The effects of ZnO doping on microstructure and microwave dielectric properties of Li$_3$Mg$_2$TaO$_6$ ceramics with rock salt structure

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Abstract. In this study, the ZnO doping Li$_3$Mg$_2$TaO$_6$ were prepared by solid state reaction method. The correlations between microstructure and microwave dielectric characterizations of Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$($x=0$--$0.5$) ceramics were systematically investigated. All the samples showed the single phase of Li$_3$Mg$_2$TaO$_6$ with orthorhombic structure in Fddd (70) space group, and the structure refinement results showed the increase of the cell volume with the increasing $x$. The SEM images indicated that the dense structures were obtained in the range of 0--0.3, and a small amount of ZnO impurity phase was observed in grain boundaries because of the evaporation of ZnO in the high sintering temperature. The $\varepsilon_r$ and $\tau_f$ increased as the ZnO content increased. The $Q\times f$ value increase firstly with the increasing $x$, to the maximum at $x=0.3$, and then decreased. As sintered at 1270 °C for 4h, the Li$_3$Mg$_{1.7}$Zn$_{0.3}$TaO$_6$ ($x=0.3$) ceramics showed the excellent microwave properties: $\varepsilon_r = 20.61$, $Q\times f = 106,863$ GHz and $\tau_f = -21.6$ ppm/°C.

1. Introduction

With the rapid development of integrated microwave devices for wireless telecommunications industry, microwave dielectric ceramics are widely used in the field of microwave components, including resonators, filters, waveguides and antennas. In regard to dielectric resonators, they exhibit resonance for a narrow range of microwave frequencies, and they enable the filter components in the mobile database station to remove secondary signals and unwanted sidebands. To meet the specific requirements of transmission of high-quality primary signals, the dielectric material should have the comprehensive microwave dielectric properties: a suitable dielectric constant ($\varepsilon_r$), a high $Q\times f$ value for selectivity and a high temperature stability (near zero $\tau_f$). However, it is difficult to optimize these three properties simultaneously. In general, low-permittivity ceramics with $\varepsilon_r$ below 20 are used for millimeter-wave communications. The medium-permittivity ($\varepsilon_r=25$--$50$) ceramics are used for cellular phone base stations and satellite communication. High-permittivity materials are used in integrated circuit where miniaturization of components is necessary [1-3]. Much work so far has focused on the high $Q$ and versatile tunable microwave dielectric ceramics, such as Mg$_2$SiO$_4$ [4], Nd(Co$_{1/2}$Ti$_{1/2}$)$_2$O$_3$ [5], Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ [6] and Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ [7], etc. Most ultra-high $Q$ dielectrics are found in complex
perovskite structures, and the Ta containing complex perovskite ceramics usually correlate to the higher $Q\times f$ values. But the complex manufacturing process of high-temperature prolonged sintering is required to ensure high Q value for perovskites. The exploration of a new high-Q microwave dielectric system is still advancing.

The AX (A=cation, X=anion) rock salt structure is one of the most well-known structures, it is unique in displaying regular edge-sharing octahedra coordination for both cations and anions. According to previous studies, many Li containing dielectric ceramics with rock salt structure were reported to have good dielectric properties, such as Li$_3$MO$_3$ (M=Ti, Zr, Sn) [8], Li$_3$NbO$_4$ [9], Li$_2$TiO$_3$-MgO [10], Li$_2$Mg$_2$BO$_6$ (B=Ti, Zr, Sn) [11], Li$_3$Mg$_2$NbO$_6$ [12], etc. Among of these excellent Li containing materials, Li$_3$Mg$_2$NbO$_6$ (LMNO) was a promising candidate for application in a microwave circuit due to its remarkable dielectric properties: $\varepsilon_r = 16.8$, $Q\times f = 79,643$GHz, $\tau_f = -27.2$ ppm/°C when sintered at 1250°C for 2h [12]. But the dielectric loss and temperature coefficient of resonant frequency of LMNO were also relatively high. Recently, Zuo et al. [13] reported the microwave dielectric properties of Li$_3$(Mg$_{0.93}$Zn$_{0.08}$)$_2$Nb$_6$O$_{24}$ ceramics of $\varepsilon_r = 16.30$, $Q\times f = 50,084$GHz, $\tau_f = 1.5$ ppm/°C sintered in 950°C. Wang et al. [14] investigated the Li$_3$Mg$_{1.8}$Ca$_0.2$NbO$_6$ ceramics with LMZBS glass, and obtained good microwave dielectric properties of $\varepsilon_r = 16.70$, $Q\times f = 31,000$GHz, $\tau_f = -1.3$ ppm/°C sintered in 950°C for 4h. Zhang et al. [15] improved the $Q\times f$ values by Sb doping in Nb site of Li$_3$Mg$_3$(Nb$_{1-x}$Sb$_x$)$_6$O$_{24}$ ceramics, and reported the good dielectric properties of: $\varepsilon_r = 15.79$, $Q\times f = 95,487$GHz, $\tau_f = -24.53$ ppm/°C. However, to our knowledge, there were no studies have reported the dielectric properties of Li$_3$Mg$_2$TaO$_6$ (LMTO) single phase, and the effects of Mg site substitution on the dielectric properties of LMTO were also remained to be explored.

In this study, we synthesized the Li$_3$Mg$_{2.2}$Zn$_{0.5}$TaO$_6$ ($x=0\sim0.5$) (LMZxTO) ceramics by solid-state reaction method, and the effects of ZnO doping on sintering behaviour, crystal structure, and microwave dielectric properties were investigated.

2. Experiment procedures

The LMZxTO ceramics were prepared by solid state reaction technic. The raw materials of Mg(OH)$_2$, 4MgCO$_3$·5H$_2$O (>99.5%), Li$_2$CO$_3$(99.9%), Ta$_2$O$_5$(99.9%), and ZnO(99.9%) were weighed according to the stoichiometry of Li$_3$Mg$_{2.2}$Zn$_{0.5}$TaO$_6$($x=0\sim0.5$). These raw powders were ball milled in alcohol for 7h in nylon jars with zirconia balls. After drying, the mixtures were calcined at 1000°C for 4h, then reground for 3h, dried and mixed with an 6wt% PVA as a binder. The resultant powders were axially pressed into cylinders with diameter of 15 mm and 7.5mm in thickness under the pressure of 20 MPa. To control Li volatilization, these pellets were muffled in ZrO$_2$ powders and Li$_2$CO$_3$ were used to provide Li-rich atmosphere in high temperature circumstances. Then the pellets were sintered from 1230°C to 1310°C.

Phase composition was determined by X-ray diffraction (XRD) using CuKα radiation (Philips X’Pert Pro MPD, Netherlands) and the structure refinement were carried out by analyzing XRD data using the GSAS software [16]. Archimedes principle was employed to measure the apparent density (or bulk density) of the sintered samples. The relative density ($D$) was the ratio of the measured apparent density ($\rho_a$) to the calculated theoretical density ($\rho_{theo}$): $D = \frac{\rho_a}{\rho_{theo}}$. And the theoretical density ($\rho_{theo}$) was obtained by: $\rho_{theo} = \frac{Z\cdot A}{\nu \cdot N_A}$, where $Z$ is the number of molecules in the unit cell, $A$ is the formula weight, $\nu$ is the cell volume, $N$ is Avogadro's number ($N=6.022\times10^{23}$/mol). The porosity of the ceramics: $P=1-D$. Scanning electron microscopy (SEM, FEI Inspect F, the United Kingdom) was employed to study the surface microstructure of the ceramics. And the average grain sizes were analyzed from SEM graphs using Image-Pro Plus software. The network analyzer (Agilent Technologies E5071C, the United States) and a temperature chamber (DELTA 9023, Delta Design, USA) were used to measure the microwave dielectric properties by the Hakki–Coleman dielectric resonator method using the TE011 mode [17]. The temperature coefficient of resonant frequency was
determined by the variation of the resonant frequency from 25 °C to 85 °C, using the equation: 
\[ \tau_f = \frac{f_{t_2} - f_{t_1}}{f_{t_1}(t_2 - t_1)} \]
where \( f_{t_1} \) and \( f_{t_2} \) are the resonant frequencies at \( t_1 = 25 \) °C and \( t_2 = 85 \) °C, respectively.

3. Results and discussion

3.1. Crystal structures

Figure 1(a) shows the XRD patterns of \( \text{Li}_3\text{Mg}_2\text{Zn}_x\text{TaO}_6 \) \((x=0~0.5)\) ceramics sintered at 1270°C for 4h. For \( x=0 \) to 0.5, the diffraction patterns all showed the single \( \text{Li}_3\text{Mg}_2\text{TaO}_6 \) (JCPDS No. 36-1017) phase with orthorhombic structure in Fddd (70) space group. There was no trace of the secondary phase in these samples, this finding indicated the formation of the solid solutions due to the proximal ion radius of \( \text{Zn}^{2+}(0.74\text{Å}) \) to \( \text{Mg}^{2+}(0.72\text{Å}) \). And as seen from Figure 1(b), the character peak of (426) shifted to lower angle as \( x \) increased, this shift revealed an increase in cell volume based on Bragg’s law \( (2\sin\theta = n\lambda) \). In addition, the intense peaks of (111) and (004) at the 2θ=18° were relevant to the long-range ordering (LRO). For the “degree of order” \( s \) was closely related to the properties of dielectric loss in perovskites, the order parameter \( s \) was widely calculated by the formula of:
\[ s = \frac{l_{\text{sup}}}{l_{\text{sub,obs}}} \]

(1) for perovskite structures[18]; \( l_{\text{sup}} \) is the ratio of the observed intensities of the superstructure reflection to that of the reflection of the subcell, and \( l_{\text{sub,calc}} \) is the corresponding ratio calculated from the structure using the published structural data[19]. Similarly, the order parameter \( s \) for ordered orthorhombic \( \text{Li}_3\text{Mg}_2\text{TaO}_6 \) can be defined as:
\[ s = \frac{\sqrt{l_{111}^{111}}}{\sqrt{l_{026}^{026}}} \]

where \( I_{(111)} \) is the superlattice reflection of (111) peak and \( I_{(026)} \) is the reflection of the (026) subcell peak. As shown in Table.1, the \( s \) value slightly decreased with the increasing \( x \), showing that the introduction of \( \text{Zn} \) lowered the ordering degree of the \( \text{Li}_3\text{Mg}_2\text{Zn}_x\text{TaO}_6 \) \((x=0~0.5)\) ceramics. Based on the measured X-ray diffraction data, the Rietveld refinement technique was carried out to understand the crystal structure change. The representative result of refinement was shown in Figure 2. The R values and refined crystal parameters of \( \text{Li}_3\text{Mg}_2\text{Zn}_x\text{TaO}_6 \) \((x=0~0.5)\) ceramics are shown in Table 1. The refinement factors of \( R_{\text{wp}}, R_p, \) and \( \chi^2 \) for refinement were in the range of 6~9%, 4~7% and 1.6~2.3, hence, highly reliable structural models were established. In addition, with the increasing \( x \), the lattice parameters increased from 897.155 to 907.495. The increase of cell volumes was caused by the larger ion radius of \( \text{Zn}^{2+}(0.74\text{Å}) \) ions to \( \text{Mg}^{2+}(0.72\text{Å}) \) ions, which was in accord with the peak shift in XRD patterns.

Figure 3 displays the Scanning Electron Microscope (SEM) photographs for \( \text{LMZ}_x\text{TO} \) \((x=0~0.5)\) ceramics which were sintered at 1270°C for 4h in an atmosphere-controlled environment. All samples showed the polygonal grains. The dense structures were achieved among the range of 0 to 0.3, and pores were observed for \( x\geq0.4 \). There seemed to be some white impurity phase in the grain boundary regions for \( x\geq0.1 \). The EDS analyses for the matrix by spot A and C showed the composition that is close to the pure \( \text{Li}_3\text{Mg}_2\text{TaO}_6 \). The white areas marked by spot B and D, however, demonstrated Zn-rich composition which containing small amounts of Mg and Ta, and the similar concentrations of Zn and O in white regions indicated that these white areas might be contaminated from the \( \text{ZnO} \). Besides, the inhomogeneous and very partial distribution of the white impurity phase illustrated that very small amount of \( \text{ZnO} \) impurity phase existed in the grain boundaries. There have been study declared that \( \text{ZnO} \) can be evaporated when the sintering temperature was above 1250°C [20]. And the possible reason for the formation of the \( \text{ZnO} \) phase was the volatilization of \( \text{ZnO} \) in 1270°C, and because of the atmosphere-controlled sintering condition in this study, the \( \text{ZnO} \) steam couldn’t enter in air, so it deposited in the grain boundaries. Coupled with the XRD results, the \( \text{Li}_3\text{Mg}_2\text{Zn}_x\text{TaO}_6 \) solid solutions
indeed formed, but the amount of the evaporative ZnO was insufficient to be detected in XRD patterns. The results of the measured average grain size were shown in Table 2. Average grain size increased with the increasing $x$, this result suggested that zinc substitution facilitated the grain growth. With further increasing the ZnO content up to 0.4 mol, an abrupt extension of grain size was observed, and some grains began to grow abnormally, leading to the indistinct grain boundaries. It suggested that the Zn-substitution had a remarkable effect on the grain growth owing to the formation of the liquid phase, which were in consistent with the case of ZnO doped Li$_3$(Mg$_{0.92}$Zn$_{0.08}$)$_2$NbO$_6$ ceramics that the liquid phase was formed when sintered at 1240°C for 4h [21].

![Figure 1](image1.png)

**Figure 1.** (a) The XRD patterns of Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0$–0.5) microwave ceramics sintered at 1270°C for 4h. (b) The amplified spectra of the XRD patterns from 62° to 63°.

![Figure 2](image2.png)

**Figure 2.** Experimental (red circles) and calculated (black line) X-ray powder diffraction profiles for Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0.1$) microwave ceramics sintered at 1270°C for 4h. The bottom continuous line is the differences between the observed and the calculated intensity.
Table 1. Refined crystal parameters and R values versus composition in Li₃Mg₂ₓZnₓTaO₆ (x=0–0.5) ceramics sintered at 1270°C for 4h.

| x (mol) | 0   | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|---------|-----|-----|-----|-----|-----|-----|
| a (Å)   | 5.881 | 5.902 | 5.904 | 5.903 | 5.905 | 5.909 |
| b (Å)   | 8.617 | 8.620 | 8.624 | 8.635 | 8.651 | 8.656 |
| c (Å)   | 17.704 | 17.703 | 17.733 | 17.729 | 17.739 | 17.742 |
| V(Å³)   | 897.155 | 900.667 | 902.913 | 903.680 | 906.148 | 907.495 |
| Rwp (%) | 6.53 | 7.21 | 8.62 | 6.34 | 8.12 | 8.17 |
| Rp (%)  | 4.69 | 4.36 | 5.53 | 4.52 | 6.23 | 6.34 |
| χ²      | 1.65 | 1.83 | 2.32 | 1.84 | 2.15 | 2.26 |
| s       | 1.162 | 1.054 | 0.983 | 0.976 | 0.945 | 0.932 |
| P.F (%) | 70.18 | 69.92 | 69.86 | 69.75 | 69.53 | 69.44 |

Figure 3. The SEM images of Li₃Mg₂ₓZnₓTaO₆ (x=0–0.5) ceramics for (a) x=0, (b) x=0.1, (c) x=0.2, (d) x=0.3, (e) x=0.4, (f) x=0.5 sintered at 1270°C for 4h; The EDS analyses for (g) A and (h) B point marked in (b) and for (i) C and (D) point marked in (d).

Table 2. The average grain size of the of Li₃Mg₂ₓZnₓTaO₆ (x=0–0.5) ceramics sintered at 1270°C for 4h.

| x (mol) | 0   | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|---------|-----|-----|-----|-----|-----|-----|
| Avg. grain size (μm) | 18.92 | 20.58 | 21.96 | 23.62 | 29.32 | 30.66 |
3.2. dielectric properties

Figure 4 (a) shows the apparent densities of LMZxTO (x=0–0.5) ceramics sintered from 1230°C to 1310°C with the step size of 20°C for 4h and Figure 4(b) displays relative densities of LMZxTO (x=0–0.5) ceramics sintered at 1230°C, 1270°C and 1310°C for 4h, as a function of Zn contents. The apparent densities increased with the increasing x in the range of 0–0.5, and the increase of sintering temperature also contributed to the increase of apparent densities. In addition, the relative densities were calculated to better understand the densification process. As shown in Figure 4(b), the relative densities of LMZxTO (x=0–0.5) ceramics sintered at 1270°C firstly increased from 97.56% to 98.28% with the increased x, reached the maximum at x=0.3, and then decreased to 97.40%. It also was worth noting that, in the range of 0.2 to 0.5, the relative densities of LMZxTO ceramics sintered at 1310°C were lower than that of which the ceramics were sintered at 1270°C. The drastic evaporation of ZnO at the sintering of 1310°C might be responsible for this increase of porosity. The values of the cell volumes of the LMZxTO ceramics (x=0–0.5, 1230°C/4h, 1270°C/4h and 1310°C/4h) carried out from the Rietveld refinement results of the samples were shown in Table 3. The growth rate of the cell volume (ΔV) of LMZTO ceramics sintered at 1310°C was much lower than that of which the samples were sintered at 1230°C and 1270°C. From above we have discussed that the Zn substitution contributed to the increase of the cell volumes, thus the low growth rate of cell volumes might be related to the drastic evaporation of ZnO when the ceramics were sintered at the high temperature of 1310°C. And the specific data of densities of ceramics which were sintered at 1270°C and 1310°C were listed in Table 4. The apparent and theoretical densities were all increased with the increasing x, however, the turning point of x=0.3 were found in relative densities. The increase of porosity were attributed to the liquid phase sintering characteristics for x≥0.4 associate with Figure 3(e)–(f).

![Figure 4](image_url)
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Table 3. Refined cell volumes ($V$) of Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0$–$0.5$) ceramics sintered at 1230°C, 1270°C and 1310°C for 4h.

| x (mol) | S.T. (°C) | Z | Formula weight | Apparent density ($\rho_o$) | Theoretical density ($\rho_{theo}$) | Relative density ($D$) (%) | Porosity ($P$) (%) |
|---------|-----------|---|----------------|-----------------------------|----------------------------------|--------------------------|-----------------|
| 0       | 1230° C   | 8 | 346.38         | 5.004                       | 5.129                            | 97.56                    | 2.44            |
| 0.1     | 1270° C   | 8 | 350.49         | 5.058                       | 5.170                            | 97.83                    | 2.17            |
| 0.2     | 1270° C   | 8 | 354.60         | 5.116                       | 5.172                            | 97.98                    | 2.02            |
| 0.3     | 1270° C   | 8 | 358.71         | 5.183                       | 5.217                            | 98.28                    | 1.72            |
| 0.4     | 1270° C   | 8 | 362.82         | 5.207                       | 5.319                            | 97.90                    | 2.10            |
| 0.5     | 1310° C   | 8 | 366.93         | 5.251                       | 5.406                            | 97.14                    | 2.86            |

Table 4. The specific data of formula weight, apparent density ($\rho_o$), theoretical density ($\rho_{theo}$), relative density ($D$) (%), porosity ($P$) (%) of Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0$–$0.5$) ceramics sintered at 1270°C and 1310°C for 4h.

| x (mol) | S.T. (°C) | Z | Formula weight | Apparent density ($\rho_o$) | Theoretical density ($\rho_{theo}$) | Relative density ($D$) (%) | Porosity ($P$) (%) |
|---------|-----------|---|----------------|-----------------------------|----------------------------------|--------------------------|-----------------|
| 0       | 1230° C   | 8 | 346.38         | 5.004                       | 5.129                            | 97.56                    | 2.44            |
| 0.1     | 1270° C   | 8 | 350.49         | 5.058                       | 5.170                            | 97.83                    | 2.17            |
| 0.2     | 1270° C   | 8 | 354.60         | 5.116                       | 5.172                            | 97.98                    | 2.02            |
| 0.3     | 1270° C   | 8 | 358.71         | 5.183                       | 5.217                            | 98.28                    | 1.72            |
| 0.4     | 1270° C   | 8 | 362.82         | 5.207                       | 5.319                            | 97.90                    | 2.10            |
| 0.5     | 1310° C   | 8 | 366.93         | 5.251                       | 5.406                            | 97.14                    | 2.86            |

Table 5. The observed and theoretical polarizabilities of Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0$–$0.5$) ceramics sintered at the optimal temperature of 1270°C for 4h.

| x (mol) | Theoretical $\alpha_{theo}$ ($\AA^3$) | Observed $\epsilon_r$ | Z | Observed $\alpha_{obs}$ ($\AA^3$) | $\Delta\alpha=\alpha_{obs}-\alpha_{theo}$ (%) |
|---------|--------------------------------------|----------------------|---|---------------------------------|-----------------------------------|
| 0       | 23.030                               | 19.89                | 8 | 23.103                          | 0.32                              |
| 0.1     | 23.102                               | 20.02                | 8 | 23.216                          | 0.49                              |
| 0.2     | 23.174                               | 20.15                | 8 | 23.295                          | 0.52                              |
| 0.3     | 23.246                               | 20.61                | 8 | 23.389                          | 0.61                              |
| 0.4     | 23.318                               | 20.63                | 8 | 23.456                          | 0.59                              |
| 0.5     | 23.390                               | 20.93                | 8 | 23.538                          | 0.63                              |

Figure 4(c) displays the dielectric constants of the Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0$–$0.5$) ceramics sintered from 1230°C to 1310°C for 4h. The $\epsilon_r$ increased with the increasing x, and the variations of dielectric constants as a function of Zn content were similar to the variations of the apparent densities as a function of x. The increasing sintering temperature also was correlated with the higher $\epsilon_r$. It is widely reported that the dielectric constant were relevant to the factors of pores, secondary phases, intrinsic factor of ion polarizability and ion vibrations [22]. For Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ ($x=0$–$0.5$) ceramics sintered at the optimal sintering temperature of 1270°C for 4h, the relatives densities were all high (>97%), thus the effects of porosities to dielectric constants were insignificant. Therefore, the dielectric constants were mainly attributed to the ion polarizability. The theoretical polarizabilities $\alpha_{theo}$ were calculated by summing the molecular polarizabilities of each ionic substance [23]:

$$\alpha_{theo}(\text{Li}_3\text{Mg}_{2-x}\text{Zn}_x\text{TaO}_6)=3\alpha_{O}(\text{Li}^{3+})+(2-x)\alpha_{O}(\text{Mg}^{2+})+x\alpha_{O}(\text{Zn}^{2+})+\alpha_{O}(\text{Ta}^{5+})+6\alpha_{O}(\text{O}^{2-})$$

(2)
The observed ionic polarizabilities and dielectric constant were associated according to the Clausius-Mosotti equation [24] in the uniform dielectric materials: 

\[ \alpha_{obs} = \frac{V_m (\varepsilon_2 - 1)}{b (\varepsilon_2 + 2)} \]  

(3) where \( \varepsilon_2 \) is the measured dielectric constant, \( \alpha_{obs} \) is the observed dielectric polarizability, \( V_m \) is the molar volume, \( b \) has the value of \( 4\pi/3 \). The results of \( \alpha_{theo} \) and \( \alpha_{obs} \) of LMZTO \((x=0-0.5)\) ceramics sintered at 1270°C are shown in Table 5. The \( \alpha_{theo} \) and \( \alpha_{obs} \) all increased as \( x \) increased, therefore, the increase of dielectric constants was mainly attributed to the increase of ionic polarizabilities. In addition, it was noticeable that the \( \Delta \alpha \) has an increasing tendency with the increasing \( x \), the deviations of \( \alpha_{obs} \) from \( \alpha_{theo} \) were increased due to the increase of rattling effect and the decrease of bond strength [25].

Figure 4(d) shows the quality factors \((Q\times f)\) of the \( \text{Li}_3\text{Mg}_{2-x}\text{Zn}_x\text{TaO}_6 \((x=0-0.5)\) ceramics sintered from 1230°C to 1310°C for 4h as a function of \( x \). The variations of \( Q\times f \) values of all the samples sintered at the different temperatures were similar, therefore they firstly increased in the range of 0 to 0.3, then decreased. The \( Q\times f \) values were varied from 75,219 GHz to 106,863 GHz, the wide range of the \( Q\times f \) values indicated that the quality factors of \( \text{Li}_3\text{Mg}_{2-x}\text{Zn}_x\text{TaO}_6 \((x=0-0.5)\) ceramics were highly dependent on Zn content and the optimal sintering temperature in this study. It is generally accepted that \( Q\times f \) value is largely dependent on the extrinsic factors such as density, pores and secondary phase, and intrinsic ones associated with with composition and crystal structure of the materials, such as packing fraction [26].

As seen from Figure 4(b) and Figure 4(d), the variation of \( Q\times f \) values of LMZTO \((x=0-0.5)\) ceramics sintered at 1230°C, 1270°C and 1310°C showed a similar tendency to the relative densities as a function of \( x \). Hence, the best \( Q\times f \) values achieved in 1270°C due to the porosity was lowest in these samples seen from Figure 4(b). And the worst quality factors of the ceramics were obtained when the samples were sintered at 1310°C, implying that the samples were over-sintered when sintered at high temperature of 1310°C. However, the \( Q\times f \) values and the relative densities did not show the strictly same tendency because that the quality factor was affected by the comprehensive reasons. As one of the most important factor of intrinsic loss, the packing fraction is widely considered to be responsible for the changing of quality factors in ceramics with relative density lager than 97% [27]. In this work, the packing fraction was calculated using the following formula:

\[ \text{Packing fraction(\%)} = \frac{\text{volume of the atoms in the cell} \times 2}{\text{volume of the unit cell}} = \frac{4\pi}{2} \times (r_1^3 \times 3 + (2-x) \times r_2^3 + r_3^3 + x \times r_4^3 + r_5^3 + 6 \times 8) \]  

(4)

The results of packing fraction is presented in Table 1, as shown in Table 1 (last row) the packing fraction decreased with the increasing Zn content, and an abrupt decrease was also shown in LMZTO \((x=0.4)\) ceramics as Zn content added from 0.3 to 0.4 mol. Therefore, in general, the improvement of the quality factors might be mainly attributed to the increase of relative densities, and the decrease of quality factors might be ascribed to the appearance of pores (increase of porosity) and the abrupt decrease of packing fractions as ZnO content \( x \geq 0.4 \) mol.

Figure 4(e) shows the temperature coefficient of resonant frequency \((\tau_r)\) of \( \text{Li}_3\text{Mg}_{2-x}\text{Zn}_x\text{TaO}_6 \((x=0-0.5)\) ceramics sintered at 1270°C for 4h. The \( \tau_r \) increased from -26.47 to -17.78 ppm/°C with the increasing \( x \). It is reported that the magnitude of \( \tau_r \) are highly correlated with the temperature coefficient of permittivity \((\tau_e)\) [28]. According to Bosman et al. [29], \( \tau_e \) is made up of three terms: \( A \), \( B \) and \( C \). The term \( A \) expresses the direct relationship between the polarizability and temperature per unit volume. \( B \) term represents the increase of the polarizability per unit cell and \( C \) represents the decrease in the number of polarizable ions in a single cell, these \( B \) and \( C \) effects have similar absolute value but the opposite sign, thus the terms \( A \) plays a primary role on \( \tau_e \). And the \( A \) term effect was considered to be related to the restoring force affecting on ions, which depends mainly on the lattice parameters [30]. Therefore, the increase of \( \tau_r \) in this study was mainly attributed to the increase of cell volume, which were shown in Table 1.

4. Conclusions

The \( \text{Li}_3\text{Mg}_{2-x}\text{Zn}_x\text{TaO}_6 \((x=0-0.5)\) microwave dielectric ceramics were prepared by traditional solid-state reaction method through atmosphere controlled sintering technique. The correlations between the microstructures and microwave dielectric properties were investigated. The XRD patterns showed the
single phase of Li$_3$Mg$_2$TaO$_6$ (JCPDS No. 36-1017) with orthorhombic structure in Fddd (70) space group, and indicated the solid solutions of Li$_3$Mg$_{2-x}$Zn$_x$TaO$_6$ were formed in the range of 0~0.5. The SEM images showed that zinc substitution facilitated the grain growth, but ZnO impurity phase was observed because of the evaporation of ZnO in high sintering temperature, and with further increasing the ZnO content up to 0.4 mol, the liquid phase were formed during sintering. The apparent densities and dielectric constants increased with the increasing $x$. The $Q\times f$ values and relative densities firstly increased, reached maximum at $x=0.3$, and then decreased. The $\tau_f$ values increased as Zn content increased, the increase of $\tau_f$ was mainly attributed to the increase of cell volume. Typically, when sintered at 1270 °C for 4h, the excellent microwave properties were obtained for Li$_3$Mg$_{1.7}$Zn$_{0.3}$TaO$_6$ ($x=0.3$) ceramics: $\varepsilon_r=20.61$, $Q\times f=106,863$ GHz and $\tau_f=-21.6$ ppm/°C.

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