Sintering behavior and microwave dielectric properties of Li$_4$Mg$_3$[Ti$_{0.8}$(Mg$_{1/3}$Ta$_{2/3}$)$_{0.2}$]$_2$O$_9$ ceramics with LiF additive for LTCC applications

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Abstract

Novel low temperature sintered Li$_4$Mg$_3$[Ti$_{0.8}$(Mg$_{1/3}$Ta$_{2/3}$)$_{0.2}$]$_2$O$_9$ (LMT$_{0.8}$MT$_{0.2}$) ceramics with 1–5 wt% LiF additives were successfully prepared by the solid-state reaction method. The effects of LiF additives on the phase composition, sintering characteristic, microstructure and microwave dielectric properties of LMT$_{0.8}$MT$_{0.2}$ ceramics were investigated in detail for the first time. The sintering temperature of LMT$_{0.8}$MT$_{0.2}$ ceramics could be effectively lowered to 950 °C by the addition of LiF. A single rock salt crystalline phase structure belonging to a space group of Fm-3m (No.225) was obtained through X-ray diffraction patterns. Dense uniform morphology was observed at 950 °C for LMT$_{0.8}$MT$_{0.2}$ ceramics with 3–5 wt% LiF in terms of scanning electron microscopy photographs. Particularly, the LMT$_{0.8}$MT$_{0.2}$-4 wt% LiF ceramics sintered at 950 °C for 4 h possessed optimum microwave dielectric properties of $\varepsilon_r=16.10$, $Q\times f = 114,313$ GHz (at 8.18 GHz) and $\tau_f = -7.72$ ppm/°C. In addition, the excellent chemical compatibility with silver metal electrodes indicated that the LMT$_{0.8}$MT$_{0.2}$-4 wt% LiF ceramics might be a promising candidate for the low-loss low temperature co-fired ceramics (LTCC) applications in microwave devices. © 2020 Elsevier B.V. All rights reserved.

1. Introduction

As the critical materials of multifunctional electronic components, microwave dielectric materials with superior dielectric properties at microwave frequencies have been considered to play a key role in the field of microwave electronic devices, such as dielectric substrates, resonators, radar, and Internet of Things (IoT), etc. [1–4]. Nowadays, low-temperature co-fired ceramics (LTCC) technology has attracted more and more attention because of the increasing demand of higher miniaturization and integration ability for modern microwave circuit system. However, whether microwave dielectric ceramics could be practically applied in the fabrication of LTCC devices depend upon the following essential requirements: high-permittivity ($\varepsilon_r$) values facilitate devices miniaturization, low dielectric-loss (great $Q\times f$, $Q = \tan \delta^{-1}$, $f = $ resonant frequency) values for a good frequency selectivity, near zero temperature coefficient of resonant frequency ($\tau_f$) values to ensure thermal stabilities, and the internal metallic electrodes (such as Al, Cu, Ag, etc.) could compatible with the studied dielectric materials at relatively low sintering temperatures [5,6]. At present, much more researches were focus on new findings about microwave dielectric ceramic systems [7–10], the improvements on properties by equivalent ion substitution [11–15] and the enhancements on sintering characteristics by adding sintering additives [16–18]. Especially, a great number of dielectric materials with low sintering temperatures, such as NaCa$_2$V$_2$O$_7$, 0.35Ag$_2$MoO$_4$-0.65Ag$_{0.5}$Bi$_{0.5}$MoO$_4$, SrMv$_2$O$_7$ (M = Mg, Zn), Li$_{1-x}$Z$_x$Na$_{0.6}$Sn$_{2.8}$O$_8$ ceramics, etc., might be promising candidates for LTCC applications [19–29].

Recently, it has been found that the new Li$_4$Mg$_3$Ti$_2$O$_9$ ceramics with rock salt structure have received enormous attention owing to the excellent microwave dielectric properties ($\varepsilon_r=15.97$, $Q\times f = 135,800$ GHz, and $\tau_f = -7.06$ ppm/°C) at 1450 °C [30]. Subsequently, the enhancement in dielectric properties of Li$_4$Mg$_3$Ti$_2$O$_9$ ceramics were successfully achieved by the partial isovalent complex ions of (Mg$_{1/3}$Ta$_{2/3}$)$_{4/3}$-co-substitution for tetravalent transition metal cations (Ti$^{IV}$), and the best $Q\times f$ of 160,575 GHz was obtained...
in Li₂Mg₃[Ti₀.₈(Mg₁₃Ta₂₃)₀₂]O₉ sample along with \( \tau_f = 15.77 \) and \( \tau_f = 0 \) ppm°C when sintered at 1550 °C for 4 h [31]. However, the sintering temperature is too high to satisfy the possible LTCC applications. In general, sintering aid, such as fluoride (BaF₂, SrF₂, and LiF, etc.), oxides (CuO, B₂O₃, SiO₂, etc.) with low melting points or glass (Li₂O–B₂O₃–SiO₂ (LBS), ZnO–B₂O₃–SiO₂ (ZBS), BaCuO(B₂O₃), etc.), are added to lower the higher sintering temperature of the matrix materials [32–37]. Among them, lithium fluoride (LiF) is an effective sintering additive to accelerate densification and to lower the sintering temperature of microwave dielectric materials due to its low melting point of 845 °C [32]. For example, Lai et al. observed the sintering temperature of the CaMgSi₂O₆ ceramics with monoclinc structure from 1250 °C to 900 °C with 2 wt% LiF [38]. 0.63Li₂Mg₂SnO₆·0.37Ba₃(VO₄)₂ ceramic by using 3 wt% LiF sintered at 850 °C for 6 h was reported with good properties of \( \varepsilon_r = 12.8 \), \( Q_f = 101,705 \) GHz and \( \tau_f = -2.9 \) ppm°C [39]. Furthermore, Zhang et al. discovered that 0.85Li₂Mg₁₃Ta₂₃O₉·0.15LiF ceramics exhibited an excellent combination of microwave dielectric (\( \varepsilon_r = 27.8 \), \( Q_f = 63,000 \) GHz, and \( \tau_f = -4.1 \) ppm°C) with sintering temperature of 850 °C [40].

To our best knowledge, the influences of LiF additives on sintering behavior and microwave dielectric properties of LMTₙ₀ₓ(MT)ₐ₂ solid solutions have not been reported up to now. Therefore, the improvement in sintering characteristics of LMTₙ₀ₓ(MT)ₐ₂ ceramics by selecting LiF as sintering aid, and the LMTₙ₀ₓ(MT)ₐ₂ + x wt% LiF samples (\( x = 1–5 \)) were prepared successfully through the solid-state route in the present study. The phase purity, sinterability, microstructures, densification, microwave dielectric properties and the chemical compatibility with silver electrode of the novel LiF-doped LMTₙ₀ₓ(MT)ₐ₂ ceramics also were investigated scientifically.

2. Experimental procedure

The LiF-doped LMTₙ₀ₓ(MT)ₐ₂ composite ceramics were prepared by solid-state process. High-purity starting materials Li₂CO₃ (99.99% metals basis, Aladdin), Ta₂O₅ (99.5% metals basis, Aladdin), MgO (AR, 98%, Macklin) and TiO₂ (99.8% metals basis, Macklin) were weighed according to the desired stoichiometric ratio of LMTₙ₀ₓ(MT)ₐ₂ compounds, and ball-milled using ZrO₂ balls for 24 h in anhydrous alcohol medium. Then all the dried slurries were calcined at 1050 °C for 2 h to form LMTₙ₀ₓ(MT)ₐ₂ phase. The powders were re-ground with different quantities (1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%) of LiF (99%, Aladdin) for 24 h, and dried at 80 °C once again. Afterwards, 8 wt% paraffin wax as the adhesion agent was added to the obtained mixture powders and then uniaxially pressed into green cylindrical samples with dimension of 10 mm and height of about 6 mm under a pressure of 200 MPa. Finally, these formed LMTₙ₀ₓ(MT)ₐ₂ + x wt% LiF (\( x = 1, 2, 3, 4 \) and 5) pellets were sintered at 800–1150 °C for 4 h in air after all specimens were pretreated at 500 °C for 4 h to remove the organic binder.

The phase constitutions of the sintered LMTₙ₀ₓ(MT)ₐ₂–x wt% LiF (\( 1 \leq x \leq 5 \)) ceramics were investigated in the 2-theta range from 30 ° to 100° to collect intensity data by means of X-ray powder diffractometer (XRD, 40 kV/40 mA) using Cu-Kα (\( \lambda = 1.542 \) A) radiation. The apparent densities (\( \rho_{app} \)) of as-sintered pellets were measured through liquid Archimedean method. Scanning electron microscopy (SEM, FEI Co., United States) equipped with X-MAX-50 type Energy Dispersive X-ray spectroscopy (EDXS) was employed to analyze the surface micro-structure and chemical compatibility of the sintered specimens. The \( \varepsilon_r \) and \( Q_f \) values in microwave frequencies ranging from 8.0 to 12.5 GHz were measured by Hakki–Coleman dielectric resonator method [41] using the N5234A-200 vector network analyzer (Agilent Co., USA) and TEO1d shielded cavity method [42], respectively. The \( \tau_f \) (ppm/°C) values were calculated on the basis of the following equation:

\[
\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \times 10^6 \text{ppm/°C}
\]

where, \( f_{85} \) and \( f_{25} \) denoted the resonant frequency at 85 °C and 25 °C, respectively.

3. Results and discussion

Fig. 1 presented the typical room temperature powder XRD diffraction patterns of LMTₙ₀ₓ(MT)ₐ₂ ceramics with different LiF doping contents (1–5 wt%) sintered at different temperatures for 4 h. It is visible from Fig. 1 that all the diffraction peaks were well indexed to the cubic-type LiFeO₂ (JCPDS#70-2711) phase structure. And no obvious impure phases were detected in the LiF-doped LMTₙ₀ₓ(MT)ₐ₂ ceramics, which indicated a single rock-salt crystaline phase with a space group Fm-3m (No. 225) in the prepared LMTₙ₀ₓ(MT)ₐ₂ with x wt% LiF (\( 1 \leq x \leq 5 \)) solid solution samples were successfully formed, which was corresponding to the results reported by Xing et al. [31]. No any LiF phase could be obviously detected except for the bottom phase peaks owing to the replacement of larger O²⁻ ion (ionic radius of 1.40 Å) with F⁻ ion (ionic radius of 1.33 Å), this similar phenomenon also could be found in LiF-doped LMS-CST system [43]. Notably, the angle 2θ position and intensity of the diffraction peaks did not change dramatically with the increase amount of LiF, which were considered that the crystal structure of the LMTₙ₀ₓ(MT)ₐ₂ ceramic matrix [31] did not change by introduction of LiF additives.

The variations in apparent densities of LMTₙ₀ₓ(MT)ₐ₂–x wt% LiF (\( 1 \leq x \leq 5 \)) ceramics as a function of sintering temperatures were shown in Fig. 2. The apparent densities of LiF-doped LMTₙ₀ₓ(MT)ₐ₂ ceramics exhibited an upward tendency at first, which was ascribed to the reduction of porosity caused by the formation of liquid phase during the sintering process, and then kept stable when the sintering temperature was further increased. For the LMTₙ₀ₓ(MT)ₐ₂ samples doped with 3–5 wt% LiF, the relatively saturation apparent density value of ~3.61 g/cm³ was obtained in the sintering temperature region of 950 °C–1050 °C, which was closed to the apparent density (around 3.60 g/cm³) of the matrix sintered at 1550 °C for 4 h [31]. Yet, the maximum apparent densities (2.93 g/cm³ for \( x = 1 \) and 3.40 g/cm³ for \( x = 2 \)) of the samples were lower.
than others, indicating that doping amount of 1–2 wt% LiF was not sufficient to promote the densification process of LMT0.8(MT)0.2 ceramics and has little contribution to reducing sintering temperature during sintering process. Therefore, it could be proved that adding appropriate LiF as a sintering additive is one of the effective methods for promoting the sintering characteristics of the LMT0.8(MT)0.2 ceramics at low temperature.

Fig. 3 illustrated the SEM micrographs of LMT0.8(MT)0.2-x wt% (1 ≤ x ≤ 5) LiF ceramics sintered at 950 °C for 4 h. As exhibited in Fig. 3 (a)–(b), it was clear that some intergranular pores existed on the surface of the sample accompanied by small grain size of approximately 1–2 μm, which indicated that a small amount of liquid phase resulted in the incomplete growth of grains. When 3–5 wt% LiF were added to the samples (Fig. 3 (c)–(e)), the compactness gradually increased and average grain sizes enlarged above 2 μm as well as more uniform, and the grain boundaries were also well defined, which could be attributed to LiF liquid phase promoted the growth of grains. Therefore, the moderate LiF addition could obtain a dense and uniform micro-structure with well-packed grains and significantly promote the sintering behaviors of LMT0.8(MT)0.2 ceramics, which were in accordance with the results of apparent densities.

Fig. 4 exhibited the curves of dielectric constants (εr) for LMT0.8(MT)0.2 ceramics with various LiF doping contents (1–5 wt%) sintered at 800–1150 °C. Generally, the εr values were mainly dependent on the secondary phases, grain boundaries, density and pores etc. extrinsic factors [44]. The formation of pure phase for all LiF-doped LMT0.8(MT)0.2 ceramics were confirmed through XRD patterns shown in Fig. 1. When LiF doping contents were larger than 3 wt%, the relative permittivity varied from 12.81 to 16.20 with the sintering temperature increased from 800 °C to 900 °C, then saturation value was observed in the range of 900 °C–1150 °C. For the LMT0.8(MT)0.2 specimens doped with 1–2 wt% LiF, the variations in εr values were not remarkable with rising in temperature,
and the maximum $\varepsilon_r$ values of 11.64 for $x = 1$ and of 14.78 for $x = 2$ all no more than the $\varepsilon_r$ values of above 3 wt% LiF additions, which was ascribed to the porous micro-structure shown in Fig. 3(a)–(b). It was obvious that the variation in dielectric constant was in good agreement with that of the change tendency in apparent density (Fig. 2). The higher density corresponded to higher dielectric constant, suggesting that density played a major factor in the $\varepsilon_r$ value. In addition, it was worth noting that the $\varepsilon_r$ value (16.10) of the 4 wt% LiF doped LMT$_{0.8}$(MT)$_{0.2}$ ceramic densified at 950 °C was quite closed to the $\varepsilon_r$ value (15.77) of the pure LMT$_{0.8}$(MT)$_{0.2}$ ceramic sintered at 1550 °C for 4 h [31].

Fig. 5 displayed the quality factors ($Q_f$) of LMT$_{0.8}$(MT)$_{0.2}$ samples with various amounts of LiF additives sintered at different temperature. In general, the $Q_f$ values at the microwave frequencies were greatly affected by both extrinsic factors and intrinsic factors. The extrinsic factors mainly arose from the second phases, compactness, oxygen vacancies, porosity, and grain sizes, while the intrinsic factors involved the structure characteristics and lattice vibration modes [45,46]. The variations of $Q_f$ had something to do with the extrinsic dielectric loss when lied in a region of lower vibration modes [47]. The dielectric loss of the LMT$_{0.8}$(MT)$_{0.2}$ ceramic by adding 2 wt% LiF was lower than that of previous work [31], which indicated the increase in dielectric loss of the LMT$_{0.8}$(MT)$_{0.2}$ samples led by the addition of LiF. Notably, the $Q_f$ values went up first with the increase of LiF doping, and the subsequent decreased with further increase of LiF content, implying that the quality factor was closely related to the quantity of LiF additive.

The microwave dielectric properties ($\varepsilon_r$, $Q_f$, $\tau_f$) of LMT$_{0.8}$(MT)$_{0.2}$-x wt% (1 ≤ x ≤ 5) ceramics sintered at optimum temperature were presented in Fig. 6. The dielectric constant increased from 11.38 at $x = 1$ to 16.10 at $x = 3$, and then stable value was observed at $x = 3$–5. Meanwhile, the lower $Q_f$ values of 22.342 GHz at $x = 1$ sharply increased to the peak values of 114.313 GHz at $x = 4$, then decreased to 103,003 GHz when LiF doping content exceeded 4 wt %. In particular, no obvious change was observed for the measured $\tau_f$ values with the increase of LiF addition, and varied from -4.54 to -9.32 ppm/°C, suggesting that the amount of LiF additives account for the $\tau_f$ values. Typically, LMT$_{0.8}$(MT)$_{0.2}$ ceramic with 4 wt% LiF sintered at 950 °C for 4 h exhibited good microwave dielectric properties of $\varepsilon_r = 16.10$, $Q_f = 114,313$ GHz and $\tau_f = -7.72$ ppm/°C.

In order to investigate the chemical compatibility with silver (Ag) electrode so that better serve for LTCC applications, XRD patterns of 4 wt% LiF-doped LMT$_{0.8}$(MT)$_{0.2}$ ceramic pellet co-fired with 20 wt% Ag powders (99.9%, Macklin, 10 μm) at 950 °C for 4 h were shown in Fig. 7. It was observed that the detectable diffraction patterns corresponded well to the standard card of LiFeO$_2$ (JCPDS#70-2711) and of Ag (JCPDS#04-0783), respectively. Besides, no existence of additional peaks in the range of 30–100°, indicating that no any chemical reaction taken place between the Ag and the LMT$_{0.8}$(MT)$_{0.2}$-4 wt% LiF ceramic. In addition, the SEM image of fracture surface and EDXS line scan were performed to analysis the interface between the 4 wt% LiF-doped LMT$_{0.8}$(MT)$_{0.2}$ ceramic sheet and the Ag coating co-fired at 950 °C, as shown in Fig. 8(a) and (b). The Ag profile increased sharply on the right side of the boundaries, which suggested that Ag did not spread into zone of LMT$_{0.8}$(MT)$_{0.2}$+x wt% LiF (x = 4) ceramics during co-fired. At the same time, these results were also further confirmed by the corresponding EDXS elemental mapping analysis (Fig. 8(c)–(g)). Hence,
the LMT$_{0.8}$($MT$)$_{0.2}$–4 wt% LiF ceramic is a suitable candidate for LTCC applications because of its outstanding microwave dielectric properties and good chemical compatibility with silver electrode.

4. Conclusion

A series of rock-salt structured LMT$_{0.8}$($MT$)$_{0.2}$+$x$ wt% LiF ($x$ = 1, 2, 3, 4, 5) ceramics were prepared by the solid-state reaction method at a low temperature. The formation of single crystalline phase with Fm-3m space group in experimental specimens was confirmed by the X-ray diffractometer. The compact samples with 3–5 wt% LiF sintered at 950 °C with homogeneous microstructures were characterized by scanning electron microscopy, indicated the appropriate content of LiF additive could obviously lower the densification sintering temperature of LMT$_{0.8}$($MT$)$_{0.2}$ ceramics to a certain extent. The optimal properties with $\varepsilon_r = 16.10$, $Q_f = 114,313$ GHz and $\tau_f = -7.72$ ppm/°C were achieved in LMT$_{0.8}$($MT$)$_{0.2}$ ceramics with 4 wt% LiF sintered at 950 °C. Furthermore, a good chemical compatibility with Ag electrodes made LMT$_{0.8}$($MT$)$_{0.2}$+4 wt% LiF ceramics as a promising candidate materials for LTCC applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

acquisition.

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References