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Abstract

The low-loss $Li_2Mg_4TiO_7$ dielectric ceramics were prepared by the conventional solid-state method. The relationship among sintering behavior, phase composition, microstructure and dielectric properties of $Li_2Mg_4TiO_7$ ceramics was investigated. All the sintered samples exhibited the single phase with rock-salt structure belonging to Fm-3m space group. The higher $Q\cdot f$ values of samples above 1500°C were depending on crystal structure and phase composition. IR reflectivity spectrum indicated that the dielectric constant of $Li_2Mg_4TiO_7$ was mainly affected by the polar optical phonons. Typically, the ceramics sintered at 1600°C exhibited excellent microwave dielectric properties with ε_r=13.43, $Q\cdot f$ =233,600GHz and τ_f=-7.24ppm/°C.

Keywords: $Li_2Mg_4TiO_7$; Electroceramics; Microwave dielectric properties; FTIR

1. Introduction

Microwave dielectric ceramics have been utilized extensively in the microwave communication systems such as microwave resonators, antennas, and microwave filters as the key materials [1, 2]. In order to meet the requirements of wireless communication applications, the microwave dielectric materials should show a higher dielectric constant for the miniaturization of electronic components, a higher quality factor for the maximum signal intensity and a near-zero temperature coefficient of resonant frequency for adapting to environmental temperature changes [3, 4].

Recently, much research has been carried out to investigate Li_2O-MgO-TiO_2 ceramics due to their excellent microwave dielectric properties [5-13]. For example, Sebastian et al. reported that the cubic spinel $Li_2MgTi_3O_8$ ceramics showed a microwave dielectric property of ε_r=27.2, $Q\cdot f$=42,000GHz and τ_f=3.2ppm/°C [5]. A higher $Q\cdot f$ value of 153,000GHz could be obtained by the rock-salt structured $Li_2Mg_3TiO_6$ ceramics with ε_r=14.42 and τ_f=-11.07ppm/°C [6]. In addition, Huang et al. investigated that the Li_2MgTiO_4 ceramics could be obtained at 1350°C with ε_r=17.25, $Q\cdot f$=97,300GHz and τ_f=-27.2ppm/°C [8]. A pseudo phase diagram of Li_2O-MgO-TiO_2 ternary system was firstly established by Zhou et al[13]. Recently, Zhou et al reported that $Mg_{1-x}Li_{2x}Ti_xO_{1+2x}$ solid solution ceramics exhibited an adjustable microwave dielectric performance[14]. Based on above work, it was found that the ratio of Li:Mg:Ti played an important role in affecting phase composition and microwave dielectric properties of the Li_2O-MgO-TiO_2 ceramics. In this work, the rock-salt structured $Li_2Mg_4TiO_7$ ceramics were synthesized to optimize dielectric properties according to the phase diagram of Li_2TiO_3-MgO

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reported by A.R. West [15]. The relationship among chemical composition, microstructure, sintering characteristics, infrared spectra and microwave dielectric properties of $Li_2Mg_4TiO_7$ ceramics were also investigated.

2. Experimental procedure

The $Li_2Mg_4TiO_7$ ceramics were prepared via the conventional solid-state method. Proportionate amounts of the starting materials(analytical-grade Li_2CO_3, MgO and TiO_2) were collected in an ethanol container with ZrO_2 balls. The powders were milled for 24h with anhydrous ethanol, then dried and calcined at 1150°C for 2h in alumina crucibles. The calcined powders were re-milled for 24h, dried, mixed with polyvinyl alcohol as a binder, granulated and pressed into cylindrical disks of 10mm diameter and about 6mm height at a pressure of about 200MPa. The resulting pellets were preheated at 500°C for 4h to expel the binder,then covered with sacrificial powders with the same composition and sintered at 1450-1700°C for 4h in tightly closed platinum crucibles with a heating rate of 5°C/min.

Phase analysis of samples was conducted with the help of a Rigaku diffractometer using Ni filtered CuKα radiation (λ=0.1542nm) at 40kV and 40mA settings. The morphology on the surface of samples was examined using a scanning electron microscopy. The apparent densities were measured using the Archimedes method. The infrared reflectivity spectra were measured using a Bruker IFS 66v FTIR spectrometer on Infrared beamline station (U4) at National Synchrotron Radiation Lab. (NSRL), China. A network analyzer (N5234A, Agilent Co., America) was used for measuring microwave dielectric properties. Dielectric constants were measured using Hakki-Coleman post-resonator method by exciting the TE011 resonant mode of dielectric resonator by using an electric probe as suggested by Hakki and Coleman [16]. Unloaded quality factors were measured using TE01d mode by the cavity method [17]. The temperature coefficients of the resonant frequency were calculated from data in the temperature range of 25-85°C according to $\tau_f=\Delta f/(f_0\Delta T)$, where f_0 was the frequency measured at 25°C.

3. Results and discussion

Fig. 1(a) illustrated the variation of the apparent densities and diametric shrinkage ratio of $Li_2Mg_4TiO_7$ ceramics as a function of sintering temperatures. As the sintering temperatures increasing from 1450°C to 1700°C, the apparent density gradually increased from 3.04g/cm^3 to 3.28g/cm^3. The shrinkage ratio showed the similar tendency, which increased from 9.51% to 11.37% in the temperature region of 1450-1700°C. The XRD patterns of $Li_2Mg_4TiO_7$ samples sintered at different temperatures were also shown in Fig. 1(b). All the patterns that matched with JCPDS PDF#70-2711 could be fully indexed as the single phase with Fm-3m space group (No. 225). As the sintering temperature increasing from 1500°C to 1650°C, there was an increasing tendency in the intensity of the diffraction peaks, which indicated the grain growth of the ceramics. The lattice parameters of ceramics sintered at 1600°C were calculated to be a=b=c=4.1934Å and V=73.14Å^3, which were higher than that of cubic structured Li_2MgTiO_4 and $Li_2Mg_3TiO_6$ [7, 12]. In addition, the theoretical density and relative density were calculated as Equ. 1 and Equ. 2.

$$\rho_{th} = \frac{nM}{NV} \tag{1}$$

$$\rho_{re} = \frac{\rho_{ap}}{\rho_{th}} \times 100\% \tag{2}$$

where *M* was atomic weight, *V* was unit-cell volume calculated by JADE software, and *N* was Avogadro number. As shown in the inset of Fig. 1(a), the relative density was nearly 94.6% at 1600°C, which indicated that the well-dense samples could be obtained above 1600°C.

The SEM micrographs of samples sintered at different temperatures for 4h were shown in Fig. 2(a-f). Undeveloped microstructure with small pores could be observed below 1500°C, and the average grain sizes gradually increased from 19.37μm to 59.11μm with the sintering temperature increasing from 1550°C to 1650°C. In addition, some pores and partial melting grains caused by the evaporation of lithium could be observed in Fig. 2(f), which indicated that it was very difficult to obtain highly densified $Li_2Mg_4TiO_7$ samples above 1700°C. EDS analysis about grains chosen randomly from the samples sintered at 1600°C was shown in Fig. 2(d). It could be seen that the ratio of Mg:Ti was about 4:1, which was consistent with the chemical formula of $Li_2Mg_4TiO_7$.

Microwave dielectric properties of $Li_2Mg_4TiO_7$ ceramics as a function of sintering temperature were shown in Fig. 3(a), thorough which the optimum properties could be obtained. The variation of dielectric constants was consistent with that of apparent densities and a saturated value of 13.43 could be achieved from specimen sintered at 1600°C. As the ceramics possessed around 95% of their theoretical density, the polarization characteristics were mainly dependent on the crystal structure of $Li_2Mg_4TiO_7$. According to Shannon's additive rule and Clausius-Mosotti equation [18, 19], the theoretical dielectric polarizability ($\alpha_{theo.}$) and observed dielectric polarizability ($\alpha_{obs.}$) of the ceramics were calculated as follows.

$$\alpha_{theo.} = \alpha(Li_2Mg_4TiO_7) = 2\alpha(Li^+) + 4\alpha(Mg^{2+}) + \alpha(Ti^{4+}) + 7\alpha(O^{2-}) \tag{3}$$

$$\alpha_{obs.} = \frac{1}{b} V_m \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \tag{4}$$

where $\alpha(Li^+)$, $\alpha(Mg^{2+})$, $\alpha(Ti^{4+})$ and $\alpha(O^{2-})$ represented oxides polarizability abilities reported by Shannon [17]. Moreover, V_m, and b indicated the unit-cell volume and constant value (4π/3), respectively. By comparison, the values of $\alpha_{theo.}$(24.68) and $\alpha_{obs.}$(24.62) were in agreement with each other.

The Q·*f* values gradually increased from 175,400GHz to 233,600GHz with the increasing relative densities and fluctuated around 200,000-220,000GHz in the range of 1500-1700°C as shown in Fig.3(a). In general, the intrinsic factors such as crystal structure and phase composition played an important role in affecting dielectric loss for the densified specimens [1]. In this work, the maximum Q·*f* value of 233,600GHz could be obtained at 1600°C, which was higher than the Q·*f* values reported in other Li_2O-MgO-TiO_2 systems [5-13]. Fig. 3(a) also illustrated variation of temperature coefficient of resonant frequency as a function of sintering temperatures. The τ_f values increased from -11.67ppm/°C to -7.23ppm/°C with temperature increasing from 1450°C to 1600°C and slightly decreased to around -10 ppm/°C after 1600°C.

The measured and calculated IR reflectivity spectrum of $Li_2Mg_4TiO_7$ ceramic sintered at 1600°C was shown in Fig. 3(b). According to the classical oscillator model, the complex dielectric function was written as Equ. 5, and the fitted data could be obtained by Fresnel formula shown in Equ. 6.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{S_j}{\omega_j^2 - \omega^2 + i\omega\gamma_j} \tag{5}$$

$$R = \left| \frac{\sqrt{\varepsilon^*} - 1}{\sqrt{\varepsilon^*} + 1} \right|^2 \tag{6}$$

where $\varepsilon^*(\omega)$ was complex dielectric function, R(ω) was IR reflectivity, n was number of transverse phonon modes, ε_∞ was dielectric constant caused by electronic polarization, S_j, ω_j and γ_j were intensity, resonant frequency and damping constant of *J*th mode. The spectrum of $Li_2Mg_4TiO_7$ was fitted based on 5 resonant modes and the calculated IR reflectivity spectrum matched well with measured one, which could be observed in Fig. 3(b) and Table 1. In addition, the complex dielectric constants, ε' and ε'', were also calculated and shown in Fig. 3(c). The calculated ε' value was little higher than measured one at same frequency, which indicated ε' was mainly affected by polar optical phonons [20]. In contrast, the ε'' value measured at 1600°C was equal to that of calculated one, which suggested the intrinsic factors played a dominant role in increasing the Q·*f* values of $Li_2Mg_4TiO_7$ at 1600°C.

4. Conclusion

Ultra-low loss $Li_2Mg_4TiO_7$ ceramics were successfully prepared by the conventional solid-state method. The ε_r values were mainly determined by the apparent densities at lower sintering temperature, while the polar optical phonons played a dominated role in affecting polarization behavior for densified ceramics. The saturated Q·*f* values could be found in the range of 1500-1650°C, which were mainly controlled by crystal structure and phase composition of $Li_2Mg_4TiO_7$. The best microwave dielectric properties could be obtained at 1600°C with ε_r=13.43, Q·*f*=233,600GHz and τ_f=-7.24ppm/°C.

Acknowledgments

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Reference

[1] S. Nishigaki, H. Kato, S. Yano, R. Kamimure, Am. Ceram. Soc. Bull. 66 (1987) 1405-1410.

[2] K. Wakino, K. Minai, H. Tamura, J. Am. Ceram. Soc. 67 (1984) 278-281.

[3] T. Takada, S.F. Wang, S. Yoshikawa, S.J. Jang, R.E. Newnham, J. Am. Ceram. Soc. 77 (1994) 1909-1916.

[4] H.T. Wu, L.P. Zhao, Journal of University of Jinan (Sci. and Tech.) 30 (2016) 177-183.

[5] S. George, M.T. Sebastian, J. Am. Ceram. Soc. 93 (2010) 2164-2166.

[6] Z.F. Fu, P. Liu, J.L. Ma, X.G. Zhao, H.W. Zhang, J. Eur. Ceram. Soc. 3 (2016) 625-629.

[7] H.T. Wu, E.S. Kim, RSC Adv. 6 (2016) 47443-47453.

[8] Y.W. Tseng, J.Y. Chen, Y.C. Kuo, C.L. Huang, J. Alloys. Compd. 509 (2015) L308-L310.

[9] C.J. Pei, G.G. Yao, P. Liu, J.P. Zhou, Mater. Lett. 184 (2016) 57-59.

[10] H.F. Zhou, X.H. Tan, J. Huang, X.L. Chen, Ceram. Int. 43 (2017) 3688-3692.

[11] J.J. Bian, Y.F. Dong, J. Eur. Ceram. Soc. 2 (2010) 325-330.

[12] H.L. Pan, C.F. Xing, X.S. Jiang, H.T. Wu, J. Alloy. Compd. 688 (2016) 416-421.

[13] Y.D. Zhang, D. Zhou, J. Am. Ceram. Soc. 99 (2016) 3645-3650.

[14]H.F. Zhou, X.H. Tan, J. Huang, N. Wang, G.C. Fan, X.L. Chen, J. Alloy. Compd. 696(2017) 1255-1259.

[15] M. Castellanos, A.R. West, J. Mater. Sci. 14 (1979) 450-454.

[16] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave. Theory Tech. 8 (1960) 402-410.

[17] W.E. Courtney, IEEE Trans. 18 (1970) 476-485.

[18] R.D. Shannon, G.R. Rossman, Am. Miner. 77 (1992) 94-100.

[19] R.D. Shannon, J. Appl. Phys. 73 (1993) 348-366.

[20] J. Petzelt, S. Kamba, Mater. Chem. Phys. 79 (2003) 175-180.

Figures captions

Fig. 1 (a) Apparent densities, shrinkage ratio and relative densities of $Li_2Mg_4TiO_7$ ceramics as a function of sintering temperatures from 1450°C to 1700°C (b) XRD patterns of $Li_2Mg_4TiO_7$ ceramics sintered at 1500-1700°C for 4h

Fig. 2 SEM micrographs of $Li_2Mg_4TiO_7$ ceramics sintered at different temperatures for 4h (a-f corresponding to 1450°C~1700°C) and the inset of Fig.(d) was EDS analysis about grains chosen randomly from the samples sintered at 1600°C

Fig. 3 (a) Curves ε_r, Q·*f* and τ_f values for $Li_2Mg_4TiO_7$ ceramics sintered at different temperatures (b) Measured (black line) and fitted (red circle) IR reflectivity spectrum of $Li_2Mg_4TiO_7$ ceramic sintered at 1600°C (c) The real and imaginary parts of complex permittivity of $Li_2Mg_4TiO_7$ ceramic sintered at 1600°C

Table caption

Table 1 Fitted parameters of resonant modes in $Li_2Mg_4TiO_7$

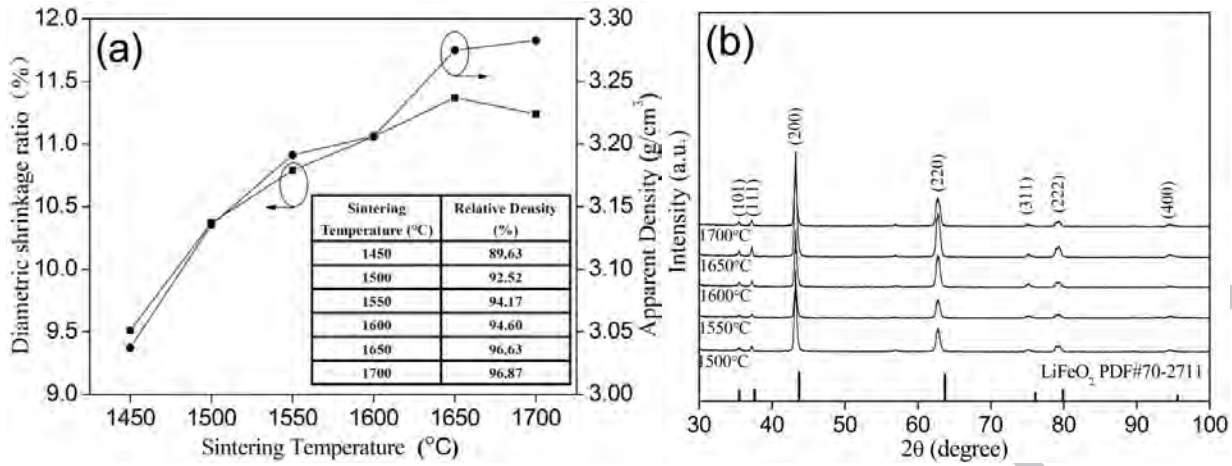
(a)
Diametric shrinkage ratio (%)
Apparent Density (g/cm3)
Sintering Temperature (°C)
Sintering Temperature (°C)
Relative Density (%)
1450 89.63
1500 92.52
1550 94.17
1600 94.60
1650 96.63
1700 96.87
(b)
Intensity (a.u.)
2θ (degree)
(101)
(111)
(200)
(220)
(311)
(222)
(400)
1700°C
1650°C
1600°C
1550°C
1500°C
LiFeO2 PDF#70-2711

Fig. 1

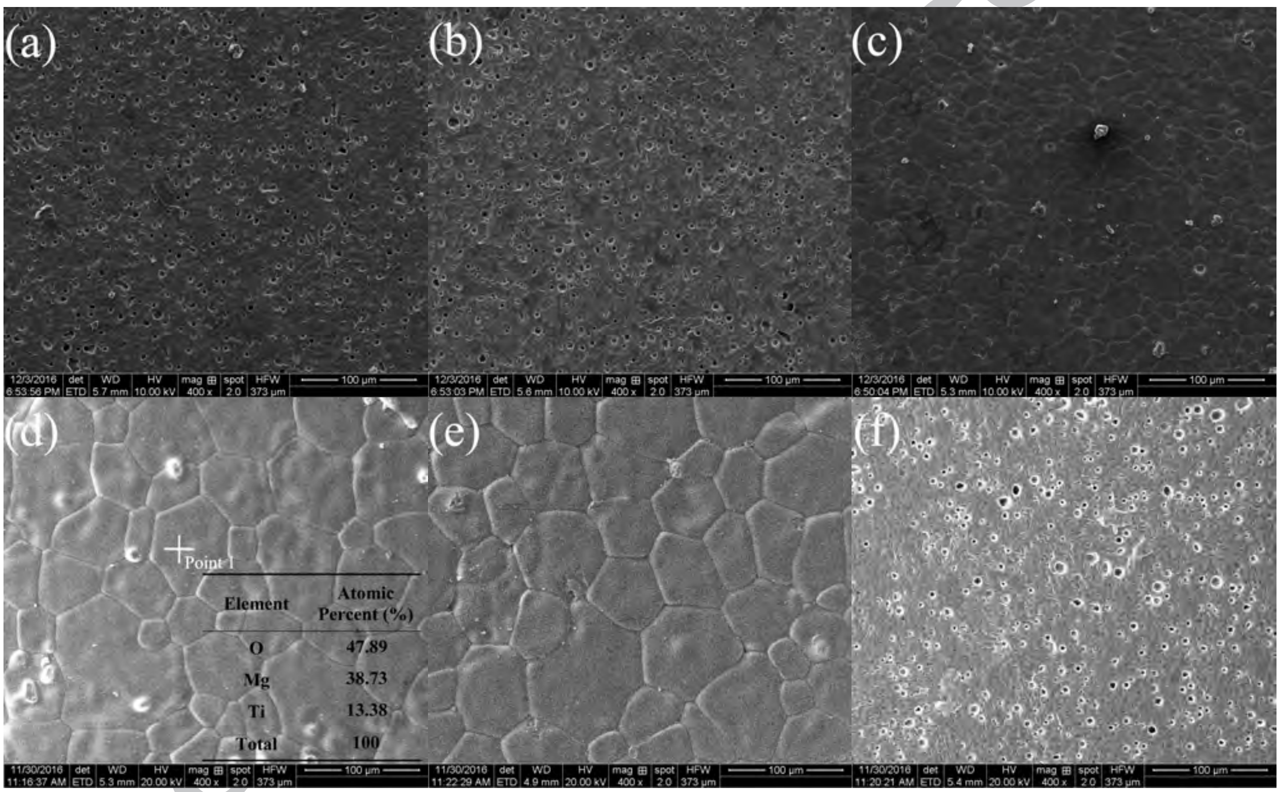
(a)
(b)
(c)
(d)
(e)
(f)
Point 1
Element Atomic Percent (%)
O 47.89
Mg 38.73
Ti 13.38
Total 100
100 μm

Fig. 2

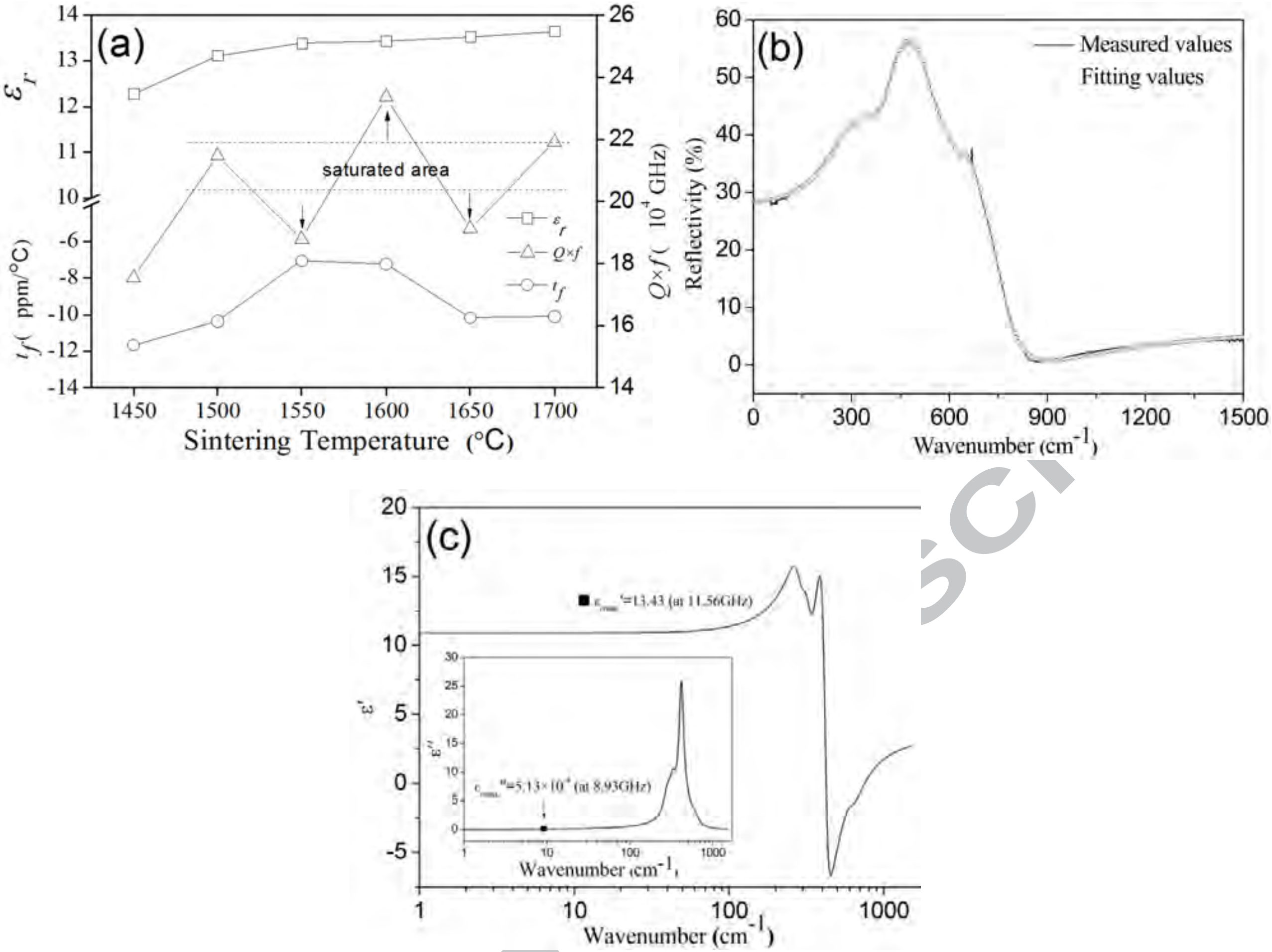

Fig. 3

Table 1

Mode	$Li_2Mg_4TiO_7$		ε_∞=3.34	
	ω_{oj}	ω_{pj}	γ_j	$\Delta_{\varepsilon j}$
1	284.22	281.22	68.223	0.979
2	328.85	301.91	61.759	0.843
3	417.49	737.16	64.143	3.120
4	457.48	697.28	207.99	2.320
5	615.54	330.28	143.38	0.288

Research highlights

- Rock-salt structured $Li_2Mg_4TiO_7$ was firstly prepared with excellent microwave properties
- Excellent property of $\varepsilon_r=13.43$, $Q\cdot f=233{,}600GHz$ and $\tau_f=-7.24ppm/℃$ was obtained at 1600 ℃
- IR reflectivity spectrum was firstly used to analyze resonant modes in $Li_2Mg_4TiO_7$