Temperature Stable and Low Loss Microwave Dielectric Ceramics of Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$

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Abstract: In this paper, a series of Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) ceramics were prepared by the conventional solid-state reaction method. The effects of Sr$^{2+}$ substitution on the structure, morphology and microwave dielectric properties of Li$_2$Mg$_3$TiO$_6$ ceramics were investigated. The X-ray diffraction (XRD) results indicated that Li$_2$Mg$_3$TiO$_6$ and SrTiO$_3$ phases stably coexisted with each other and formed composite materials. The appearance of porous structure mainly originated from the volatilization of lithium at high sintering temperatures. As the Sr$^{2+}$ content increased from 0 to 0.08, the optimum dielectric constant ($\varepsilon_r$) increased from 13.61 to 17.32, the quality factor ($Q\times f$) decreased monotonously and the temperature coefficient of resonant frequency ($\tau_f$) changed from -34.4 to +16.8 ppm/$^\circ$C. The variations of $\varepsilon_r$, $Q\times f$ and $\tau_f$ could be explained by the Lichtenecker logarithmic model and mixing rule, respectively. In particular, optimal microwave dielectric properties of $\varepsilon_r=16.08$, $Q\times f=82100$ GHz, $\tau_f=+1.7$ ppm/$^\circ$C were obtained for Li$_2$Mg$_{2.94}$Sr$_{0.06}$TiO$_6$ ceramic sintered at 1310 $^\circ$C for 5h.

1. Introduction

Over the past decades, with the rapid development of mobile communications and satellites broadcasting, microwave dielectric materials have attracted more and more attentions due to their widespread applications such as filters, resonators, antennas and oscillator [1-4]. In order to meet the requirements of future microwave communication systems, microwave dielectric materials should possess dielectric characteristics: adjustable dielectric constant ($\varepsilon_r$) for different applications, high quality factor ($Q\times f$) for excellent selectivity and near-zero temperature coefficient of the resonant frequency ($\tau_f$) for thermostability [5, 6].

In recent years, several excellent Li-containing compounds such as Li$_3$Mg$_2$NbO$_6$, Li$_2$Mg$_3$Ti$_4$O$_{12}$, Li$_2$Zn$_3$Ti$_4$O$_{12}$, Li$_2$MgTiO$_4$, Li$_2$TiO$_3$ and Li$_2$Mg$_3$BO$_6$ (B = Zr, Sn or Ti) have received considerable attentions as a potential candidate for microwave dielectric materials [7-12]. For example, Wang et al. reported that the strategy of Li non-stoichiometric could be adopted to promote densification and reduce losses of Li$_3$Mg$_2$NbO$_6$ ceramics. Zhou et al. reported that the novel low loss Li$_2$Mg$_3$Ti$_4$O$_{12}$ (M=Mg or Zn) ceramic systems exhibited dense microstructure, pure cubic phase at optimum temperature. Both of them possessed outstanding dielectric characteristics: $\varepsilon_r=20.2$, $Q\times f=62300$ GHz, $\tau_f=-27.1$ ppm/$^\circ$C (Li$_2$Mg$_3$Ti$_4$O$_{12}$) and $\varepsilon_r=20.6$, $Q\times f=106700$ GHz, $\tau_f=-48$ ppm/$^\circ$C (Li$_2$Zn$_3$Ti$_4$O$_{12}$). Liu et al. reported the novel cubic structure ceramic systems of Li$_2$Mg$_3$BO$_6$. Among these various compounds, Li$_2$Mg$_3$TiO$_6$ with rock salt structure has been extensively investigated because of their remarkable microwave dielectric characteristics: $\varepsilon_r=15.2$, $Q\times f=152000$ GHz, $\tau_f=-39$ ppm/$^\circ$C. Up to now, many researchers have

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focused their attention on the Li$_2$Mg$_3$TiO$_6$ material and a number of efforts and attempts have been made to control dielectric characteristics. For instance, Pan et al. established the relationship between intrinsic structure characteristics and dielectric properties by prepared Li$_2$Mg$_{3-x}$Co$_x$TiO$_6$ solid solutions [13]. Yang et al. studied the influences of Zn$^{2+}$ doping on the crystal structure, morphology and microwave dielectric properties of Li$_2$(Mg$_{1-x}$Zn$_x$)TiO$_6$ ceramics and found the solid solubility limit was located about 0.15 [14]. Zhang et al. fabricated Li$_2$(Ni$_{1-x}$Mg$_x$)$_3$TiO$_6$ (0 ≤ x ≤ 1) materials through the conventional solid sintering method, the relationship between crystalline structures and microwave dielectric properties were studied [15]. However, the application of Li$_2$Mg$_3$TiO$_6$ were hampered due to the bigger negative $\tau_f$. In general, the near-zero $\tau_f$ could be achieved by following methods: (1) directly added the opposite $\tau_f$ materials, (2) introduced the suitable ions to obtained corresponding materials with opposite $\tau_f$ value [16].

In this article, given the larger positive $\tau_f$ of SrTiO$_3$ and remarkable thermal stability of Li$_2$Mg$_{3-x}$Ca$_x$TiO$_6$ composite ceramics, the Sr$^{2+}$ doped Li$_2$Mg$_3$TiO$_6$ materials were synthesized by the solid-state reaction and the influences of Sr$^{2+}$ ions doping on the structure, morphology and microwave dielectric properties of Li$_2$Mg$_3$TiO$_6$ ceramics were investigated. The excellent microwave dielectric properties such as low loss and near-zero $\tau_f$ make Li$_2$Mg$_{2.94}$Sr$_{0.06}$TiO$_6$ ceramic a possible applications in microwave domains.

### 2. Experimental Procedure

The Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ samples were synthesized by the conventional solid-state reaction progress. The high purity starting raw materials of SrCO$_3$, Li$_2$CO$_3$, MgO and TiO$_2$ were weighed accurately according to chemical formula of Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) and milled with zirconia ball in anhydrous alcohol medium for 6 h. The mixtures were dried and calcined at 1000 °C for 4 h. After re-milling and drying, the binder of polyvinyl alcohol (13 wt.% PVA) was mixed with the finely milled calcined powders. Subsequently, the mixtures were granulated and vertically pressed into cylinders sheets (12mm*6mm). Finally, the samples were preprocessed at 550 °C for 2 h and sintered at 1220–1340 °C for 4 h.

The crystalline structure of Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) samples were analyzed by X-ray diffraction (DX-2700, XRD). The particle morphology were visualized by scanning electron microscope (JOEL JSM6490LV, SEM). The bulk densities of ceramics were measured by the Archimedes method with medium of distilled water. The dielectric properties of all samples were measured by the network analyzer (N5230A, Agilent, TE011 mode). The temperature coefficient resonant frequency ($\tau_f$) of specimens were calculated with the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(85 - 25)} \times 10^6 \text{ (ppm/°C)}$$

where $f_1$ and $f_2$ represent the resonant frequency obtained at 85 °C and 25 °C, respectively.

### 3. Results and Discussion.
The XRD patterns of the pure Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_3$-xSr$_x$TiO$_6$ (x = 0.02, 0.04, 0.06, 0.08) ceramics sintered at 1310 °C were shown in Fig. 1. The peaks of pure Li$_2$Mg$_3$TiO$_6$ sample were indexed as the rock salt structure with space group Fm3m (225). On the basis of previous research [17], the structure of Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_3$SnO$_6$ (JCPDS: 39-0932) seemed very similar, which could be ascribed to the similar Shannon’s effective ionic radius between Ti$^{4+}$ ions and Sn$^{4+}$ ions (Coordination number = 6, $R_{Ti^{4+}}$ = 0.605 Å, $R_{Sn^{4+}}$ = 0.69 Å). However, the additional phase compositions of SrTiO$_3$ (JCPDS: 79-0176, space group: Pm-3m) could be detected, which may be due to the big difference of radius between Sr$^{2+}$ ions and Mg$^{2+}$ ions (Coordination number = 6, $R_{Sr^{2+}}$ = 1.18 Å, $R_{Mg^{2+}}$ = 0.72 Å). Moreover, with the increase of Sr$^{2+}$ content, the phase content of SrTiO$_3$ gradually increases. The similar results were detected in Ca$^{2+}$ doped Li$_2$Mg$_3$TiO$_6$ ceramics. All these results show that Sr$^{2+}$ can react preferentially with Ti$^{4+}$, which result in the coexist of Li$_2$Mg$_3$TiO$_6$ and SrTiO$_3$ structure.

The surface SEM images of pure Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_3$-xSr$_x$TiO$_6$ ceramics sintered at 1310 °C for 4h were displayed in Fig. 2. Obviously, the pure Li$_2$Mg$_3$TiO$_6$ ceramic presents the porous microstructure, which is due to the lithium volatile and evaporate at elevated sintering temperatures [12]. With the increase of Sr$^{2+}$ content, the microstructure of Li$_2$Mg$_3$TiO$_6$/SrTiO$_3$ composite materials turn from porous structure into almost dense structure, which is similar to previous reports about Li$_2$Mg$_3$-xCa$_x$TiO$_6$ [16]. In addition, the average grain size gradually increase with the Sr$^{2+}$ doping content increase as shown in Fig. 2 (b-e). The results indicate that the Sr$^{2+}$ doped could improve densification of samples, which may pave an alternative way to cure the porous structure.

![Fig. 1 XRD patterns of pure Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_3$-xSr$_x$TiO$_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) ceramics sintered at 1310 °C.](image1)

![Fig. 2 SEM images of pure Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_3$-xSr$_x$TiO$_6$ ceramics sintered at 1310 °C: (a) x=0, (b) x=0.02, (c) x=0.04, (d) x=0.06, (e) x=0.08, (f) x=0.08.](image2)
Fig. 3 The bulk densities of the pure Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x = 0.02, 0.04, 0.06, 0.08) ceramics sintered at different temperatures.

The bulk densities of the pure Li$_2$Mg$_3$TiO$_6$ and Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x = 0.02, 0.04, 0.06, 0.08) ceramics sintered at different temperatures were shown in Fig. 3. It can be seen that the bulk densities increase first and then decrease with the increase of the sintering temperature. In the range of 1220-1310 °C, the gradually increase of bulk densities should be due to the densification process. However, the decreases inversely when sintering temperature is beyond 1310 °C could be ascribed to the lithium evaporation. In addition, the bulk densities increase and relative densities of 92%, 92.4%, 93.1%, 93.9%, 94.3% can be obtained with the increase of x value. The results prove once again the Sr$^{2+}$ doped could eliminate pores of Li$_2$Mg$_3$TiO$_6$ ceramics, which was in accordance with the SEM images.

Fig. 4 shows the change trend of $\varepsilon_r$ as functions of Sr$^{2+}$ doped content and sintering temperatures. It is noticeable that the trend of $\varepsilon_r$ sintered at different temperatures is similar to that of densities with each certain Sr$^{2+}$ concentration, which means the densification play an important role in dielectric constant. In addition, the $\varepsilon_r$ values of Li$_2$Mg$_3$TiO$_6$/SrTiO$_3$ composite materials increase with increasing Sr$^{2+}$ concentration. The increasing trend is reasonable related to the incremental relative densities, increasing SrTiO$_3$ ($\varepsilon_r$=290) according to the mixture rule: $ln\varepsilon_r = \sum v_i ln\varepsilon_{ri}$ [6].

Fig. 4 The change trend of dielectric constant as functions of Sr$^{2+}$ doped content and sintering temperatures.

Fig. 5 displays the change trend of $Q\times f$ as functions of Sr$^{2+}$ doped content and sintering temperatures. It is clear that the $Q\times f$ of Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x =0.00, 0.02, 0.04, 0.06, 0.08) materials sintered at different sintering temperature displayed a similar trend to bulk densities. As we all know, the $Q\times f$ usually associated with the intrinsic losses and extrinsic losses. The intrinsic losses depend on lattice vibration modes, and the extrinsic losses are depend on porosity, secondary phase and grain sizes. In this paper, given the results of SEM, the gradually reduce of $Q\times f$ mainly because of the increasing secondary phase...
SrTiO$_3$ ($Q\times f = 4800$ GHz). The results demonstrate that, compared with densification, the secondary phase plays a more important role on $Q\times f$ value.

Fig. 5 The change trend of $Q\times f$ as functions of Sr$^{2+}$ doped content and sintering temperatures.

Fig. 6 shows the change trend of $\tau_f$ as functions of Sr$^{2+}$ doped content. It can be seen that the $\tau_f$ vary from -34.4 to +16.8 ppm/°C with increasing Sr$^{2+}$ concentration. As we all know, the $\tau_f$ usually associated with the sample components and secondary phase. According to the XRD patterns, the phase proportion of SrTiO$_3$ in composite materials increase with increasing Sr$^{2+}$ concentration. The near-zero $\tau_f$ of Li$_2$Mg$_{2.94}$Sr$_{0.06}$TiO$_6$/SrTiO$_3$ composite materials could be explained by the increasing large positive $\tau_f$SrTiO$_3$ ($\tau_f$ = +1650 ppm/°C) based on Lichtenecker empirical logarithmic rule: $\tau_f = v_1\tau_{f1} + v_2\tau_{f2}$ [17].

Fig. 6 The change trend of $\tau_f$ as functions of Sr$^{2+}$ doped content.

4. Conclusion.

In this paper, the Li$_2$Mg$_{3-x}$Sr$_x$TiO$_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) ceramics were prepared by the conventional solid-state reaction method. The effects of Sr$^{2+}$ substitution on the structure, morphology and microwave dielectric properties of Li$_2$Mg$_3$TiO$_6$ ceramics were investigated. The X-ray diffraction (XRD) results indicated that Sr$^{2+}$ ions did not replace Mg$^{2+}$ ions in Li$_2$Mg$_3$TiO$_6$ due to the bigger radius of Sr$^{2+}$ ions, which lead to the formation of Li$_2$Mg$_{2.94}$Sr$_{0.06}$TiO$_6$/SrTiO$_3$ composite materials. The appearance of porous structure mainly originated from the volatilization of lithium at higher sintering temperatures. As the Sr$^{2+}$ content increased from 0 to 0.08, the optimum dielectric constant ($\varepsilon_r$) increased from 13.61 to 17.32, the quality factor ($Q\times f$) decreased monotonously and the temperature coefficient of resonant frequency ($\tau_f$) changed from -34.4 to +16.8 ppm/°C. The variations of $\varepsilon_r$, $Q\times f$ and $\tau_f$ could be explained by the Lichtenecker logarithmic model and mixing rule, respectively. In particular, excellent microwave dielectric properties of $\varepsilon_r = 16.08$, $Q\times f = 82100$ GHz, $\tau_f = +1.7$ ppm/°C were obtained for Li$_2$Mg$_{2.94}$Sr$_{0.06}$TiO$_6$ ceramic sintered at 1310 °C for 5h. The excellent comprehensive properties make the Li$_2$Mg$_{2.94}$Sr$_{0.06}$TiO$_6$ ceramic a suitable candidate for microwave applications.
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