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Sintering behavior and microwave dielectric properties of High-Q $Li_2(Mg_{1-x}Zn_x)_3Ti(O_{0.96}F_{0.08})_6$ ceramics for LTCC application

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ABSTRACT

$Li_2(Mg_{1-x}Zn_x)_3Ti(O_{0.96}F_{0.08})_6$ (LMZTF) ceramics were fabricated through the solid-state reaction method. All samples diffraction peaks belong to Zn_2TiO_4 and $Li_2Mg_3TiO_6$. The SEM characterization and bulk density testing demonstrated the uniform microstructure of LMZTF ceramics. In this work, the dielectric loss of $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics was greatly reduced through ion doping. The High-Q $Li_2(Mg_{0.98}Zn_{0.02})_3Ti(O_{0.96}F_{0.08})_6$ ceramics sintered at 950 °C for 6 h possessed outgoing microwave dielectric properties: ε_r ~14.64, Q × f ~128,000 GHz, τ_f ~ −33.9 ppm/°C, which made it a promising candidate for low temperature co-fired ceramic (LTCC) applications.

1. Introduction

Microwave dielectric ceramics have excellent characteristics such as low loss, high resonance frequency stability, and low production costs [1–3]. Quality factor (Q × f values), dielectric constant (ε_r) and temperature stability (τ_f) are the important evaluation criteria of microwave ceramics [4,5]. The commonly used silver electrode layer has a melting point of 961 °C. Therefore, ceramic materials with excellent dielectric performance that can be co-fired with Ag or Cu electrodes at low temperatures are an important research object in the current era [6–11].

It has been reported that Li-based ceramics such as Li_2MgTiO_4, $Li_2MgTi_3O_8$, and $Li_2Mg_3TiO_6$ exhibit the advantages of adjustable dielectric constant and ultra-low dielectric loss [12–14]. In 2015, Fu et al. [14] explored the $Li_2Mg_3TiO_6$ ceramics. In 2016, Zhang et al. [15] reported the effects of Ni^{2+}, Ca^{2+}, Mn^{2+}, and Zn^{2+} on dielectric properties of $Li_2Mg_3TiO_6$ ceramics. Among them, $Li_2(Mg_{0.95}Zn_{0.05})_3TiO_6$ ceramics possessed excellent microwave properties. Then, the impact of the non-stoichiometric ratio on the properties of $Li_2Mg_3TiO_6$ ceramics was discussed. $Li_2Mg_{3.6}TiO_{6.6}$ ceramics sintered at 1375 °C obtained outgoing properties [16]. Co^{2+} was used to replace Mg^{2+} to systematically analyze the influences of crystal structure on the performance of $Li_2Mg_3TiO_6$ ceramics [17]. Wu et al. [18,19] used composite ions $(Mg_{1/3}Sb_{2/3})^{4+}$ and $(Mg_{1/3}Nb_{2/3})^{4+}$ to replace Ti^{4+} ions of $Li_2Mg_3TiO_6$ ceramics. $Li_2Mg_3Ti_{0.95}(Mg_{1/3}Nb_{2/3})_{0.05}O_6$ ceramics sintered at 1575 °C for 4 h possessed outgoing microwave dielectric properties: ε_r ~14.79, Q × f ~204, 900 GHz, τ_f ~ −18.43 ppm/°C. In 2017, Xie et al. [11] used $Ca_{0.8}Sr_{0.2}TiO_3$ to improve the τ_f value of $Li_2Mg_3TiO_6$ ceramics. When the composition was $0.9Li_2Mg_3TiO_6$-$0.09Ca_{0.8}Sr_{0.2}TiO_3$, the value of τ_f was −3.65 ppm/°C.

However, there are few studies on the low-temperature sintering of $Li_2Mg_3TiO_6$ ceramics. In 2017, Fu et al. [20] used LiF as a sintering aid and $Ca_{0.8}Sr_{0.2}TiO_3$ as a τ_f compensator to successfully prepare a dielectric material that met the requirements of LTCC technology. The sintering temperature of the $Li_6Mg_7Ti_3O_{16}$ + 4 wt%LiF, $Li_2Mg_3SnO_6$ + 5 wt%LiF and $Li_2Mg_3TiO_6$ + 4 wt%LiF ceramics was reduced to below 950 °C and the ceramics had satisfactory dielectric properties [21–23]. Liu et al. [24] reported that $Mg_{0.85}Zn_{0.15}SiO_3$ ceramics obtained outgoing dielectric properties when sintered at 1360 °C. In addition, compared with other ions, the F^- ion has excellent chemical stability. Therefore, replacing O^{2-} ion with F^- ion can reduce the sintering temperature of $Li_2Mg_3TiO_6$ ceramics and maintain its outgoing dielectric properties [25]. Since the radius of Zn^{2+} ions is similar to Mg^{2+} ions, the Mg^{2+} ions in $Li_2Mg_3TiO_6$ ceramics can be replaced by Zn^{2+} ions. Appropriate amounts of Zn^{2+} replacing Mg^{2+} may have a positive impact on the performance of the $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics.

In this paper, the Mg^{2+} ions in $Li_2(Mg_{1-x}Zn_x)_3Ti(O_{0.96}F_{0.08})_6$ (LMZTF) were replaced by different contents of Zn^{2+} ions. The

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change law of microstructure and dielectric properties were researched. Finally, LMZTF ($0.02 \le x \le 0.08$) ceramics with excellent properties and low sintering temperature were successfully prepared.

2. Experimental section

LMZTF ($0.02 \le x \le 0.08$) ceramics were fabricated using Li_2CO_3, MgO, TiO_2, LiF, and ZnO as raw materials. The raw materials were mixed with ZrO_2 balls and deionized water, and the ball-milling time was 8 h. After drying and sieving, all mixtures were pre-fired at 700 °C for 4 h. Then, the calcined powders were ball-milling again for 8 h. After drying and sieving, the paraffin wax was added to the powder for granulation, which was pressed into a cylindrical body of Φ10 mm × 5 mm. Finally, these LMZTF samples were sintered at 850–975 °C.

In this paper, the X-ray diffractometer (Rigaku D/max 2550 PCX) produced in Japan was used to test the phase composition of LMZTF ceramics. A scanning electron microscope (ZEISS MERLIN Compact, Germany) was used to observe the surface microstructure. The Agilent N5234A vector network analyzer was used to measure the dielectric constant and $Q \times f$ values of LMZTF ceramics. The τ_f was calculated according to Eq. (1):

$$\tau f = \frac{f2 - f1}{f1(T2 - T1)} \times 10^6 (ppm/°C) \quad (1)$$

where f_2 and f_1 were the resonant frequencies at T_2 (85 °C) and T_1 (25 °C), respectively.

Fukuda et al. [26] studied the variation law of the temperature coefficient of the resonance frequency of the TiO_2-Bi_2O_3 composite system, and proposed that τ_f could be expressed by the following mixing rule:

$$\tau_f = \nu_1 \tau_{f1} + \nu_2 \tau_{f2} \quad (2)$$

where ν_1 and ν_2 are the volume fractions of each component, respectively. τ_{f1} and τ_{f2} are the temperature coefficients of the resonance frequency of each component, respectively.

The bulk densities were measured by the Archimedes method. The theoretical density was obtained by Eq. (3):

$$\rho_{theory} = \frac{ZA}{V_C N_A} \quad (3)$$

where Z, A, V_C, and N_A were the number of atoms in the unit cell, atomic weight (g/mol), the volume of the unit cell (cm^3), and Avogadro constant (mol^{-1}), respectively. The relative density was obtained as the following formula:

$$\rho_{relative} = \frac{\rho_{bulk}}{\rho_{theory}} \quad (4)$$

3. Results and discussion

The XRD pattern of LMZTF ceramics sintered at 950 °C for 6 h is shown in Fig. 1. The diffraction peaks of LMZTF ceramics correspond to the $Li_2Mg_3SnO_6$ (PDF#39-0932) standard card. When $0.02 \le x \le 0.08$, the second phase Zn_2TiO_4 is detected in the samples. The research by Yang et al. [27] showed that when the amount of Zn^{2+} ion substitution was greater than 0.02 mol, the second phase was generated in $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ceramics. However, in this study, the Zn_2TiO_4 phase appeared when the amount of Zn^{2+} ions

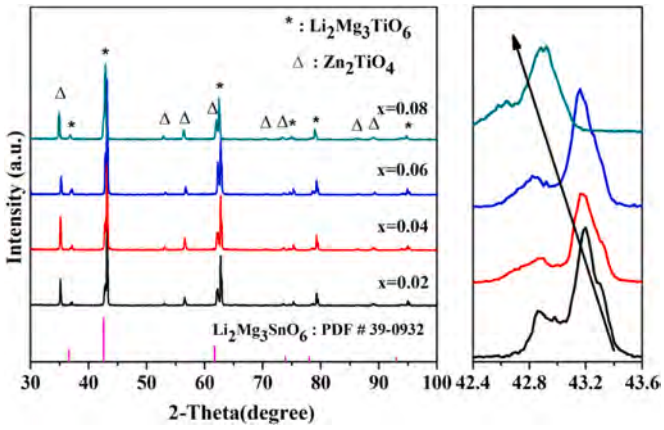

Fig. 1. The XRD patterns of LMZTF ceramics sintered at 950 °C for 6 h.

substitution was greater than or equal to 0.02 mol. It is shown that the substitution of F^- ions affect the solid solubility of $Li_2Mg_3TiO_6$ ceramics. As shown in Fig. 1, the main peaks of LMZTF shift slightly to the lower angle because of the difference in ionic radius between Zn^{2+} ion (0.740 Å) and Mg^{2+} ion (0.720 Å).

The microstructure of LMZTF ceramics sintered at 950 °C for 6 h is shown in Fig. 2. To characterize the influence of Zn^{2+} substitution on the grain size of LMZTF ceramics, the grain size distribution histograms of sintered samples with different x values are shown in Fig. 3. When x = 0.02, the sample surface is dense and uniform. When $0.04 \le x \le 0.08$, the grain size of the sample is not compact and uniform, and there are fine pores. In general, material composition and sintering temperature affect the microstructure and porosity of ceramics. All the components in Fig. 2 exhibit similar polygonal grains with clear grain boundaries. Compared with SEM images of Zhang et al. [25] on $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics, Zn^{2+} ions increase the grain size of ceramics. The average grain sizes are 2.16, 2.36, 2.28, and 2.35 μm, respectively. This may be because the addition of Zn^{2+} ions to the grain of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics weakens the free energy and promotes the grain growth of LMZTF ceramics.

The dispersion degree of particle size distribution is used to test the uniformity of particle size. The formula in the reference

$$\bar{S} = \frac{1}{n} \sum_{i=1}^{n} S_i \quad (5)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (S_i - \bar{S})^2}{n}} \quad (6)$$

where $\bar{S}$ and σ are average particle size and dispersion degree of particle size distribution, respectively. Fig. 4 shows the average particle size area and dispersion degree of particle size distribution respectively. From 0.02 to 0.04, the average particle size area increases with the increase of Zn^{2+} content. When x = 0.06, the average particle size area decreases. When x = 0.02, the value is about 3.664 μm^2. When x = 0.04, the value is about 4.374 μm^2. When x = 0.06, the value is about 4.083 μm^2. When x = 0.08, the value is about 4.374 μm^2. When x = 0.02, the particle size dispersion is the smallest, and when x = 0.08, the maximum particle size dispersion is

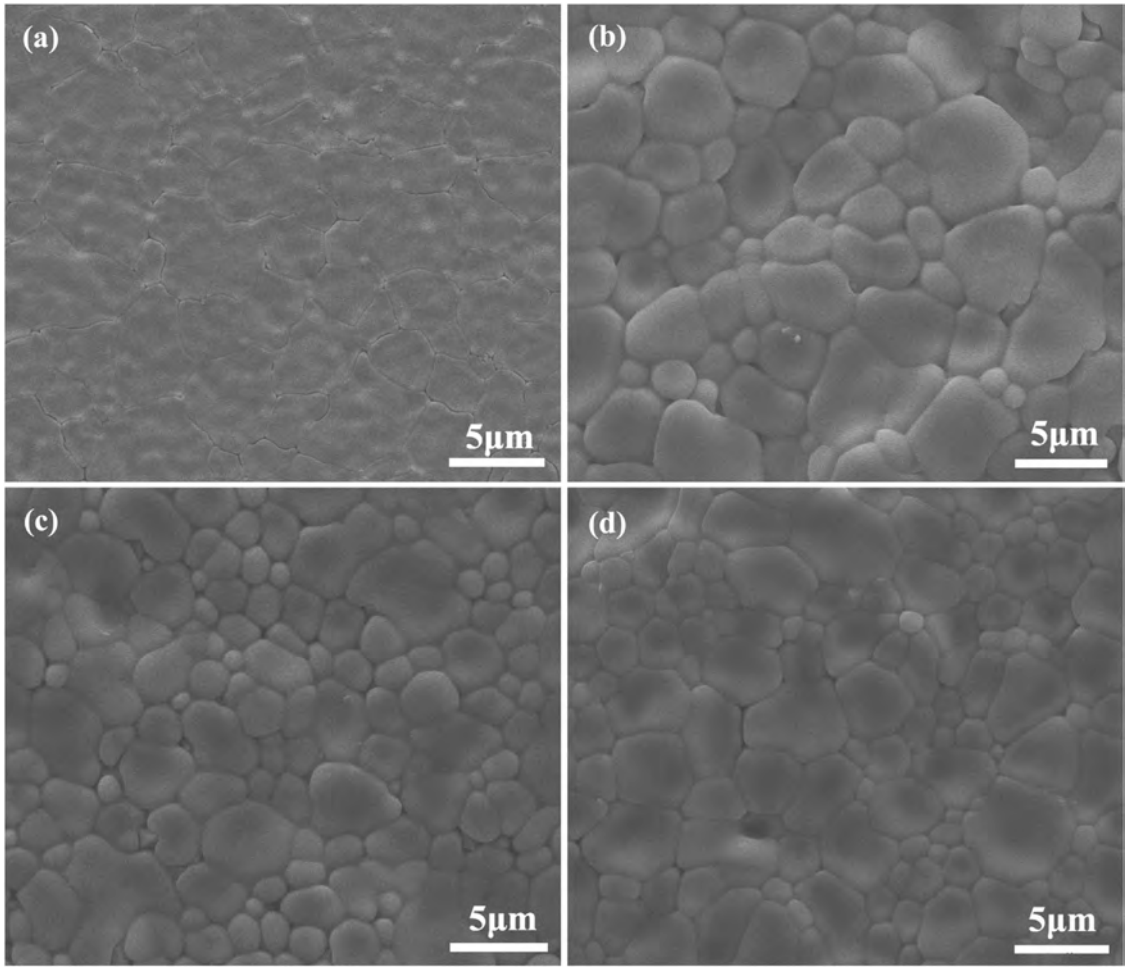

Fig. 2. The surface microstructures of LMZTF ceramics sintered at 950 °C for 6 h: (a) x = 0.02; (b) x = 0.04; (c) x = 0.06; (d) x = 0.08.

obtained, indicating that as the value of x increases, the particle size distribution gradually becomes uneven.

Fig. 5(a) is the change curve of the relative density of LMZTF ceramics at different sintering temperatures. Overall, the relative density of LMZTF ceramics shows a trend of increasing first and then decreasing with the increase of sintering temperature. In addition, the relative density of LMZTF ceramics reaches a maximum of 95.3% at x = 0.02, and it declines with the increase of x. The change of the lattice structure weakens the free energy of LMZTF ceramics and facilitates the sintering process, so the sample has a high degree of densification. When $0.04 \le x \le 0.08$, the point defects generated by excessive Zn^{2+} ions are converted into line defects and surface defects during the sintering process, which affects the density of the LMZTF ceramics, so the density gradually decreases [28].

The dielectric constant of LMZTF ceramics is illustrated in Fig. 5(b). The ε_r increases rapidly with the sintering temperature rising, which is similar to the tendency of relative densities. The ε_r of the LMZTF ceramics gradually increases, reaching the maximum value at 950 °C, and then gradually decreases. However, the ε_r of LMZTF ceramics increases with the increase of doping amount when the sintering temperature is 950 °C, which is opposite to the changing trend of relative density. This result is mainly caused by the formation of the second phase. It can be known from the XRD pattern that when $x \ge 0.02$, the Zn_2TiO_4 phase is detected in the sample, indicating that the sample is a multi-phase composite. For heterogeneous composite ceramic materials, the dielectric constant depends on the combination of the volume fraction of the component materials and the dielectric constants of the component materials [29], which can be derived from the following mixing rules [30]:

$$\ln \varepsilon = \sum_i V_i \ln \varepsilon_i \tag{7}$$

where ε_i and V_i are the dielectric constant and volume fraction of the i-th phase, respectively. The dielectric constant of Zn_2TiO_4 is higher than that of $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$, so the dielectric constant of LMZTF ceramics gradually increases with the increase of x.

Fig. 5(c) is the changing trend of $Q \times f$ values of LMZTF ceramics at different sintering temperatures. The $Q \times f$ value of LMZTF ceramics reaches its maximum value at 950 °C as the temperature increases. Besides, at 950 °C, the quality factor of LMZTF ceramics is between 115,000 GHz and 128,000 GHz, and the maximum value of

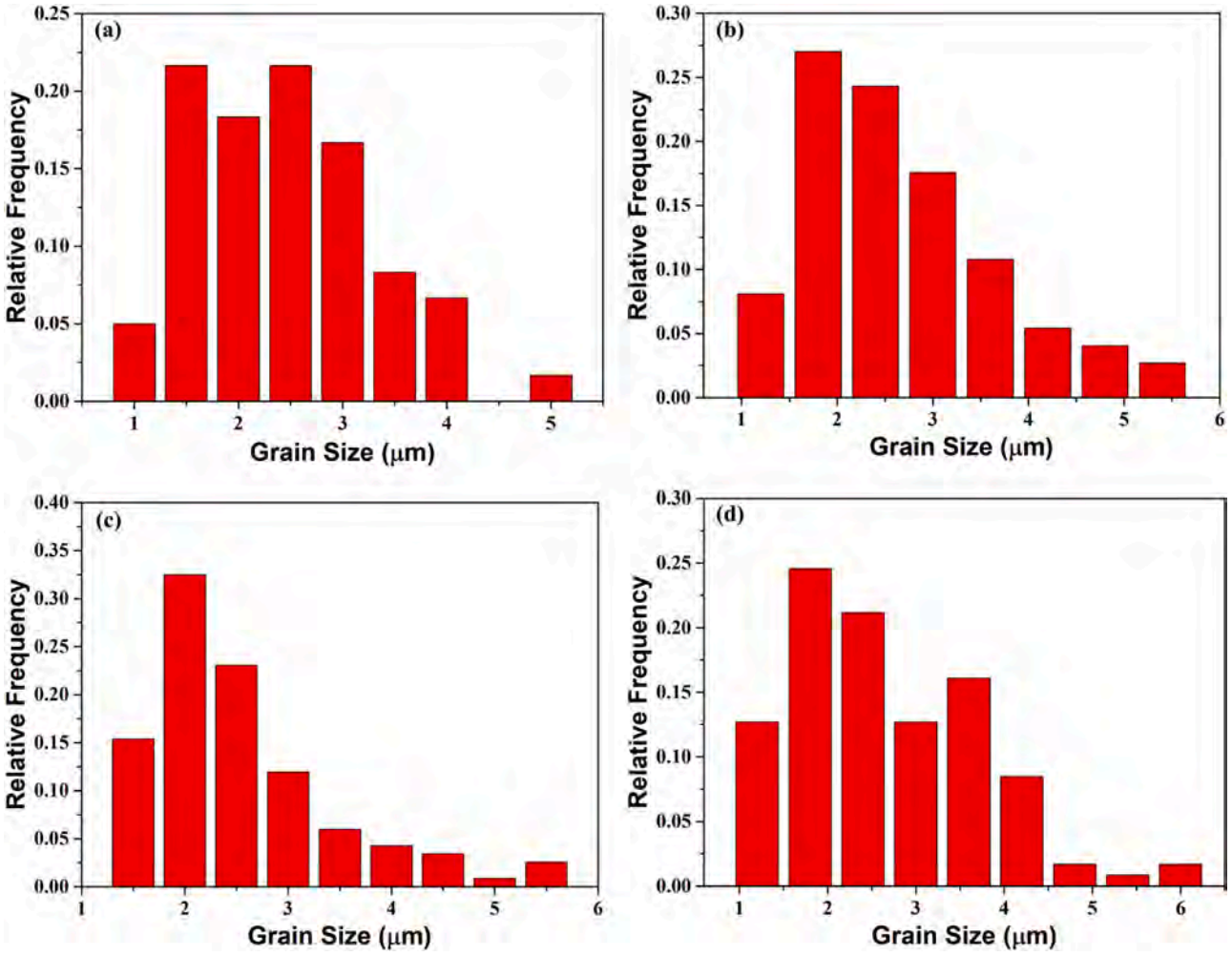

Fig. 3. Grain size distribution of LMZTF ceramics sintered at 950 °C for 6 h: (a) x = 0.02; (b) x = 0.04; (c) x = 0.06; (d) x = 0.08.

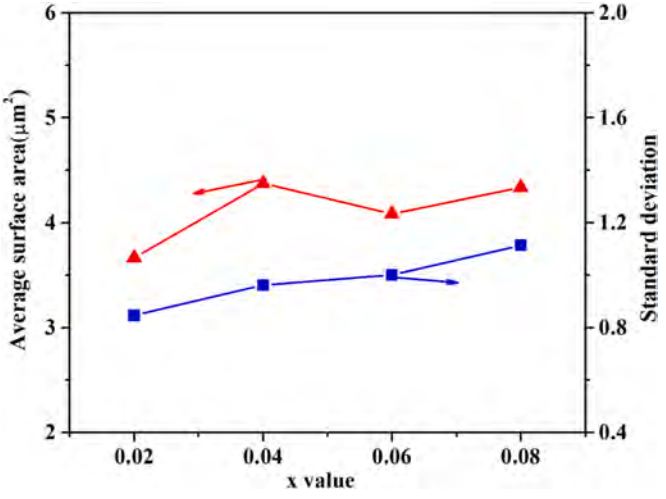

Fig. 4. The average surface area and dispersion degree of particle size sintering at 950 °C for 6 h.

128,000 GHz is obtained at x = 0.02. The relative density and second phase affect the $Q \times f$ values greatly. The research results show that the substitution of Zn^{2+} effectively improves the $Q \times f$ value of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics. This is because the substitution of Zn^{2+} ions causes lattice distortion and introduces point defects to promote sintering and obtain a larger bulk density. Also, the decrease in $Q \times f$ values when the amount of Zn^{2+} substitution is greater than 0.02 mol is due to the increase of the content of the second phase Zn_2TiO_4. The quality factor of Zn_2TiO_4 is about 1000–2000 GHz, which will reduce the $Q \times f$ value of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics.

The τ_f values of LMZTF ceramics sintered at 950 °C for 6 h are shown in Fig. 6. We observe that due to the small distinction between the temperature coefficient of $Li_2Mg_3TiO_6$ ceramics and Zn_2TiO_4 ceramics, the τ_f of $Li_2Mg_3TiO_6$ ceramics changes slightly with the increase of Zn^{2+} content ($Li_2Mg_3TiO_6$: −39 ppm/°C; Zn_2TiO_4: −67 ppm/°C). The dielectric properties of LMZTF ceramics are shown in Table 1. It can be concluded that $Li_2(Mg_{0.98}Zn_{0.02})_3Ti(O_{0.96}F_{0.08})_6$ ceramic has the largest relative density and high performance: ε_r ~ 14.64, $Q \times f$ ~ 128,000 GHz, τ_f ~ −33.9 ppm/°C.

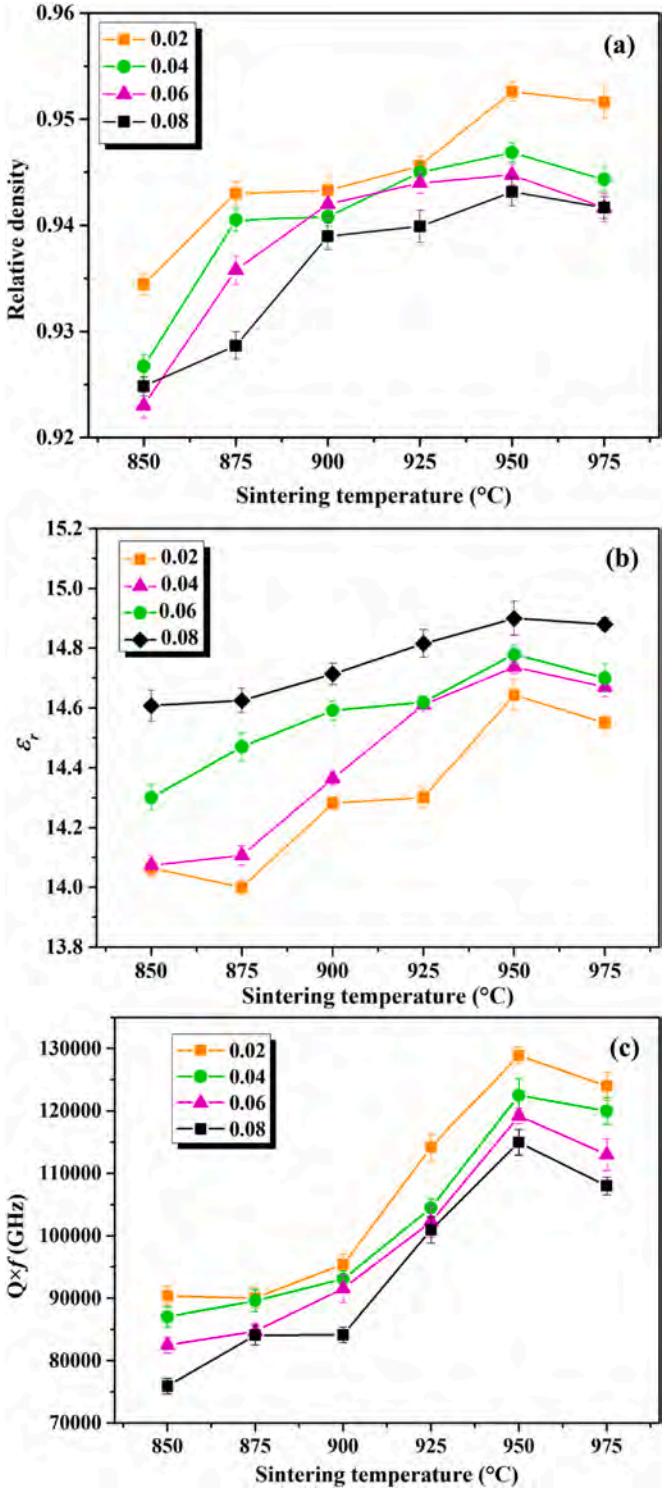

Fig. 5. The variations in relative density, dielectric constant, and Q × *f* values of LMZTF ceramics sintered at various temperature for 6 h as a function of Zn^{2+} ions content.

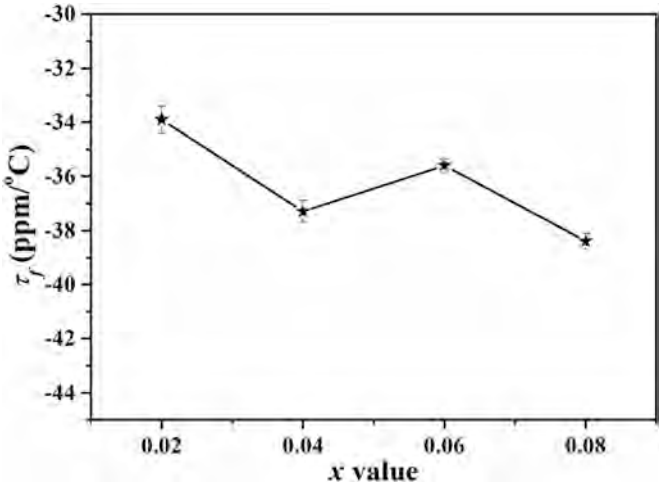

Fig. 6. The τ_f values of LMZTF ceramics sintered at 950 °C for 6 h.

Table 1
Relative density and microwave dielectric properties of LMZTF ceramics sintered at 950 °C.

LMZTF	Relative density (%)	ε_r	Q × *f* (GHz)	τ_f (ppm/°C)
x = 0.02	95.2	14.64	128,000	−33.9
x = 0.04	94.6	14.73	122,000	−37.3
x = 0.06	94.4	14.78	119,000	−35.6
x = 0.08	94.3	14.9	115,000	−38.4

4. Conclusions

In this work, when x = 0.02, the substitution of Zn^{2+} ions reduced the free energy, promoted the sintering process, and obtained optimal relative density value and dielectric properties. When 0.04 ≤ x ≤ 0.08, the increase of the content of the second phase Zn_2TiO_4 had a certain adverse impact on the density and performance. In summary, this paper showed that the $Q \times f$ values of $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics could be improved through ion doping. Particularly, when the sintering temperature is 950 °C, $Li_2(Mg_{0.98}Zn_{0.02})_3Ti(O_{0.96}F_{0.08})_6$ ceramic has the best dielectric properties: ε_r ~14.64, $Q \times f$ ~ 128,000 GHz, τ_f ~ − 33.9 ppm/°C.

CRediT authorship contribution statement

Ping Zhang: Conceptualization, Methodology, Validation, Investigation, Writing-original draft, Writing-review & editing, Resources. **Manman Hao:** Methodology, Validation, Writing-original draft, Formal analysis, Data curation, Software. **Xin Tian:** Data curation. **Sheng Xie:** Methodology, Validation, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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