Journal of Materials Science: Materials in Electronics (2018) 29:15523–15528
https://doi.org/10.1007/s10854-018-9107-z

Low temperature sintering and microwave dielectric properties of $Li_3Mg_2NbO_6$ ceramics

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Received: 20 July 2017 / Accepted: 13 April 2018 / Published online: 19 April 2018

Abstract
The $Li_3Mg_2NbO_6$ (LMN) ceramics were synthesized through the traditional solid-state process. The sintering characteristics, microwave dielectric properties and the morphology of LMN ceramics with various $BaCu(B_2O_5)$ (BCB) addition were investigated. No secondary phase was found in the BCB added ceramics. Low-level doping of BCB (≤ 2 wt%) could significantly improve the densification of LMN ceramics due to the liquid phase sintering mechanism. The dielectric constant and the quality factor value had the same variation trend with bulk density. The temperature coefficient of resonant frequency (τ_f) value presented descending tendency as the BCB content increased. Besides, the X-ray diffraction result and the back scattered electron image of the sample confirmed the chemical compatibility silver electrodes. The optimum microwave dielectric of $\varepsilon_r = 14.27$, $Q \times f = 55521$ GHz and $\tau_f = -18.2$ ppm/°C was obtained, when the LMN ceramics with 0.1 wt% BCB sintered at 950 °C for 4 h, which could be a promising candidate material for low temperature co-fired ceramics applications.

1 Introduction

Microwave dielectric materials not only have widely application in automatic, medical, communication, Aerospace and the other field, but also play a key role in the emerging industry, Such as the Internet of Things (IoT), the Tactile Internet (fifth generation wireless systems), intelligent transport systems (ITS) [1]. As a result, it attracts tremendous research interest. The main requirements for microwave dielectric materials are relative high permittivity ε_r (for miniaturization), high Q (for selectivity), near zero τ_f (for stability) [2–4]. Unfortunately, most of these materials with excellent properties have high sintering temperatures, which lead to large energy consumption, evaporation of volatile components, reactions with other materials, even fail to meet the requirements of low-temperature co-fired ceramics (LTCC). The sintering temperature of LTCC should be below 961 °C owing to the melting temperature of Ag electrode [5, 6]. Therefore, it is of significance to lower the sintering temperature of microwave dielectric ceramics since LTCC have been widely investigated as a means of miniaturizing microwave devices [7, 8].

LMN ceramics with rock salt structure were prepared by Yuan and Bian [9], and the LMN ceramic sintered at 1250 °C for 4 h had excellent properties of $\varepsilon_r = 16.8$, $Q \times f = 79643$ GHz and $\tau_f = -27.2$ ppm/°C. Latter, they discovered that $Q \times f$ values of the $Li_{3-3x}Mg_{4x}Nb_{1-x}O_4$ ceramics increased greatly with the increasing x and saturated within the composition range of 0.1–1/3 [10]. Plenty of work about the Mg-site and enhanced microwave dielectric properties of $Li_3(Mg_{1-x}Zn_x)_2NbO_6$ (Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}) have been done [11–13], the $Q \times f$ value of the ceramics varied from 52,700 to 14,2331 GHz. Nevertheless, it is impossible to be co-fired with Ag electrode due to the over 1000 °C sintering temperature. Thus, it is necessary to lower the sintering temperature of ceramics. Adding the glass or oxides with low melting temperature as sintering aids is generally known to be the most effective way [14]. Zhang et al. discovered that the $0.7Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6 + 0.3Ba_3(VO_4)_2$ ceramic possessed excellent microwave dielectric properties with $\varepsilon_r = 16.3$, $Q \times f = 50{,}084$ GHz, $\tau_f = 1.5$ ppm/°C sintered at 950 °C for 4 h [15]. Besides, the microwave dielectric properties with $\varepsilon_r = 14.0$, $Q \times f = 67{,}451$ GHz, $\tau_f = -16.82$ ppm/°C were obtained for $Li_3Mg_2NbO_6 + 0.1$ wt% B_2O_3 ceramics sintered at 925 °C [16]. The sintering temperature of $BaTi_4O_9$ and $Li_2MgTi_3O_8$ could be dramatically lowered by adding BCB [17, 18]. In order to

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make LMN fulfill the requirements of LTCC, BCB was added into LMN ceramic to decrease their sintering temperature. In this paper, the effect of BCB on the sintering characteristics, microstructures and microwave dielectric properties of LMN ceramics were investigated systematically.

2 Experiment

The $Li_3Mg_2NbO_6$ ceramics were synthesized by conventional solid-state process. High purity (> 99%) Li_2CO_3, MgO and Nb_2O_5 were used as the starting material compositions. Stoichiometric amounts of the chemical powders were weighed and ball-milled by planetary ball mill (Nanjing University Instrument Factory) in a nylon jar with ZrO_2 ball for 6 h. The mixture was then dried and heat treated at 1050 °C for 4 h. As a consequence, the sizes of powders were about 5 µm. For the preparation of BCB, high purity (> 99%) $BaCO_3$, CuO and H_3BO_3 were mixed, ball-milled, dried and heat treated at 800 °C for 3 h. Then, LMN powders were re-milled for 6 h with different content (0.05, 0.1, 0.5, 1, 1.5 wt%) of BCB. After drying and sieving, the mixed powders were granulated and pressed into cylindrical samples with 12 mm in diameter and 6 mm in thickness. Finally, all of the samples were sintered at 850–950 °C for 4 h. To improve the reliability of the measurement, six samples were prepared at each point, the value Q × f of per data point was the mode, while the value of ε_r and bulk densities had a little difference.

The bulk densities of the sintered samples were measured by the Archimedes method. The crystalline phases were characterized by XRD (D/max 2400, Rigaku, Tokyo Japan) with Cu-Kα radiation. Scanning Electron Microscope (JSM 6490LV, JEOL, Tokyo Japan) coupled with energy dispersive X-ray spectroscopy (EDX) was used to analyze the microstructure of the samples. The dielectric properties at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method using a HP83752A network analyzer [19, 20]. The temperature coefficients of resonant frequency (τ_f) were calculated as follows:

$$\tau_f = \frac{f_{t2} - f_{t1}}{f_{t1} \times (t_2 - t_1)} \quad (1)$$

where f_{t1} and f_{t2} represented the frequencies at $t_1 = 25$ °C and $t_2 = 80$ °C, respectively.

3 Results and discussion

The XRD patterns of the LMN with different amount of BCB (x = 0.05, 0.1, 0.5, 1 and 1.5 wt%) sintered at 950 °C for 4 h are given in Fig. 1a. All the reflections were well matched with JCPDS file 36-1018 for LMN, no secondary phase was detected in the BCB-doped ceramics, which might be its low mass fraction. In addition, the intensity of the diffraction peak had no significant change with different content of BCB additive.

The cross-sectional SEM images of 0.05–1.5 wt% BCB-added LMN ceramics sintered at 950 °C for 4 h are shown in Fig. 2a–e. In Fig. 2a, there were lots of pores which indicated that the amount of the liquid phase was insufficient for the densification process of LMN ceramics. The microstructure illustrated in Fig. 2b was relatively homogeneity and the size grains ranged from 3 to 8 µm. The micro morphology as shown in Fig. 2c was dense and no pores were observed. With further increasing the content of additives up to 1.5 wt%, some grains began to melt and grow abnormally, leading to the indistinct grain boundaries, which might result in the deterioration of the microwave dielectric. As a consequence, we concluded that the content of the additives exerted a significant effect on the grain growth owing to the formation of the liquid phase [21].

Figure 3 depicts the variations of the bulk densities, dielectric constants, Q × f values and the temperature coefficient of the resonant frequency of LMN with various BCB additions as a function of sintering temperature. The apparent density of the specimens was easily affected not only by the amount of the additive but also by the sintering temperature. The density went up quickly as the ascending of the sintering temperature. What could be inferred from the Fig. 3a was the 0.05 wt% BCB was not enough to densify the LMN ceramics at low sintering temperature and the porous microstructure shown in Fig. 2a supported this. Meanwhile, it was found that the apparent density of 1.5 wt% BCB + LMN ceramics reached the saturation value slowly as the sintering temperature increase from 900 to 950 °C, the maximum bulk density (3.495 g/cm^3) of the ceramics with 1.5 wt% BCB sintered at 950 °C was achieved, which reached 92% of the theoretical density (3.8 g/cm^3). Therefore, it demonstrated

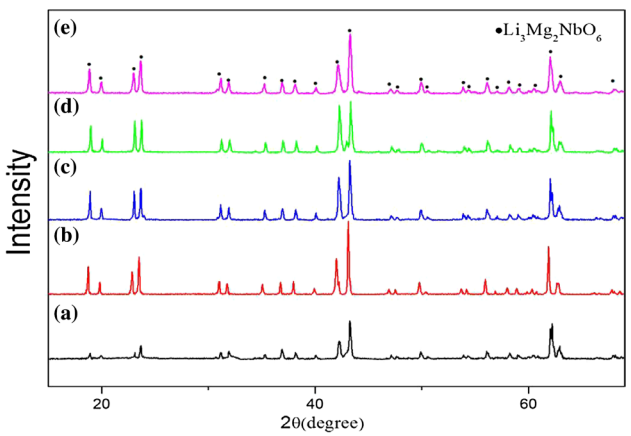

Fig. 1 The XRD patterns of the LMN ceramics sintered at 950 °C for 4 h doped with (*a*) 0.05 wt%, (*b*) 0.1 wt%, (*c*) 0.5 wt%, (*d*) 1.0 wt% and (*e*) 1.5 wt% BCB

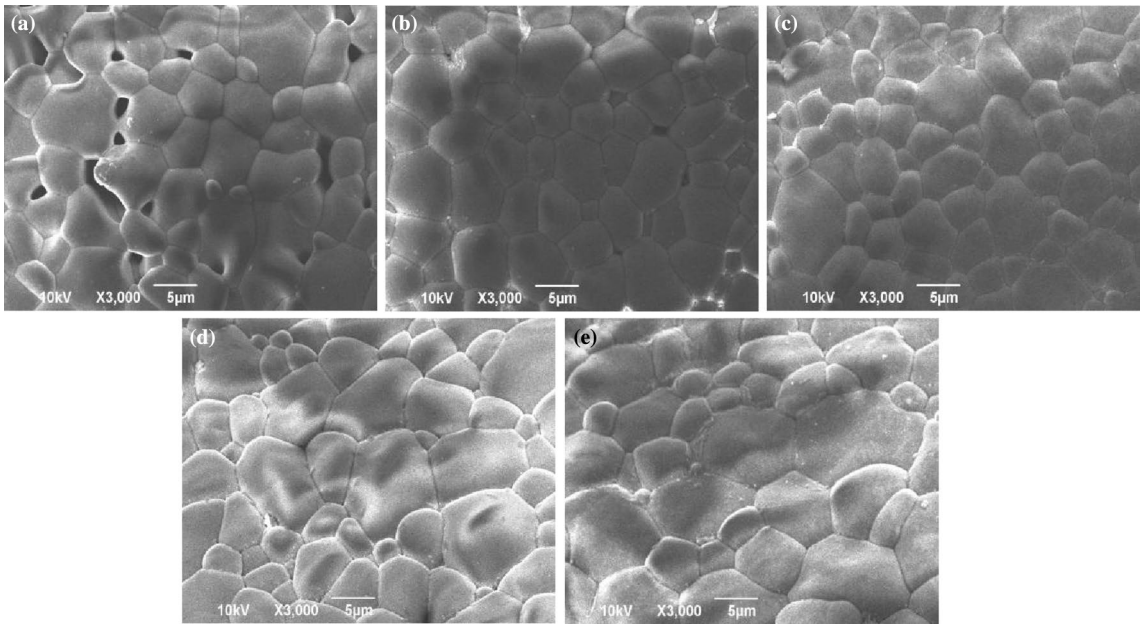

Fig. 2 The cross-sectional SEM images of 0.05–1.5 wt% BCB-added LMN ceramics sintered at 950 °C for 4 h

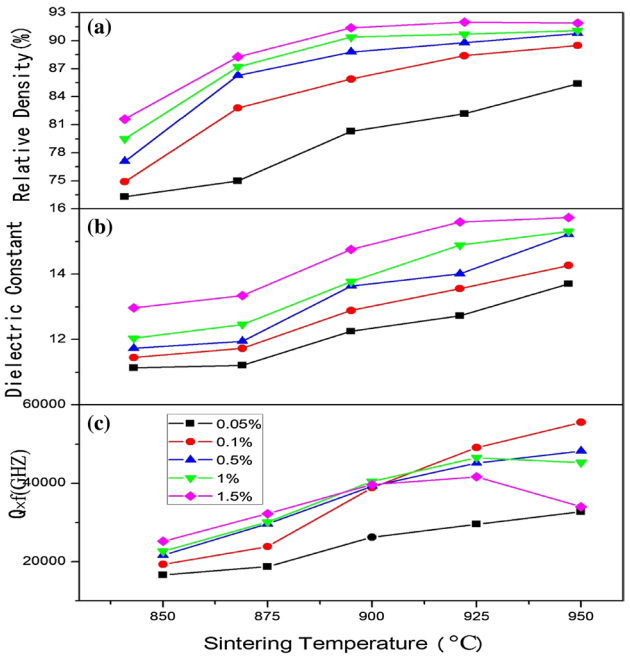

Fig. 3 The variations of bulk densities (**a**), ε_r (**b**) and Q × f (**c**) values of LMN ceramics with various BCB additions as a function of sintering temperature

that the addition of BCB was beneficial to the densification by the liquid sintering mechanism. As is known to us that dielectric constant is generally dependent on the dielectric polarizabilities and structural characteristics including the distortion, tilting and rattling spaces of oxygen octahedron in the unit cell [22, 23]. The variation tendency of ε_r was closely in accord with the change of the apparent density in the Fig. 3b. When the sintering temperature was 900 °C, the dielectric constant increased from 11.73 to 15.22 with BCB range from 3.0511 to 3.474, since the high densification meant there were more polarized particles in a unit volume, which contributed to the increasing of dielectric constant.

Figure 3c presents the Q × f values of LMN + x wt% BCB ceramics as a function of sintering temperature. The Q × f value of LMN with fixed content of additives went up quickly with the increase of the sintering temperature due to the promoted densification, while the Q × f values of the samples (x = 1 and 1.5) increased to a maximum initially, then decreased with ascending the apparent densification. Generally, the Q × f values rely on the intrinsic loss and extrinsic loss. The intrinsic losses are mainly caused by lattice vibration modes, while the extrinsic losses are dominated by second phases, oxygen vacancies, grain boundaries, and densification or porosity [24, 17]. In addition, the excess additives deteriorate the microwave dielectric properties. Hence, the increasing of Q × f value of LMN + x wt% BCB (x = 0.05, 0.1 and 0.5) was attributed to the promotion of the densification. As the increasing of apparent density, the decrease of Q × f value was due to the excess liquid phased and the abnormal grain growth shown in Fig. 2e.

Figure 4 displays the τ_f value of LMN with various BCB contents sintered for 4 h at 950 °C. The τ_f value presented descending tendency as BCB content increased. Since the temperature coefficient of resonant frequency was correlated with the composition, additives as well as secondary phase

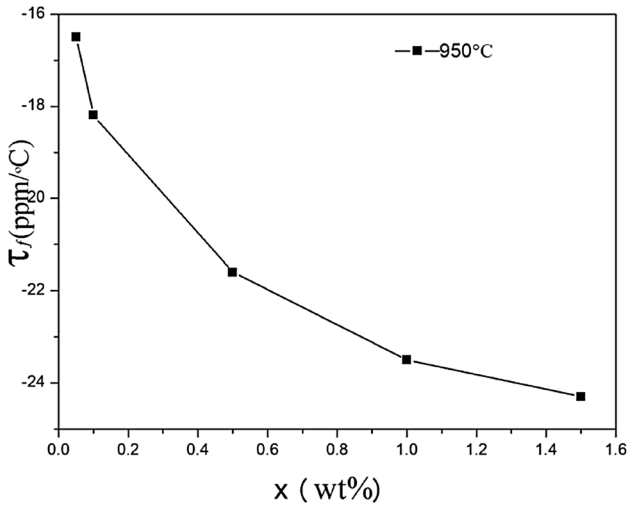

Fig. 4 The τ_f values of LMN ceramics with x wt% BCB sintered at 950 °C for 4 h

of the materials [25], there was only one phase that was detected in the Fig. 1, so the addition could be responsible for the decrease of τ_f value. Particularly, the optimum microwave dielectric properties of $\varepsilon_r = 14.7$, $Q \times f = 55{,}521$ GHz and $\tau_f = -18.2$ ppm/°C could be obtained when the LMN ceramics with 0.1 wt% addition sintered at 950 °C.

Aiming to test the chemical compatibility with the silver electrode, the LMN ceramics with 1.5 wt% sintering aids and 20 wt% Ag sintered at 950 °C for 4 h were characterized by X-ray diffraction (XRD), SEM and EDS. The results of EDS together with back scattered electron (BSE) micrograph are illustrated in Fig. 5 and Table 1. The Ag particles as directed by the white arrow in Fig. 5a could be found easily because the extent of brightness was closely related to the compound in the BSE image. Figure 5c Compared with Fig. 1 presented no other phases except the cubic silver phase. As a consequence, there were no reactions between the LMN + 1.5 wt% BCB and Ag. None of elements was detected other than the elements used in the experiment, which verified the results of XRD. The lithium and boron ion can't be detected owing to the limitation of EDS. Besides, the 1.5 wt% BCB doped LMN ceramic sample with Ag electrode coating was co-fired

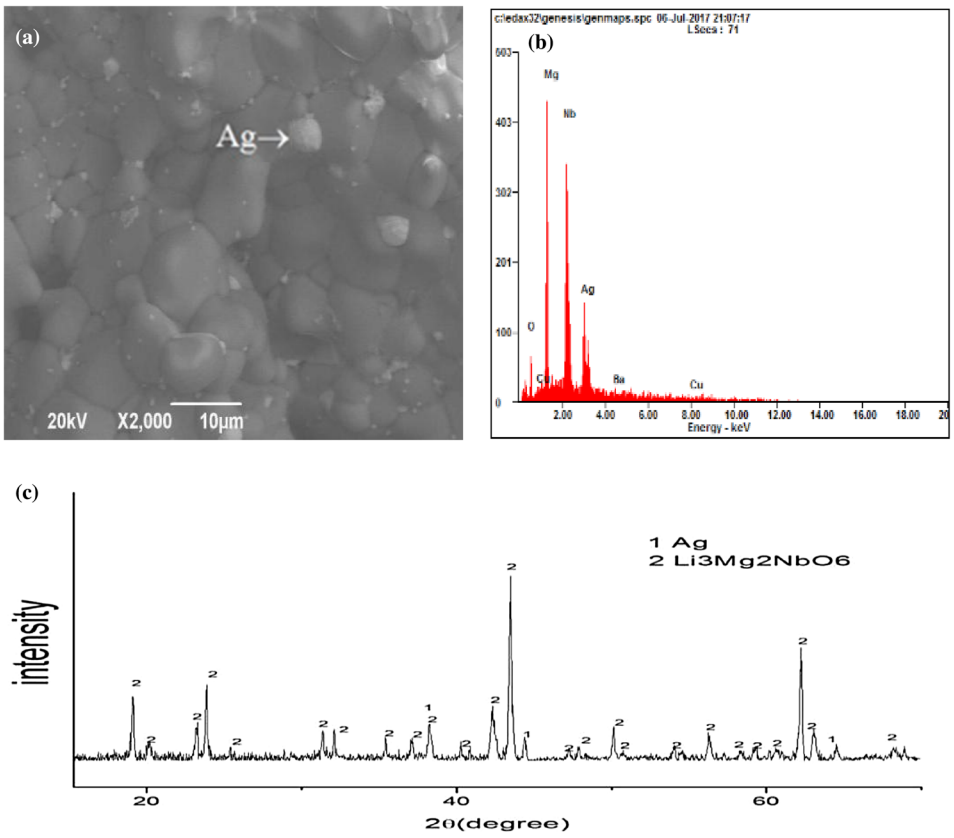

Fig. 5 The XRD pattern, EDS analysis and the BSE image of the LMN ceramic with 1.5 wt% BCB and 20 wt% Ag particles sintered at 950 °C for 4 h

Table 1 The quantitative EDS analysis of the sample

Element	Nb	Mg	O	Ba	Cu	Ag
wt%	21.43	47.45	10.96	1.22	0.31	18.63

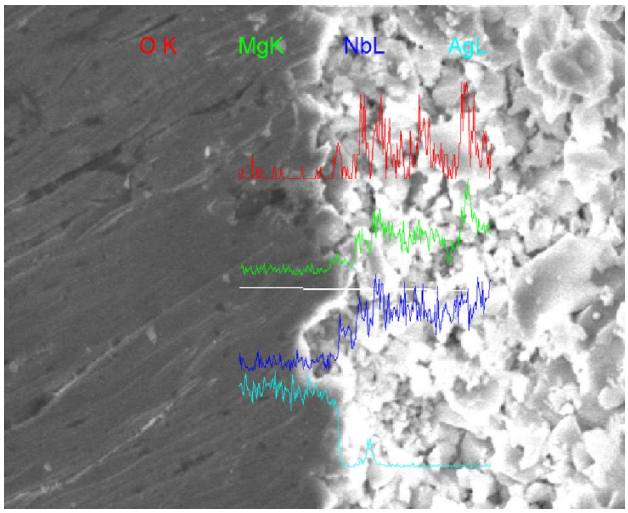

Fig. 6 The EDX line scanning analysis of 1.5 wt% BCB + LMN ceramic with Ag coating

at 900 °C for 4 h in air and analyzed to detect interactions between the sample and the Ag electrode, Fig. 6 present the SEM micrographs and the EDX line scanning analysis of the sample. A good contact between the ceramic and Ag was observed from the SEM, the EDX line scanning analysis confirmed that Ag did not diffuse into LMN ceramic. Therefore, the BCB doped LMN ceramic had a good chemical compatibility with Ag electrode.

4 Conclusion

Microwave dielectric properties of LMN ceramics were investigated as a function of BCB content and sintering temperature. The dielectric constant and the Q × f values had the same variation trend with bulk density. The τ_f value presented descending tendency as BCB content increased. Optimum dielectric properties were obtained as the sample with 0.1 wt% BCB sintered at 950 °C for 4 h: $\varepsilon_r = 14.27$, Q × f = 55521 GHz and $\tau_f = 18.2$ ppm/°C. From the analysis of 1.5 wt% BCB doping sample co-fried with 20 wt% Ag, the BCB doped LMN ceramics were chemically compatible with Ag powder, which made it be a suitable candidate material for LTCC applications.

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