Low temperature sintering and microwave dielectric properties of novel temperature stable $Li_3Mg_2NbO_6$-0.1TiO_2 ceramics

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Abstract

Novel temperature stable $Li_3Mg_2NbO_6$-0.1TiO_2 (LMNT) ceramics doped with Li_2O-B_2O_3-Bi_2O_3-SiO_2 (LBBS) glass were synthetized by a solid-state route. The sintering temperature of the LBBS glass doped LMNT ceramics can be effectively lowered to 900 °C. The experimental results revealed that the addition of the LBBS glass can assist to improve the Q×f values while shifting the τ_f values toward negative direction. Particularly, the 1wt.% of LBBS glass doped LMNT ceramic sintered at 900 °C for 4 h possessed excellent microwave dielectric properties: ε_r=16, Q×f=42648 GHz, τ_f=-1ppm/°C., which is potential for LTCC applications.

Key words: Ceramics, Dielectrics, Low temperature firing

1. Introduction

Dielectric materials have contributed to the rapid development of communication systems including mobile telecommunication and satellite broadcasting. In recent years, many works have been conducted to search

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for appropriate dielectric ceramics and new technology to satisfy the demands for miniaturization and integration. One solution is the low temperature co-fired ceramics (LTCC) technology enabling combining multi-layer and highly conductive internal electrode metals, such as silver and copper [1]. For practical application, the dielectric materials for LTCC should have a low sintering temperature (lower than 960°C) [2-4]. In previous works, low temperature sintering has been achieved by adding glass frits, such as ZnO-B_2O_3-SiO_2, ZnO-P_2O_5-MnO_2 and B_2O_3-CuO [5-8].

Recently, Yuan et al. reported that the $Li_3Mg_2NbO_6$ ceramics exhibited good dielectric properties: ε_r=16.8, Q×f=79643 GHz, τ_f=-27.2 ppm/°C when sintered at 1250 °C [9]. However, the high sintering temperature forbids potential for LTCC applications. Zhang et al. successfully lowered the sintering temperature of $Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6$ ceramics to 925 °C by adding 0.5.wt% $0.17Li_2O$-$0.83V_2O_5$[10]. Afterwards, Zhang et al. reported that the $Li_3Mg_2NbO_6$ ceramics sintered at 875 °C maintained excellent dielectric properties of ε_r=14.89, Q×f=86720 GHz, τ_f=-15.46 ppm/°C when doped with 1wt% Li_2O-B_2O_3-SiO_2 glass [11]. However, all of them above exhibit inappropriate negative τ_f. Rutile TiO_2 was widely utilized to compensate the negative τ_f due to large positive τ_f (+465 ppm/°C) [12, 13].

In this work, we selected TiO_2 to compensate the τ_f for $Li_3Mg_2NbO_6$-TiO_2 (LMNT) system. And then we chose Li_2O-B_2O_3

-Bi_2O_3-SiO_2 (LBBS) glass to lower the sintering temperature. The effects of LBBS glass on the sintering, microstructures and microwave dielectric properties of LMNT ceramics were investigated.

2. Experiment procedure

All the samples were prepared by using predecessors of Li_2CO_3, MgO, Nb_2O_5 and TiO_2 (all purity>99%). The raw materials were mixed according to the stoichiometric composition $Li_3Mg_2NbO_6$ and ball-milled in distilled water for 12 h. The mixtures were dried and calcined at 1000 °C for 4 h. And then the calcined powers were mixed with the TiO_2 according to the composition $Li_3Mg_2NbO_6$-0.1TiO_2. Afterwards, the 0.5-2wt. % LBBS glass powders were added to the LMNT ceramics. After re-milling another 12 h, the mixtures were pressed into pellets of 12 mm in diameter and 6 mm in thickness. The pellets were sintered from 850 °C to 1000 °C for 4 h.

The bulk densities were measured by Archimedes method. The crystalline phases were examined by X-ray diffractometer (DX-2700, Haoyuan Co.) with CuKα radiation at 40kV and 30mA. The microstructures of fracture surface were observed using a scanning electron microscope (JSM-6490, JEOL, Japan). The dielectric properties were measured by the Hakki-Coleman dielectric resonator method in TE011 mode by using a network analyzer (Agilent N5230A, USA). The temperature coefficient of resonant frequency value (TCF, τ_f) can be calculated by the equation:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times 60} \times 10^6 \,(\text{ppm/°C}) \qquad (1)$$

Where f_{80} and f_{20} were the resonant frequencies at 80 °C and 20 °C, respectively.

3. Results and discussions

Fig. 1 shows the XRD patterns of the LMNT ceramics with different amounts of LBBS glass sintered at 900 °C. It is obvious that all the specimens show an orthorhombic structure $Li_3Mg_2NbO_6$ phase (JCPDS No. 36-1018) with little MgO phase (JCPDS No. 45-0946). Besides, no TiO_2 phase can be detected, indicating that solid solutions are formed or amount of TiO_2 is insufficient to be detected. The residual MgO phase is mainly induced by the evaporation of lithium. With the LBBS content increasing, the diffraction peaks of MgO phase remains unchanged and the diffraction peak position of $Li_3Mg_2NbO_6$ phase shifts to the left, which might be due to the formation of impurity[11].

Fig. 2 shows the SEM micrographs of the LMNT ceramics with various contents of LBBS glass sintered at 900 °C. In the Fig. 3 (a)-(b), the grain sizes have an increasing trend and dense microstructures with no visible pore can be observed. The calculated average grain sizes are 3.1μm, 3.8μm, 2.5μm, 2.3μm as the LBBS contents increasing, respectively. This result indicates that moderate addition of LBBS glass can promote the grain growth. However the microstructures with substantial pores can be observed when doped with 1.5-2wt. % LBBS glass. This can be attributed to massive LBBS glass liquid phase, which promotes the abnormal growth of grains and some pores are trapped in grain boundaries, thus deteriorating the dielectric performances of the LMNT ceramics.

Fig. 3 illustrates the bulk densities and dielectric properties of the LMNT ceramics with various amounts of LBBS glass sintered at different temperatures. With the sintering temperature increasing from 850 °C to 950 °C, the bulk densities and the ε_r increase approaching to a maximum at 900 °C and then decrease. Moreover, the bulk densities and the ε_r reach a maximum value for 1wt. % LBBS glass addition. Therefore, the ε_r is depended on the bulk densities. The Q×f is related with intrinsic losses and extrinsic losses. The intrinsic losses are mainly depended on structure characteristics, whereas the extrinsic losses are relevant to second phase, grain size, and porosity[11]. Fig. 1 indicates that the effect of MgO phase can be neglected. So in this study, the Q×f values are dependent on the bulk density. The Q×f values increase approaching to a maximum at 900 °C and then decrease, presenting a similar tendency with the bulk density. For all the samples sintered at 900 °C, the Q×f values initially increase, reaching to a maximum (42648 GHz) for 1wt. % LBBS glass addition and then decrease. This phenomenon implies that appropriate LBBS glass can enhance the Q×f values of the LMNT ceramics duo to decrease of porosity and larger grain sizes, as shown in Fig. 2 (a)-(b).

Fig. 4 exhibits the temperature coefficients of resonant frequency (τ_f) of the LMNT ceramics with various amounts of LBBS glass sintered at 900°C. It can be observed that the τ_f values shift towards to the negative direction with LBBS content increasing, which may be explained by the relatively high negative τ_f of LBBS glass. Kang et al. also found that the τ_f value shifted to negative direction with XRD peak shifting to the left[14]. Therefore, the variation of τ_f values can be explained by integrated effects from both lowered 2θ angles and the contribution of LBBS glass.

4. Conclusions

In this work, $Li_3Mg_2NbO_6$-0.1TiO_2 (LMNT) ceramics doped with Li_2O-B_2O_3-Bi_2O_3-SiO_2 (LBBS) glass were synthesized by the conventional solid-state reaction route. The effects of LBBS glass on the sintering behaviors, microstructures and microwave dielectric properties of LMNT ceramics were investigated. Particularly, the 1wt. % LBBS glass doped LMNT ceramics sintered at 900 °C for 4 h possessed excellent microwave dielectric properties: ε_r=16, Q×f=42648 GHz, τ_f=-1 ppm/°C, exhibiting a potential for temperature stable applications.

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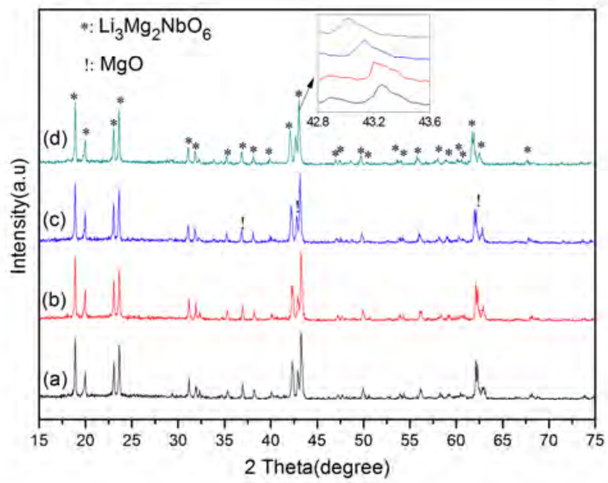
Figure Captions:

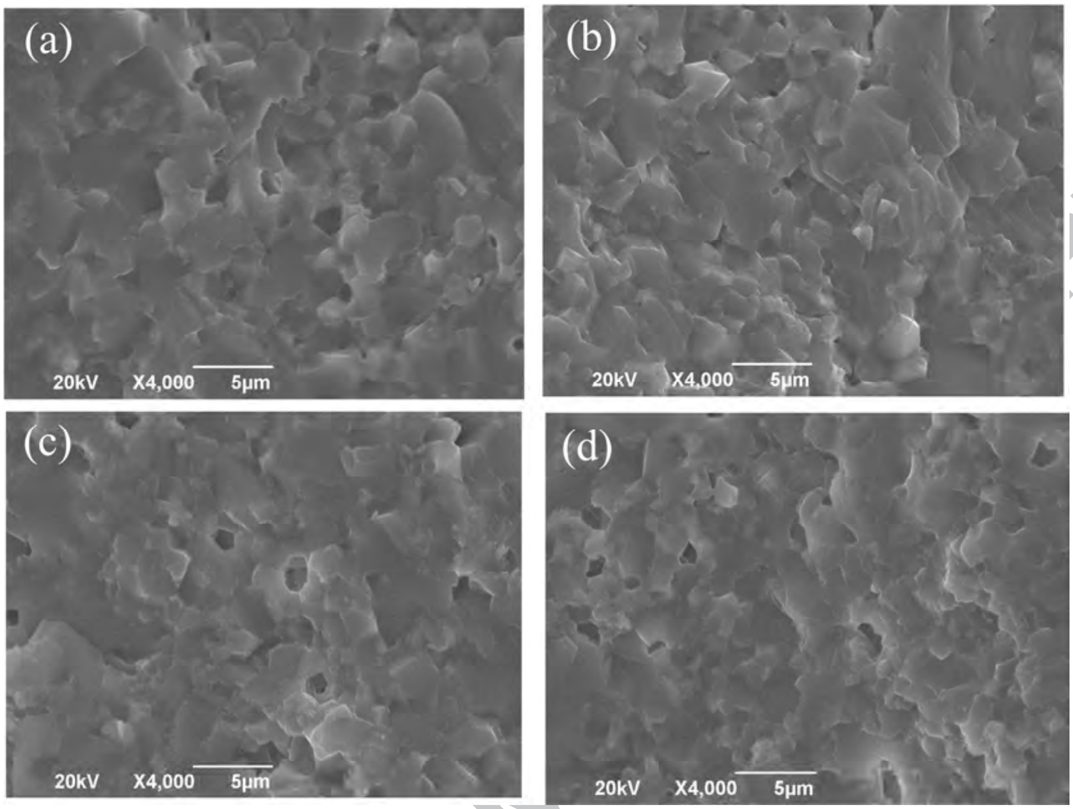
Fig.1. The XRD patterns of the LMNT ceramics sintered at 900 °C with (a) 0.5 wt. %, (b) 1 wt. %, (c) 1.5 wt. %, (d) 2 wt. % LBBS glass.

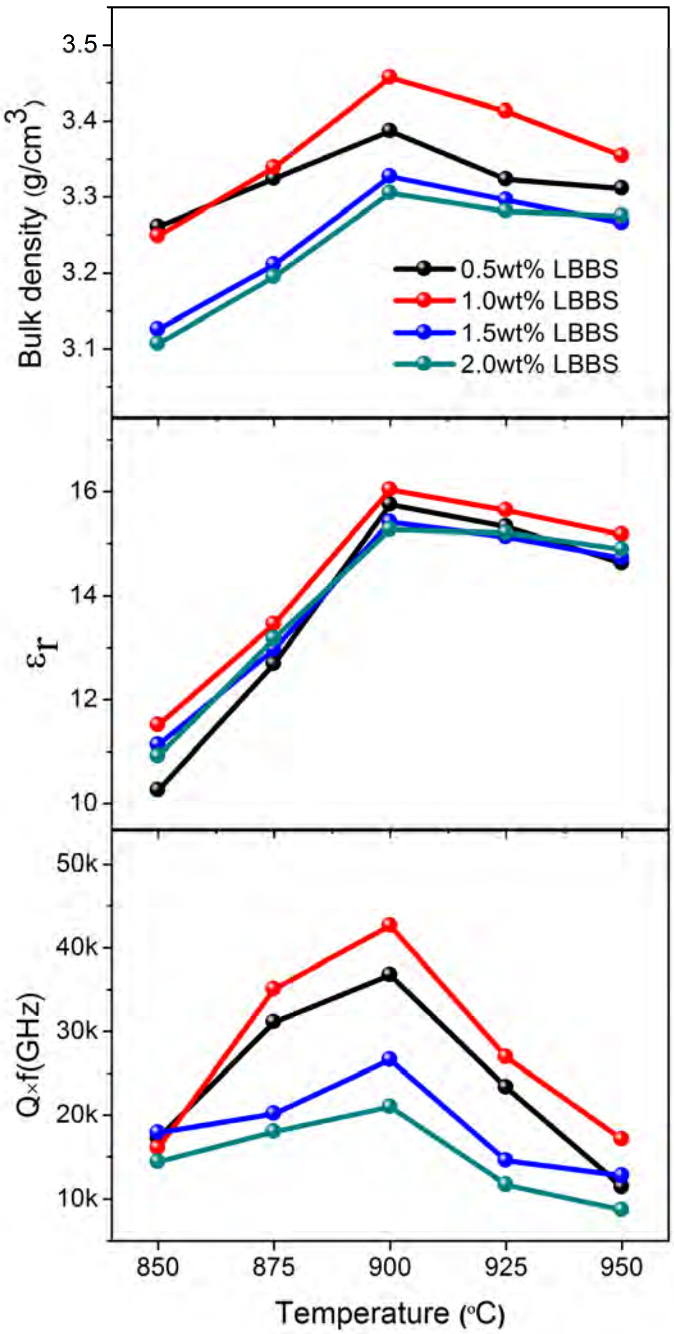
Fig.2. The SEM micrographs of the LMNT ceramics with x wt. % of LBBS glass sintered at 900 °C for 4h. (a)x=0.5, (b) x=1, (c) x=1.5, (d) x=2.

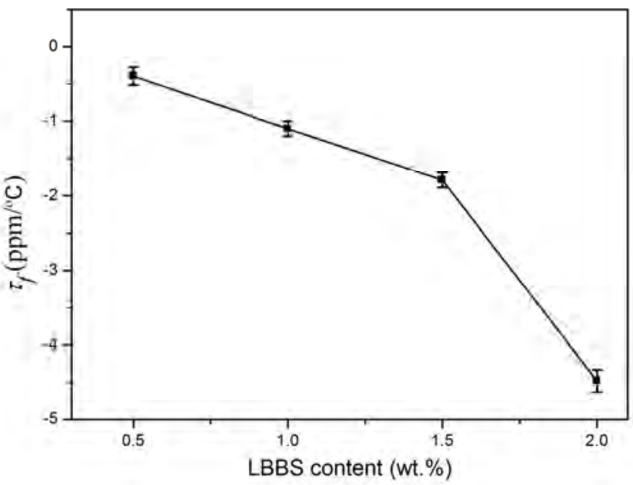
Fig.3. The bulk densities and dielectric properties of the LMNT ceramics with various amounts of LBBS glass sintered at different temperatures.

Fig.4. The τ_f values of the LMNT ceramics doped with different amounts of LBBS glass sintered at 900°C.


*: Li3Mg2NbO6
!: MgO
(d)
(c)
(b)
(a)
Intensity(a.u)
2 Theta(degree)
15
20
25
30
35
40
45
50
55
60
65
70
75
42.8
43.2
43.6


(a)
20kV X4,000 5μm
(b)
20kV X4,000 5μm
(c)
20kV X4,000 5μm
(d)
20kV X4,000 5μm


Bulk density (g/cm3)
3.5
3.4
3.3
3.2
3.1
0.5wt% LBBS
1.0wt% LBBS
1.5wt% LBBS
2.0wt% LBBS
εr
16
14
12
10
Q×f(GHz)
50k
40k
30k
20k
10k
850
875
900
925
950
Temperature (°C)


τ_f (ppm/°C)
LBBS content (wt.%)
0
-1
-2
-3
-4
-5
0.5
1.0
1.5
2.0

- Novel temperature stable ceramics were synthetized with $Li_3Mg_2NbO_6$ and TiO_2.
- Dense and uniform LMNT ceramics were obtained doped with LBBS glass.
- LBBS glass lowered sintering temperature of LMNT ceramics to 900 °C.
- The LMNT + 1wt. % LBBS composites possessed excellent dielectric properties.