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Sintering behavior and microwave dielectric properties of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics for LTCC application

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Abstract

A novel system $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics were synthesized through the solid stated reaction method. The calcining temperature, sintering behavior and microwave dielectric properties of samples were investigated systematically. The effects of different calcining temperatures for $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics on sintering behavior and microwave dielectric properties were discussed. The optimum calcining temperature was obtained at 700°C because the high point defect concentrations with associated high diffusivities promoted the solid state synthesis reaction. In addition, the phase compositions, microstructure and microwave dielectric properties of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics were studied. The ε_r and $Q\times f$ values showed the similar tendency with the relative density as x increased. Moreover, the amount of liquid phase also could be a significant factor affecting dielectric properties, which could be confirmed from the change of morphology of grains. Furthermore, the $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics calcined at 700°C and sintered at 950°C for 6 hours exhibited the excellent microwave dielectric properties of ε_r~14.57, $Q\times f$~92,450GHz and τ_f~-32.91 ppm/°C.

Keywords: $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$; Microwave dielectric properties; Calcining temperature; Liquid phase sintering

1. Introduction

Microwave dielectric ceramics are a kind of important electronic functional materials, widely used in the microwave frequency band (300MHz ~ 300GHz), and are the key materials for dielectric resonators, oscillators, phase shifters and other components which are used in modern communication devices [1-3]. The inorganic electronic functional materials and organic electronic functional materials both have extensive researches [4-6]. In recent years, LTCC (Low Temperature Co-fired Ceramic) technology has become the preferred way for electronic components integration and modularization

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due to the excellent electronic, mechanical and thermal properties. It is widely used in the field of substrates, packaging and microwave devices [7]. To meet the application of LTCC technology, the materials should have these characteristics: lower sintering temperature (below the melting point of common metals such as Ag, Al, Cu, Au), excellent dielectric properties, low-cost and environmental protection [8-10].

$Li_2Mg_3TiO_6$ ceramics with excellent microwave dielectric properties of ε_r~15.2, $Q\times f$~152,000GHz and τ_f~39ppm/°C sintered at 1280°C for 6h were reported by Fu firstly [11]. Afterwards, the improvements of microwave dielectric properties for $Li_2Mg_3TiO_6$ ceramics were widely studied. There were some researches improved the $Q\times f$ values by the methods of ion substitutions and non-stoichiometry [12]. For example, divalent cations of Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} substituted for Mg^{2+} ions, tetravalent ions ($Ge^{4+}$and Zr^{4+}) and compound ions of $(Mg_{1/3}Nb_{2/3})^{4+}$and $(Mg_{1/3}Sb_{2/3})^{4+}$ substituted for Ti^{4+} ions [13-17]. What's more, Fu and Ma etc. reported that the τ_f values could be adjusted to near zero by adding $SrTiO_3$ and $Ca_{0.8}Sr_{0.2}TiO_3$ [18-19].

With regard to low-temperature sintering of $Li_2Mg_3TiO_6$ ceramics, some sintering additives such as LC (2wt%LiF+2wt%CuO), LV (2wt%LiF+2wt%V_2O_5) and LB (2wt%LiF+2wt%Bi_2O_3) were added to reduce the sintering temperature [20]. Besides, LiF was routinely used as sintering additive to reduce the sintering temperature for Li-based microwave dielectric ceramics, for instance, the $Li_6Mg_7Ti_3O_{16}$-4wt%LiF, $Li_2Mg_3SnO_6$-2~5wt%LiF and $Li_2Mg_3TiO_6$-4wt%LiF had good dielectric properties and the sintering temperatures were reduced to below 950°C[21-24]. However, the addition of LiF as sintering additive after calcination reduced the sintering temperature, but the calcining temperature remained high. Previous studies showed that the F^- ions could substitute for O^{2-} ions during sintering process when adding LiF after calcining [23]. Besides, F^- ions possessed excellent chemical stability compared to other anions. Therefore, it is worthwhile for us to investigate whether it is possible to reduce both the calcining temperature and sintering temperature of $Li_2Mg_3TiO_6$ ceramics and keep the excellent dielectric properties by the substitution of F^- anions for O^{2-} ions.

In this paper, the $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics were synthesized through the solid stated reaction method. The effects of the substitution of F^- anions for O^{2-} ions on the calcining temperature were discussed, and the microwave dielectric properties of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics with different calcining temperatures were analyzed. Furthermore, the influence of different F^- ions amounts on the sintering temperature and dielectric properties for $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$)

ceramics at the optimum calcining temperature were investigated. In addition, the phase compositions, morphology and sintering characteristics of ceramics were discussed.

2. Experimental procedure

$Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06 \le x \le 0.15$) ceramics were prepared using high-purity (≥99%) oxide powders of Li_2CO_3, MgO, TiO_2 and LiF. The raw materials were mixed according to the formula of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06 \le x \le 0.15$) ceramics. The mixed powders were milled with ZrO_2 balls for 8h in distilled water. All mixtures were dried and calcined at 650-750°C for 4h. The calcined powders were remilled with ZrO_2 balls for 8h in distilled water, and then dried. These mixtures were mixed together with 6wt% -9wt% paraffin as a binder. Afterwards, the granulated powders were pressed into cylinders with 10mm in diameter and about 5mm in height. Finally, the pellets were first heated at 550°C in air for 3h to burn out the organic binder, then sintered at 850-975°C for 6h in the air.

The crystalline phases of the sintered samples were investigated by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Tokyo, Japan) with Cu Ka radiation generated at 40kV and 40mA. The microstructures of the ceramic surfaces were performed and analyzed by a scanning electron microscopy (SEM, ZEISS MERLIN Compact, Germany). The microwave dielectric properties of the sintered samples were measured by a network analyzer (N5234A, Agilent Co, America) in the frequency range of 8–13 GHz. The dielectric constants were measured by exciting the $TE_{01\sigma}$ resonant mode of the dielectric resonator as suggested by Hakki-Coleman [24]. The unload quality factors were measured using $TE_{01\sigma}$ mode by the cavity method [25]. The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range from 25 °C to 85 °C and was calculated by the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6 (ppm/^oC) \quad (1)$$

where f_{85} and f_{25} were the resonant frequencies at 85°C and 25°C, respectively.

The bulk densities(ρ_{bulk}) of the sintered samples were measured by using the Archimedes method and the theoretical density was obtained using the following:

$$\rho_{theory} = \frac{ZA}{V_c N_A} \quad (2)$$

where A is the atomic weight (g/mol), Z is the number of atom in a unit cell, N_A is Avogadro number (mol^{-1}) and V_c is the volume of unit cell (cm^3). The relative density could be calculated as follows:

$$\rho_{relative} = \frac{\rho_{bulk}}{\rho_{theory}} \times 100\% \quad (3)$$

3. Results and discussions

Fig. 1(a) exhibits the XRD patterns of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at different temperatures. From this figure, the phases like LiF and $MgTiO_3$ are detected when samples were calcined at 650°C, which can be attributed to the lower calcining temperature resulting in the powders cannot react completely. However, as the calcining temperature rises to 700°C, the main crystalline phases of $Li_2Mg_3TiO_6$ ceramics are formed and no other phases are detected. However, as the calcining temperature continues rising, the powder particles become coarsen and even tend to block and agglomerate, which will have significant negative effects on the secondary ball milling and the final sintering of samples. A model was proposed by W. Rhodes et al. that there were two different mechanisms for promoting sintering reaction on both sides of LiF melting points [26]. So in our system, the calcination below LiF melting points is mainly the process of forming the solid solution. Furthermore, the high point defect concentrations will be caused which could be responsible for high diffusion rates for ions in a solid solution zone. The introduction of crystal defects leads to a contraction of the crystal lattice [26]. The synthetic reaction is promoted significantly.

On the other hand, from the view point of energy, the forming of the solid solution will reduce the chemical potential and free energy, which will also improve the reaction rate. What's more, a liquid phase sintering mechanism probably becomes operative when the sintering temperature is higher than the melting point of LiF. The XRD patterns of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics sintered at 950°C under different calcining temperatures are shown in Fig. 1(b). All the samples exhibited $Li_2Mg_3SnO_6$-like (JCPDS#39-0932) cubic phase, it indicates that although the powders cannot completely react at the calcining temperature of 650°C, the reaction can be continued during the final sintering process, but it will shorten the sintering time and affect the densification of ceramics. Fig. 2 displays the XRD patterns of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06 \leq x \leq 0.15$) ceramics calcined at 700°C and sintered at 950°C for 6h. Similarly, all the samples exhibit $Li_2Mg_3SnO_6$-like cubic phase and no others are detected. The main peaks angle are higher compared to $Li_2Mg_3SnO_6$-like because the ionic radius of Ti^{4+}(R=0.605Å, CN=6) is smaller than that of Sn^{4+}(R=0.69Å, CN=6) [11].

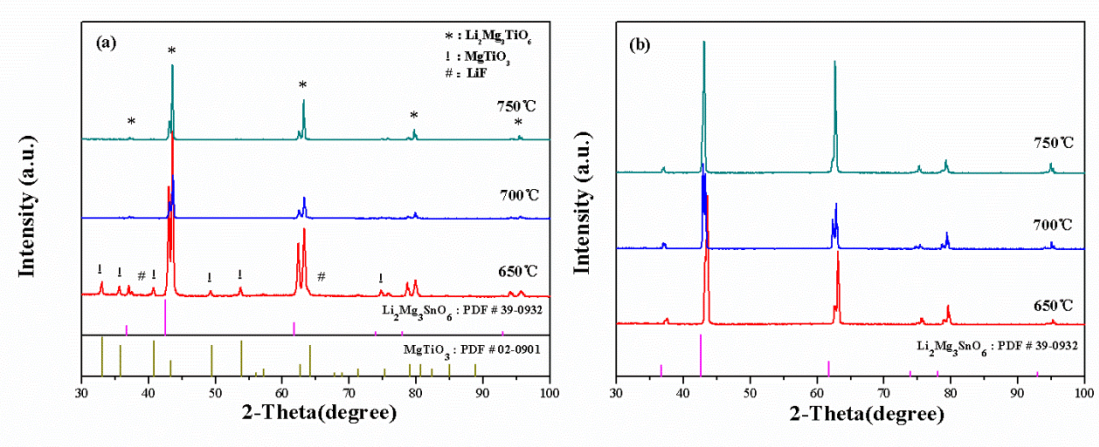

Fig. 1 (a) The XRD patterns of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at different temperatures. (b) The XRD patterns of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics sintered at 950°C under different calcining temperatures

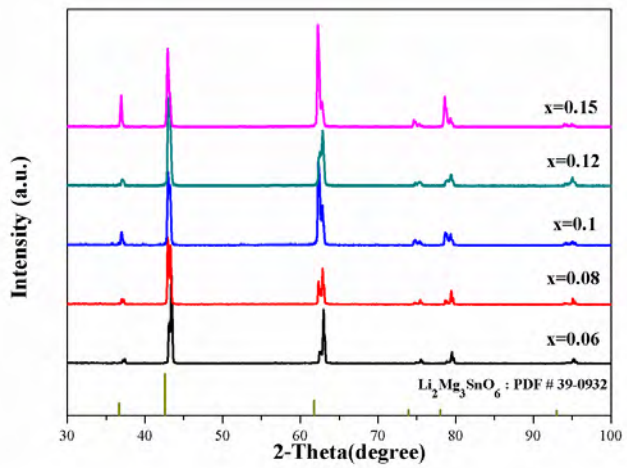

Fig. 2 The XRD patterns of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06 \leq x \leq 0.15$) ceramics sintering at 950°C for 6h

Fig. 3(a)-(c) present the SEM photographs of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at (a) 650°C, (b) 700°C and (c) 750°C and all sintered at 950°C for 6h. The homogeneous and dense crystalline morphology is obtained at the calcining temperature of 700°C. However, when the calcining temperature is 650°C or 750°C, the pores are found at the grain boundaries and the distributions of grain size are nonuniform, which leads to a harmful influence to dielectric properties [27]. Fig. 3(d)-(h) show the SEM photographs of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06 \leq x \leq 0.15$) ceramics calcined at 700°C and sintered at 950°C for 6h. It is because of that the liquid phase produced at 950°C cannot ensure the effective process of particle re-arrangement, and the liquid phase sintering cannot be finished

adequately, there are still some pores at the grain boundaries with x=0.06. Nevertheless, the dense and compact grain microstructure is obtained at x=0.08. In addition, it can be observed that the size of the crystal increases gradually due to elevated boundary and the diffusion coefficient caused by liquid phase sintering [23]. Moreover, there are some serious deformation and distortion of grain microstructure when x=0.12 and 0.15, it is mainly due to the excessive liquid phase produced that results in the decrease of viscosity.

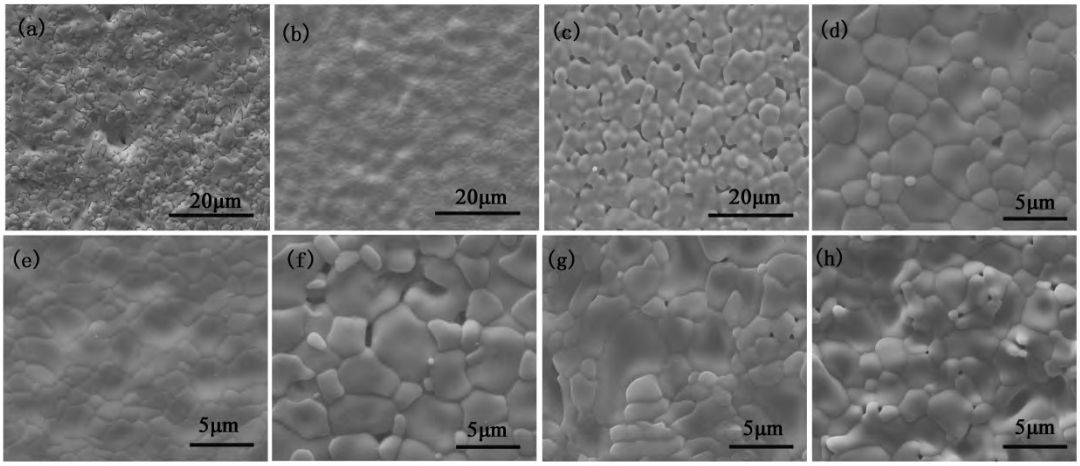

Fig. 3(a)-(c) The SEM photographs of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at (a) 650°C, (b) 700°C and (c) 750°C and all sintered at 950°C; (d)-(h) the SEM photographs of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics calcined at 700°C and sintered at 950°C for 6h (d-h corresponding to x=0.06, x=0.08, x=0.1, x=0.12, x=0.15)

Fig. 4(a)-(c) illustrate the relative density, dielectric constant ε_r and $Q\times f$ value of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at 650°C-700°C and sintered at different temperatures. From Fig. 4(a), the $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at 700°C own the highest relative density, which increases with the rise of sintering temperature and is up to 96.9% at 950°C, but it decreases when the sintering temperature is higher than 950°C. When the calcining temperature is 650°C, the relative density tendency of samples is consistent with the calcining temperature of 700°C in spite of 950-975°C, which still increases above 950°C. This may be attributed to that the solid reaction which is not sufficiently performed in the calcining process will continue during the sintering process, and the sintering time may be shortened. Besides, because of the lower calcining temperature, the calcined powders are loose and spongy. The ceramics bodies shrink quickly during sintering process so that some pores are not removed and occur at grain boundaries, which reduce the densification of samples.

In addition, there are many influencing factors of the liquid phase sintering, such as particles shape, green density, sintering temperature, heating rate and cooling rate etc, especially granularity. The fine particles are favorable for improving the rate of sintering densification and obtaining a high final sintering density, because the capillary force and mass transfer rate are enhanced and improved. Therefore, the particles are coarse when calcined at 750°C, which causes the lower relative density of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics.

The variations of dielectric constant ε_r and $Q\times f$ value of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at 650°C-700°C and sintered at different temperatures are shown in Fig. 4(b) and (c). The values of ε_r and $Q\times f$ are significantly affected by extrinsic losses which are caused by second phases, grain boundaries, porosity and densification [28-30]. It can be observed that the ε_r value and $Q\times f$ value have a similar trend with the relative density of samples, which indicates that the densification is a significant factor that affects the dielectric properties. The maximum ε_r and $Q\times f$ values of 14.57 and 92450GHz are obtained as a result of the highest density of 96.9% at the calcining temperature of 700°C and sintering temperature of 950°C. In addition, the trends of dielectric properties for different calcining temperatures also can be confirmed from the microstructure shown in Fig. 3. The dense and homogeneous morphology of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at 700°C and sintered at 950°C is obtained, thereby the most excellent properties could be acquired. Therefore, the ε_r and $Q\times f$ values for samples with different calcining temperatures are mainly affected by the relative density.

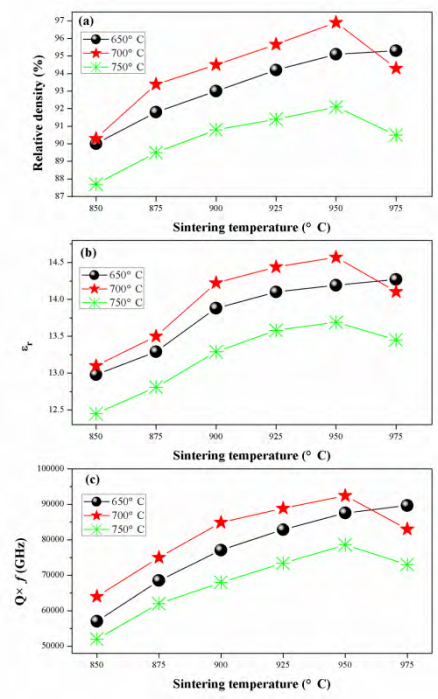

Fig. 4 The relative density, dielectric constant ε_r and $Q\times f$ value of $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics calcined at 650°C-700°C and sintered at different temperatures

Fig. 5 shows the relative density, dielectric constant ε_r and $Q\times f$ value of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics with the calcining temperature of 700°C and sintered at 950°C for 6h. From Fig. 5(a), the relative density increases gradually with the rise of temperature from 850°C to 975°C when x=0.06, meaning that the ceramics bodies are gradually densified but the amount of liquid phase produced below 975°C cannot ensure the liquid phase sintering process [31]. The relative density of samples ceramics increases first, reaching the maximum value at respective optimum temperatures and then decrease for $0.08\leq x\leq 0.15$. Moreover, the greatest relative density of 96.9% for samples is gained sintered at 950°C when x=0.08，which has a close relation to the dense and uniform morphology shown in Fig. 3. The maximum density for x=0.1 and 0.12 is obtained sintered at 925°C for 6h, while the relatively high value for x=0.15 is 92.7% acquired at 900°C.

The trends of ε_r and $Q\times f$ values for $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics shown in Fig. 5(b) and (c) are consistent with that of relative density. The ε_r and $Q\times f$ values mainly depend on the densification of ceramics [32]. Similarly, the ceramics have a correspondingly higher ε_r value and $Q\times f$ value sintered with x=0.08 and the optimal values of dielectric properties are 14.57 and 92450GHz are obtained at 950°C, which indicates that the liquid phase produced is sufficient for the requirement of liquid phase sintering mechanism when the substitution amount of F^- ions is 0.08. However, both the dielectric constant ε_r and $Q\times f$ values for x=0.1 and 0.12 are obtained the relatively higher values at 925°C, what's more, the peak values of dielectric properties for $Li_2Mg_3Ti(O_{0.935}\ F_{0.15})_6$ ceramics are achieved when sintered at 900°C. These results illustrate that the optimal sintering temperature for $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ($0.06\leq x\leq 0.15$) ceramics can be reduced gradually, it may be beneficial to the application in LTCC technology, but at the same time, the increase of x contributes to the quantity of liquid phase [33]. Too much amount of liquid phase will result in a deformation of grains and the reduction of relative density. Furthermore, the dielectric constant ε_r and $Q\times f$ value of ceramics could be lowered.

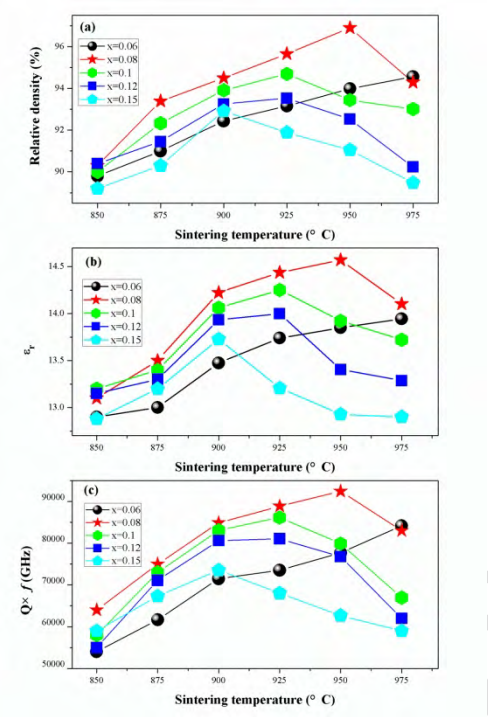

Fig. 5 The relative density, dielectric constant ε_r and Q×f value of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ (0.06≤x≤0.15) ceramics with the calcining temperature of 700°C and sintered at 950°C for 6h

The microwave dielectric properties of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ (0.06≤x≤0.15) ceramics calcined at different temperatures and sintered at 950°C for 6h are shown in Table. 1. The temperature coefficient of resonant frequency floats in the range of -30~-40 ppm/°C. But it can be observed that the τ_f value shows a decreasing trend generally [34]. In general, the $Li_2Mg_3Ti(O_{0.94}F_{0.08})_6$ ceramics has excellent microwave properties of ε_r~14.57, Q×f~92,450GHz and τ_f~31.84ppm/°C calcined at 700°C and sintering at 950°C for 6h. It not only reduces the sintering temperature to meet LTCC technology, but also lowers the calcining temperature.

Table. 1 The microwave dielectric properties of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ (0.06≤x≤0.15) ceramics calcined at different temperatures and sintered at 950°C for 6h

$Li_2Mg_3Ti(O_{1-x/2}F_x)_6$	calcining temperature(°C)	sintering temperature(°C)	ε_r	Q×f (GHz)	τ_f(ppm/°C)
x=0.08	650	950	14.19	87,570	-33.58
x=0.08	750	950	13.69	78,600	-32.73
x=0.06	700	950	13.84	77,670	-30.34
x=0.08	700	950	14.57	92,450	-32.91
x=0.1	700	950	13.92	79,920	-39.40
x=0.12	700	950	13.40	76,791	-38.37
x=0.15	700	950	12.90	62,671	-39.80

Table. 2 shows the microwave dielectric properties for different $Li_2Mg_3TiO_6$ based ceramics calcining and sintering at their optimum temperatures. For $Li_2Mg_3TiO_6$ ceramics, the highest Q×*f* value and the relative stable τ_f value are obtained calcined at 1000°C and sintered at 1350°C finally. But the higher calcining temperature and sintering temperature hinder its application. The addition of LiF as a common sintering aid to $Li_2Mg_3TiO_6$ ceramics reduces the sintering temperature to 950°C. The decrease of properties for $Li_2Mg_3TiO_6$-4wt%LiF compared with $Li_2Mg_3TiO_6$ ceramics can be attributed that the grain size deducts significantly while adding LiF promote sintering densification. Furthermore, the F^- ions are introduced as a substitute before calcination for $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics. Some decrease in Q×*f* value is due to the unevenness of the liquid phase, which causes partial grain deformation, and some impurities might be introduced. However, what's important is that the $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics reduce the calcining temperature and sintering temperature both. It can be applied to LTCC effectively.

Table. 2 The optimum calcining temperature, sintering temperature and the most excellent microwave dielectric properties of $Li_2Mg_3TiO_6$ based ceramics

Component	calcining temperature(°C)	sintering temperature(°C)	ε_r	Q×*f* (GHz)	τ_f(ppm/°C)
$Li_2Mg_3TiO_6$	1000	1350	15.2	152,000	-39 [11]
$Li_2Mg_3TiO_6$-4wt%LiF	1000	950	16.2	131,000	-44 [23]
$Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$	700	950	14.57	92,450	-32.91

4. Conclusions

The $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ceramics were prepared by the solid state reaction. The effect of F^- ions substituting for O^{2-} anions on sintering behaviors and microwave properties of $Li_2Mg_3TiO_6$ ceramics were studied systematically for the first time. Taking $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics as an example, the optimum calcining temperature was explored. Furthermore, the sintering characteristics and microwave dielectric properties at different calcining temperatures were discussed. The calcining temperature could be reduced from 1000°C to 700°C compared with $Li_2Mg_3TiO_6$ ceramics, because the solid state synthesis reaction was promoted by the high point defect. Besides, the reduction of calcining temperature might be also attributed to the decrease of the chemical potential and free energy. In addition, the sintering behaviors and properties of $Li_2Mg_3Ti(O_{1-x/2}F_x)_6$ ceramics were investigated at the optimum calcining temperature. The optimum sintering temperature was reduced gradually as F^- ions

increased, which could be applied to the LTCC technology. Furthermore, the dielectric constant ε_r and $Q\times f$ values had a similar trend with relative density with the increase of x. The $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ ceramics calcined at 700°C and sintered at 950°C for 6h exhibited the better microwave dielectric properties of ε_r~14.57, $Q\times f$~92,450GHz and τ_f~-32.91 ppm/°C.

Acknowledgments

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Highlights

- $Li_2Mg_3Ti(O_{1-x/2}F_x)_6(0.06\leq x\leq 0.15)$ ceramics were prepared by solid stated reaction
- The calcining temperature was reduced by the substitution of F^- anions for O^{2-} ions
- The $Li_2Mg_3Ti(O_{0.96}F_{0.08})_6$ exhibited excellent microwave dielectric properties