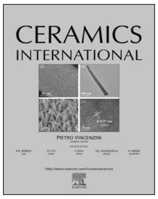
ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



$Li_4Mg_3Ti_2O_9$: A novel low-loss microwave dielectric ceramic for LTCC applications

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A R T I C L E I N F O

Keywords:
$Li_4Mg_3Ti_2O_9$
Microwave dielectric properties
Infrared spectroscopy
LTCC

A B S T R A C T

Low-loss novel $Li_4Mg_3Ti_2O_9$ dielectric ceramics with rock-salt structure were prepared by a conventional solid-state route. The crystalline structure, chemical bond properties, infrared spectroscopy and microwave dielectric properties of the abovementioned system were initially investigated. It could be concluded from this work that the extrinsic factors such as sintering temperatures and grain sizes significantly affected the dielectric properties of $Li_4Mg_3Ti_2O_9$ at lower sintering temperatures, while the intrinsic factors like bond ionicity and lattice energy played a dominant role when the ceramics were densified at 1450 °C. In order to explore the origin of intrinsic characteristics, complex dielectric constants (ε' and ε'') were calculated by the infrared spectra, which indicated that the absorptions of phonon oscillation predominantly effected the polarization of the ceramics. The $Li_4Mg_3Ti_2O_9$ ceramics sintered at 1450 °C exhibited excellent properties of ε_r=15.97, $Q{\cdot}f$=135,800 GHz and τ_f=−7.06 ppm/°C. In addition, certain amounts of lithium fluoride (LiF) were added to lower the sintering temperatures of matrix. The $Li_4Mg_3Ti_2O_9$−3 wt% LiF ceramics sintered at 900 °C possessed suitable dielectric properties of ε_r=15.17, $Q{\cdot}f$ =42,800 GHz and τ_f=−11.30 ppm/°C, which made such materials promising for low temperature co-fired ceramic applications (LTCC).

1. Introduction

With the rapid development of mobile communication, microwave dielectric ceramics have attracted more and more attentions due to their remarkable advantages in microwave devices such as dielectric resonators, antennas, microwave filters and so on [1,2]. These materials are basically required to possess an appropriate dielectric constant to reduce devices sizes, a high quality factor for frequency selectivity and a near-zero temperature coefficient of resonant frequency for temperature stability [3,4]. Moreover, in order to meet the requirements of miniaturization and integration, the ceramics should also be sintered below 960 °C for being co-fired with Ag electrode (LTCC) [5,6].

Recently, the Li_2O-MgO-TiO_2 ceramics have been extensively investigated due to their excellent microwave dielectric properties and potential applications in LTCC [7–18]. For example, Sebastian et al. reported that the cubic spinel $Li_2MgTi_3O_8$ ceramics showed the dielectric property of ε_r=27.2, $Q{\cdot}f$=42,000 GHz and τ_f=3.2 ppm/°C [7]. The densified $Li_2Mg_3Ti_4O_{12}$ ceramics, which belonged to a space group of Fd-3m, could be obtained at 1125 °C with ε_r=20.2, $Q{\cdot}f$=62,300 GHz and τ_f=−27.1 ppm/°C [8]. A pseudo phase diagram of Li_2O-MgO-TiO_2 ternary system was firstly established by Zhou et al. on the basis of various data reported in previous works [9], which indicated that the phase compositions and dielectric properties of ceramics were significantly affected by the ratio of Li:Mg:Ti. More specifically, there were a great number of reports about the rock-salt structured Li_2O-MgO-TiO_2 compounds owing to their higher $Q{\cdot}f$ values [11–16]. According to the partial subsolidus phase diagram of Li_2TiO_3-MgO, monoclinic structured Li_2TiO_3 might be transformed into cubic rock salt phase when MgO content was beyond 40 mol% [10]. The structural evolution in the above system was also confirmed by Bian et al.. In their report, the $0.6Li_2TiO_3$+0.4MgO ceramics sintered at 1350 °C possessed dielectric properties of ε_r=17.25, $Q{\cdot}f$=97,300 GHz and τ_f=~−25 ppm/°C with a space group of Fm-3m [11]. A higher $Q{\cdot}f$ value of 152,000 GHz could be obtained by rock-salt structured $Li_2Mg_3TiO_6$ ($0.75Li_2TiO_3$+0.25MgO) ceramics with ε_r=15.2 and τ_f=−39 ppm/°C [12]. Huang et al. investigated that the Li_2MgTiO_4 ($0.5Li_2TiO_3$+0.5MgO) ceramics possessed the properties of ε_r=18, $Q{\cdot}f$=90,000 GHz and τ_f=−27.2 ppm/°C at a lower sintering temperature (1350 °C) [13]. In addition, Zhou et al. investigated that the adjustable dielectric properties could be achieved by using a series of $Mg_{1-x}Li_{2x}Ti_xO_{1+2x}$ ($Li_2Mg_4TiO_7$, $Li_2Mg_3TiO_6$, $Li_2Mg_2TiO_5$ and Li_2MgTiO_4) solid solutions [14]. However, the evaporation of lithium seriously affected the densification and structure-property relationship

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http://dx.doi.org/10.1016/j.ceramint.2017.03.041
Received 3 February 2017; Received in revised form 1 March 2017; Accepted 6 March 2017
0272-8842/

Please cite this article as: Bi, J., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.03.041

of samples in all the above-mentioned reports. In our previous works, the Li_2MgTiO_4 and $Li_2Mg_3TiO_6$ compounds were synthesized by the atmosphere-protective sintering method to suppress lithium evaporation. The former possessed a higher dielectric constant (15.07) and a near-zero τ_f value (−3.81 ppm/°C), while the latter exhibited an excellent $Q{\cdot}f$ value of 153,000 GHz [15,16].

Based on the above results, the $Li_4Mg_3Ti_2O_9$ ceramics, which could be divided into $0.4Li_2TiO_3+0.6MgO$, were chosen as a candidate for optimizing a balanced property in Li_2O-MgO-TiO_2 system. However, there were insufficient data to predict the crystal structure and dielectric properties of these ceramics. Hence, the rock-salt structured $Li_4Mg_3Ti_2O_9$ ceramics were synthesized via the solid state method in this work. The relationships among phase composition, microstructure, sintering characteristics, infrared spectra and microwave dielectric properties of the system were systematically investigated. Complex chemical bond theory was used to characterize the bond ionicity and lattice energy of individual bonds. In addition, the lithium fluoride (LiF) was used as sintering aids to decrease the sintering temperature of the matrix. The sintering behaviors as well as dielectric properties of $Li_4Mg_3Ti_2O_9$-xwt%LiF compounds were studied in the present work.

2. Experimental procedure

The $Li_4Mg_3Ti_2O_9$ ceramics were prepared via the conventional solid-state route. High purity Li_2CO_3, MgO and TiO_2 (99.99%, Aladdin Shanghai Biochemical Technology Co., Ltd. Shanghai, China) were weighted according to the stoichiometric formulation of $Li_4Mg_3Ti_2O_9$. The starting powders were mixed with anhydrous ethanol for 24 h in a nylon container, dried and calcined at 1050 °C for 2 h in the alumina crucibles. After subsequent ball-milling with 0–5 wt% lithium fluoride, the resultant powders were mixed with 8 wt% polyvinyl alcohol, granulated and pressed into cylindrical disks of 10 mm diameter and about 6 mm height at a pressure of about 200 MPa. All the obtained pellets were preheated at 500 °C for 4 h to expel the organic binder. In order to suppress the lithium evaporation, the matrix were covered with sacrificial powders and sintered at 1300–1450 °C for 4 h in platinum crucibles at a heating rate of 5 °C/min, while the LiF-doped $Li_4Mg_3Ti_2O_9$ samples were sintered at 700–1200 °C in air.

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. The microstructures of $Li_4Mg_3Ti_2O_9$ were examined using a scanning electron microscope (Model JEOL JEM-2010, FEI Co., Japan) coupled with energy dispersive X-ray spectroscopy (EDS). The apparent densities of sintered samples were measured using the Archimedes method (Mettler ToledoXS64). Infrared reflectivity spectra were measured using a Bruker IFS 66v FTIR spectrometer on Infrared beamline station (U4) at National Synchrotron Radiation Lab. (NSRL) in China. 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 [19]. Unloaded quality factors were measured using TE01d mode by the cavity method [20]. All measurements were finished at room temperature and in the frequency of 8–12 GHz. The temperature coefficients of the resonant frequency (τ_f) were calculated from the data collected in the temperature range of 25–85 °C according to $\tau_f=\Delta f/(f_0\Delta T)$, where f_0 was the frequency at 25 °C.

3. Results and discussion

Fig. 1 showed the variation of diametric shrinkage ratio and apparent densities with sintering temperature for $Li_4Mg_3Ti_2O_9$ samples. As the sintering temperature increasing from 1350 to 1425 °C, the apparent density gradually increased from 2.92 to 3.15 g/cm^3. After that, the values stabilized at 3.15 g/cm^3 in the temperature region of 1425–1450 °C. The variation of shrinkage ratio showed a similar tendency that the values increased from 9.58% to 10.5% with temperature increasing from 1350 to 1450 °C. The SEM micrographs of $Li_4Mg_3Ti_2O_9$ samples obtained at various sintering temperatures were illustrated in Fig. 2(a-e). The microstructure with small pores could be observed when the samples were sintered at 1350 °C. By contrast, grain growth of samples with closely-packed grains and discernable grain boundaries was recognized when the sintering temperature increasing from 1375 to 1450 °C, which resulted in the elimination of pores in the matrix. The well-dense sample was comprised of large grains of around 30 μm and small grains of around 10 μm when it was sintered at 1450 °C, which indicated that the evaporation of lithium could be neglected in this work. EDS analysis about grains chosen randomly from specimen sintered at 1450 °C was displayed in Fig. 2(f). The atom ratio of Mg to Ti was approximately to be 3:2, which was corresponded to the theoretical composition of $Li_4Mg_3Ti_2O_9$.

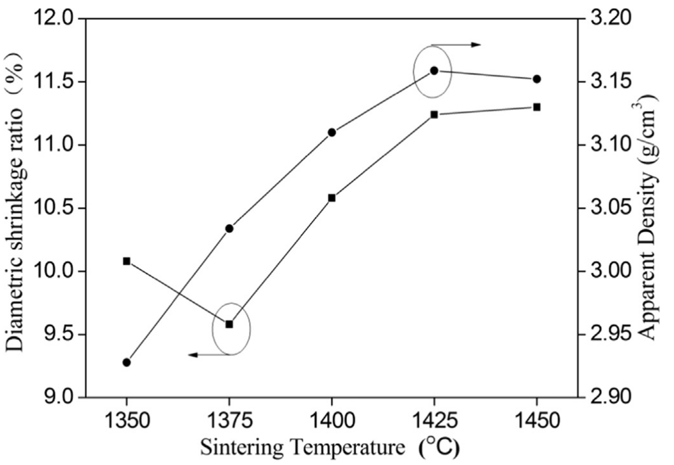

Fig. 1. Apparent densities and shrinkage ratio of $Li_4Mg_3Ti_2O_9$ ceramics as a function of sintering temperatures from 1350 to 1450 °C.

XRD patterns of $Li_4Mg_3Ti_2O_9$ specimens sintered at different temperatures were presented in Fig. 3. All the diffraction peaks could be indexed as the standard pattern of rock-salt structured $LiFeO_2$ (JCPDS #70–2711), which indicated that $Li_4Mg_3Ti_2O_9$ possessed the same structure with Li_2MgTiO_4 and $Li_2Mg_3TiO_6$. There were no significant changes in the angle and intensity of the diffraction peaks, implying the good crystallinity of all the samples. The unit cell volume of $Li_4Mg_3Ti_2O_9$ specimen sintered at 1450 °C was calculated to be V=72.12 Å^3 with a=b=c=4.1626 Å, which was higher than that of Li_2MgTiO_4 (V=71.90 Å^3) and was lower than that of $Li_2Mg_3TiO_6$ (V=73.14 Å^3) reported in our previous works [15,16]. Based on the atomic coordinate information of $LiFeO_2$, the bond length of Li/Mg/Ti-O was calculated to be 2.0816 Å. The schematic crystal structure of rock-salt structured $Li_4Mg_3Ti_2O_9$ was shown in the inset of Fig. 3. It could be observed that three kinds of cations occupied the same atomic positions and were connected with other six oxygen ions, thus the ratio of Li:Mg:Ti would enlarge or compress single Li/Mg/Ti-O octahedral.

In order to initially characterize the structure-property relationship, intrinsic parameters such as lattice energy and bond ionicity were calculated in this work. Based on the crystallographic data reported in our previous works and generalized P-V-L theory reported by Zhang et al., the complex crystal of $Li_4Mg_3Ti_2O_9$ was decomposed as Eq. (1) [21–23].

$$Li_4Mg_3Ti_2O_9 \rightarrow \sum A_mB_n = Li_4O_4 + Mg_3O_3 + Ti_2O_2 \tag{1}$$

Due to the fact that $Li_4Mg_3Ti_2O_9$ had the same crystal structure as Li_2MgTiO_4 and $Li_2Mg_3TiO_6$ compounds, the valence electron numbers and effective valence electron numbers of oxygen anions in every bond could refer to our previous work [15,16]. The bond ionicity of