a Rigaku D/max-2500 (Cu $K\alpha$ radiation, Tokyo, Japan). The microstructures of the sintered ceramics were observed by scanning electron microscopy (SEM, JSM-6301F, JEOL, Tokyo, Japan). A network analyzer (HP8720ES, Hewlett-Packard, Santa, Rosa, CA) was used to measure the microwave dielectric properties. The dielectric constants were measured using the Hakki–Coleman [24] post-resonator method by exciting the TE_{011} resonant mode of the dielectric resonators using the electric probe of an antenna as suggested by Courtney [25]. The unloaded quality factors were measured using the $TE_{01\delta}$ mode in the cavity method [26]. The temperature coefficients of the resonant frequencies of the TE_{011} mode were obtained in the temperature range from 25 to 80 °C. The τ_f values were calculated by the following relationship:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 are the resonant frequency at T_1 and T_2, respectively.

3. Results and discussion

3.1. $CaMg_{1-x}Zn_xSi_2O_6$ ceramics

X-ray diffraction experiments were performed on the well-sintered $CaMg_{1-x}Zn_xSi_2O_6$ ceramics, and the results are shown in Fig. 1. It can be noted that the XRD patterns for all samples can be identified as diopside structure similar to the $CaMgSi_2O_6$ compound (JCPDS 19-0239). $CaMgSi_2O_6$ and $CaZnSi_2O_6$ are chain silicates, crystallizing in monoclinic symmetry with a space group of $C2/c$. It was reported that they can form quaternary solid solutions together with $CaFeSi_2O_6$ and $CaMnSi_2O_6$ [15]. Moreover, the ionic radius of Zn^{2+} (0.736 Å, CN=6) is nearly close to Mg^{2+} (0.728 Å, CN=6) [27], making it easy to substitute the magnesium site by the zinc ion. Thus, the solid solutions of $CaMg_{1-x}Zn_xSi_2O_6$ seemed to be easily formed. And yet, some peaks of $Ca_2ZnSi_2O_7$ hardystonite phase (JCPDS 35-0745) appear in the samples of x=0.2 and 0.3, implying the limited solid solutions formed from $CaMgSi_2O_6$ and $CaZnSi_2O_6$ end compounds. These results suggest that the solid solutions of $CaMg_{1-x}Zn_xSi_2O_6$ can be formed in the sintered bodies with a small amount of Zn^{2+} substitution for Mg^{2+}.

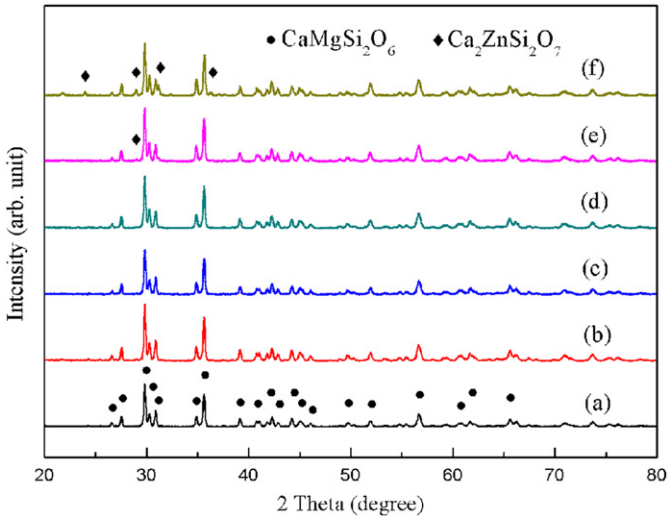

Fig. 1. XRD patterns of well-sintered $CaMg_{1-x}Zn_xSi_2O_6$ (x=0, 0.05, 0.1, 0.15, 0.2, and 0.3) ceramics.

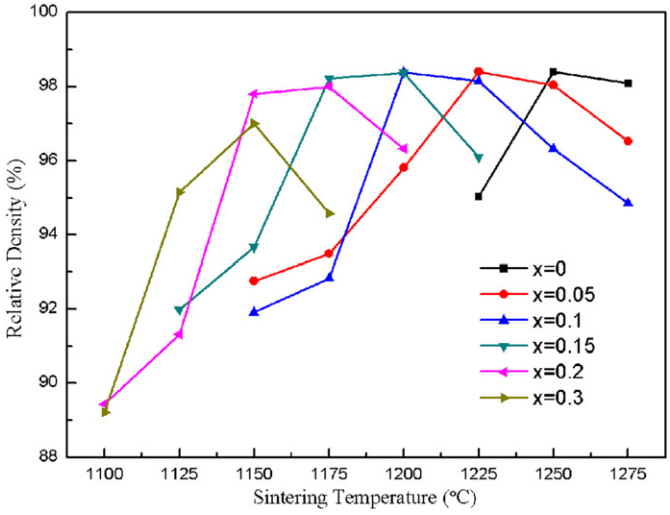

Fig. 2. Relative densities of $CaMg_{1-x}Zn_xSi_2O_6$ ceramics as a function of sintering temperature.

The relative densities of $CaMg_{1-x}Zn_xSi_2O_6$ ceramics as a function of sintering temperature are shown in Fig. 2. For each composition, the relative densities initially increase with increasing temperature and then decrease after reaching a maximum value, through which the optimized sintering temperatures of the ceramics were determined, i.e. 1250 °C for x=0, 1225 °C for x=0.05, 1200 °C for x=0.1, 1175 °C for x=0.15, and 1150 °C for x=0.2 and x=0.3. It is clear that a higher Zn^{2+} content shifts the obtainable maximum density to a lower temperature. This result implies that the substitution of Zn^{2+} for Mg^{2+} can markedly lower the sintering temperature in the $CaMg_{1-x}Zn_xSi_2O_6$ system.

The microstructure observations were performed on the well-sintered $CaMg_{1-x}Zn_xSi_2O_6$ ceramic samples by scanning electron microscopy, and the typical micrographs are shown in Fig. 3. All samples have dense microstructures with low porosity. As shown in Fig. 3(a), the average grain size of pure $CaMgSi_2O_6$ is about 1 μm except some abnormal growth grains. It can be also seen that pores exist in these abnormally grown grains. These phenomena may be due to the fast growth of the grains, thereby some pores were been trapped in the bodies of the abnormal growth grains [4]. As shown in Fig. 3(b), the grain sizes are more uniform and hardly any pore is observed in the large grains. It is interesting to note that the sample with x=0.1 seems to possess a homogeneous microstructure with equiaxed grains in Fig. 3(c). This might be related to the improvement of the sintering process caused by the formation of solid solutions [20]. However, the abnormal grain growth reappears for the sample x=0.15 in Fig. 3(d), probably because of the fast growth of the grains by excessive amount of Zn^{2+} substitution for Mg^{2+}.

The microwave dielectric properties of $CaMg_{1-x}Zn_xSi_2O_6$ ceramics were characterized as a function of sintering temperature and Zn^{2+} content, and the results are shown in Fig. 4 and Table 1. For each composition (see Fig. 4(a, b)), the relationship between dielectric properties (ε_r and Qf values) and sintering temperature share the similar trend with that between density and sintering temperature. According to Penn et al. [28], porosity plays a significant role in the dielectric properties (ε_r and Qf values) of microwave materials. Generally, both ε_r and Qf values decrease with increasing porosity volume, while pores directly lower the densities. In this case, ε_r and Qf increase with densification [11].

To better know the effects of secondary phase on the microwave dielectric properties of $CaMgSi_2O_6$-based ceramics, $Ca_2ZnSi_2O_7$ ceramics were also synthesized in the present work. When sintered at 1325 °C, the ceramic shows an ε_r of 10.2, Qf of 14,000 GHz and τ_f of −30.0 ppm/°C.

It can be seen from Fig. 4(a), that the maximum ε_r values increase from 7.80 to 7.99 as x varies from 0 to 0.15. In the case of microwave dielectrics, the dielectric constant is intrinsically determined by ionic polarizability [3,28]. Shannon [29] reported that the polarizability of Zn^{2+} (2.09 Å^3) is larger than that of Mg^{2+} (1.33 Å^3), thereby ε_r increases in the solid solution series [30]. Beyond the solid solution limit, $Ca_2ZnSi_2O_7$ has a larger dielectric constant than $CaMgSi_2O_6$, the appearance of which causes ε_r to increase in the samples of x=0.2 and 0.3. These results basically agreed with the well-known Lichtenecker empirical rule [31].

The dielectric loss is found to depend very strongly on pore volume, purity, and grain size [28]. To better interpret the variation of Qf values with Zn^{2+} content, the Qf values of representative samples are listed in Table 1. As the relative densities of these samples are all above 96%, the effect of porosity on the dielectric loss can be neglected [5]. In this case, the grain size and unexpected impurities mainly dominate the dielectric loss. Among $CaMg_{1-x}Zn_xSi_2O_6$ solid solutions (x=0–0.15), no secondary phase was observed from Fig. 1. So the effect of impurities on the dielectric loss can be also neglected. It is worthy to note

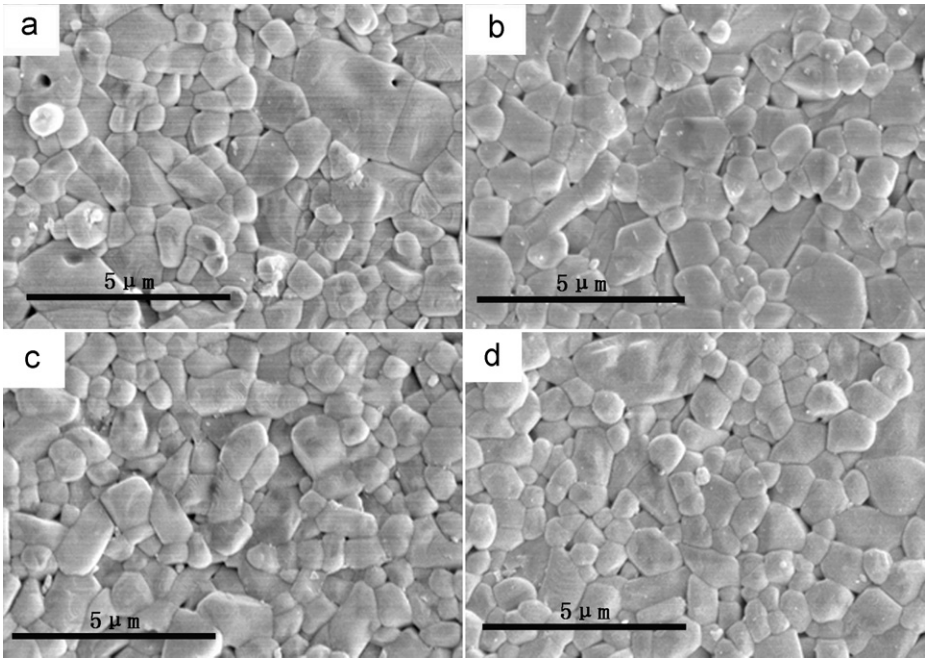

Fig. 3. SEM micrographs of the surfaces of well-sintered $CaMg_{1-x}Zn_xSi_2O_6$ ceramics: (a) $x=0$, 1250 °C, (b) $x=0.05$, 1225 °C, (c) $x=0.1$, 1200 °C, and (d) $x=0.15$, 1175 °C.

that $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramic has the highest *Qf* value due to its homogeneous microstructure with equiaxed grains, which leads to decrease in the inevitable pores caused by the abnormally grown grains and thereby lowering the dielectric loss. This results are consistent with the pertinent literatures [20,32]. Beyond the solid solution limit, *Qf* values degrade rapidly from 61,400 GHz to 37,200 GHz as x varies from 0.2 to 0.3, owing to the fact that the $Ca_2ZnSi_2O_7$ phase has a very low *Qf* value of 14,000 GHz and deteriorates the quality factors of diopside ceramics consequently.

Meanwhile, the variations of τ_f with Zn^{2+} content are also given in Fig. 4(c) and Table 1. The τ_f initially shows no remarkable variations when x increases from 0 to 0.15, and then slightly decreases to more negative values. The result is closely related to $Ca_2ZnSi_2O_7$ (-30.0 ppm/°C) has a little more negative τ_f than that of $CaMgSi_2O_6$ (-24.1 ppm/°C).

3.2. $CaMg_{0.9}Zn_{0.1}Si_2O_6+y$ wt% LiF ceramics

A small amount of LiF was considered as a sintering assistant to further lower the sintering temperature of $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics. The bulk densities of LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics sintered under various conditions are shown in Fig. 5. The concentration of LiF strongly influences the density. Doped with 0.6 wt% LiF, the optimal sintering temperature is significantly lowered from 1200 °C to 975 °C. With increasing LiF content from 0.6 wt% to 3 wt%, the sintering temperature at which the maximum densities occur decreases from 975 °C to 800 °C. This result suggests that LiF is a very effective sintering additive for $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics. It can be ascribed to the fact that LiF (melting point 845 °C) can melt to form a liquid phase to promote the densification process of $CaMg_{0.9}Zn_{0.1}Si_2O_6$, thereby significantly lowering the sintering temperature and enhancing the sintering behaviors [23]. In general, Fig. 5 shows a decrease in density at higher LiF contents, probably due to liquid phase sintering in the presence of molten LiF and the volatilization of LiF. It is reported that the porous microstructure can be also caused by volatilization of the lithium salt [33], thereby decreasing the apparent density and degrading the dielectric properties consequently. It can be also noted that LiF addition broadens the process window, which will be highly beneficial for practical LTCC applications.

Fig. 6 shows the XRD patterns of $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics doped with different amounts of LiF. Hardly any additional phase is present other than the $CaMgSi_2O_6$ phase in 0.6 wt% LiF-doped ceramics sintered at 900 °C and higher to 1000 °C. From Fig. 6(c), new peaks of $Li_{0.6}Zn_{1.1}Si_{1.3}O_4$ (JCPDS 34-1231) are observed in 3 wt% LiF-doped sample sintered at 900 °C, which indicates that the reactions between LiF and matrix material take place during the sintering process, leading to degradation of the apparent density and the dielectric properties [33].

Fig. 7 shows the SEM micrographs of 0.6 wt% LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics sintered at different temperatures. From Fig. 7(a), some pores can be observed on the sample surface. These pores could be related to the poor densification with low temperature. Dense microstructures with low porosity can be observed in Fig. 7(b,c), which is related to the grain growth with increasing sintering temperature. Compared with pure $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics shown in Fig. 3(c), the average grain size slightly

increases by doping 0.6 wt% LiF. This could be due to the effect of low melting point of LiF on the grain growth behavior of $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics.

The microwave dielectric properties of LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics are shown in Fig. 8 and Table 2. As for glass added ceramics, the microwave dielectric properties are more likely relying on density and the presence of secondary phases [7,18]. Likewise, the variations of ε_r and Qf values with sintering temperature nearly follow the similar trend with the relationship between bulk densities and sintering temperature. As shown in Fig. 8(a, b) and Table 2, ε_r and Qf values decrease with increasing amount of LiF addition. This result might be due to the volatility of lithium and the unexpected secondary phases [33]. Especially for the

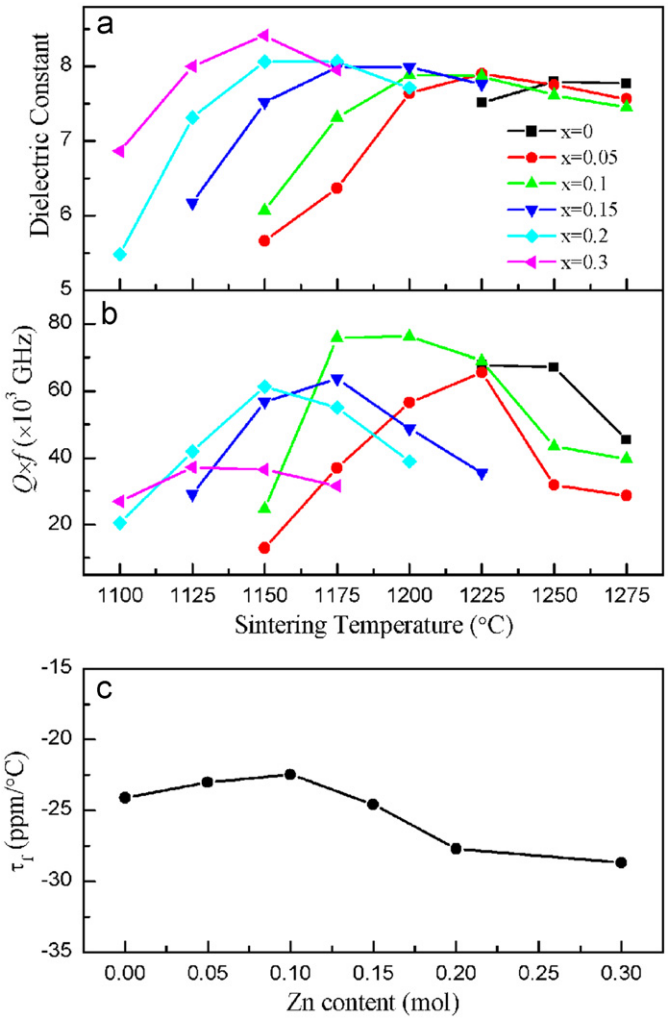

Fig. 4. Microwave dielectric properties of $CaMg_{1-x}Zn_xSi_2O_6$ ceramics: (a) ε_r, (b) Qf vs. sintering temperature, and (c) τ_f vs. Zn content.

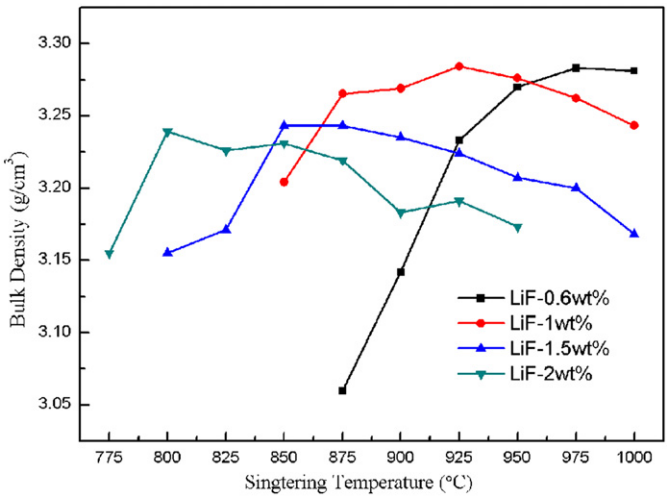

Fig. 5. Bulk densities of LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics as a function of sintering temperature.

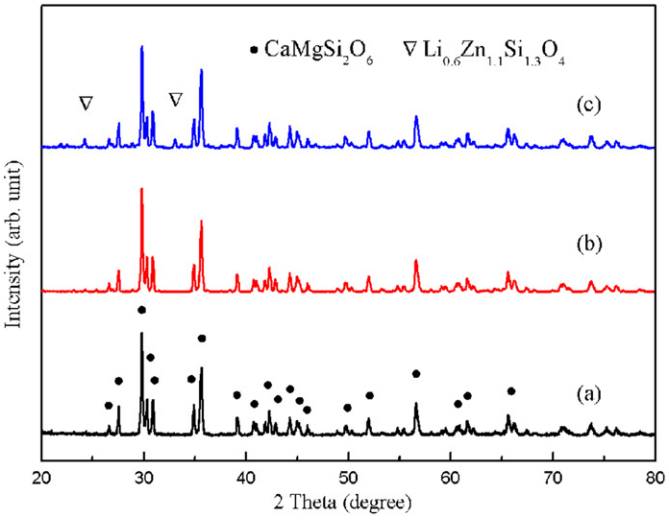

Fig. 6. XRD patterns of LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics: (a) 0.6 wt% LiF, 900 °C, (b) 0.6 wt% LiF, 1000 °C, and (c) 3 wt% LiF, 900 °C.

Table 1
Relative densities and microwave dielectric properties of $CaMg_{1-x}Zn_xSi_2O_6$ ceramics sintered at optimized temperatures.

Samples, x	Sintering temperature (°C)	Relative density (%)	ε_r	Qf (GHz)	τ_f (ppm/°C)
0	1250	98.39	7.80	67,100	−24.1
0.05	1225	98.40	7.90	65,600	−23.0
0.10	1200	98.38	7.88	76,100	−22.5
0.15	1175	98.22	7.99	63,700	−24.6
0.20	1150	97.80	8.06	61,400	−27.7
0.30	1150	97.00	8.41	36,400	−28.7

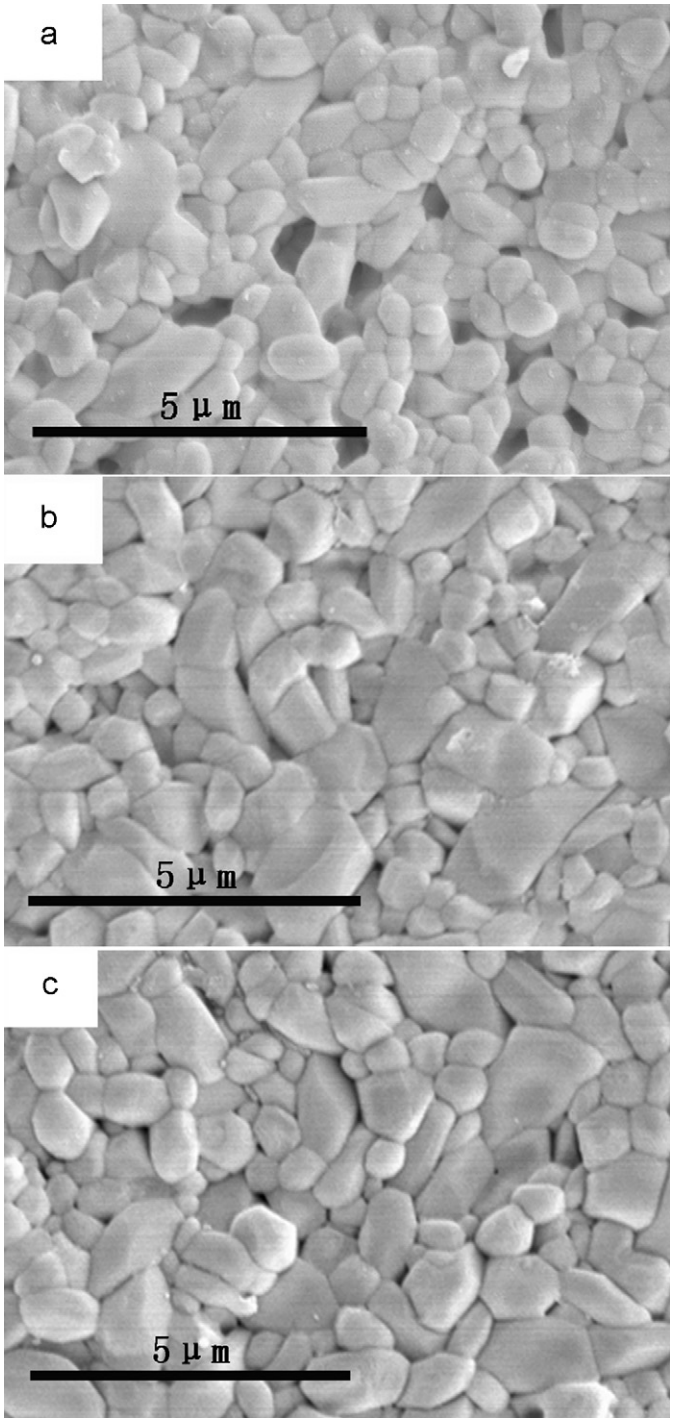

Fig. 7. SEM micrographs of the surfaces of 0.6 wt% LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics sintered at different temperatures: (a) 900 °C, (b) 925 °C, and (c) 950 °C.

samples added with excess amount of 2 wt% LiF, the quality factor almost becomes independent of sintering temperature, which seriously degrades to about 24,000 GHz because of the appearance of $Li_{0.6}Zn_{1.1}Si_{1.3}O_4$. From Fig. 8(c), τ_f basically decreases nonlinearly to more negative values as x increases. These results can be closely related to the $Li_{0.6}Zn_{1.1}Si_{1.3}O_4$ phase which might have a more negative τ_f.

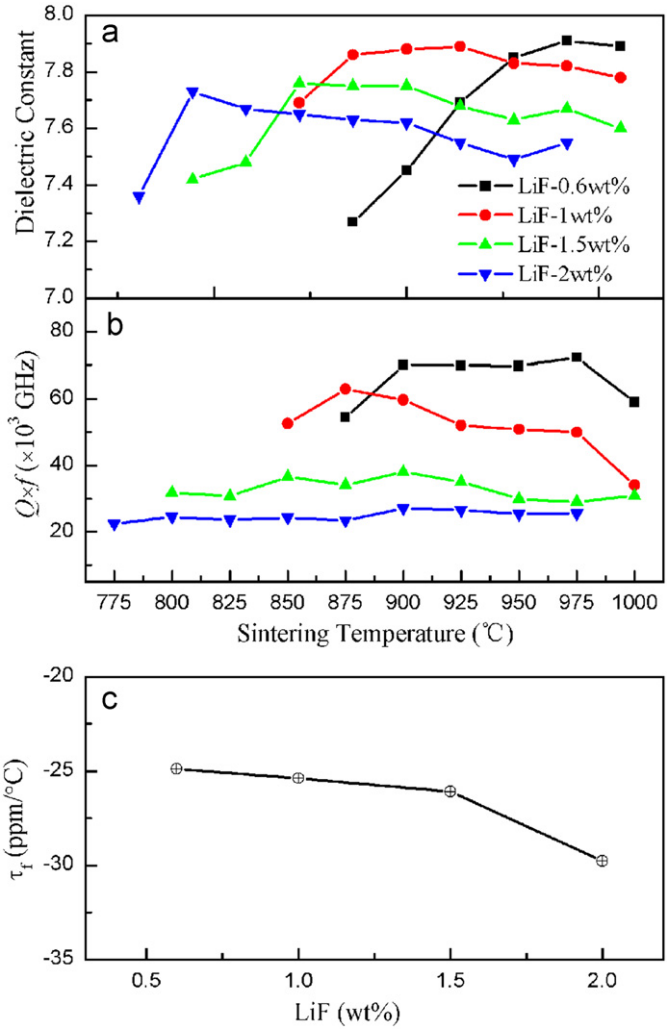

Fig. 8. Microwave dielectric properties of LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics: (a) ε_r, (b) Qf vs. sintering temperature, and (c) τ_f vs. LiF content.

It is noteworthy that 0.6 wt% LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics, sintered in the temperature range of 900–975 °C, maintain relatively high Qf values about 70,000 GHz. As no apparent peaks of secondary phases were examined from XRD patterns in Fig. 6(a, b), these samples hence possess relatively high Qf values. These results indicate that a small amount of LiF can effectively decrease the sintering temperature without degrading the microwave dielectric properties of host materials. It is obvious that these ceramics are promising to be co-fired with Ag electrode materials for further LTCC applications.

4. Conclusions

In this work, we utilized two steps to obtain the low-temperature co-fired ceramics with excellent dielectric properties in the diopside material system. Firstly, $CaMg_{1-x}Zn_xSi_2O_6$ solid solutions through Zn^{2+} substitution for Mg^{2+} can markedly lower the sintering temperature and enhance the microwave dielectric properties.

Table 2
Bulk densities and microwave dielectric properties of $CaMg_{0.9}Zn_{0.1}Si_2O_6+y$ wt% LiF ceramics.

y (wt%)	Sintering temperature (°C)	Bulk density (g/cm^3)	ε_r	Qf (GHz)	τ_f (ppm/°C)
0.6	925	3.270	7.69	69,900	−24.9
1	900	3.269	7.88	59,700	−25.4
1.5	850	3.243	7.76	36,500	−26.1
2	850	3.231	7.65	24,300	−29.8

$CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramic exhibits good dielectric properties of $\varepsilon_r=7.88$, $Qf=76{,}100$ GHz and $\tau_f=-22.5$ ppm/°C. Then, LiF was considered to further reduce the densification temperature of $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics. A small amount of LiF addition can lower the sintering temperature prominently. In particular, 0.6 wt% LiF-doped $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics can be sintered in the temperature range of 900–975 °C and have relatively high Qf values of ~70,000 GHz. These materials possess a pretty wide process window, promising to be the potential candidates for LTCC applications.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Grant nos. 50972074, 51102141, and 50921061) and the Ministry of Science and Technology of China through 973- Project under 2009CB623306.

References

[1] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, International Materials Reviews 53 (2008) 57–90.
[2] R.R. Tummala, Ceramic and glass-ceramic packaging in the 1990s, Journal of the American Ceramic Society 74 (1991) 895–908.
[3] I.M. Reaney, D. Iddle, Microwave dielectric ceramics for resonators and filters in mobile phone networks, Journal of the American Ceramic Society 89 (2006) 2063–2072.
[4] Q. Zeng, W. Li, J.L. Shi, J.K. Guo, M.W. Zuo, W.J. Wu, A new microwave dielectric ceramic for LTCC applications, Journal of the American Ceramic Society 89 (2006) 1733–1735.
[5] H. Zhuang, Z.X. Yue, F. Zhao, L.T. Li, Low-temperature sintering and microwave dieletric properties of $Ba_5Nb_4O_{15}$–$BaWO_4$ composite ceramics for LTCC applications, Journal of the American Ceramic Society 91 (2008) 3275–3279.
[6] M.R. Joung, J.S. Kim, M.E. Song, J.H. Choi, J.W. Sun, S. Nahm, J.H. Paik, B.H. Choi, Effect of $LiCO_3$ addition on the sintering temperature and microwave dielectric properties of $Mg_2V_2O_7$ ceramics, Journal of the American Ceramic Society 92 (2009) 2151–2154.
[7] P.V. Bijumon, M.T. Sebastian, Influence of glass additives on the microwave dielectric properties of $Ca_5Nb_2TiO_{12}$ ceramics, Materials Science and Engineering B 123 (2005) 31–40.
[8] H.P. Wang, S.Q. Xu, B. Zhang, Q.L. Zhang, H. Yang, Synthesis and microwave dielectric properties of CaO–MgO–SiO_2 submicron power doped with Li_2O–Bi_2O_3 by sol–gel method, Materials Research Bulletin 44 (2009) 619–622.
[9] D. Thomas, M.T. Sebastian, Temperature-compensated $LiMgPO_4$: a new glass-free low temperature cofired ceramic, Journal of the American Ceramic Society 93 (2010) 3828–3831.
[10] D.K. Kwon, M.T. Lanagan, T.R. Shrout, Microwave dielectric properties and low-temperature cofiring of $BaTe_4O_9$ with aluminum metal electrode, Journal of the American Ceramic Society 88 (2005) 3419–3422.
[11] J. Pei, Z.X. Yue, F. Zhao, Z.L. Gui, L.T. Li, Microwave dielectric ceramics of hexagonal$(Ba_{1-x}A_x)La_4Ti_4O_{15}$ (A=Sr, Ca) for base station applications, Journal of Alloys and Compounds 459 (2008) 390–394.
[12] J.Wang, Z.X. Yue, Z.L. Gui, L.T. Li, Low-temperature sintered $Zn(Nb_{1-x}V_{x/2})_2O_{6-2.5x}$ microwave dielectric ceramics with high Q value for LTCC application, Journal of Alloys and Compounds 392 (2005) 263–267.
[13] M. Thirumal, I.N. Jawahar, K.P. Surendiran, P. Mohanan, A.K. Ganguli, Synthesis and microwave dielectric properties of $Sr_3Zn_{1-x}Mg_xNb_2O_9$ phases, Materials Research Bulletin 37 (2002) 185–191.
[14] H. Jantunen, R. Rautioaho, A. Uusimäki, S. Leppävuori, Preparing low-loss low-temperature cofired ceramic materials without glass addition, Journal of the American Ceramic Society 83 (2000) 2855–2857.
[15] A.L. Huber, M. Heuer, K.T. Fehr, K. Bente, E. Schmidbauer, G.D. Bromiley, Characterization of synthetic hedenbergite ($CaFeSi_2O_6$)-petedunnite ($CaZnSi_2O_6$) solid solution series by X-ray powder diffractionand 57Fe Mössbauer spectroscopy, Physics and Chemistry of Minerals 31 (2004) 67–79.
[16] H.P. Sun, Q.L. Zhang, H. Yang, J.L. Zou, $Ca_{1-x}Mg_x)SiO_3$: a low-permittivity microwave dielectric ceramic system, Materials Science and Engineering B 138 (2007) 46–50.
[17] H.P. Wang, S.Q. Xu, S.Y. Zhai, D.G. Deng, H.D. Ju, Effect of B_2O_3 additives on the sintering and dielectric behaviors of $CaMgSi_2O_6$ ceramics, Journal of Materials Science and Technology 26 (2010) 351–354.
[18] T. Joseph, M.T. Sebastian, H. Sreemoolanadhan, V.K.S. Nageswari, Effect of glass addition on the microwave dielectric properties of $CaMgSi_2O_6$ ceramics, International Journal of Applied Ceramic Technology 7 (2010) E98–E106.
[19] Q.L. Zhang, H. Yang, H.P. Sun, A new microwave ceramic with low-permittivity for LTCC applications, Journal of the European Ceramic Society 28 (2008) 605–609.
[20] Y.C. Zhang, J. Wang, Z.X. Yue, Z.L. Gui, L.T. Li, Effect of Mg^{2+} substitution on microstructure and microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics, Ceramics International 30 (2004) 87–91.
[21] H.T. Kim, S. Nahm, J.D. Byun, Y. Kim, Low-fired (Zn, Mg)TiO_3 microwave dielectrics, Journal of the American Ceramic Society 82 (1999) 3476–3480.
[22] J.X. Tong, Q.L. Zhang, H. Yang, J.L. Zou, Low-temperature firing and microwave dielectric properties of $Ca[(Li_{0.33}Nb_{0.67})_{0.9}Ti_{0.1}]O_{3-\delta}$ ceramics with LiF addition, Materials Letters 59 (2005) 3252–3255.
[23] U. Intatha, S. Eitssayeam, K. Pengpat, K.J.D. MacKenzie, T. Tunkasiri, Dielectric properties of low temperature sintered LiF doped $BaFe_{0.5}Nb_{0.5}O_3$, Materials Letters 61 (2007) 196–200.
[24] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacitance in the millimeter range, IEEE Transactions on Microwave Theory and Techniques 8 (1960) 402–410.
[25] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators, IEEE Transactions on Microwave Theory and Techniques 18 (1970) 476–485.

[26] J. Krupka, K. Derzakowski, B. Riddle, J.B. Jarvis, A dielectric resonator for measurements of complex permittivity of low loss dielectric materials as a function of temperature, Measurement Science and Technology 9 (1998) 1751–1756.
[27] R.D. Shannon, Revised effective ionic radii and systematic of interatomic distance in halides and chalcogenides, Acta Crystallographica A 32 (1976) 751–767.
[28] S.J. Penn, N.M. Alford, A. Templeton, X.R. Wang, M.S. Xu, M. Reece, K. Schrapel, Effect of porosity and grain size on the microwave dielectric properties of sintered alumina, Journal of the American Ceramic Society 80 (1997) 1885–1888.
[29] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, Journal of Applied Physics 73 (1993) 348–366.
[30] M.S. Fu, X.Q. Liu, X.M. Chen, Y.W. Zeng, Effects of Mg substitution on microstructures and microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ perovskite ceramics, Journal of the American Ceramic Society 93 (2010) 787–795.
[31] R.W. Vest, Ceramic Meterials for Electronics, Second ed., Marcel Dekker Inc, New York, 1991 435 pp.
[32] H. Zhuang, Z.X. Yue, F. Zhao, J. Pei, L.T. Li, Microstructure and microwave dielectric properties of $Ba_5Nb_4O_{15}$–$BaWO_4$ composite ceramics, Journal of Alloys and Compounds 472 (2009) 411–415.
[33] M. Pollet, S. Marinel, Low temperature sintering of $CaZrO_3$ using lithium fluoride addition, Journal of the European Ceramic Society 23 (2003) 1925–1933.