J. Am. Ceram. Soc., **99** [4] 1122–1124 (2016)
DOI: 10.1111/jace.14132

Journal
Rapid Communication

Novel Low-Firing Forsterite-Based Microwave Dielectric for LTCC Applications

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A novel low-temperature sintering microwave dielectric based on forsterite (Mg_2SiO_4) ceramics was synthesized through the solid-state reaction method. The effects of LiF additions on the sinterability, phase composition, microstructure, and microwave dielectric properties of Mg_2SiO_4 were investigated. It demonstrated that LiF could significantly broaden the processing window (~300°C) for Mg_2SiO_4, and more importantly the sintering temperature could be lowered below 900°C, maintaining excellent microwave dielectric properties simultaneously. The 2 wt% LiF-doped samples could be well-sintered at 800°C and possessed a $\varepsilon_r \sim 6.81$, a high $Q\times f \sim 167\ 000$ GHz, and a $\tau_f \sim -47.9$ ppm/°C, having a very good potential for LTCC integration applications.

I. Introduction

Recently, the low-temperature cofired ceramic (LTCC) has received much attention as the base materials for electronic components and substrates in global advanced integration, electronic packaging, and interconnection technologies.[1–3] For a particular LTCC material, dielectrics are required to have a low dielectric constant ($\varepsilon_r < 10$), a high quality factor ($Q\times f$), and a near-zero temperature coefficient of resonant frequency (τ_f). In addition, the low sintering temperature (T_s, below 900°C) is the key issue because ceramics must be cofired with highly conductive electrode materials like silver (melting point, T_m, 961°C).[2,3] With the ever-increasing demand for such microwave components, many strategies have emerged to lower T_s of dielectrics.[3–7] Among those, the idea of adding low melting point materials like B_2O_3 and glass is widely used as it is the cheapest and easiest way to be realized.

Mg_2SiO_4 is a typical low-ε_r (6.8) and high-Q (270 000 GHz) microwave ceramic, promising to be the ideal candidate for LTCC applications in terms of many merits such as it is inexpensive, easy to process, chemically stable, highly insulating even at higher temperatures, etc.[5,6,8] However, its high T_s (1500°C) limits the practical use in microwave integrated circuits. Some glasses like Li_2O-B_2O_3-SiO_2 and Li_2O-MgO-ZnO-B_2O_3-SiO_2 (15 wt%) could lower T_s to about 900°C ~ 950°C.[5,6] However, the $Q\times f$ values were deteriorated a lot at such a high amount of glasses. Moreover, some unexpected problems would arise during LTCC fabrications as host materials and glasses undergo different thermal expansion, thermal resistance, mechanical strength, etc.[1,3] Thus, more effective sintering aids are essential to realize low-fired forsterite ceramics with good microwave dielectric performances.

In our previous works, fluorides like LiF and MgF_2 have been demonstrated to be the effective sintering aids for $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics.[9,10] At a low amount of LiF (0.6 wt%), particularly the $CaMg_{0.9}Zn_{0.1}Si_2O_6$, ceramics could be sintered at 900°C with high $Q\times f$ values (~ 70 000 GHz).[9] Herein, LiF was chosen as the sintering aid for Mg_2SiO_4, and its effects on the sintering behaviors, phase composition, microstructure, and microwave dielectric properties of Mg_2SiO_4 were investigated.

II. Experimental Procedure

Analytical purity MgO, SiO_2, and LiF (Sinopharm Chemical Reagent Co. Ltd., Beijing, China) powder were used as the raw materials. Stoichiometric amounts of MgO and SiO_2 were ball-mixed in ethanol for 4 h with zirconia balls. The slurry was then dried and calcined at 1150°C for 4 h in air. Added with different weight percentages (0.5, 1, 2, 3 wt%) of LiF, the as-prepared powder was remilled and then uniaxially pressed together with the organic binder (5 wt% polyvinyl alcohol) under a pressure of 200 MPa into cylinders and pellets with appropriate specifications. Samples were sintered in the temperature range of 750°C–1450°C for 4 h in air at a heating rate of 5°C/min.

The crystal phases of the sintered ceramics were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany). The microstructures of the samples were observed by scanning electron microscopy (SEM, MERLIN VP Compact, Carl Zeiss, Germany). The bulk densities were measured by the Archimedes method. The microwave dielectric properties were measured by a network analyzer (HP8720ES, Hewlett-Packard, Santa, Rosa, CA) and a temperature chamber (MC-811T, Espec, Osaka, Japan). The τ_f values were obtained in the temperature range from 25°C to 80°C.

III. Results and Discussion

Figure 1 shows the XRD patterns of the LiF-doped Mg_2SiO_4 ceramics. As shown in Figs. 1(a) and (b), almost all the recognizable reflections of the 0.5 wt% LiF-doped counterparts sintered from 1100°C to 1450°C are identified to orthorhombic forsterite structure according to the JCPDS data file no. 34-0189 (indicated by red lines). At a higher LiF content of 3 wt% in Fig. 1(c), there seems no detectable reflections of secondary phases for the samples even sintered at 1050°C.

Figure 2(a)–(c) display the microstructures for the 0.5 wt % LiF-doped Mg_2SiO_4 sintered at different temperatures. A relatively poor densification is found for the sample sintered at 1150°C [Fig. 2(a)]. The average grain size is about 1 μm

M. Sebastian—contributing editor

Manuscript No. 37572. Received September 26, 2015; revised October 22, 2015; approved December 26, 2015.
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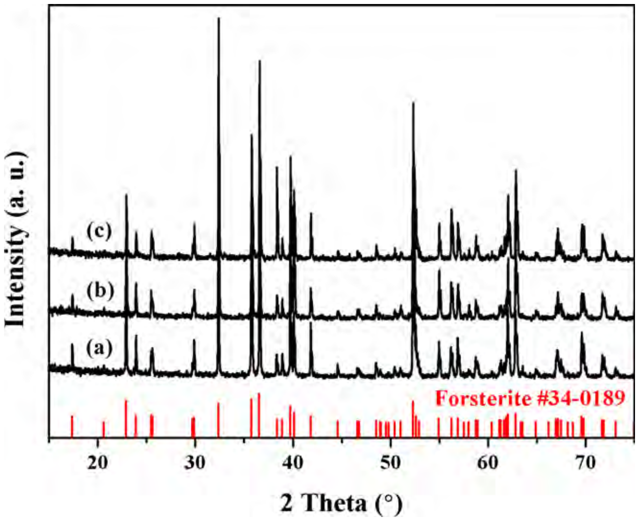

Fig. 1. XRD patterns of LiF-doped Mg_2SiO_4 ceramics: (a) 0.5 wt% LiF, 1100°C; (b) 0.5 wt% LiF, 1450°C; and (c) 3 wt% LiF, 1050°C.

except for abnormal grain growth (AGG, indicated by arrows). When T_s is increased to 1200°C, more pronounced AGG can be seen from Fig. 2(b) and the grain size (~10 μm) is much larger than the rest ones. This is likely due to the LiF-related liquid phase that promotes the sintering process for Mg_2SiO_4 and results in AGG.[3,11] At a higher T_s of 1300°C in Fig. 2(c), the average grain size is ~ 20 μm, and some pores are trapped inside grains caused by fast grain growth.[11] Doped with 2 wt% LiF shown in Fig. 2(d), the sample sintered at 800°C has a relatively dense microstructure with some angular (approximately cubic-like) grains, which is somewhat different from that of 0.5 wt% LiF-doped counterparts. In this case, the obtained T_s is lower than the melting point of LiF (845°C). In our previous reports, 2 wt % LiF could allow $CaMg_{0.9}Zn_{0.1}Si_2O_6$ to be sintered at 775°C ~ 975°C, and 1000°C for 5 wt% MgF_2 (T_m ~1266°C).[9,10] As sintering is an interface-related process for ceramics in terms of driven force and kinetics,[11] it seems possible for fluorine to enter the network of silicon–oxygen tetrahedron motivated by mass transfer. The increase in LiF content could also enhance the chance of fluorine to substitute for oxygen within silicon–oxygen tetrahedron. With respect to the differences in valence bonds between oxygen and fluorine, the replacement of networking Si-O bonds by non-networking Si-F bands could decrease the continuity of the host network,[12] and the lattices could also be activated by this substitution. Moreover, fluorine is an effective nucleation agent in LTCC-based materials,[12] which could also improve the sintering role of LiF in Mg_2SiO_4 and further induce a decrease in T_s. Hence, these samples could be sintered below the melting point of sintering aids. And further investigations are needed to better understand it yet. As a result, the interface structures might be changed and different microstructures (AGG and angular grains) occur in the orthorhombic forsterite.

The buck densities and microwave dielectric properties of the LiF-doped Mg_2SiO_4 ceramics are displayed in Fig. 3 and Table I. It is worth noting that LiF can significantly improve the sintering process of Mg_2SiO_4, resulting in a wide sintering window of ~300°C shown in Fig. 3(a). This is highly beneficial for practical LTCC device fabrications.[1,3] Overall, at a fixed content of LiF, the bulk density initially increases with T_s and thereafter decreases, suggesting that T_s can be effectively decreased from 1200°C to approximately 800°C when the content of LiF varies from 0.5 to 3 wt%.

Fully considering the microwave dielectric response of the LiF-doped Mg_2SiO_4 ceramics, the variations in ε_r and $Q \times f$ with T_s basically share a similar trend with that of the bulk densities, as shown in Figs. 3(b) and (c). Generally, for glass (liquid phase) added ceramics, microwave dielectric properties are dependent on densification (porosity) and the presence of secondary phases.[9,13] Nearly pure forsterite structures were detected in the LiF-doped samples. The effect of densification on the behaviors of ε_r and $Q \times f$ becomes much important. Likewise, they initially increase and then decrease after a crucial T_s. To be noted that the well-sintered samples exhibit high $Q \times f$ values over 160 000 GHz listed in Table I. Meanwhile, τ_f does not show much change with different contents of LiF, lying in a range of −45 to −55 ppm/°C.

Table II lists the microwave dielectric properties of some Mg_2SiO_4-based ceramics in terms of different low-firing approaches.[5,6,8,14,15] Low-temperature sintering (~800°C) and excellent microwave properties can be simultaneously

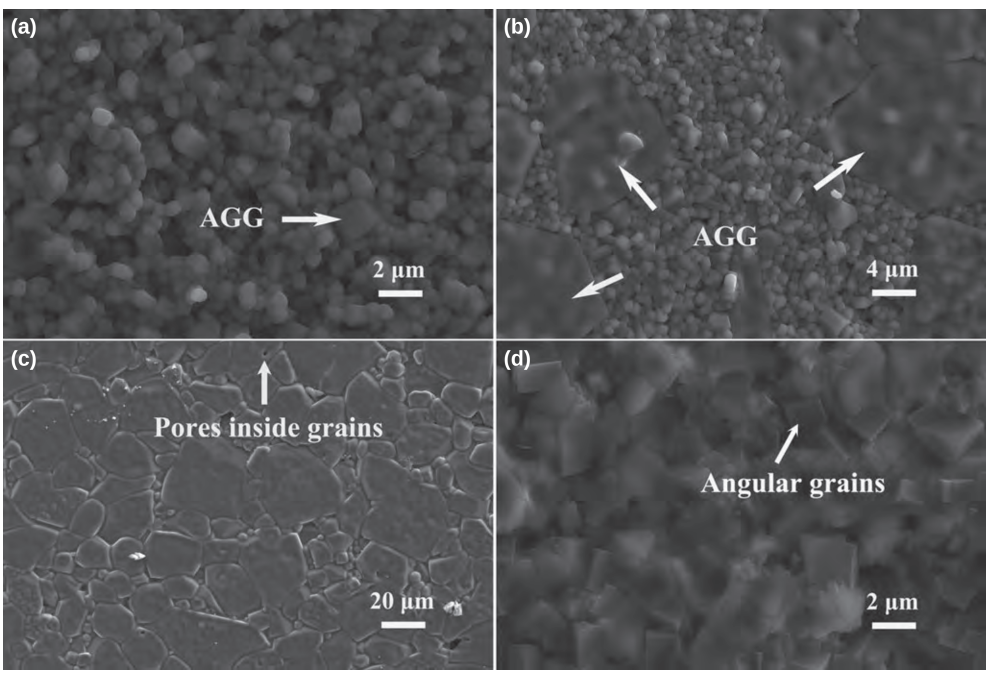

Fig. 2. SEM micrographs of LiF-doped Mg_2SiO_4 ceramics: (a) 0.5 wt% LiF, 1150°C; (b) 0.5 wt% LiF, 1200°C; (c) 0.5 wt% LiF, 1300°C; and (d) 2 wt% LiF, 800°C.

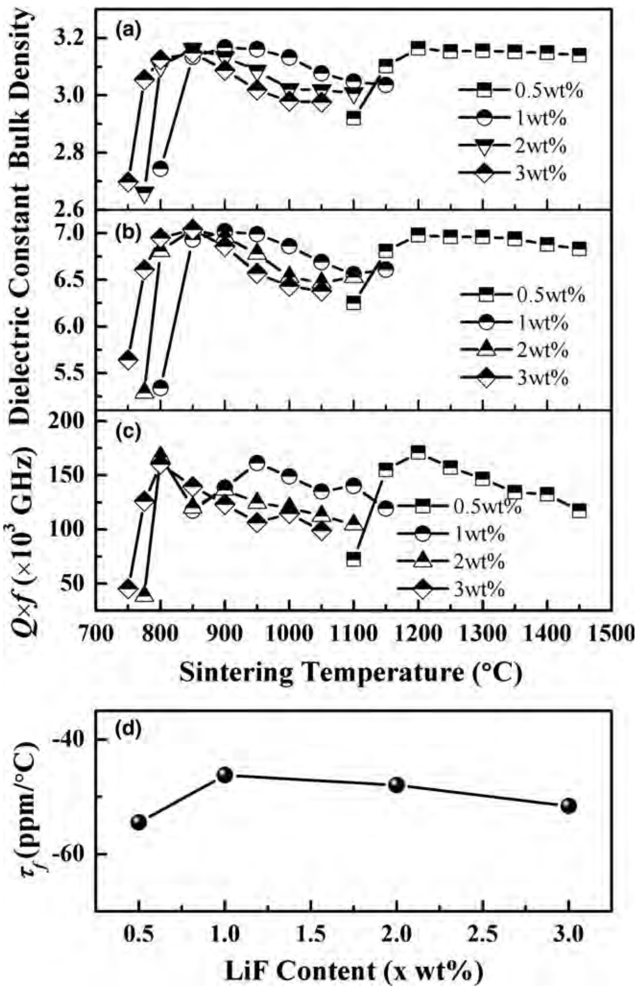

Fig. 3. Bulk densities and microwave dielectric properties of LiF-doped Mg_2SiO_4 ceramics: (a) bulk densities, (b) microwave dielectric constant, (c) $Q\times f$ values, and (d) temperature coefficient of resonant frequency.

Table I. Bulk Densities and Microwave Dielectric Properties of LiF-Doped Mg_2SiO_4 Ceramics Sintered at Optimized Temperatures

x (wt%)	T_s(°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
0.5	1200	6.98	171 000	−54.5
1	950	7.02	162 300	−46.2
2	800	6.81	167 000	−47.9
3	800	6.95	160 300	−51.6

Table II. Comparison of Microwave Dielectric Properties of Some Mg_2SiO_4-Related Ceramics

Methods (or additions)	T_s (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	References
–	1500	6.8	270 000	−70	[8]
Mg/Si = 2.05	1500	7.5	114 730	−59	[14]
High-energy ball milling	1075	7.2	193 800	−58	[15]
Li_2O-B_2O_3-SiO_2 glass (@7 GHz)	950	5.0	1 000	—	[5]
Li_2O-MgO-ZnO-B_2O_3-SiO_2 glass	950	6.75	30 600	—	[6]
LiF	800	6.95	160 300	−51.6	This work

obtained for Mg_2SiO_4 ceramics by doping 2 wt% LiF. With the merits of inexpensive, chemically stable, and highly insulating nature in silicates, these LiF-doped Mg_2SiO_4 ceramics have a high potential for LTCC applications. Considering the important roles of fluorides particularly LiF in the low-fired Mg_2SiO_4 and $CaMg_{0.9}Zn_{0.1}Si_2O_6$ ceramics,[9,10] it seems reasonable to deduce that fluorides could be an effective sintering aid for alternative silicate materials, such as Zn_2SiO_4, $MgSiO_3$, etc.

IV. Conclusions

Novel low-fired microwave dielectrics based on Mg_2SiO_4 were synthesized through the solid-state reaction approach. LiF could markedly improve the sintering process for Mg_2SiO_4, resulting in a sintering temperature window of ~300°C. More importantly, it could lower the densification temperature to ~800°C and maintain excellent microwave dielectric properties of a ε_r ~ 6.81, a high $Q\times f$ ~ 167 000 GHz, and a τ_f ~ −47.9 ppm/°C for the 2 wt% LiF-doped samples. With the advantages of low sintering temperature and good dielectric properties, these LiF-doped forsterite ceramics have a very good potential for practical LTCC integration applications.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (grant nos. 51472138, 51221291, 51302142, and 51102141), and the Ministry of Science and Technology of China through 973-Project under no. 2015CB654605.

References

[1]Y. Imanaka, *Multilayered Low Temperature Cofired Ceramics (LTCC) Technology*. Springer, New York City, New York, 2005.

[2]R. R. Tummala, "Ceramic and Glass-Ceramic Packaging in the 1990s," *J. Am. Ceram. Soc.*, **74** [5] 895–908 (1991).

[3]M. T. Sebastian and H. Jantunen, "Low Loss Dielectric Materials for LTCC Applications: A Review," *Int. Mater. Rev.*, **53** [2] 57–90 (2008).

[4]J. S. Kim, et al., "Low-Temperature Sintering and Microwave Dielectric Properties of the Zn_2SiO_4 Ceramics," *J. Am. Ceram. Soc.*, **91** [2] 671–4 (2008).

[5]T. S. Sasikala, M. N. Suma, P. Mohanan, C. Pavithran, and M. T. Sebastian, "Forsterite-Based Ceramic-Glass Composites for Substrate Applications in Microwave and Millimeter Wave Communications," *J. Alloys Compd.*, **461**, 555–9 (2008).

[6]T. S. Sasikala, C. Pavithran, and M. T. Sebastian, "Effect of Lithium Magnesium Zinc Borosilicate Glass Addition on Densification Temperature and Dielectric Properties of Mg_2SiO_4 Ceramics," *J. Mater. Sci.: Mater. Electron.*, **21**, 141–4 (2010).

[7]Y. Z. Hao, Q. L. Zhang, J. Zhang, C. R. Xin, and H. Yang, "Enhanced Sintering Characteristics and Microwave Dielectric Properties of Li_2TiO_3 Due to Nano-Size and Nonstoichiometry Effect," *J. Mater. Chem.*, **22**, 23885–92 (2012).

[8]H. Ohsato, T. Tsunooka, T. Sugiyama, K.-I. Kakimoto, and H. Ogawa, "Forsterite Ceramics for Millimeterwave Dielectrics," *J. Electroceram.*, **17**, 445–50 (2006).

[9]J. Zhang, Y. Y. Zhou, and Z. X. Yue, "Low-Temperature Sintering and Microwave Dielectric Properties of LiF-Doped $CaMg_{1-x}Zn_xSi_2O_6$ Ceramics," *Ceram. Int.*, **39**, 2051–8 (2013).

[10]J. Zhang, Y. Y. Zhou, B. Peng, Z. K. Xie, X. H. Zhang, and Z. X. Yue, "Microwave Dielectric Properties and Thermally Stimulated Depolarization Currents of MgF_2-Doped Diopside Ceramics," *J. Am. Ceram. Soc.*, **97** [11] 3537–43 (2014).

[11]W. Jo, D.-Y. Kim, and N.-M. Hwang, "Effect of Interface Structure on the Microstructural Evolution of Ceramics," *J. Am. Ceram. Soc.*, **89** [8] 2369–80 (2006).

[12]J. Zhou, "Towards Rational Design of low-Temperature co-Fired Ceramic (LTCC) Materials," *J. Adv. Ceram.*, **1** [2] 89–99 (2012).

[13]S. J. Penn, et al., "Effect of Porosity and Grain Size on the Microwave Dielectric Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, **80** [7] 1885–8 (1997).

[14]K. X. Song, X. M. Chen, and X. C. Fan, "Effects of Mg/Si Ratio on Microwave Dielectric Characteristics of Forsterite Ceramics," *J. Am. Ceram. Soc.*, **90** [6] 1808–11 (2007).

[15]L. Cheng, et al., "Fabrication of Nanopowders by High Energy Ball Milling and Low Temperature Sintering of Mg_2SiO_4 Microwave Dielectrics," *J. Alloys Compd.*, **513**, 373–7 (2012). □