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Sintering Behavior, Microstructure and Microwave Dielectric Properties of Novel Temperature Stable $Li_3Mg_2NbO_6$–tio_2 Composite Ceramics

Gang Wang*, Dainan Zhang*, Huaiwu Zhang

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

Abstract

A novel series of temperature stable $Li_3Mg_2NbO_6$–$xTiO_2$ ceramics were prepared by the conventional solid-state route. The effects of TiO_2 addition on the sintering behavior, phase composition, microstructure and microwave dielectric properties were investigated systematically. The dense microstructure could be obtained in low TiO_2 content (x=0.1) samples sintered at 1100 °C. The dielectric constant ε_r was attributed to the bulk density and TiO_2 content. The variation in $Q\times f$ values is related to the bulk density, and improved values could be obtained for $Li_3Mg_2NbO_6$–$0.1TiO_2$ ceramics. The quality factor ($Q\times f$) had a maximum for x=0.1 and the temperature coefficient of resonant frequency (τ_f) value shifted towards positive direction with the increase of TiO_2 addition. Notably, $Li_3Mg_2NbO_6$–$0.1TiO_2$ ceramics sintered at 1100 °C possessed excellent microwave dielectric properties: ε_r=15, $Q\times f$ =74,000 GHz(9.93GHz), τ_f= −3.4 ppm/°C, which made the ceramics as promising low loss and temperature stable candidates for millimeter-wave applications.

INTRODUCTION

Dielectric materials have promoted the rapid development of wireless communication systems including mobile telecommunication and satellite broadcasting. In recent years, many groups have performed some methods to search for new technology and appropriate dielectric ceramics for practical application to satisfy the demands for

* Corresponding author:

Email address: wang_toward@163.com(G. W.);dnzhang@uestc.edu.cn(D. Z.)

miniaturization, multifunction and integration. For practical applications, the dielectric materials should satisfy several essential requirements: (i) an appropriate dielectric constant (ε_r), (ii)a high quality factor (Q×f) and (iii) a near-zero temperature coefficient of resonant frequency (τ_f) [1]. However, most of dielectric ceramics have a low quality factor (Q×f) and high temperature coefficient of resonant frequency (τ_f). Hence, it is necessary to develop new microwave materials [2-4].

Recently, the $Li_3Mg_2NbO_6$ ceramics with orthorhombic structure was reported by Yuan et al. exhibiting good microwave dielectric properties: ε_r=16.8, Q×f=79,643 GHz, τ_f=-27.2 ppm/°C [5]. Afterwards, many types of research were conducted to lower the sintering temperature and improve the Q×f values. Zhao et al. reported the remarkable dielectric properties of τ_f-adjusted $Li_3(Mg_{0.95}Ca_{0.05})_2NbO_6$: ε_r=15.62, Q×f=96,160 GHz, τ_f=-18.49 ppm/°C by Ca^{2+} substitution on the Mg sites [6]. However, all of them above exhibit inappropriate negative τ_f. Rutile structure TiO_2 was widely utilized to compensate the negative τ_f due to large positive τ_f (+465 ppm/°C) [7-9].

In this work, we selected TiO_2 to compensate the τ_f for $Li_3Mg_2NbO_6$-$x$$TiO_2$ system. The effects of TiO_2 on the microstructure, sintering behaviors and microwave dielectric properties of the LMNT ceramics were investigated.

EXPERIMENT PROCEDURE

$Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics were synthetized by using predecessors of MgO, Li_2CO_3, Nb_2O_5 and TiO_2 (all purity>99%). The raw materials were mixed and ball-milled in distilled water for 12 h using zirconia spheres as milling media. The mixtures were sieved through a 120 mesh sieve and calcined in air at 1050 °C for 4 h. And then the calcined powers were mixed with the TiO_2 according to the composition $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4). After re-milling another 12 h, the mixture was mixed with polyvinyl alcohol (PVA) and pressed into cylindrical pellets of 12 mm in diameter and 6 mm in thickness. The pellets were sintered from 1050 °C to 1200 °C for 4 h.

The bulk densities were measured by Archimedes method using distilled water as the buoyancy liquid and the theoretical density of $Li_3Mg_2NbO_6$-0.1TiO_2 can be calculated as 3.52 g/cm^3. The phase structures were determined by X-ray diffractometer (XRD: Philips X' pert Pro MPD, Holland). The microstructures and morphology of as-sintered samples were observed by a scanning electron microscope (JSM-6490, Japan). The dielectric properties were measured by the Hakki-Coleman dielectric resonator method in TE011 mode combining 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} are the resonant frequencies at 80 °C and 20 °C.

RESULTS AND DISCUSSIONS

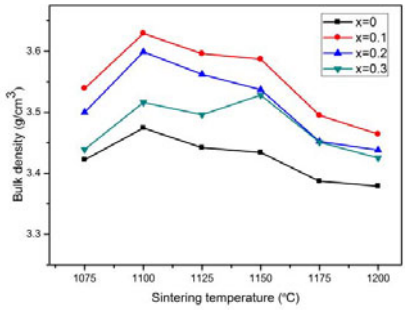

Fig.1. Bulk densities of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ceramics.

The bulk densities of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics sintered at different temperatures are shown in Fig. 1. It is obvious that the bulk densities depend strongly on the sintering temperature. When the sintering temperature increases from 1075 °C to 1200 °C, the bulk density values of all specimens increase approaching to a maximum value at 1100 °C and then decrease, indicating that 1100 °C is the optimal temperature of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics. When sintered at 1100 °C, the relative density initially increases, reaching a maximum value for x=0.1 and then decreases. Therefore, we select the samples sintered at 1100 °C for further investigation in detail.

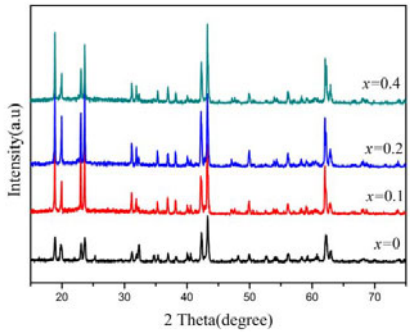

Fig.2. The XRD diffraction patterns of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics.

Fig. 2 shows the XRD patterns of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics sintered at 1100 °C. It is obvious that all the specimens show an orthorhombic structure $Li_3Mg_2NbO_6$ phase (JCPDS file No. 36-1018) with a little MgO phase (JCPDS file No. 45-0946). Besides, no TiO_2 phase can be detected, indicating that continuous solid solutions are formed in the entire composition ranges or content of TiO_2 is insufficient to be detected. And the diffraction peaks of MgO phase remained unchanged, indicating that the addition of TiO_2 has no significant effect on MgO phase.

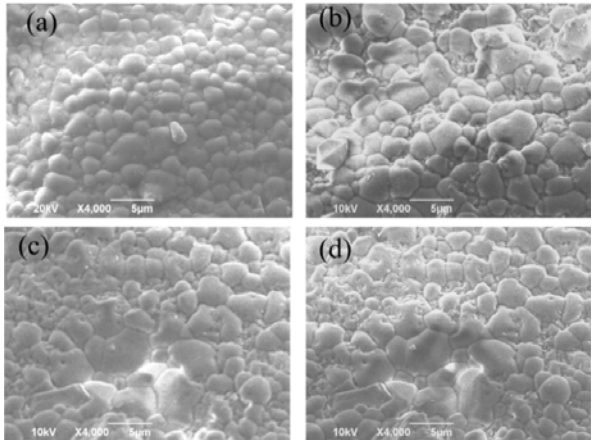

Fig.3. The SEM micrographs of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics sintered at 1100 °C for 4h: (a)x=0.5,(b)x=1,(c)=1.5,(d)x=2.

Fig. 3 shows the SEM micrographs of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics sintered at 1100 °C. In the Fig. 3 (a)-(b), the grain sizes have an increasing trend and dense microstructures with no visible pores can be observed, which agrees well with the relative density. This result indicates that moderate addition of TiO_2 can promote the grain growth. However, excess TiO_2 inhibits the grain growth by hindering grain boundary migrating from the small grains to the contiguous large ones. Moreover, when x=2 and 4, the microstructures with inhomogeneous grains can be observed.

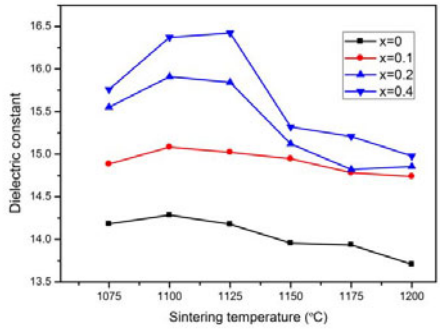

Fig.4. Dielectric constant of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics.

Fig. 4 illustrates the dielectric constant (ε_r) of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics sintered at different temperatures. In general, the dielectric constant is related with extrinsic factors (such as the bulk density and the second phase) and intrinsic factors. Fig. 2 indicates that the second phase (MgO phase) exists in the entire composition range and the content of MgO phase remains unchanged. Therefore, the effect of MgO phase can be neglected. So the dielectric constant of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics is dependent on the content of TiO_2. As shown in Fig. 4, when the sintering temperature ranges from 1075 °C to 1200 °C, the ε_r values of all samples increase approaching to a maximum at 1100 °C, and then decreases as the sintering temperature increases further. So in this study, the TiO_2 content plays a critical role in ε_r value.

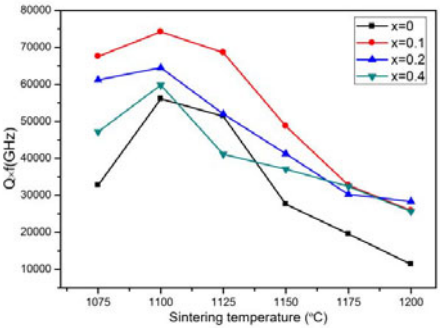

Fig.5. Q×f values of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics sintered at different temperatures.

Fig. 5 exhibits the Q×f values of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics. The dielectric Q×f value is related with intrinsic losses and extrinsic losses. The intrinsic losses are mainly depended on structure characteristics, whereas the extrinsic losses are relevant to oxygen vacancies, second phase, grain size, and porosity [10]. In this study, the Q×f values are dependent on the extrinsic factors. With regard to the extrinsic losses, the XRD diffraction patterns show that the second phase (MgO phase) exists in the entire composition ranges and the content of MgO phase remains unchanged. Therefore, the effect of MgO phase can be neglected. The Q×f values of all samples increase approaching to a maximum at 1100 °C and then decrease, presenting a similar tendency with the bulk density. And in this work, the bulk density and TiO_2 addition affected the Q×f value. The change of Q×f value was similar to that of the bulk density. So the bulk density dominates the Q×f value. For all the samples sintered at 1100 °C, the Q×f values initially increase, reaching to a maximum value (74,000 GHz) for x=0.1 and then decrease. This phenomenon implies that appropriate TiO_2 can enhance the Q×f values of the LMNT ceramics duo to reduce of porosity, as shown in Fig. 3 (a)-(b). However, the subsequent decrease of Q×f values may be attributed to the porosity and the excessively higher intrinsic dielectric loss of the TiO_2 than LMNT ceramic.

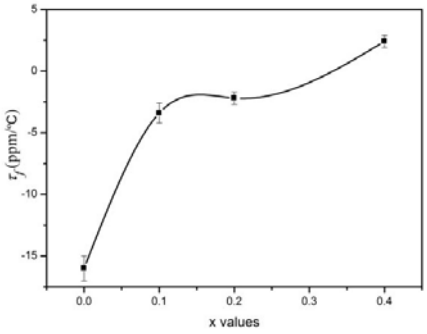

Fig.6. τ_f values of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics sintered at 1100°C.

Fig. 6 exhibits the temperature coefficients of resonant frequency (τ_f) of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics d sintered at 1100°C for 4 h. In general, the τ_f value is influenced by the composition and additive. The theoretical τ_f values of the mixture can be predicted by the following equation:

$$\tau_f = y_1\tau_{f1} + y_2\tau_{f2} \quad (2)$$

Where y_1, y_2 and τ_{f1}, τ_{f2} are the volume fractions and the τ_f values of the $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics and the TiO_2, respectively. It can be observed that the τ_f values shift towards to the positive direction with TiO_2 content increasing, which may be explained by the relatively high positive τ_f of TiO_2 glass. Table 1

show a comparison of microwave properties among several ceramics. Compared with other composite ceramics, $Li_3Mg_2NbO_6$-0.1TiO_2 ceramics possesses excellent microwave dielectric properties: high Q×f value and near zero τ_f value, satisfying the requirement of the practical application.

Table 1

A comparison among several ceramics

Compounds	S.T (°C)	ε_r	Q×f (GHz)	τ_f (ppm/°C)	Ref
0.7CaP2O7-0.3 TiO_2	1120	10.9	44000	-11	[11]
0.74CaWO4-0.26TiO_2	1300	17.48	27000	0	[9]
0.7MgMoO4-0.3TiO_2	950	9.13	11900	3.2	[8]
$Li_3Mg_2NbO_6$-0.1TiO_2	1100	15	74,000	-3.4	This work

CONCLUSIONS

In this work, $Li_3Mg_2NbO_6$-$x$$TiO_2$ (x=0, 0.1, 0.2 and 0.4) ceramics were synthesized via the conventional solid-state reaction route. The effects of TiO_2 addition on the microstructures, sintering behaviors and microwave dielectric properties of $Li_3Mg_2NbO_6$-$x$$TiO_2$ ceramics were investigated. Particularly, the $Li_3Mg_2NbO_6$-0.1TiO_2 ceramics sintered at 1100 °C for 4 h possessed excellent microwave dielectric properties: ε_r=15, Q×f=74,000 GHz, τ_f= −3.4 ppm/°C, exhibiting a potential for temperature stable microwave applications.

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