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Low temperature sintering and microwave dielectric properties of $Li_6Mg_7Ti_3O_{16}$ ceramics with LiF additive for LTCC applications

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Abstract $Li_6Mg_7Ti_3O_{16}$ ceramics were prepared by the conventional solid-state method with 1–5 wt% LiF as the sintering aid. Effects of LiF additions on the phase compositions, sintering characteristics, micro-structures and microwave dielectric properties of $Li_6Mg_7Ti_3O_{16}$ ceramics were investigated. The LiF addition could effectively lower the sintering temperature of $Li_6Mg_7Ti_3O_{16}$ ceramics from 1550 to 900 °C. For different LiF-doped compositions, the optimum dielectric permittivity (ε_r) and quality factor ($Q{\cdot}f$) values first increased and then decreased with the increase of LiF contents, whereas the temperature coefficient of resonant frequency (τ_f) fluctuated between − 14.39 and − 8.21 ppm/°C. Typically, $Li_6Mg_7Ti_3O_{16}$ ceramics with 4 wt% LiF sintered at 900 °C exhibited excellent microwave dielectric properties of $\varepsilon_r = 16.17$, $Q{\cdot}f = 80{,}921$ GHz and $\tau_f = -8.21$ ppm/°C, which are promising materials for the low temperature co-fired ceramics applications.

1 Introduction

Low temperature co-fired ceramics (LTCC) technology has played an important role in the wireless communication system due to its advantage in low-cost and miniaturization of multilayer microwave devices [1–3]. In general, LTCC materials should meet some requirements: a low sintering temperature (below 960 °C), an appropriate ε_r, a high $Q{\cdot}f$ for the frequency selectivity, a near-zero τ_f for temperature stability and co-fired with metal electrodes (such as Ag and Cu) [4, 5]. Lowering the sintering temperature is a key issue to apply this technology. Generally speaking, there are several methods to reduce the sintering temperature: using the wet chemistry route [6, 7], searching for novel glass-free low-sintering dielectric ceramics [8, 9] and adding low melting temperature sintering aids [10, 11]. Adding sintering aids has been known to be the effective and cheap method. LiF is usually introduced to develop low-fired dielectric materials for LTCC applications. For example, 4 wt% LiF significantly lowered the sintering temperature from 1500 to 1600 °C to 900–975 °C for $Ba(Mg_{1/2}W_{1/2})O_3$ ceramics [12]. Besides, Yue et al. [13] reported that 0.6 wt% LiF doped $CaMg_{1-x}Zn_xSi_2O_6$ ceramics sintered at 900 °C possessed the excellent microwave dielectric properties of $\varepsilon_r = 7.7$, $Q{\cdot}f = 70{,}000$ GHz and $\tau_f = -25$ ppm/°C.

Recently, many compounds based on the Li_2O–MgO–TiO_2 systems have been investigated due to their excellent microwave dielectric properties [14–17]. For instance, Huang et al. reported that Li_2MgTiO_4 ceramics sintered at 1360 °C exhibited good microwave dielectric properties of $\varepsilon_r = 17.25$, $Q{\cdot}f = 97{,}300$ GHz and $\tau_f = -27.2$ ppm/°C [14]. Liu et al. reported that $Li_2Mg_3TiO_6$ ceramics sintered at 1280 °C exhibited excellent microwave dielectric properties of $\varepsilon_r = 15.2$, $Q{\cdot}f = 152{,}000$ GHz and $\tau_f = -39$ ppm/°C [15]. In addition, Bi et al. investigated the crystal structure of $Li_2Mg_4TiO_7$ phase and reported the excellent microwave dielectric properties of $\varepsilon_r = 13.43$, $Q{\cdot}f = 233{,}600$ GHz and $\tau_f = -7.24$ ppm/°C [16]. In our previous work, $Li_6Mg_7Ti_3O_{16}$ (LMT) ceramics sintered at 1550 °C exhibited excellent microwave dielectric properties of $\varepsilon_r = 15.27$, $Q{\cdot}f = 20{,}9416$ GHz and $\tau_f = -11.32$ ppm/°C [17]. However, the high sintering temperature would limit the application in LTCC devices. Therefore, it was significant to decrease the sintering temperature (below 960 °C). In this study, LiF was used to lower the sintering temperature of

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LMT ceramics and meet the requirements of LTCC applications. Effects of LiF additions on the phase compositions, sintering characteristics and microwave dielectric properties of LMT ceramics were investigated systematically.

2 Experimental procedure

LMT ceramics doped with 1–5 wt% LiF were prepared by the conventional solid-state method. High-purity powders of Li_2CO_3 (99.9%, Aladdin), MgO (99.99%, Aladdin), TiO_2 (99.8%, Aladdin) and LiF (99.9%, Aladdin) were used as raw materials. Firstly, the powders were weighed according to the stoichiometric ratio of LMT and ball-milled for 24 h in a nylon container. After drying, the mixed powders were calcined at 1100 °C in air to obtain LMT phase. Secondly, different weight percentages of LiF were added to the calcined powders. After re-milling and sieving, the powders mixed with 8 wt% wax were pressed into pellets of 10 mm in diameter and 5 mm in thickness under the pressure of 6 MPa. Finally, these pellets were heated at 500 °C for 4 h to eliminate the binder and then sintered at 800–1500 °C for 4 h with the heating rate of 5 °C/min.

Phase analysis of samples was conducted with the help of a Rigaku diffractometer using Ni filtered Cu Kα radiation (λ = 0.1542 nm) at 40 kV and 25 mA settings. The morphology of sintered samples was examined using a scanning electron microscopy. The apparent densities of the sintered samples were measured using Archimede's method. A network analyzer was used to measure the microwave dielectric properties. Dielectric constants were measured by exciting the TE_{011} resonant mode of dielectric resonator as suggested by Hakki-Coleman [18]. Unloaded quality factors were measured using $TE_{01\delta}$ mode by the cavity method [19]. The temperature coefficient of the resonant frequency was calculated from data collected in the temperature range of 25–85 °C based on the following equation.

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

where f_1 and f_2 are the resonant frequencies at the temperature of T_1 and T_2, individually.

3 Results and discussion

Figure 1 shows XRD patterns of LMT ceramics doped with 1–5 wt% LiF sintered at optimum temperatures for 4 h. The main peaks can be indexed to be the cubic rock-salt structure (JCPDS PDF#39–0932) with Fm-3m (No. 225) space group. With the increase of LiF contents, the main peaks (200) shift toward higher angle due to the substitution of

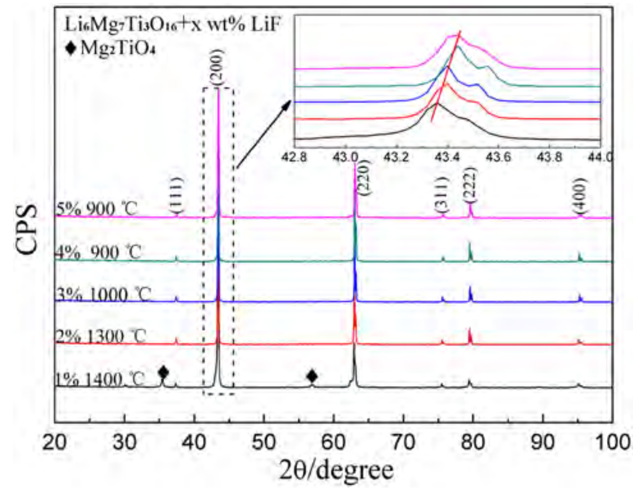

Fig. 1 XRD patterns of $Li_6Mg_7Ti_3O_{16}$ ceramics doped with 1–5 wt% LiF sintered at the optimum temperatures for 4 h

F^- (R = 1.33 Å) for O^{2-} (R = 1.40 Å) sites. Similar phenomena were reported in other ceramics [15, 20]. When 1 wt% LiF is doped into the samples, a small amount of Mg_2TiO_4 phase (JCPDS PDF#25-1157) is detected, which may be attributed to the volatilization of Li element at the high temperatures [21]. With the increase of LiF additions from 2 to 5 wt%, a single phase LMT is synthesized at respective optimal sintering temperatures. The results may be explained by the reason that the sintering temperatures decrease significantly and the volatilization of the Li element becomes weakened with the increase of the LiF addition. It can be concluded that the LiF addition contributes to reduce the sintering temperature and inhibit the appearance of Mg_2TiO_4, which is conducive to the improvement of performances.

Apparent densities of LMT ceramics doped with different LiF contents sintered at 800–1500 °C are exhibited in Fig. 2. It can be observed that the apparent densities of the samples doped with 1 wt% LiF increase with the increase of the sintering temperatures from 1000 to 1500 °C and the samples doped with 2 wt% LiF exhibit no obvious change. However, with the increase of the sintering temperatures, the apparent densities of the samples doped with 3–5 wt% LiF increase to a maximum value and thereafter slightly decrease. At the sintering temperatures of 850–1000 °C, the maximum values can be obtained for ceramics doped with 3–5 wt% LiF. It is difficult to densify samples doped with 1–2% LiF at the relatively low temperatures (< 1000 °C), which may be explained by the Li volatilization. So, it can be concluded that a small quantity of LiF additions can effectively lower the sintering temperature to 900 °C.

Figure 3 illustrates SEM images of LMT ceramics doped with 1–5 wt% LiF sintered at optimum temperatures. Ceramics possess lots of pores and the grain boundaries become vague in Fig. 3a–c. The pores may be due to

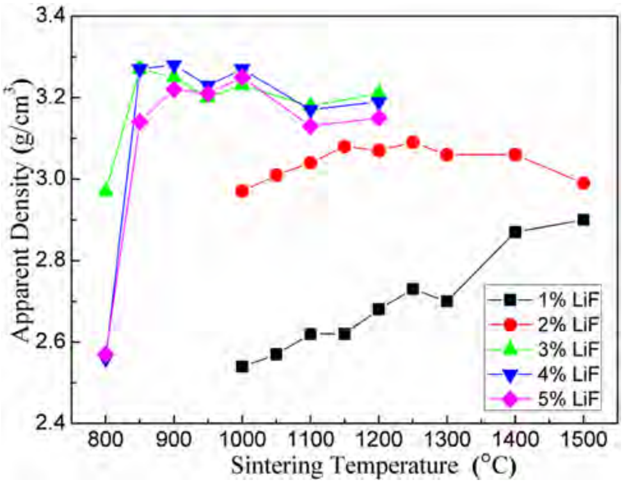

Fig. 2 Apparent density of $Li_6Mg_7Ti_3O_{16}$ ceramics doped with different LiF contents sintered at 800–1500 °C

the volatilization of Li element and melting grain boundaries can be explained by the high temperatures. As LiF contents increase to 4 wt%, the grain boundaries become clear gradually and the grains exhibit uniformity in Fig. 3d. When LiF contents increases to 5 wt%, the grain boundaries become vague. This phenomenon will produce adverse effects on microwave dielectric properties. LiF possess a low melting point (845 °C) and liquid phase is formed during the sintering, which enhances grain boundary mass transport significantly. Moreover, the substitution of smaller F^- for O^{2-} weaken the oxygen bond strength, which facilitates the diffusion process and thus reduces the intrinsic sintering temperature [15]. Therefore, appropriate LiF is conducive to the decrease of the sintering temperatures.

ε_r values of LMT ceramics doped with 1–5 wt% LiF sintered at 800–1500 °C are given in Fig. 4. It has been reported that ε_r values are dependent on the density, dielectric polarizabilities and structural characteristics [22, 23]. In our study, ε_r values of the samples doped with 1–2 wt% LiF increase with the increase of the sintering temperature from 1000 to 1500 °C, which can be explained by the decrease of the pores. ε_r values of the sintered samples doped with 3–5 wt% LiF increase to the maximum values and thereafter slightly decrease with the increase of the sintering temperatures from 800 to 1200 °C. The increase of ε_r values is due to the decrease of pores and the decrease may be explained by the abnormal grain growth [24]. The ε_r values show the similar tendency with the apparent densities. The maximum values can be obtained for the ceramics doped with 3–5 wt% LiF sintered at 900–1000 °C. Based on the above analysis, it can be concluded that the density plays an important effect on the ε_r values.

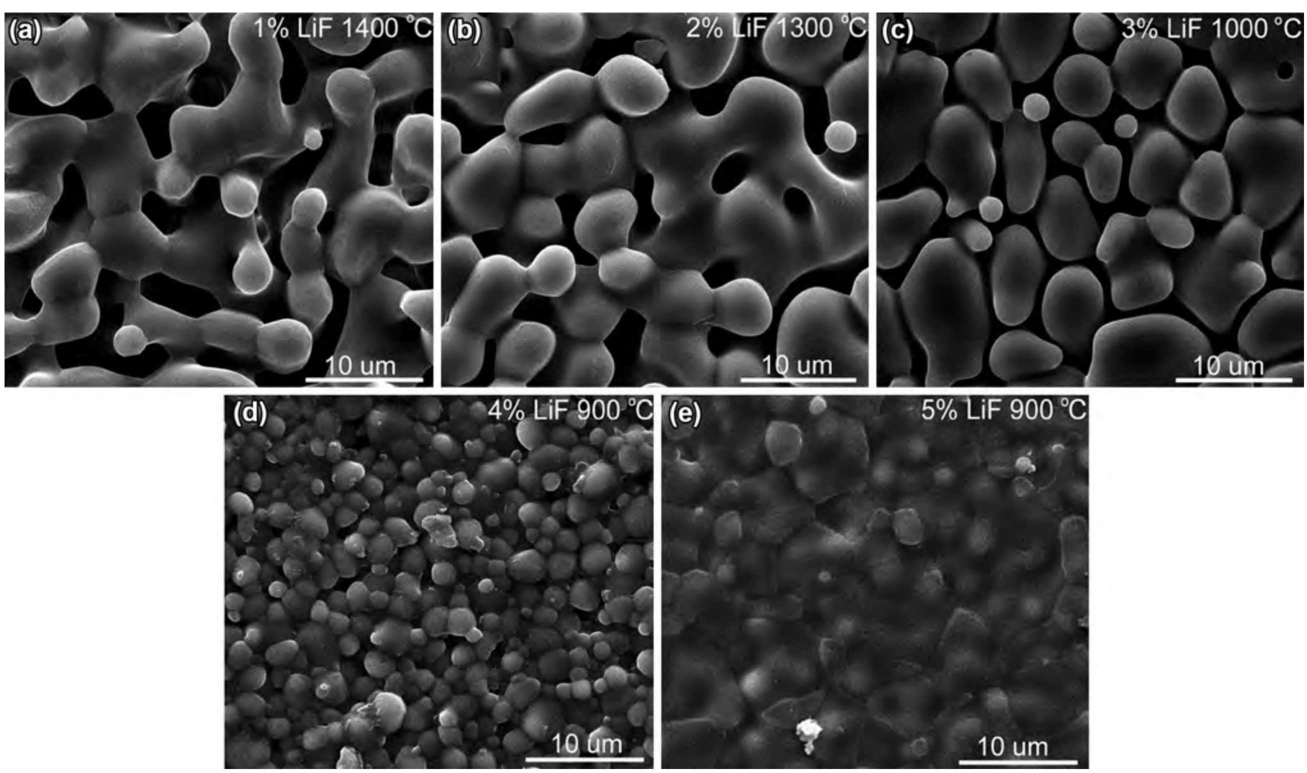

Fig. 3 SEM micro-graphs of $Li_6Mg_7Ti_3O_{16}$ ceramics doped with 1–5 wt% LiF sintered at the optimum temperatures

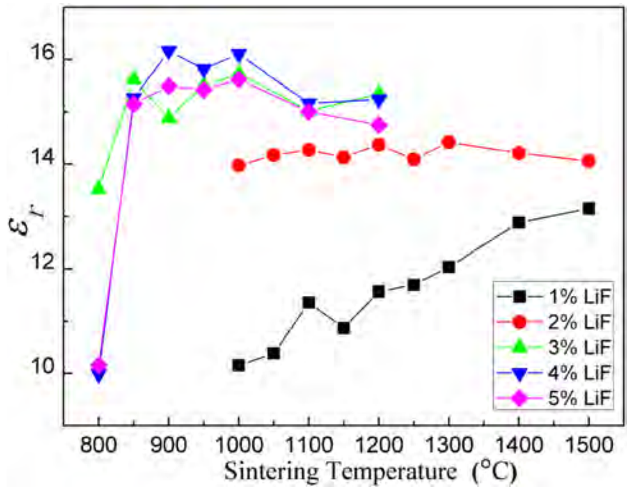

Fig. 4 ε_r values of $Li_6Mg_7Ti_3O_{16}$ ceramics doped with 1–5 wt% LiF sintered at 800–1500 °C

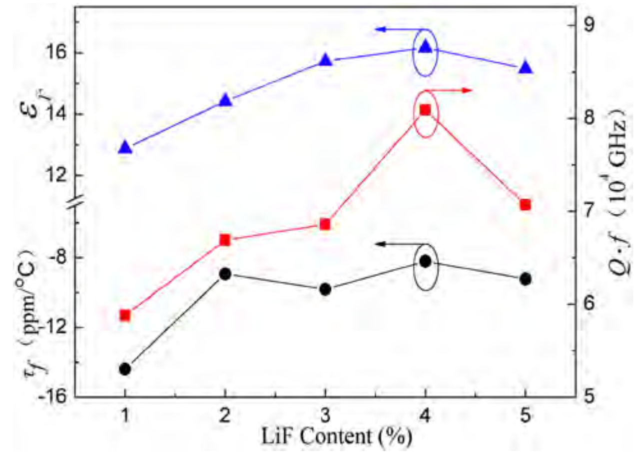

Fig. 6 Microwave dielectric properties of $Li_6Mg_7Ti_3O_{16}$ ceramics doped with 1–5 wt% LiF sintered at the optimum temperatures

Figure 5 shows $Q{\cdot}f$ values of LMT ceramics doped with 1–5 wt% LiF sintered at 800–1500 °C. It has been reported that $Q{\cdot}f$ values are dependent on the density, impurity, secondary phase, grain size and crystal structure, etc. [22, 23]. In this work, $Q{\cdot}f$ values of the ceramics doped with 1–5 wt% LiF show the similar tendency that $Q{\cdot}f$ values increase to the maximum values and thereafter slightly decrease. The increase of $Q{\cdot}f$ values is because of the decrease of the pores and the decrease may be explained by the abnormal grain growth [24]. The optimum temperatures of ceramics doped with 1–5 wt% LiF are 1400, 1300, 1000 and 900 °C, individually. In addition, the curves of $Q{\cdot}f$ values show the similar tendencies with those of the apparent densities and ε_r values, which portends that the density plays an important effect on $Q{\cdot}f$ values.

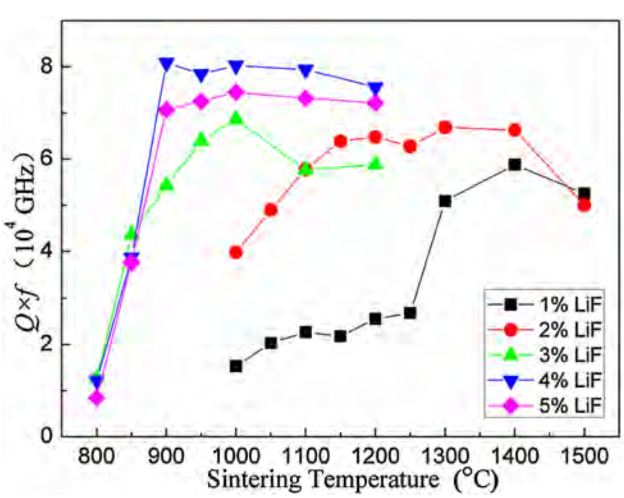

Fig. 5 $Q{\cdot}f$ values of $Li_6Mg_7Ti_3O_{16}$ ceramics doped with 1–5 wt% LiF sintered at 800–1500 °C

Microwave dielectric properties of LMT ceramics doped with 1–5 wt% LiF sintered at the optimum temperatures are exhibited in Fig. 6. With the increase of the LiF additions from 1 to 5 wt%, ε_r values first increase and then decrease. The increase attributes to the decrease of pores and the decrease of ε_r values can be explained by the excessive LiF and abnormal grain growth. $Q{\cdot}f$ values exhibit first increase and then decrease. The increase of $Q{\cdot}f$ values attributes to the growth of grains and decrease of Mg_2TiO_4 phase. The decrease of $Q{\cdot}f$ values may be caused by the excessive LiF and abnormal grain growth. Figure 6 also exhibits that τ_f values fluctuate around −9 ppm/°C. LMT ceramics doped with 4 wt% LiF sintered at 900 °C possess the excellent microwave dielectric properties of $\varepsilon_r = 16.17$, $Q{\cdot}f = 80{,}921$ GHz and $\tau_f = -8.21$ ppm/°C.

4 Conclusions

In this paper, the phase compositions, sintering characteristics, micro-structures and microwave dielectric properties of LMT ceramics doped with 1–5 wt% LiF were studied in detail. The results showed that density played an important role in influencing the microwave dielectric properties. A small quantity of LiF additions could effectively reduce the sintering temperatures to 900 °C. LMT ceramics doped with 4 wt% LiF sintered at 900 °C exhibited the excellent microwave dielectric properties of $\varepsilon_r = 16.17$, $Q{\cdot}f = 80{,}921$ GHz and $\tau_f = -8.21$ ppm/°C.

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