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Microwave dielectric properties of $Li_2Mg_3ZrO_6$ ceramics doped with LiF for LTCC applications

L. Cheng[1] · H. L. Pan[1] · M. F. Li[1] · F. Ling[1] · H. T. Wu[1]

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Abstract $Li_2Mg_3ZrO_6$ (LMZ) ceramics doped with 1–5 wt% LiF were prepared by the conventional solid-state reaction method. The influences of LiF addition on the phase compositions, micro-structure, sintering behavior and microwave dielectric properties of LMZ ceramics were explored. A small quantity of LiF addition could obviously reduce the sintering temperature to 950 °C while maintaining the excellent dielectric properties. The optimized quality factor values for different doping components firstly increased and then decreased with the increase of the LiF content, whereas the optimized dielectric permittivity increased with the increase of the LiF content. LMZ ceramics sintered at 950 °C doped with 4 wt% LiF additives possessed the excellent microwave dielectric properties of $\varepsilon_r = 12.66$, $Q{\cdot}f = 89{,}325$ GHz and $\tau_f = -14.46$ ppm/°C, which demonstrated that the materials were promising for the low temperature co-fired ceramics applications.

1 Introduction

Due to the rapid development of miniaturized multi-layer microwave devices, low temperature co-fired ceramics (LTCC) technology has obtained much attention in electronic industries and modern wireless communication systems [1–3]. LTCC should meet some requirements: a low sintering temperature (below melting points of Ag, Cu, etc.), a high quality factor ($Q{\cdot}f$), an appropriate dielectric permittivity (ε_r), a near-zero temperature coefficient of resonant frequency (τ_f) and a good chemical compatibility [4, 5]. How to decrease the sintering temperature is a key issue in applying this technology. Generally speaking, there are several methods to lower the sintering temperature, such as using ultra fine particles as raw materials [6], searching for novel glass-free low-sintering dielectric ceramics [7, 8] and adding low melting temperature sintering aids [9, 10]. Adding sintering aids has been known to be the effective and cheap method and LiF is usually introduced to develop low-fired dielectric materials for LTCC applications. For instance, 4 wt% LiF doped $Ba(Mg_{1/2}W_{1/2})O_3$ ceramics significantly decreased the sintering temperatures from 1500–1600 to 900–975 °C [11]. Besides, Yue and colleagues [12] reported that 2 wt% LiF doped Mg_2SiO_4 ceramics sintered at 800 °C possessed the excellent microwave dielectric properties of $\varepsilon_r = 6.81$, $Q{\cdot}f = 167{,}000$ GHz and $\tau_f = -47.9$ ppm/°C.

Recently, LMZ ceramics have received a lot of attentions due to their excellent microwave dielectric properties [13–15]. For example, the superior microwave dielectric properties of $Li_2Mg_3ZrO_6$ ceramics sintered at 1380 °C were $\varepsilon_r = 12.6$, $Q{\cdot}f = 86{,}000$ GHz and $\tau_f = -36$ ppm/°C, which was reported by Liu and colleagues [13]. Subsequently, Zuo and colleagues [14] researched the atmosphere-controlled sintering of $Li_{2(1+x)}Mg_3ZrO_6$ ceramics and reported the desirable microwave dielectric properties $\varepsilon_r = 12.8$, $Q{\cdot}f = 307{,}319$ GHz and $\tau_f = -35$ ppm/°C for $Li_{2.12}Mg_3ZrO_6$ ceramics sintered at 1275 °C. In our earlier work [15], the correlations between the crystal structure and microwave dielectric properties of LMZ ceramics were investigated, and the optimal microwave properties of $\varepsilon_r = 12.17$, $Q{\cdot}f = 113{,}000$ GHz and $\tau_f = -17.13$ ppm/°C were reported. therefore, the focus of our research was further on finding new attempts to decrease their sintering temperature below 961 °C (the melting point of Ag) for

✉ H. T. Wu
mse_wuht@ujn.edu.cn

1 School of Materials Science and Engineering, University of Jinan, Jinan 250022, China

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their applications in LTCC microwave devices. In our current study, LiF was selected as the sintering aid to decrease the sintering temperature of LMZ ceramics. Afterwards, the effects of LiF additions on the sintering behavior, micro-structure, phase compositions and microwave dielectric properties of LMZ ceramics were investigated systematically.

2 Experimental procedure

LMZ ceramics were prepared by the conventional solid state method. High purity powders of LiF (99%, Aladdin), MgO (99.99%, Aladdin), ZrO_2 (99.99%, Aladdin) and Li_2CO_3 (99.99%, Aladdin) were used as starting materials. The powders were weighed according to the stoichiometric amount of raw materials and ball milled for 24 h in a nylon container using ethanol as the grinding medium. The resultant slurry was dried, and then calcined at 1000 °C for 4 h in air. The calcined powders mixed with different weight percentages of LiF were ground again. After re-milling and sieving, the powders together with 8 wt% wax were pressed into pellets of 10 mm in diameter and 5 mm in thickness under the pressure of 6 MPa. These pellets were heated at 500 °C for 4 h to expel the binder and then sintered at 800–1300 °C for 4 h.

Crystallization phase of the sintered samples was identified by X-ray diffraction (XRD) using Ni filtered CuKα radiation (λ = 0.1542 nm) at 40 kV and 25 mA settings. A scanning electron microscopy was utilized to observe the surface morphology of the sintered samples. The apparent densities of the sintered samples were measured employing Archimede's method. A network analyzer was used for characterizing the microwave dielectric properties. The dielectric constant and the unloaded quality factor of the samples were measured through Hakki and Coleman post resonator and resonant cavity methods [16, 17], respectively. The temperature coefficient of the resonant frequency was measured by noting the variation of TE_{01d} mode frequency and calculated from data collected in the temperature range of 25–85 °C according to the following equation.

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

where f_1 is the resonant frequency at temperature T_1 and f_2 at temperature T_2.

3 Results and discussion

Figure 1 shows the XRD patterns of LMZ ceramics doped with 1–5 wt% LiF sintered at optimum temperatures for 4 h. The main phase can be confirmed as the cubic rock salt structure (JCPDS PDF#70-2711) with space group Fm-3m (No. 225). When the sintered samples doped with 1–2 wt% LiF, a small amount of ZrO_2 (JCPDS PDF#88-2390) is discovered, which may be attributed to the volatilization of Li element at the high temperature [18]. The appearance of ZrO_2 phase would engender a detrimental impact on the microwave dielectric properties, which is consistent with the results reported by Fu et al. [13]. With the increase of the LiF addition from 2 to 5 wt%, a single phase LMZ is synthesized at respective optimal sintering temperatures, and no obvious changes are observed. The results may be explained by the reason that the sintering temperatures decrease significantly and the volatilization of Li element becomes weakened with the increase of the LiF addition. It can be concluded that LiF addition is conducive to reduce the sintering temperature and inhibit the appearance of the ZrO_2 phase, which is valuable for the improvement of microwave dielectric properties.

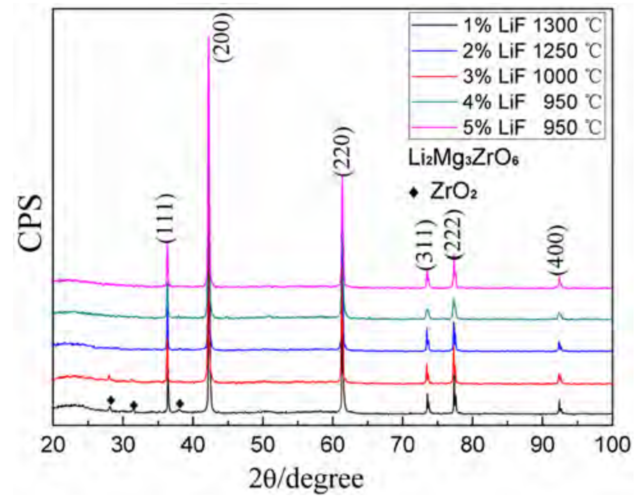

Fig. 1 XRD patterns of $Li_2Mg_3ZrO_6$ ceramics doped with 1–5 wt% LiF sintered at the optimum temperatures for 4 h

Apparent densities of LMZ ceramics doped with different LiF contents sintered at 800–1300 °C are exhibited in Fig. 2. It can be observed that the apparent densities of the samples doped with 1–2 wt% LiF increase as the sintering temperatures increase from 950 to 1300 °C. However, with the increase of the sintering temperatures from 800 to 1050 °C, 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 950–1000 °C, the maximum value can be obtained for ceramics doped with 3–5 wt% LiF. It is difficult to densify a sample doped with 1–2% LiF at a relatively low temperature (<1000 °C), which may be explained by the volatilization of Li element. So, it can be concluded that a small

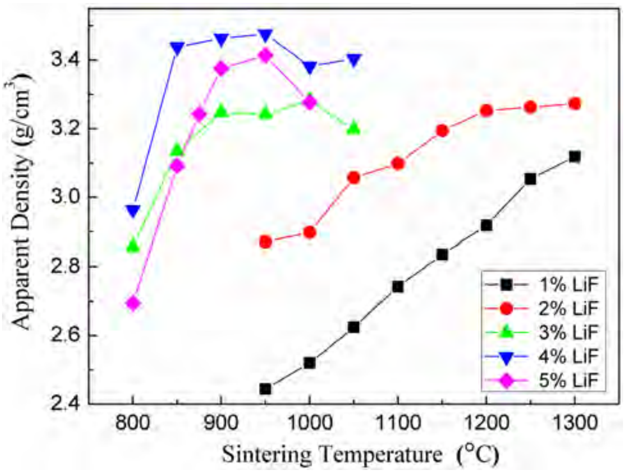

Fig. 2 Apparent density of $Li_2Mg_3ZrO_6$ ceramics doped with different LiF content sintered at 800–1300 °C

quantity of LiF addition can effectively lower the sintering temperature to 950 °C.

Figure 3 displays the SEM micro-graphs of LMZ ceramics doped with 1–5 wt% LiF sintered at optimum temperatures. As the Fig. 3a–b show, the ceramics possess lots of pores and the grain boundaries become blurred. The pores may be explained by the volatilization of Li element, and the melting grain boundaries can be interpreted by the high temperature. As the LiF content increases to 4 wt%, the grain boundaries become clear gradually, of which the sizes exhibit uniformity as shown in Fig. 3d. As the LiF content increases to 5 wt%, an excessive of LiF can be found on the grain surface as shown in Fig. 3e, which would produce negative influence on the microwave dielectric properties. LiF possess a low melting point of 845 °C and liquid phase is formed during the sintering, which enhances grain boundary mass transport significantly. Therefore, adequate LiF is conducive to the decrease of the sintering temperature. It can be concluded that LMZ ceramics doped with 4 wt% LiF reach the best state with the increase of the LiF content, which implies the optimal microwave dielectric properties.

ε_r values of LMZ ceramics doped with 1–5 wt% LiF sintered at 800–1300 °C are given in Fig. 4 It is reported that ε_r values are dependent on the density, dielectric polarizabilities and structural characteristics [19, 20]. In our study, the ε_r value of the sample doped with 1–2 wt% LiF increases with the increase of the sintering temperature from 950 to 1300 °C, which can be interpreted by the decrease of the porosity. The ε_r values of sintered samples doped with 3–5 wt% LiF increase to a maximum value and thereafter slightly decrease with the increase of the sintering temperatures from 800 to 1050 °C. The increase of ε_r values

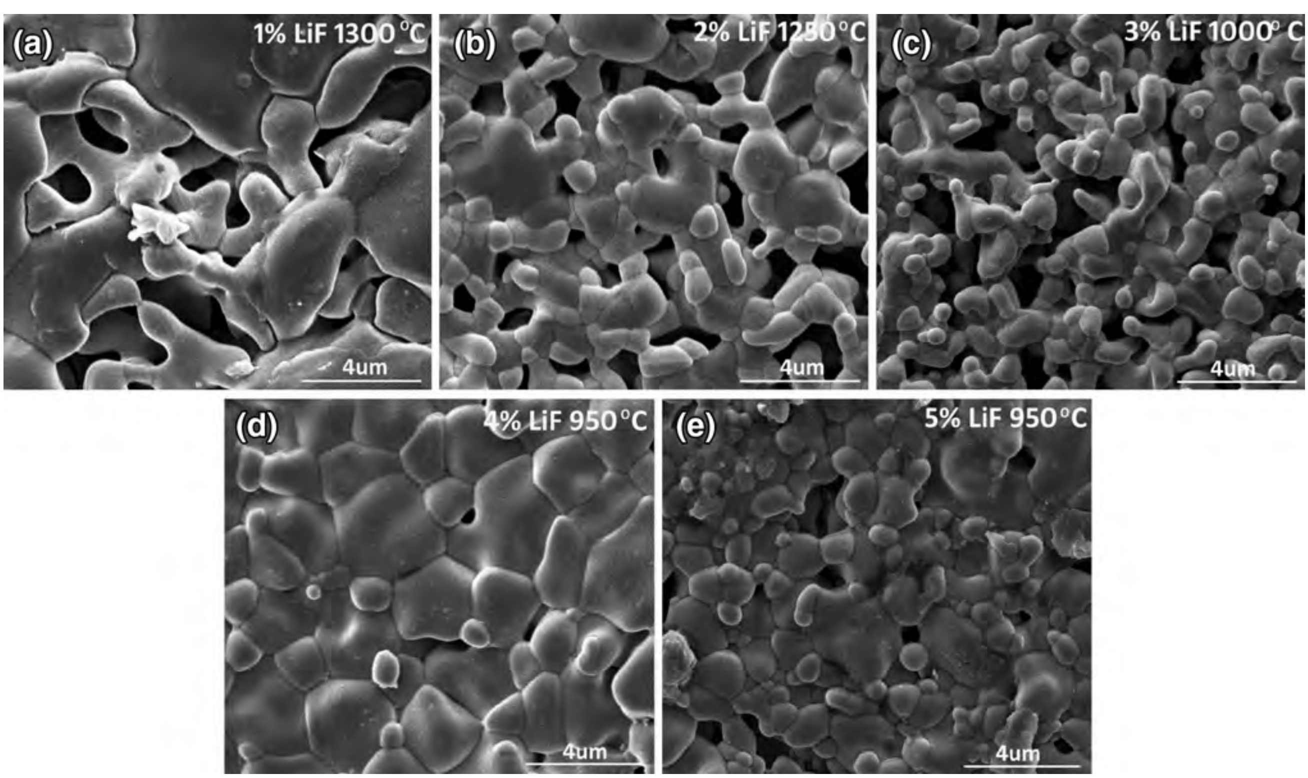

Fig. 3 SEM micrographs of $Li_2Mg_3ZrO_6$ ceramics doped with 1–5 wt% LiF sintered at optimum temperatures

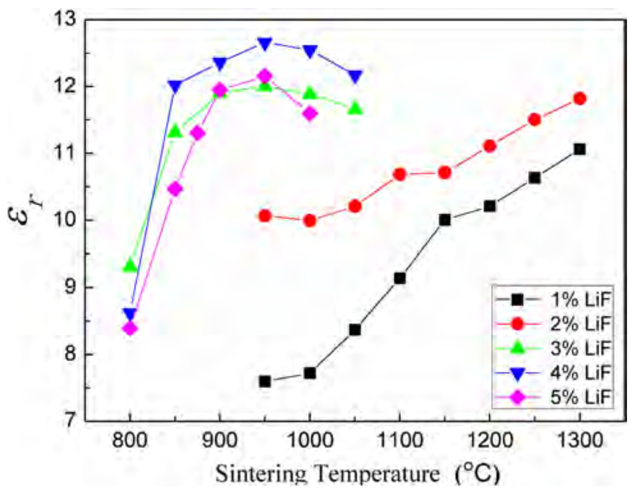

Fig. 4 ε_r values of the ceramics doped with 1–5 wt% LiF sintered at 800–1300 °C

are due to the decrease in the number of pores and the decrease may be explained by the abnormal grain growth [21]. The curves of ε_r values show a similar tendency with those of the apparent densities. The maximum value can be obtained for the ceramics doped with 3–5 wt% LiF sintered at 950 °C. Through the above analysis, it can be concluded that the density plays an important effect on the ε_r values.

Figure 5 illustrates $Q{\cdot}f$ values of the ceramics doped with 1–4 wt% LiF sintered at 800–1400 °C. It has been reported that $Q{\cdot}f$ are depended on the density, impurity, secondary phase and grain size [19, 20]. In this work, the $Q{\cdot}f$ values of LMZ ceramics doped with 1–2 wt% LiF show the increasing trend with the increase of the sintered temperatures from 950 to 1300 °C, which can be interpreted by the decrease of the pores. The $Q{\cdot}f$ values of the ceramics doped with 3–5 wt% LiF show the similar tendency that the $Q{\cdot}f$ values increase to a maximum value and thereafter slightly decrease. The increase of $Q{\cdot}f$ values are due to the decline of the pores and the decrease may be explained by the abnormal grain growth [21]. The optimum temperatures of ceramics doped with 3–5 wt% LiF are 1000–950 °C, individually. In addition, the curves of $Q{\cdot}f$ values show a similar tendency with those of the apparent densities and ε_r values, which portend that the density plays an important effect on the $Q{\cdot}f$ values.

The microwave dielectric properties of LMZ ceramics doped with 1–5 wt% LiF sintered at the optimum temperature are exhibited in Fig. 6. With the increase of the LiF addition from 1 to 5 wt%, the ε_r values firstly increase and then decrease, the increase could be attributed that liquid phase was formed during the sintering process which enhances grain boundary mass transport significantly and then increased the density. The decrease of ε_r values can be caused by the excessive LiF and the abnormal grain growth. $Q{\cdot}f$ values exhibit firstly increase and then decrease. The increase of $Q{\cdot}f$ values attribute to the increase of the apparent densities and the decrease of ZrO_2 phase. The decrease of $Q{\cdot}f$ values may be caused by the excessive LiF and the abnormal grain growth. The maximum value is 89,325 GHz for the LMZ ceramics doped with 4 wt% LiF sintered at 950 °C, which is more than the value of the previous report [13]. The main cause is that no second phase is produced compared with earlier report. Figure 6 also exhibits the variety of τ_f values, which fluctuates around −18 ppm/°C. LMZ ceramics doped with 4 wt% LiF sintered at 950 °C possess the excellent microwave dielectric properties of $\varepsilon_r = 12.66$, $Q{\cdot}f = 89{,}325$ GHz and $\tau_f = -14.46$ ppm/°C.

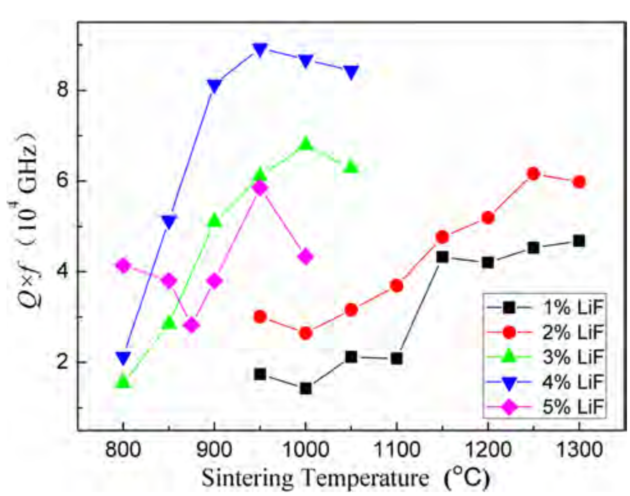

Fig. 5 $Q{\cdot}f$ values of the ceramics doped with 1–5 wt% LiF sintered at 800–1300 °C

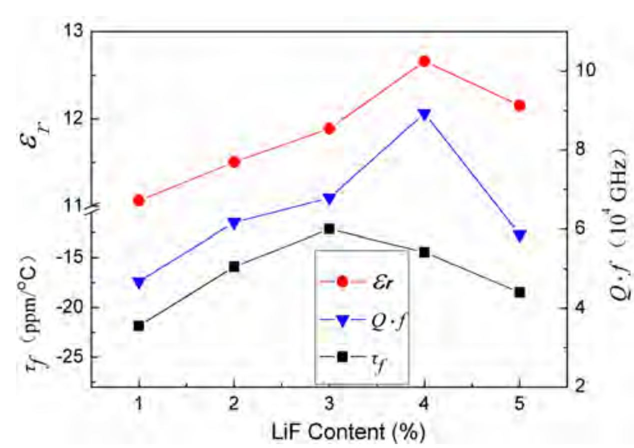

Fig. 6 Microwave dielectric properties of ceramics doped with 1–5 wt% LiF sintered at the optimum temperatures

4 Conclusion

In this paper, the phase compositions, sintering characteristics, micro-structures as well as microwave dielectric properties of LMZ ceramics doped with 1–5 wt% LiF were studied in detail. The results showed that density played an important role in microwave dielectric properties. At the same time, a small quantity of LiF addition could effectively reduce the sintering temperature to 950 °C. LMZ ceramics doped with 4 wt% LiF sintered at 950 °C exhibited the excellent microwave dielectric properties of $\varepsilon_r = 12.66$, $Q{\cdot}f = 89{,}325$ GHz and $\tau_f = -14.46$ ppm/°C.

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