Sintering Behavior and Microwave Dielectric Properties of Low-Loss Li$_6$Mg$_7$Zr$_6$O$_{16}$ Ceramics Doped with Different LiF Additives

Huarong Tian$^1$, Chunfang Xing$^1$, Haitao Wu$^1$ and Zhihao Wang$^2$

The Li$_6$Mg$_7$Zr$_6$O$_{16}$ samples were prepared with the pure cubic phase at sintering temperatures of 1300-1550 °C using the traditional solid state method in our previous work. Sintering characteristics and microwave properties were investigated as a function of sintering temperatures. The samples sintered at 1500 °C showed the best properties of the $Q\cdot f$ value of 81,284 GHz (at 8.94 GHz), dielectric constant value of 14.22 and the $\tau$ value of $-21.56$ ppm/°C. Now complex permittivity value of Li$_6$Mg$_7$Zr$_6$O$_{16}$ ceramic sintered at 1500 °C were characterized by the infrared spectra based on the classical harmonic oscillator model. In order to reduce the sintering temperature, lithium fluoride were used as sintering additives, and then the apparent densities, phase compositions and dielectric properties of Li$_6$Mg$_7$Zr$_6$O$_{16}$-5 wt% LiF were discussed as a function of lithium fluoride additions. As a result the densification temperatures for Li$_6$Mg$_7$Zr$_6$O$_{16}$-5 wt% LiF were reduced to be 1100 °C, which were significantly lower than that of the matrix (1500 °C). Excellent microwave dielectric properties were obtained in Li$_6$Mg$_7$Zr$_6$O$_{16}$-5 wt% LiF ceramics sintered at 1100 °C with $\varepsilon_r=13.67$, $Q\cdot f=132,600$ GHz (at 9.26 GHz) and $\tau=-18.89$ ppm/°C.

**Keywords:** Low-temperature sintering; Li$_6$Mg$_7$Zr$_6$O$_{16}$ ceramics; Infrared spectra; Microwave dielectric properties; LiF addition

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1. Introduction

With the rapid development of the wireless communication industry, microwave dielectric ceramics with high performances have been widely investigated and used for microwave components, such as filters, antennas, oscillators and resonators. To satisfy the specific requirements of current and future microwave devices, high-performance ceramics with an appropriate dielectric constant ($\varepsilon_r$), a high quality factor ($Q\cdot f$) and a near-zero temperature coefficient of the resonant frequency ($\tau$) are required. Nowadays a great number of new materials with excellent microwave dielectric properties have been widely investigated, such as the ReNbO$_3$ system, Mo-based microwave dielectric ceramics, and the rock salt systems or others. For example, the LaNiO$_2$-0.5MgO ceramics sintered at 1425 °C possessed excellent performance: $\varepsilon_r=19.8$, $Q\cdot f=94,440$ GHz, $\tau=6.1$ ppm/°C. The La$_2$Zr$_5$Ti$_3$(MoO$_4$)$_2$ ceramics achieved the best dielectric properties with $\varepsilon_r=10.33$, $Q\cdot f=80,658$ GHz and $\tau=-16.80$ ppm/°C. It was found in our previous work that the Li$_2$ZrO$_3$-MgO system sintered at 1500 °C exhibited excellent dielectric properties of $\varepsilon_r=12.65$, $Q\cdot f=165,924$ GHz and $\tau=-34.66$ ppm/°C. However, the high sintering temperature restricted its possible applications. In order to lower the sintering temperature, it is one of efficient methods to add or substitute sintering aids, such as LiF, CuO, H$_2$BO$_3$, Bi$_2$O$_3$ and glass in the past report. For example, when LiF content increased from 0 to 5 wt%, the optimum sintering temperature of CaMgSi$_2$O$_6$ ceramics reduced from 1250 °C to 900 °C. Zhou et al. reported that Bi$_4$(Li$_3$Ta$_7$)O$_{19}$ ceramics were densified at 1025 °C, the sintering temperature was lowered to 920 °C by the addition of 2 mol% excess Bi$_2$O$_3$. The H$_2$BO$_3$-doping in (1-x)LiAl$(Zn$_{0.5}$Si$_{0.5}$)O$_3$ + xCaTiO$_3$ (0.05 ≤ x ≤ 0.20) ceramics was used to decrease the sintering temperature from 1150 °C to 900 °C. Among them, LiF is one of inexpensive as well as the most effective sintering additives to reduce the sintering temperature of microwave dielectric materials. Hence, a conventional solid-state reaction method was used to prepare Li$_6$Mg$_7$Zr$_6$O$_{16}$ ceramics doped with different amounts of LiF. The microstructures, sintering characteristics as well as microwave dielectric properties of Li$_6$Mg$_7$Zr$_6$O$_{16}$-x (0 wt% LiF ≤ x ≤ 5 wt% LiF) were investigated scientifically.

2. Experimental procedure

Li$_6$Mg$_7$Zr$_6$O$_{16}$ compositions was prepared using reagent-grade powders of MgO (99.99%, Aladdin), Li$_2$CO$_3$ (99.99%, Aladdin) and ZrO$_2$ (99.99%, Aladdin). The raw materials were mixed by ball-milling for 24 h with zirconia balls and alcohol. The resulting slurry was dried after milling. After drying, powders were calcined at 1100 °C for 2 h thereafter. After calcination, powders were mixed together with 0-5 wt% LiF additives and then re-milled for 24 h. Powders were ground with 8 wt% PVA, and pressed into cylinders in a steel die thereafter. Finally, the matrix was sintered at 1300-1550 °C for 4 h in air, and Li$_6$Mg$_7$Zr$_6$O$_{16}$-x (1 wt% LiF ≤ x ≤ 5 wt% LiF) ceramics were sintered at 800-1150 °C.

The X-ray diffractometer (Brucker D8) was used to analyse crystal structures of Li$_6$Mg$_7$Zr$_6$O$_{16}$-x (0 wt% LiF ≤ x ≤ 5 wt% LiF). IR reflectivity spectrum was obtained via a FTIR spectrometer (Brucker IFS 66v). Microstructures of sintered samples were observed by the SEM (FESEM Quanta 250, FEI Co., USA).

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

$^2$School of Materials Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250353, China

$^*$E-mail: mse_wuht@ujn.edu.cn
Hakki-Cooley dielectric resonator method in TE_{011} resonant mode by A network analyzer (N5234A, Agilent Co., USA), the unloaded quality factor was measured using TE_{011} mode by the cavity method. τ values were calculated at 25-85 °C using the following equation:

\[ \tau_f = \frac{f_1 - f_0}{f_0 \times \Delta T} \times 10^4 \text{ (ppm/°C)} \]  

where \( f_1 \) and \( f_0 \) represented the resonant frequency at 25 °C as well as 85 °C, respectively.

3. Results and discussion

The X-ray diffraction patterns of Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) samples were shown in Fig. 1. From the recorded XRD patterns, Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) with a cubic structure (JCPDS card no. 45-0946) was identified. Moreover, no other phases could be detected, indicating that the pure cubic Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) was formed in the temperature range 1300-1500 °C. The illustrations of Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) crystal were exhibited in Fig. 2. It was noted that the oxygen octahedral sites were occupied by the Li, Mg and Zr atoms. In the structure, the cations (Li, Mg and Zr) occupied the 4a Wyckoff position, and O anions occupied the 4b Wyckoff position. According to complex chemical bond theory, the result of the decomposition of Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) was exhibited in Eq. (2). Based on our previous work, the shrinkage ratios and the apparent densities of the Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) samples could reach the saturated values at 1500 °C during the temperature increasing from 1300 to 1550°C. Correspondingly according to the curves of dielectric constants and quality factors for Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) samples from 1300 to 1550 °C, it was noted that dielectric constant increased from 13.37 to 14.28 with increasing temperature, which was caused by the elimination of pores.

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Fig. 3 presented the IR reflectivity spectrum of Li\(_{n}\)Mg\(_{n}\)Zr\(_{n}\)O\(_{6n}\) sintered at 1500 °C. Eq. (3) is used to calculate \( \varepsilon'(\omega) \) (the complex dielectric permittivity) based on the model of classical harmonic
oscillator, and $R$ (the complex reflectivity) can be obtained as Eq. (4)\textsuperscript{27}

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}$$

(3)

$$R = \frac{1 - \sqrt{\varepsilon'(\omega)}}{1 + \sqrt{\varepsilon'(\omega)}}$$

(4)

where $\omega_j$, $\omega_p$, and $\varepsilon_\infty$ are the transverse frequency, intensity and dielectric constant, respectively; $n$ as well as $\gamma$ are the number of transverse phonon modes and damping factor, respectively. In addition, the following formulas were used to calculate the $\tan \delta$ (dielectric loss tangent):

$$\tan \delta = \frac{n}{\varepsilon'} = \frac{\sum_{j=1}^{n} \Delta \varepsilon_j / \omega_j}{\varepsilon_\infty + \sum_{j=1}^{n} \Delta \varepsilon_j}$$

(5)

$$\varepsilon' = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_j^2}{\omega_j^2 - \omega^2} = \varepsilon_\infty + \sum_{j=1}^{n} \Delta \varepsilon_j$$

(6)

Fig. 4 showed the complex permittivity values and fitted IR reflectivity spectra. As shown in Table 1, there were five internal modes. The extrapolated dielectric loss and permittivity of LiMgZrO$_6$ were 0.44×10$^{-4}$ and 22.88, respectively. These calculated results were comparable with the measured ones. Hence, the microwave dielectric properties of LiMgZrO$_6$ were mainly related to the absorptions of phonon oscillation.

The apparent densities of LiMgZrO$_{6-x}$ (1 wt% LiF ≤ x ≤ 5 wt% LiF) ceramics were plotted in Fig. 5. Apparent densities of LiMgZrO$_{6-x}$ (1 wt% LiF ≤ x ≤ 5 wt% LiF) ceramics initially increased to the maximum values at their optimum temperatures and then reached saturation with further increasing the temperatures. The apparent densities of LiMgZrO$_{6-x}$ wt% LiF (x=5) increased to 3.54 g/cm$^3$ approximately at 900 °C, which was similar to that (3.66 g/cm$^3$) of LiMgZrO$_6$ sintered at 1500 °C. In addition, the apparent density increased with increasing x value. Therefore, LiF additive was an effective sintering aid to lower sintering temperature of LiMgZrO$_6$ system.

Fig. 6 showed XRD patterns of LiMgZrO$_{6-x}$ (1 wt% LiF ≤ x ≤ 5 wt% LiF) samples sintered at 1100 °C. For LiMgZrO$_{6-x}$ (1 wt% LiF ≤ x ≤ 2 wt% LiF) compositions, main cubic phase was observed. The second phases were ZrO$_2$ and Li$_x$MgZrO$_6$ for x=1 and x=2, respectively. As the LiF content increased from 3 to 5 wt%, a single phase was formed in the entire composition range, suggesting that LiMgZrO$_{6-x}$ (x=3-5 wt% LiF) was a complete solid solution with a cubic structure. Typical SEM micrographs of LiMgZrO$_{6-x}$ (1 wt% LiF ≤ x ≤ 5 wt% LiF) samples were demonstrated in Fig. 7(a-e). The porous structures were revealed in the surface of samples. It was observed that relatively dense microstructures were obtained for LiMgZrO$_6$ sample doped with 5 wt% LiF.

| Table 1 Phonon parameters obtained from the fitting of the infrared spectra of LiMgZrO$_6$ ceramic sintered at 1500 °C |
|---|---|---|---|---|---|
| mode | $\omega_{ij}$ | $\omega_{pj}$ | $\gamma_j$ | $\Delta_{ij}$ | $\varepsilon_8$ | $\varepsilon^*(\omega)$ |
| 1 | 277.41 | 855.9 | 86.452 | 9.52 | 4.06 | 22.88 |
| 2 | 308.73 | 517.36 | 44.705 | 2.81 | 184.34 | 5.11 |
| 3 | 378.39 | 855.4 | 69.187 | 0.733 | 1173.3 | 0.651 |
| 4 | 513.88 | 440.03 | 69.187 | 0.733 | 1173.3 | 0.651 |
| 5 | 1206.1 | 973.42 | 1173.3 | 0.651 |

Fig. 3 Measured (black line) and fitted (red line) IR reflectivity spectrum of LiMgZrO$_6$ ceramic sintered at 1500 °C.

Fig. 4 Real and imaginary parts of complex permittivity for LiMgZrO$_6$ ceramic sintered at 1500 °C (points are measured values at microwave region).
Fig. 5 Apparent densities of the $\text{Li}_x\text{Mg}_7\text{Zr}_3\text{O}_{16-x}$ wt% LiF ($x=1-5$) ceramics sintered at 800-1150 °C.

Fig. 6 XRD patterns of $\text{Li}_x\text{Mg}_7\text{Zr}_3\text{O}_{16-x}$ wt% LiF ($x=1-5$) ceramics sintered at 1100 °C in air.

Fig. 7 SEM micrographs of $\text{Li}_x\text{Mg}_7\text{Zr}_3\text{O}_{16-x}$ wt% LiF ($x=1-5$) ceramics sintered at 1100 °C (a-e corresponding to $x=1, 2, 3, 4, 5$).

Fig. 8 Dielectric constants of $\text{Li}_x\text{Mg}_7\text{Zr}_3\text{O}_{16-x}$ wt% LiF ($x=1-5$) ceramics sintered at 800-1150 °C.

Fig. 9 Quality factors of $\text{Li}_x\text{Mg}_7\text{Zr}_3\text{O}_{16-x}$ wt% LiF ($x=1-5$) ceramics sintered at 850-1150 °C.
Fig. 8 illustrated the variation in the dielectric constants for LiMgZrO$_{1-x}$ (1 wt% LiF $\leq x \leq 5$ wt% LiF). Generally, $\varepsilon_r$ value is closely related to density and secondary phase. For the specimens with $x=1-2$, dielectric constants had relatively lower values compared with that of LiMgZrO$_{1-x}$ (3 wt% LiF $\leq x \leq 5$ wt% LiF) ceramics, which might be caused by the second phases and the apparent densities. For $x=3-5$, the XRD patterns in Fig. 6 showed a pure phase. Therefore, $\varepsilon_r$ values of LiMgZrO$_{1-x}$ (3 wt% LiF $\leq x \leq 5$ wt% LiF) were mainly dependent on densities. With temperature increasing from 900 to 1100 °C, it was seen that the $\varepsilon_r$ values of LiMgZrO$_{1-x}$ (3 wt% LiF $\leq x \leq 5$ wt% LiF) remained stable at a given LiF content, indicating that $\varepsilon_r$ value was not significantly influenced by the temperature for the sample with high densification.$^7$

Quality factors of LiMgZrO$_{1-x}$ (1 wt% LiF $\leq x \leq 5$ wt% LiF) samples were exhibited in Fig. 9. Quality factors are mainly influenced by the intrinsic losses (lattice vibration mode) and extrinsic losses (densification of the samples, second phases as well as grain morphology).$^{33,34}$ Factors influencing the quality factors of LiMgZrO$_{1-x}$ (1 wt% LiF $\leq x \leq 5$ wt% LiF) ceramics were the extrinsic ones mainly contributing to the densification. Quality factors of LiMgZrO$_{1-x}$ (3 wt% LiF $\leq x \leq 5$ wt% LiF) ceramics were higher than that of LiMgZrO$_{1-x}$ (1 wt% LiF $\leq x \leq 2$ wt% LiF) samples, which might be related to the densities and the second phases of the ceramics. For instance, quality factor of LiMgZrO$_{1-x}$ wt% LiF ($x=1$) increased from 8,200 GHz (at 10.49 GHz) to 75,500 GHz (at 10.67 GHz) with increasing temperature, while the maximum quality factors of LiMgZrO$_{1-x}$-5 wt% LiF ceramics reached to 132,600 GHz (at 9.26 GHz) at 1100 °C, which was higher than that (81,277 GHz) of LiMgZrO$_{1-x}$ ceramics.

Microwave dielectric properties of LiMgZrO$_{1-x}$ (1 wt% LiF $\leq x \leq 5$ wt% LiF) sintered at 1100 °C were exhibited in Fig. 10. As LiF content increased from 1 to 5 wt%, the $\varepsilon_r$ value and the quality factor showed an upward tendency due to the increase of density. It is well known that the $\tau_f$ values are governed by the composition, the additives and the second phase of the materials.$^7$ The $\tau_f$ value initially decreased from -19.5 ppm/°C to -27.2 ppm/°C with increasing $x$ value, and then increased to -18.89 ppm/°C, which might be affected by additives in this work. Typically, LiMgZrO$_{1-x}$ wt% LiF ($x=5$) ceramic possessed a single phase with good properties of $\tau_f = -18.89$ ppm/°C, $Qf = 132,600$ GHz (at 9.26 GHz) and $\varepsilon_r = 13.67$.

4. Conclusion
LiMgZrO$_{1-x}$ (0 wt% LiF $\leq x \leq 5$ wt% LiF) samples were synthesized by the solid-state method. Appropriate amount of LiF additive improved the sinterability of the LiMgZrO$_{1-x}$ system. The sintering temperature of the ceramic was reduced with increasing LiF content, which was caused by the enhancement of the apparent density at low temperature by liquid phase sintering. The dielectric constants and quality factors increased gradually when temperatures and LiF additives increased. Compared with LiMgZrO$_{1-x}$ ceramics sintered at 1500 °C, 5% LiF doped-LiMgZrO$_{1-x}$ samples could be sintered well at 1100°C with excellent properties of $\varepsilon_r = 13.67$, $Qf = 132,600$ GHz (at 9.26 GHz) as well as $\tau_f = -18.89$ ppm/°C.

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References

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