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Microwave dielectric properties of low-fired Li_2TiO_3–MgO ceramics for LTCC applications

Jian-Li Ma[a], Zhi-Fen Fu[a,*], Peng Liu[b], Bing Wang[a], Yang Li[a]

[a] School of Science, Anhui University of Science and Technology, Huainan 232001, China
[b] College of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, China

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ABSTRACT

We fabricated the low-fired Li_2TiO_3–MgO ceramics doped with LiF by a conventional solid-state route, and investigated systematically their sintering characteristics, microstructures and microwave dielectric properties. The results showed that temperature stability of Li_2TiO_3 ceramics were improved by doping MgO. Well microwave dielectric properties for Li_2TiO_3–13 wt%MgO (LTM) ceramics with ε_r = 16.4, $Q \times f$ = 87,500 GHz, and τ_f = −1.2 ppm/°C were obtained at 1325 °C. Furthermore, addition of LiF enhanced the sinterability and optimized the microwave dielectric properties of LTM ceramics. A typically sample of LTM-4 wt%LiF ceramics with optimum dielectric properties (ε_r = 15.8, $Q \times f$ = 64,500 GHz, and τ_f = −0.2 ppm/°C) were achieved at 850 °C for 4 h. Such sample was compatible with Ag electrodes, suitable for the low-temperature co-fired ceramics (LTCC) applications.

1. Introduction

With the rapid development of modern microwave communication systems, high-quality microwave dielectric ceramics have attracted increasing research due to their potential application in mobile and satellite communication. Nowadays, the low-temperature co-fired ceramic (LTCC) applications has aroused considerable attention due to its advantage in enabling the fabrication of miniature modules by integrating electronic components and devices in a compact multilayer ceramic structure. The microwave dielectric materials used in LTCC field should have appropriate dielectric constant (ε_r), high $Q \times f$ value ($Q \times f \geq 5000$ GHz), a near-zero temperature coefficient of resonant frequency (τ_f), and co-fired with metal electrodes, such as Ag, Cu. Therefore, the lowering of the sintering temperature of ceramics would also have an ecological and economic impact due to a reduced consumption of electrical energy.

Recently, lithium based oxide ceramics Li_2MO_3 (M = Ti, Zr, Sn), Li_3MO_4 (M = Sb, Ta), and $Li_2ATi_3O_8$ (A = Mg, Zn) are very attractive subjects for materials research and engineering applications [1–3]. Among them, rock salt structure of Li_2TiO_3 ceramic received special attention due to its good dielectric properties: $\varepsilon_r \sim 22$, $Q \times f$ above 15,525 GHz, and τ_f = 20–38 ppm/°C [4]. However, its τ_f value is a little large and sintering temperatures (around 1200 °C) is too high to apply in LTCC. By forming a solid solution with MgO or ZnO, the quality factor of Li_2TiO_3 could be improved to about 100,000 GHz and a near-zero temperature coefficient of resonant frequency for $0.7Li_2TiO_3$–0.3MgO (ZnO) ceramics could also be obtained [5,6]. However, the high sintering temperature (1300–1325 °C) and the porous microstructure of Li_2TiO_3 based ceramics hindered their practical applications. In order to lower the sintering temperature, ultrafine nanopowders and glass frits such as H_3BO_3, and B_2O_3–CuO were usual used [1,7,8]. But the glassy phase with higher dielectric loss could be detrimental to the further enhancement of microwave dielectric properties. According to our previously work, Li_2TiO_3 ceramics were prepared at low temperature (1000 °C) by using low temperature synthesis nanopowders as a precursor [9]. Low melting fluorides such as LiF were reported to be effective as sintering flux in several microwave ceramic systems [10–13].

In this paper, we used MgO as an τ_f compensator and LiF as sintering aid for Li_2TiO_3 ceramics. The effects of MgO and LiF on the sintering characteristics, microstructures and microwave dielectric properties of Li_2TiO_3 ceramics were studied systematically, and found that the sinterability was enhanced and the microwave dielectric properties were optimized.

2. Experimental procedure

The Li_2TiO_3–13 wt%MgO–(0–6 wt%)LiF ceramics were prepared by a conventional solid-state route. Li_2CO_3 (98%, Guo-Yao Co. Ltd.,

* Corresponding authors.
E-mail address: fuzhifen80@sina.com (Z.-F. Fu).

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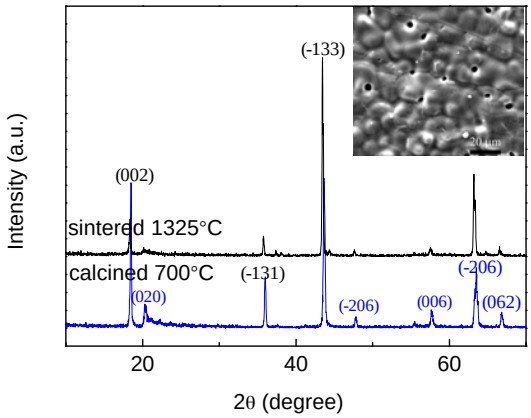

Fig. 1. The XRD pattern of the Li_2TiO_3 powders calcined at 700 °C, and the XRD pattern and SEM image of the LTM ceramics sintered at 1325 °C.

Shanghai, China), TiO_2 (99.99%, Guo-Yao Co. Ltd., Shanghai, China), MgO (99.99%, Guo-Yao Co. Ltd., Shanghai, China) and LiF (99.6%, Zhong-li Co. Ltd., Shanghai, China) powders were used as starting materials. Stoichiometric Li_2CO_3 and TiO_2 (total powders of 20 g) were mixed according to the formula of Li_2TiO_3 milled with ZrO_2 balls in ethanol (40 ml) for 8 h. Then the mixtures were dried and calcined at 700 °C for 5 h in air. The obtained Li_2TiO_3, MgO and LiF powders were weighed according to the designed molar ratios, ball-milled for 8 h, dried and sieved. Required the total powder to Ball wt% ratio is 1:20, and the size of the ball is 6 mm (twenty), 10 mm (ten) and 20 mm (two), respectively. Subsequently, the powders (the particle size at a scale of 4–10 μm) were granulated with 5 wt% PVA as binder and uniaxially pressed into cylindrical disks (11.5 mm in diameter and about 6 mm in height) under a pressure of 98 MPa. These pellets were sintered at 800–1350 °C for 4 h on alumina plates at a heating rate of 4 °C/min.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structures were analyzed using X-ray diffraction (XRD) with Cu K_α radiation (Rigaku D/MAX2550, Tokyo, Japan). The Raman spectra (RENIShaw in Via plus, UK) were excited with the 532 nm line of a semiconductor laser at a power of 250 mW and recorded in back-scattering geometry using In Via Raman Microscope equipped with a grating filter, enabling good stray light rejection in the 100–1000 cm^{-1} range. The microstructures were investigated using a scanning electron microscope (SEM, Quanta 200, FEI Company, Eindhoven, Holland) coupled with energy dispersive X-ray spectroscopy (EDS). The microwave dielectric properties of the specimens were measured using a network analyzer (ZVB20, Rohde & Schwarz, Munich, Germany) with the $TE_{01\delta}$ shielded cavity method. The temperature coefficient resonant frequency (τ_f) was calculated with the following formula:

$$\tau_f = \frac{(f_2 - f_1) \times 10^6}{f_1 (T_2 - T_1)} \quad (1)$$

where f_2 and f_1 represent the resonant frequency at T_2 and T_1, respectively. T_1 and T_2 are 20 °C and 80 °C, respectively.

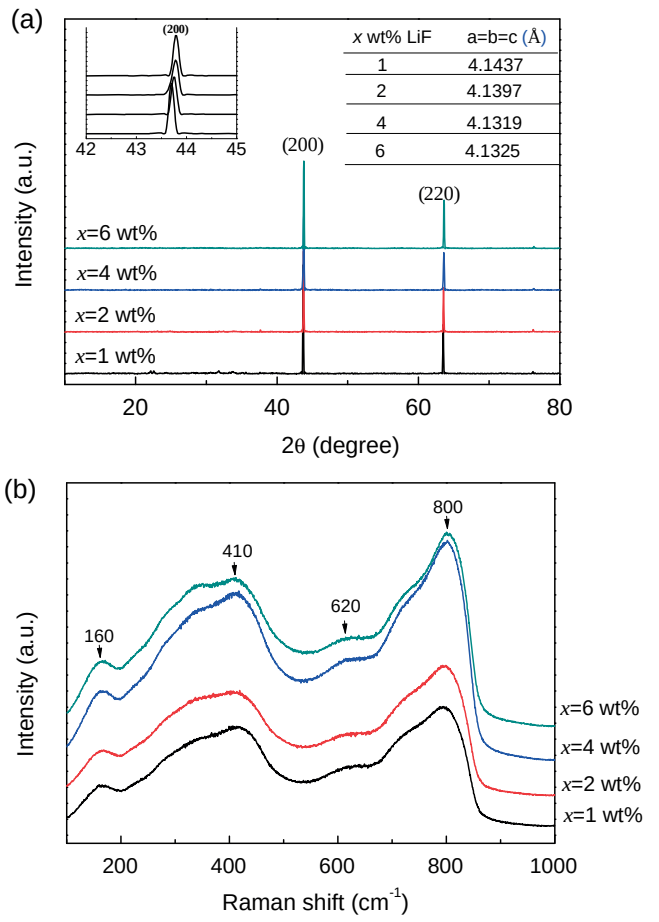

Fig. 2. (a) XRD patterns and (b) Raman spectras of *x* wt% LiF-doped LTM ceramics sintered at 850 °C as function of *x*. Inset of (a) is the profiles of (2 0 0) reflections and variation of the lattices constant of Li_2TiO_3.

3. Results and discussions

3.1. Li_2TiO_3–MgO system

Fig. 1 shows the XRD pattern of the Li_2TiO_3 powders calcined at 700 °C, and the XRD pattern and SEM image of Li_2TiO_3–13 wt% MgO (LTM) ceramic sintered at 1325 °C. The XRD pattern displays monoclinic structure (β-Li_2TiO_3 (ss), PDF# 33-0831) and no additional peaks are observed. The SEM image exhibits porous microstructure due to the volatilization of Li in the high temperature, the similar phenomenon was observed in Ref. [5]. Table 1 gives bulk density and microwave dielectric properties of LTM ceramics sintered at various temperatures. Bulk density increases with an increase in sintering temperatures, reaches a maximum (3.27 g/cm^3) at 1325 °C, and then decreased with a further increasing temperature.

Compared with Li_2TiO_3 ceramics, the higher densification temperature of MgO-doped ceramics was associated with the higher melting point of MgO [14]. The variation in ε_r and $Q \times f$ values with sintering temperatures is consistent with that of bulk density

Table 1
The density and microwave dielectric properties of LTM ceramics.

S.T. (°C)	Bulk density (g/cm^3)	Relative density	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
1250	3.05	87.9	15.2	71,800	2.1
1275	3.22	92.8	15.8	79,100	1.9
1300	3.24	93.3	16.1	84,300	1.8
1325	3.27	94.2	16.4	87,500	−1.2
1350	3.20	92.3	16.8	74,300	−2.3

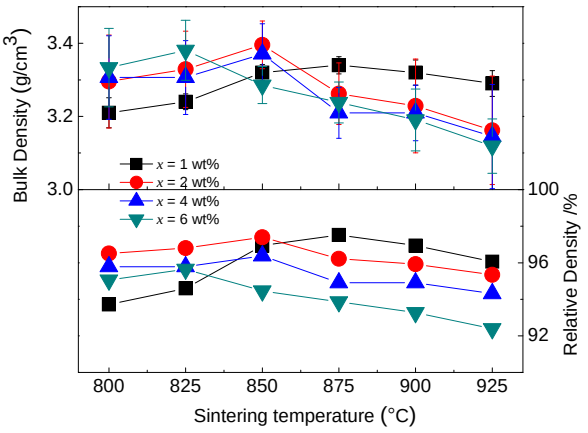

Fig. 3. The density of LTM ceramics doped with x wt% LiF as functions of sintering temperatures and x (including ± 3% error bars).

with sintering temperatures, which suggests that the density is the dominating factor to control ε_r and $Q \times f$ values in Li_2TiO_3–MgO ceramics. The τ_f values of the samples decreased from 2.1 to −2.3 ppm/°C continuously with increasing sintering temperatures. A well dielectric properties of $\varepsilon_r \sim 16.4$, $Q \times f \sim 87{,}500$ GHz, and $\tau_f = -1.2$ ppm/°C is obtained for LTM samples sintered at 1325 °C for 4 h, which is similar to reported in Li_2TiO_3–MgO [5].

3.2. Li_2TiO_3–MgO—LiF system

In order to decrease sintering temperatures to less than 950 °C for LTCC applications, LiF powders were added into LTM matrix. Fig. 2(a) presents the XRD patterns of LiF-doped LTM ceramics sintered at 850 °C. The XRD patterns exhibit disordered cubic phase (α-Li_2TiO_3 (ss), PDF# 03-1024), the similar transform of ordered monoclinic phase into disordered cubic phase was observed in Li_2TiO_3-LiF system [15]. No additional phases are detected. In the insert of Fig. 2(a), with increasing of LiF content, the intensity of (2 0 0) peak decreases implying that the disordering degree decreased. Furthermore, the peaks of (2 0 0) shift toward to a higher angle suggesting that the lattices constant of Li_2TiO_3 decreases with increasing of LiF content (x). It was reported that the LiF liquid phase is transient and would form substitutional solid solution with Li_2TiO_3 after sintering at 875 °C when content of LiF < 0.2 mol% (equivalently 5.2 wt%) [15]. So, the decreasing of lattices constant might be owing to the substitution of the F^- ion ($R = 1.33$ Å) for O^{2-} ($R = 1.4$ Å) sites, agreeing with Ref. [10]. The replacement mechanisms as following:

$$3LiF \xrightarrow{Li_2TiO_3} Li'''_{Ti} + 3F^{\bullet}_{O} + 2Li^{\times}_{Li} \quad (2)$$

According to Eq. (2), three F^- anions and one Li^+ ($R = 0.76$ Å) replaced three O^{2-} and one Ti^{4+} ($R = 0.605$ Å), respectively, resulting in lattice contraction. While LiF addition > 6 wt%, the lattices constant decrease, which is associated with that a large extent of liquid phase during sintering process inhibit the entrance or occupation of Li^+ and F^- in the Li_2TiO_3 lattice. Thus, just small amounts of F^- can be incorporated into Li_2TiO_3 lattice and the solid solubility limit of F^- in Li_2TiO_3 is about 4 wt%. Raman spectroscopy is more suitable than XRD to detect the local structure. Fig. 2(b) gives the Raman spectra of LiF-doped LTM ceramics sintered at 850 °C. All spectra exhibit similar Raman spectra at 160 cm^{-1}, 410 cm^{-1}, 620 cm^{-1} and 800 cm^{-1}. With increasing LiF content, the increase in intensity

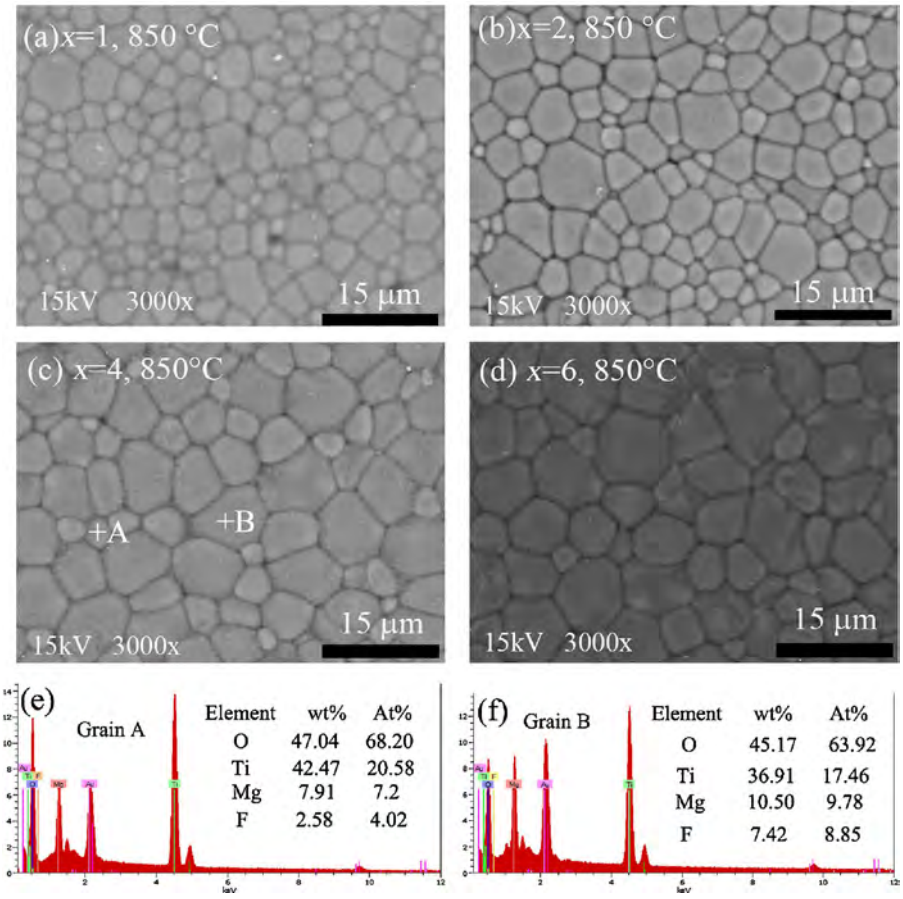

Fig. 4. (a–d) SEM images of x wt% LiF doped LTM ceramics sintered at 850 °C as function of x, and (e–f) the EDS datum of grain A and B.

of the Raman bands near 160 cm^{-1} and 800 cm^{-1} reveal that the disordering degree decreased with the increase of LiF content, which is in well agreement with that observed by XRD (Fig. 2(a)).

Fig. 3 summarizes bulk density of LiF-doped LTM ceramics as functions of sintering temperatures and x. The error is derived from the mean standard deviation and the error bars are plotted in Fig. 3. It can be seen that the densities increase with increasing sintering temperatures and then decrease after reaching their respective maximum values. Bulk density of specimens ($x \leq 4$) sintered at 825–875 °C are all above 3.27 ± 0.02 g/cm^3 (relative density of 96%), which is higher than those of pure LTM ceramics (relative density of 94%, Table 1). However, density decreases as increasing x, due to lower theoretical density of LiF (2.64 g/cm^3) than that of Li_2TiO_3 (3.42 g/cm^3). The densification temperature of sintered ceramics tends to decrease from 875 °C to 825 °C with increasing x from 1 to 6. It was obvious that additions LiF can not only successfully reduce sintering temperatures to below 875 °C but also improve densification.

The SEM images of LiF-doped LTM ceramics sintered at 850 °C are illustrated in Fig. 4(a)–(d). Compared with LTM ceramics (Fig. 1), it can be seen that LiF-doped LTM specimens show well-dense microstructure at 850 °C, which further confirmed the effectiveness of LiF in promoting the sintering behavior of Li_2TiO_3–MgO ceramics. With increasing x, the average grain size increases because of the elevated boundary diffusion coefficient. Furthermore, as shown in Fig. 4(e) and (f), a remarkable difference could be observed from the EDS analysis for the grains marked A and B. Compared with the grain A, the grain B shows much more content of F, indicating F^- ion can effectively promote grain growth. Two plausible explanations for this phenomenon are proposed here. One is that liquid phase is formed during the sintering process due to the lower melting point of LiF (845 °C). The presence of liquid phase significantly enhances the particle rearrangement and the mass transport by solution-precipitation. The other is that, the crystal defect induced by the substitution of smaller F^- for O^{2-}, as evidenced by XRD analysis, causes weakening of oxygen bond strength, which facilitates the diffusion process and thus reduces the intrinsic sintering temperatures. Since the F^- ion has a lower bonding energy and smaller ion radius compared with O^{2-}. The accurate determination of F^- ion occupation in the lattice which is crucial to the investigation of defects and grain growth deems necessary in the future.

Fig. 5(a–c) demonstrates microwave dielectric properties of samples sintered at various temperatures as functions of LiF additions. The error is derived from the mean standard deviation and the error bars are plotted in Fig. 5. As shown in Fig. 5(a), the variations in ε_r with sintering temperatures and x are consistent with that of bulk density, suggests that the density is the dominating factor to control ε_r in Li_2TiO_3–MgO ceramics. The dielectric constant of ceramic material is predominantly decided by the dipoles in unit cell volume and dielectric polarizabilities of ions [16]. To be specific, higher density exhibits higher ε_r value as a result of more dipoles and more apt to be polarized. Furthermore, the ε_r could be calculated according to the Clausius–Mossotti equation [16]:

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m + 4\pi\alpha_D} \quad (3)$$

where V_m is the molar volume and α_D is the sum of the dielectric polarizabilities of individual ions. In the Li_2TiO_3–MgO-LiF system, the substitution of F^- for O^{2-}, and Li^+ for Ti^{4+} would decrease α_D considering their relative polarizabilities [$\alpha(F^-) = 1.62$ Å^3, $\alpha(Li^+) = 1.2$ Å^3, $\alpha(O^{2-}) = 2.01$ Å^3, $\alpha(Ti^{4+}) = 2.93$ Å^3]. Thus, as illustrated in Fig. 5(a), the ε_r values decrease from 16.0 to 15.6 as increasing x due to the comparative lower dielectric polarizabilities of F^- and Li^+ than that of O^{2-} and Ti^{4+}, respectively. In Fig. 5(b), with increasing sintering temperatures and x, $Q \times f$ values increases and reaches a maximum value of 64,500 GHz at 850 °C for sample ($x = 4$), and then decreases. It is well known that dielectric loss is mainly caused not only by the lattice vibration modes, but also by impurities, second phase, pores, lattice defect, and grain boundary or grain morphology [17]. For slight amount of LiF doped samples, the increasing of $Q \times f$ values with increasing x was associated with uniform microstructures and a range of small grain sizes with a narrow distribution. In general, τ_f is well known to be influenced by the composition, the additive and the second phase of the materials [18]. It can be seen in Fig. 5(c), the τ_f value shows a continuous negative increase in magnitude as increasing LiF content. Through appropriate adjustment, a −0.2 ppm/°C of τ_f can be obtained for LTM-4 wt% LiF specimen sintered at 850 °C.

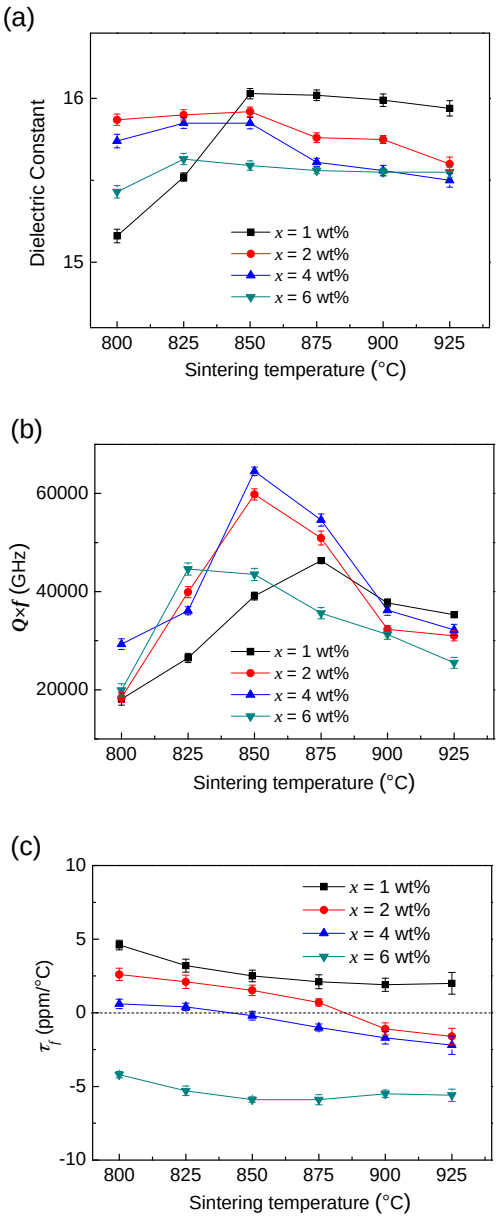

Fig. 5. Variation of microwave dielectric properties of x wt% LiF-doped LTM ceramics sintered at various temperatures with different LiF contents (including ± 2% error bars).

Fig. 6 presents the XRD pattern and SEM image of LTM-4 wt% LiF ceramics doped with 10 wt% silver (Ag) powders and sintered at 850 °C for 2 h. As is seen in Fig. 6, for the co-fired sample, only the peaks of Li_2TiO_3 phase and the respective metals (Ag) are observed. No additional peaks in the XRD patterns can be detected, implying

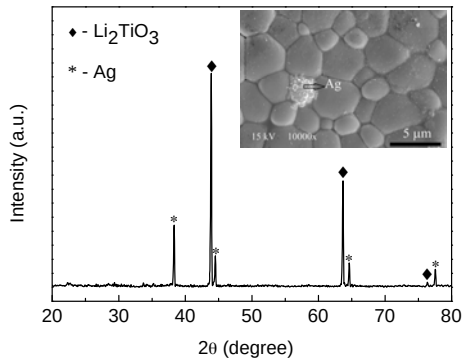

Fig. 6. The XRD pattern and SEM image of the LTM-4 wt% LiF ceramics doped with 10 wt% Ag powders sintered at 850 °C for 2 h.

that LTM composite ceramic does not react with Ag powder at 850 °C for 2 h. According to this, LiF doped LTM ceramics could be selected as suitable candidates for LTCC applications.

4. Conclusions

In this paper, the sintering characteristics, microstructures, and microwave dielectric properties of Li_2TiO_3–MgO ceramics doped with LiF were studied. The temperature stability of Li_2TiO_3 ceramics were improved by MgO additions, and a well microwave dielectric properties (ε_r = 16.4, $Q \times f$ = 87,500 GHz, and τ_f = −1.2 ppm/°C) for LTM samples were obtained at 1325 °C. Furthermore, addition of LiF successfully reduced sintering temperatures to below 875 °C and optimized the microwave dielectric properties. 4 wt% LiF doped LTM ceramics sintered at 850 °C exhibited the best microwave dielectric properties: ε_r = 15.8, $Q \times f$ = 64,500 GHz, τ_f = −0.2 ppm/°C. In addition, the chemical compatibilities of 4 wt% LiF doped composition with Ag powders were also investigated. No chemical reaction has taken place among the LTM-4 wt% LiF matrix and Ag powders after co-fired at 850 °C for 2 h. The low-temperature sintering ceramics powders are suitable for the LTCC applications.

Acknowledgments

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