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Characterization and microwave dielectric properties of new low loss Li_2MgZrO_4 ceramics

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Abstract

Low loss microwave dielectric materials Li_2MgZrO_4 were synthesized by solid-state route. The relationship among sintering characteristics, phase composition, microstructure and microwave dielectric properties of Li_2MgZrO_4 ceramics were firstly investigated using X-Ray Diffraction, Scanning Electron Microscopy and Network Analyzer. The formation of secondary phases and evaporation of lithium were observed when sintering temperatures exceeded 1175°C. Microwave dielectric properties of Li_2MgZrO_4 ceramics were affected by sintering characteristics and second phase. In addition, the bond energy of Li_2MgZrO_4 ceramics was also reported to analyze intrinsic loss. Typically, the ceramics sintered at 1175°C for 4h exhibited excellent microwave dielectric properties with ε_r=12.30, $Q \cdot f$ =40,900 GHz and τ_f=-12.31 ppm/°C.

Keywords: Ceramics; Li_2MgZrO_4; Electronic materials; Microwave dielectric properties; Bond energy

1. Introduction

Microwave dielectric materials such as duplexers, resonators, antennas, and oscillators play an important role in the rapid growth of mobile and satellite communications [1-3]. For these high frequency wireless communication applications, the microwave dielectric materials should possess high dielectric constant for miniaturization of electronic components, high quality factor for maximum signal intensity and near-zero temperature coefficient of resonant frequency for adaptation to environmental change [4, 5]. Recently, many compounds based on Li_2O-MgO-BO_2 (B=Ti, Sn, Zr) system were reported for the possible use in microwave communications [6-8]. Among several kinds of microwave dielectric ceramics, the rock-salt-structured Li_2MgTiO_4 ceramics possess a high quality factors and an appropriate dielectric constant, which are suitable candidate materials for contemporary miniaturized and integrated passive components application [9, 10]. For example, Huang et al. reported the microwave dielectric properties of Li_2MgTiO_4 ceramics were ε_r= 17.25 $Q \cdot f$=97,300 GHz and τ_f=-27.2 ppm/°C when sintered at 1360°C for 2 h [9]. As for Li_2MgZrO_4, M. Castellanos et al. reported that the Li_2MgZrO_4 powders sintered at 1050 °C had the rock-salt structure with the space group of I41/amd, which had same structure as α-$LiFeO_2$ and different structure from Li_2MgTiO_4 [11]. However, at present there were no reports of microwave dielectric properties of Li_2MgZrO_4 ceramics. In this work, the sintering characteristics, bond energy and microwave dielectric properties of the Li_2MgZrO_4 ceramics were investigated. In addition, the relationships among phase composition, microstructure, sintering characteristics and microwave dielectric properties of Li_2MgZrO_4 ceramics were also detailed.

2. Experimental procedure

The ceramics were prepared by the conventional solid-state route using Li_2CO_3 (99.99%), MgO (99.99%) and ZrO_2 (99.9%) as starting materials according to the formula of Li_2MgZrO_4. The mixed powders were milled for 24h with distilled water in a nylon container with ZrO_2 balls. All the slurries were dried and calcined at 1050°C for 4h to obtain a single phase of Li_2MgZrO_4, The calcined powders were milled for another 24h and dried. The dried powders were mixed with polyvinyl alcohol as a binder, granulated and pressed into cylindrical disks of 10 mm diameter and about 6 mm height at a pressure of about 200 MPa. These resultant pellets were preheated at 500°C for 4h to expel the binder and sintered at 1125-1225°C for 4h in air at 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=0.1542 nm) at 40 kV and 40 mA settings. To investigate the crystal structure of Li_2MgZrO_4, the X-ray diffraction patterns were analyzed by the Rietveld refinement [12]. The microstructures were examined using a scanning electron microscope. The apparent densities of the sintered pellets were measured using the Archimedes method. A network analyzer was used for the measurement of 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 [13]. Unloaded quality factors were measured using TE01d mode by the cavity method [14], which could eliminate additional losses caused by parasitic effects. All measurements were made at room temperature and in the frequency of 8-12 GHz. The temperature coefficient of the resonant frequency (τ_f) was defined as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \times 10^6 (ppm/°C) \quad (1)$$

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

3. Results and discussion

The XRD patterns of Li_2MgZrO_4 samples sintered at 1125-1225°C were shown in Fig. 1(a). It was clearly understood from this figure that all the compositions form a solid solution with rock-salt structure and I41/amd space group (No. 141 Z=2). Diffraction peaks of predominant phase gradually increased with the sintering temperature. In addition, secondary phases of ZrO_2 with monoclinic structure were observed at 28-32° in the range of 1200-1225°C. Y. Iida et al. previously reported that the volatile content of lithium element was negligibly small under 1000°C and become larger at higher temperatures [15]. Thus, it was considered that evaporation of lithium was the major factor in the formation of the second phase above 1175°C. Rietveld refinement analysis of the ceramics sintered at 1175°C was shown in Fig. 1(b). Rietveld discrepancy factors R_p, R_{wp} and R_{exp} were 5.86%, 8.72% and 2.34%, respectively. Schematic representation of single Mg/Zr-O octahedral was also shown in the inside of Fig. 1(b). Lattice parameters were calculated as a=b=4.19471Å, c=9.1686Å and V=161.3270Å^3, which were used to calculate the bond length and nature of bonding in the following section.

Fig. 2(a) illustrated the variation of the apparent densities and diametric shrinkage ratio of Li_2MgZrO_4 ceramics with sintering temperature. The apparent densities gradually increased from 2.98 to 3.33 g/cm^3 with the sintering temperature

increasing from 1125-1225°C and reached a value of 3.15 g/cm^3 at 1175°C. The shrinkage ratio showed a similar tendency that increased from 5.35% to 8.15% and reached 7.05% at 1175°C. The apparent density of the sample sintered at 1175°C was 79.02% of its theoretical densities. This lower relative density would be harmful for improving microwave dielectric properties of Li_2MgZrO_4 ceramics. The SEM micrographs of Li_2MgZrO_4 ceramics sintered at different temperatures were illustrated in Fig. 3. The grain size of the ceramics gradually increased and much pores existed in samples sintered at 1125-1175°C. Clear grain boundaries and a small amount pores could be observed in Fig 3(a)-(c). However, the sintering at 1200 and 1225°C led to indistinct-grained Li_2MgZrO_4 ceramics with irregular grain diameter and shapes. Moreover, as shown in Fig. 3(e), abnormal grain growth was observed and partial grains began to melt, which would have a detrimental effect on the $Q{\cdot}f$ value. Due to the evaporation of lithium, an appreciable amount of intergranular pores was still existed in Fig. 3(e)-(f), which was in good agreement with the lower apparent densities shown in Fig. 2(a).

The variation of microwave dielectric properties of Li_2MgZrO_4 ceramics was shown in Fig. 2(b). It was found that the dielectric constant gradually increased from 11.14 to 13.12 with the increase of sintering temperature from 1125 to 1225°C, and then reached to 12.30 at 1175°C. In order to eliminate the impact of porosity, the porosity-corrected permittivity (ε_{rc}) was calculated as Equ. 2:

$$\frac{\varepsilon_r - \varepsilon_{rc}}{3\varepsilon_r} = \frac{\delta(\varepsilon_1 - \varepsilon_{rc})}{\varepsilon_1 + 2\varepsilon_r} \tag{2}$$

where ε_r was the measured dielectric constant, ε_1 was dielectric constant of porosity, δ was the fractional porosity. To clarify effects of crystal structure on dielectric constant, theoretical dielectric polarizability ($\alpha_{theo.}$) was calculated to be 15.01 according to additive rule with ionic polarizability of composing ions or oxides [16]. Whereas the observed dielectric polarizability ($\alpha_{obs.}$) of the ceramics sintered at 1175°C was calculated to be 16.23 by Clausius-Mossotti equation with the porosity-corrected permittivity [17]. By comparison, the values of $\alpha_{theo.}$ and $\alpha_{obs.}$were in agreement with each other, and the deviation from the $\alpha_{theo.}$ and $\alpha_{obs.}$ was attributed to the evaporation of lithium.

The $Q{\cdot}f$ values gradually increased from 27,600 to 40,900 GHz with the sintering temperature increasing from 1125 to 1175°C and reached a maximum value at 1175°C. However, the values significantly reduced to 21,500 GHz when the sintering temperature was higher than 1175°C. Combining with the results shown in Fig. 1(a) and Fig. 3(d), it could be concluded that the poor microstructure and the appearance of second phase leaded to the low $Q{\cdot}f$ values at 1200°C. Although the ceramics got densified and the $Q{\cdot}f$ values increased to 28,100 GHz at 1225°C, it was considered that the formation of second phases still played an important role in increasing the dielectric loss. In addition, it was well known that intrinsic losses were mainly caused by crystal structure such as bond strength and bond energy. Shorter bond length was correlated with higher bond energy, and higher bond energy could make the system more stable [18]. Sanderson reported that the bond energy could be obtained by the chemical bond and the electronegativity [19-21]. Based on the previous

researches, the bond energy E of the Li_2MgZrO_4 ceramics sintered at 1175°C were calculated as Equ. 3-5 and the results were shown in Table 1.

$$E = \sum_{\mu} E_b^{\mu} \tag{3}$$

$$E_b^{\mu} = t_c E_c^{\mu} + t_i E_i^{\mu} \tag{4}$$

$$E_c^{\mu} = \frac{(r_{cA} + r_{cB})}{d^{\mu}} (E_{A-A} E_{B-B})^{1/2} \tag{5}$$

As shown in Table 1, total covalent energies (E_c) and ionicity energies (E_i) were 4024.7190 and 11659.2200 kJ mol^{-1}. There was a sequence of bond energy of E_{ave}(Zr-O)>E_{ave}(Li-O)>E_{ave}(Mg-O). Some reports also investigated that the bond energy between the octahedral-site cation and oxygen would affect the $Q{\cdot}f$ values [22, 23]. Thus, bond energy of E(Zr-O) took the predominant role in Li_2MgZrO_4 ceramics. Moreover, the τ_f values fluctuated from -12.57 to -15.68 ppm/°C with the sintering temperatures increasing from 1125 to 1225°C, which would possibly make the ceramics more applicable for microwave devices.

4. Conclusion

Ultra-low loss Li_2MgZrO_4 ceramics were successfully synthesized by the conventional solid-state route. Crystal structure, sintering characteristics and microwave dielectric properties were discussed. Secondary phases and evaporation of lithium were observed when sintering temperatures exceeded 1175°C. Dielectric constant was strongly dependent on the porosity and polarizability. $Q{\cdot}f$ values were mainly affected by microstructure under 1175°C, and second phase played an important role above 1175°C. τ_f values fluctuated from -12.57 to -15.68 ppm/°C with sintering temperature increasing. Moreover, the theory of the bond energy was used to analysis the variation of $Q{\cdot}f$ values. The excellent microwave property of Li_2MgZrO_4 ceramics was found at 1175°C with ε_r=12.30, $Q{\cdot}f$ =40,900 GHz and τ_f=-12.31 ppm/°C, which would make the ceramics promising for application in microwave components.

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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] J.K. Plourde, D.F. Linn, H.M.J. O'Bryan, J.J. Thompson, J. Am. Ceram. Soc.58 (1975) 418-420.

[5] P. Zhang, Z.K. Song, Y. Wang, Y.M. Han, H.L. Dong, L.X. Li, J. Alloy. Compd. 581 (2013) 741-746.

[6] P. Zhang, J. Liu, Y.G. Zhao, H.Y. Du, X.Y. Wang, Mater. Lett. 162 (2016) 173-175.

[7] Z.F. Fu, P. Liu, J.L. Ma, X.M. Chen, H.W. Zhang, Mater. Lett. 164 (2016) 436-439.

[8] P. Zhang, Y. Wang, J. Liu, Z.K. Song, Y.M. Han, L.X. Li, Mater. Lett. 123 (2016) 195-197.

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

[10] G.G. Yao, X.S. Hu, X.L. Tian, P. Liu, J.P. Zhou, Cream. Int. 41 (2015) S563-S566.

[11] M. Castellanos, A.R. West, W.B. Reid, Acta Cryst. C 41 (1985) 1707-1709.

[12] E.S. Kim, C.J. Jeon, P.G. Clem, J. Am. Ceram. Soc. 95 (2012) 2934-2938.

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

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

[15] Y. Iida, J. Am. Ceram. Soc. 43 (1960) 171-172.

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

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

[18] S.D. Ramarao, V.R.K. Murthy, Dalton Trans. 44 (2015) 2311-2324.

[19] R.T. Sandderson, Inorg. Nucl. Chem. 30 (1968) 375-393.

[20] R.T. Sandderson, Academic Press: New York 1971.

[21] R.T. Sandderson, J. Am. Chem. Soc. 105 (1983) 2259-2261.

[22] H.T. Wu, E.S. Kim, J. Alloy. Compd. 669 (2016) 134-140.

[23] P. Zhang, Y.G. Zhao, H.T. Wu, Dalton Trans. 44 (2015) 16684-16693.

Fig. 1 (a) XRD patterns of Li_2MgZrO_4 ceramics sintered at 1125-1225°C for 4 h. (b) Rietveld refinement of Li_2MgZrO_4 ceramics (R_p=5.86%, R_{wp} = 8.72%, R_{exp}=2.34%) and schematic representation of single Mg/Zr-O octahedral.

Fig. 2 (a) Apparent densities and shrinkage ratio of Li_2MgZrO_4 ceramics as a function of sintering temperatures from 1125 to 1225°C. (b) Curves of $\varepsilon_{r,}$ $Q{\cdot}f$ and τ_f values as a function of sintering temperatures for Li_2MgZrO_4 ceramics in the temperature region of 1125-1225°C.

Fig. 3 SEM micrographs of Li_2MgZrO_4 ceramics sintered at different temperatures for 4 h (a-e corresponding to 1125°C, 1150°C, 1175°C, 1200°C and 1225°C).

Table 1 Calculation of bond energy of Li_2MgZrO_4 ceramics sintered at 1175 °C.

Bond Type	*d*	*Electronegativity of cations*	*Ion coefficient*	*Covalent coefficient*	*Covalent radius of cations*	*Total of covalent radius*	*A site bond (kJ/mol)*	*B site bond (kJ/mol)*	*Ec (kJ/mol)*	*Ei (kJ/mol)*	*E (kJ/mol)*
Li-O(1)×4	2.1037	0.98	0.4100	0.5900	133	196	105.0000	498.3600	213.1270	659.9914	396.3414
Li-O(2)×2	2.4550								182.6295	565.5495	339.6267
Mg-O(1)×4	2.1037	1.31	0.3550	0.6450	139	202	11.3000	498.3600	72.0574	659.9914	280.7740
Mg-O(2)×2	2.1293								71.1910	652.0565	277.3983
Zr-O(1)×4	2.1037	1.33	0.3517	0.6483	154	217	298.2000	498.3600	397.6503	659.9914	489.9070
Zr-O(2)×2	2.1293								392.8695	652.0565	484.0169
Total	—	—	—	—	—	—	—	—	4024.7190	11659.2200	6870.1734

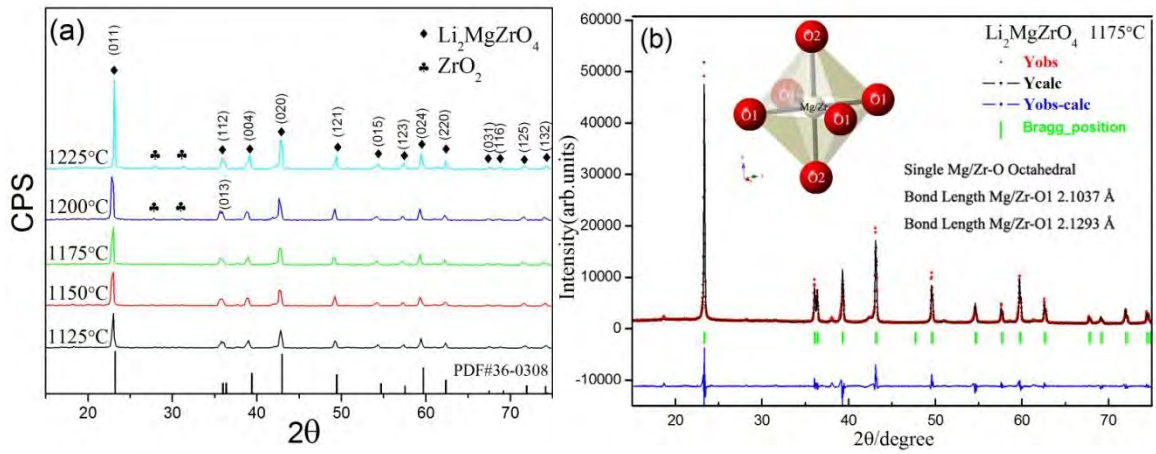

Fig. 1

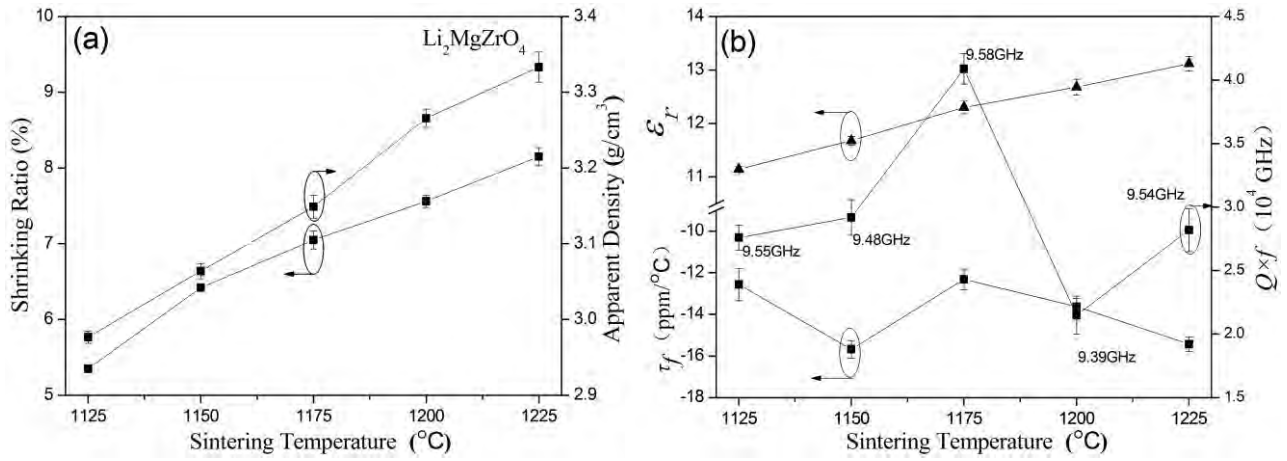

Fig. 2

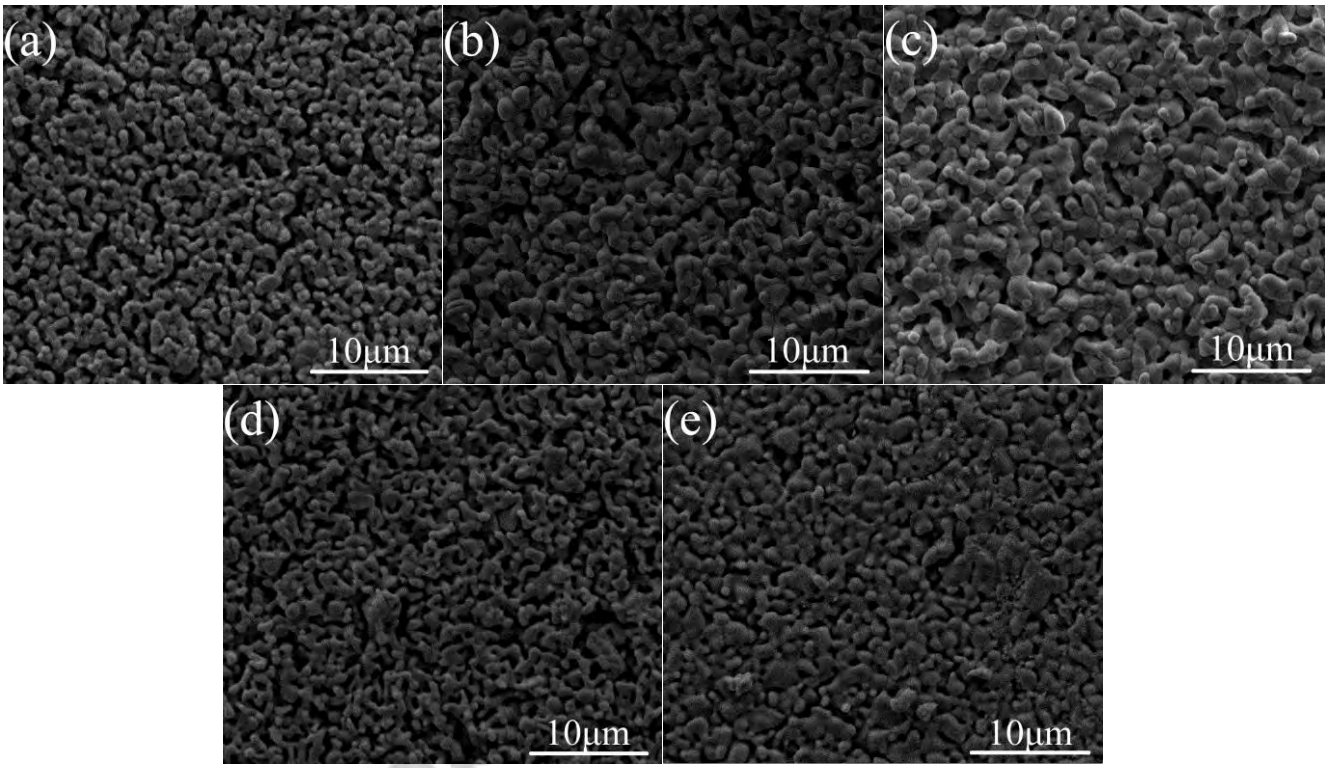

Fig. 3

Highlights

- New rock-salt structure Li_2MgZrO_4 were reported with good microwave properties
- The ceramics exhibited properties with ε_r=12.30, Q·f =40,900 GHz τ_f=-12.31 ppm/°C.
- Bond energy of ceramics was reported for first time to analyze intrinsic loss.