


 Cite this: *RSC Adv.*, 2020, 10, 29835

Microwave dielectric properties of low-temperature-fired MgNb_2O_6 ceramics for LTCC applications

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MgNb_2O_6 ceramics doped with $(\text{Li}_2\text{O}-\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2)$ glass were synthesized by the traditional solid phase reaction route. The effects of LMZBS addition on microwave dielectric properties, grain growth, phase composition and morphology of MgNb_2O_6 ceramics were studied. The SEM results show dense and homogeneous microstructure with grain size of 1.72 μm . Raman spectra and XRD patterns indicate the pure phase MgNb_2O_6 ceramic. The experimental results show that LMZBS glass can markedly decrease the sintering temperature from 1300 °C to 925 °C. Higher density and lower porosity make ceramics have better dielectric properties. The MgNb_2O_6 ceramic doped with 1 wt% LMZBS glass sintered at 925 °C for 5 h, possessed excellent dielectric properties: $\epsilon_r = 19.7$, $Q \cdot f = 67\,839$ GHz, $\tau_f = -41.01$ ppm °C⁻¹. Moreover, the favorable chemical compatibility of the MgNb_2O_6 ceramic with silver electrodes makes it as promising material for low temperature co-fired ceramic (LTCC) applications.

 Received 13th June 2020
 Accepted 6th August 2020

DOI: 10.1039/d0ra05211f

rsc.li/rsc-advances

1. Introduction

The forward evolution of electronics, power systems, satellite broadcasting and wireless communication,¹ especially the rapid development of 5G communication, have posed great demands for high integration and miniaturization.^{2,3} And considering their excellent microwave dielectric properties, microwave dielectric materials have attracted more attention in passive electronic components, such as dielectric resonators, filters and other devices.^{4,5} Additionally, LTCC technology is favored by advanced products because of their high demands for miniaturization and hybrid integration for electronic systems. For instance, Guo *et al.*^{44–46} successfully lowered the sintering temperature of ceramics by ions substitution and addition of low melting point oxide. In order to co-fire with silver electrode, ceramics must be synthesized at low temperature, less than 960 °C.^{6,7} Hence, the aim of the present work is to decrease the sintering temperature of MgNb_2O_6 ceramics and then achieve excellent chemical compatibility with silver for the first time to satisfy the demands for LTCC applications. Generally, the sintering temperature of ceramic materials can be effectively reduced by the following methods: (1) use the raw materials with lower melting temperature, such as $\text{Bi}_2\text{Mo}_2\text{O}_9$ ceramics.⁸ (2) Use ultrafine powders as raw materials to decrease the densification temperature.⁹ (3) Adopt proper synthesis process,

such as co-precipitation, sol-gel and hydrothermal methods.^{10,11} (4) Use reasonable ion substitution.^{12,13} (5) Select appropriate low-melting glass or oxide to reduce the sintering temperature. The commonly used low-melting glasses are $\text{PbO}-\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3-\text{ZnO}-\text{TiO}_2$, $\text{B}_2\text{O}_3-\text{CuO}$, $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{CaO}-\text{Al}_2\text{O}_3$.^{14,15}

Binary magnesium niobate ceramics with rhombic columnar structure are widely investigated because of their excellent microwave dielectric properties.^{16,17} However, the pure phase MgNb_2O_6 ceramic is not easy to obtain, as reported by Liou *et al.*¹⁸ Pullar *et al.*¹⁹ reported that MgNb_2O_6 ceramic sintered at 1300 °C for 2 h exhibited remarkable microwave properties: $\epsilon_r = 19.9$, $Q \cdot f = 79\,600$ GHz, $\tau_f = -64.9$ ppm °C⁻¹. Tian *et al.*²⁰ reported that MgNb_2O_6 ceramic were not only successfully sintered at 1050 °C, but also achieved remarkable microwave properties: $\epsilon_r = 21.5$, $Q \cdot f = 108\,000$ GHz, $\tau_f = -44$ ppm °C⁻¹ by adding $\text{CuO}-\text{B}_2\text{O}_3$ as sintering aid. However, the sintering temperature is still too high.

As known, the synthesis of pure-phase MgNb_2O_6 ceramics is not easy.²³ In this work, pure-phase MgNb_2O_6 ceramic was synthesized successfully by optimizing process parameters. Such as, the slightly excessive MgO , reasonable extension of the milling time and increase in the pre-sintering time. George, Sumesh, *et al.*⁴⁴ reported that the addition of LMZBS glass decreased the sintering temperature of $\text{Li}_2\text{MgSiO}_4$ ceramics from 1250 to 875 °C. Besides, the LMZBS glass melts to form a liquid phase and wet the grains of MgNb_2O_6 , thereby promoting the densification of MgNb_2O_6 .⁴⁴ In addition, magnesium oxide in LMZBS glass can compensate for the volatilization of MgO in MgNb_2O_6 , so LMZBS glass plays

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a great role in low-temperature sintering. In the present work, we have chosen LMZBS glasses as the firing aid to reduce the sintering temperature of MgNb_2O_6 ceramics. To our best knowledge, there's been no relevant report about the co-fired experiment of MgNb_2O_6 ceramics with silver electrodes. In this work, the chemical compatibility of MgNb_2O_6 ceramics with Ag electrodes have been studied for the first time. Meanwhile, the effects of LMZBS glass addition on the microstructure, density and dielectric properties of MgNb_2O_6 ceramics were also studied.

2. Experimental procedures

2.1. Materials preparation

MgNb_2O_6 ceramics were synthesized by solid-state process using high-purity MgO and Nb_2O_5 (all purity > 99.9%) as original materials were. The stoichiometric ratio of MgO and Nb_2O_5 was 1.01 : 1. (The slightly excessive MgO is beneficial to inhibit the production of the secondary phases $\text{Mg}_4\text{Nb}_9\text{O}_2$ and Nb_2O_5 ^{24,25}). The powders were milled for 24 h, dried, and finally calcined at 1000 °C for 8 h. (An appropriate increase in the pre-sintering time is conducive to the formation of single-phase MgNb_2O_6 ceramic, and a reasonable extension of the milling time will increase the uniformity of particles and decrease particle size^{23,26}). Li_2O -MgO-ZnO- B_2O_3 - SiO_2 (LMZBS) glass was synthesized by quenching method according to the mole percentage of: Li_2CO_3 : MgO : ZnO : B_2O_3 : SiO_2 = 20 : 20 : 20 : 20 : 20 (all purity > 99%). The LMZBS glass^{21,22} was melted and quenched at 900 °C. Then different weight percentages of LMZBS glasses (x = 0.1 wt%, 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%) were added to the calcined MgNb_2O_6 powders. After the second ball-milling for 12 h, the mixtures were dried, mixed with 10% PVB and then pressed into small cylinders 12 mm in diameter and 6 mm in height. Ultimately, the pressed cylinders pellets were sintered at 850–950 °C for 5 h.

2.2. Characterization analysis

The bulk density of all samples was measured by Archimedes method. The phase composition and crystal structure were analyzed by X-ray diffractometer (Philips X'Pert Pro MPD, The Netherlands). The scanning angle was ranged from 20° to 70°. The operating voltage and current of Cu K α radiation were 40 kV and 30 mA, respectively. Raman spectroscopy was used to analyze (InVia, Renishaw, UK) the crystal structure of MgNb_2O_6 ceramic. The microstructure was studied detailed by scanning electron microscope (SEM, JSM-6490LV; JEOL, Japan).²⁷ Moreover, the distribution of elements was collected by X-ray spectrometer (EDX, Genesis; EDAX, USA). The dielectric constant (ϵ_r) and quality factor ($Q \cdot f$)²⁸ were calculated by a network analyzer (N5230A, USA) combining the resonant cavity method and the Hakki-Coleman method in TE011 mode. The resonant frequency temperature coefficient (τ_f) was calculated as follows:²⁹

$$\tau_f = \frac{f_2 - f_1}{f_1 \times (t_2 - t_1)} \quad (1)$$

where t_1 = 25 °C and t_2 = 85 °C, corresponding resonance frequencies are f_{t_1} and f_{t_2} , respectively.

3. Results and discussion

3.1. Crystal structure and phase composition

Fig. 1 indicates the XRD patterns of the MgNb_2O_6 ceramics with different LMZBS additions sintered at 925 °C for 5 h. All the ceramics samples show an orthorhombic columbite structure MgNb_2O_6 phase (PDF file no. 88-0708). By comparing the diffraction peaks with the standard PDF card, no second phase was found within the measurement error range of the instrument, indicating that pure phase MgNb_2O_6 ceramics were formed through slightly excessive MgO in the synthesis process and LMZBS glass had no significant effect on phase composition for MgNb_2O_6 ceramics.

Fig. 2 shows the Raman spectra of MgNb_2O_6 ceramics at 925 °C. Raman spectral is often used to study the crystal structure of materials. According to the symmetry of crystal, the

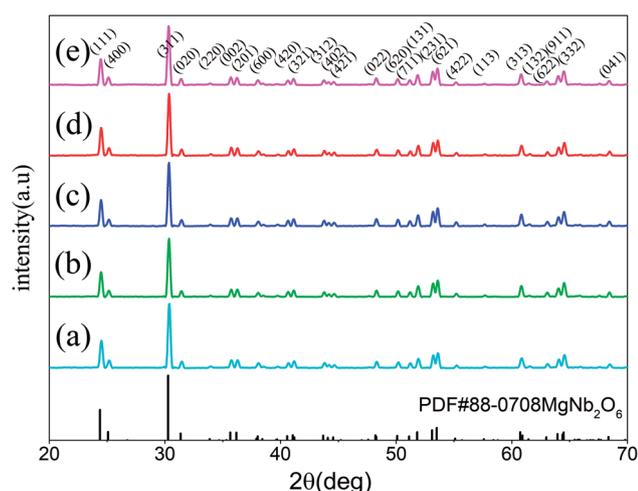


Fig. 1 XRD patterns of MgNb_2O_6 - x wt% LMZBS ceramics sintered at 925 °C for 5 h: (a) x = 0.1, (b) x = 0.5, (c) x = 1.0, (d) x = 1.5, and (e) x = 2.0.

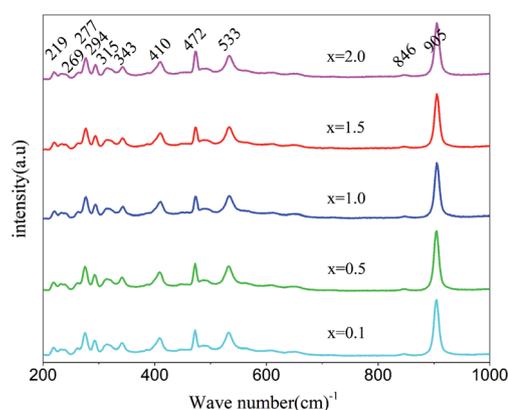


Fig. 2 Raman spectra of the MgNb_2O_6 - x wt% LMZBS (x = 0.1–2.0) ceramics sintered at 925 °C for 5 h.



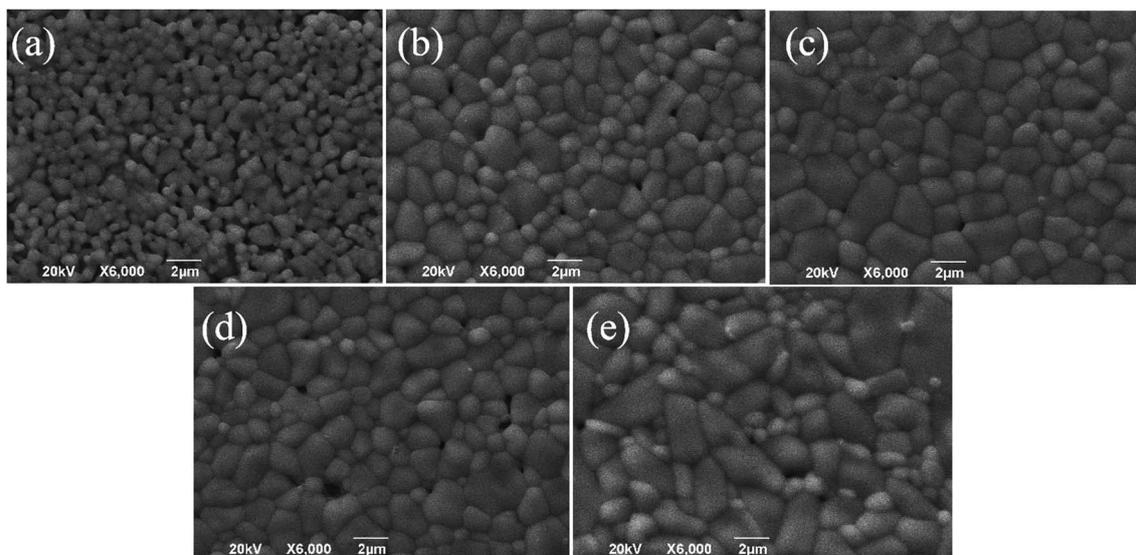


Fig. 3 Surface SEM micrographs of $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ceramics sintered at 925°C (a) $x = 0.1$, (b) $x = 0.5$, (c) $x = 1.0$, (d) $x = 1.5$, (e) $x = 2.0$.

Raman models are provided by the Bilbao Crystallographic Server for analysis:³⁰

$$\Gamma_{\text{Raman}} = 13A_g + 13A_u + 14B_{1g} + 14B_{1u} + 13B_{2g} + 13B_{2u} + 14B_{3g} + 14B_{3u} \quad (2)$$

Theoretically, MgNb_2O_6 ceramic have 108 vibration modes. However, only several Raman modes could be observed due to

the interaction or overlapping. The bands in wavelength from 200 to 250 cm^{-1} were assigned to the twisting vibration in and between chains; the bands in wavelength from 250 to 400 cm^{-1} were attributed to the twisting vibration of octahedron; the bands in wavelength from 400 to 1000 cm^{-1} were related to the stretching vibration of Nb–O bonds. Weak peak 846 cm^{-1} corresponds to the antisymmetric stretching vibration mode of Nb–Ot of NbO_6 octahedron in double chain plane (among them,

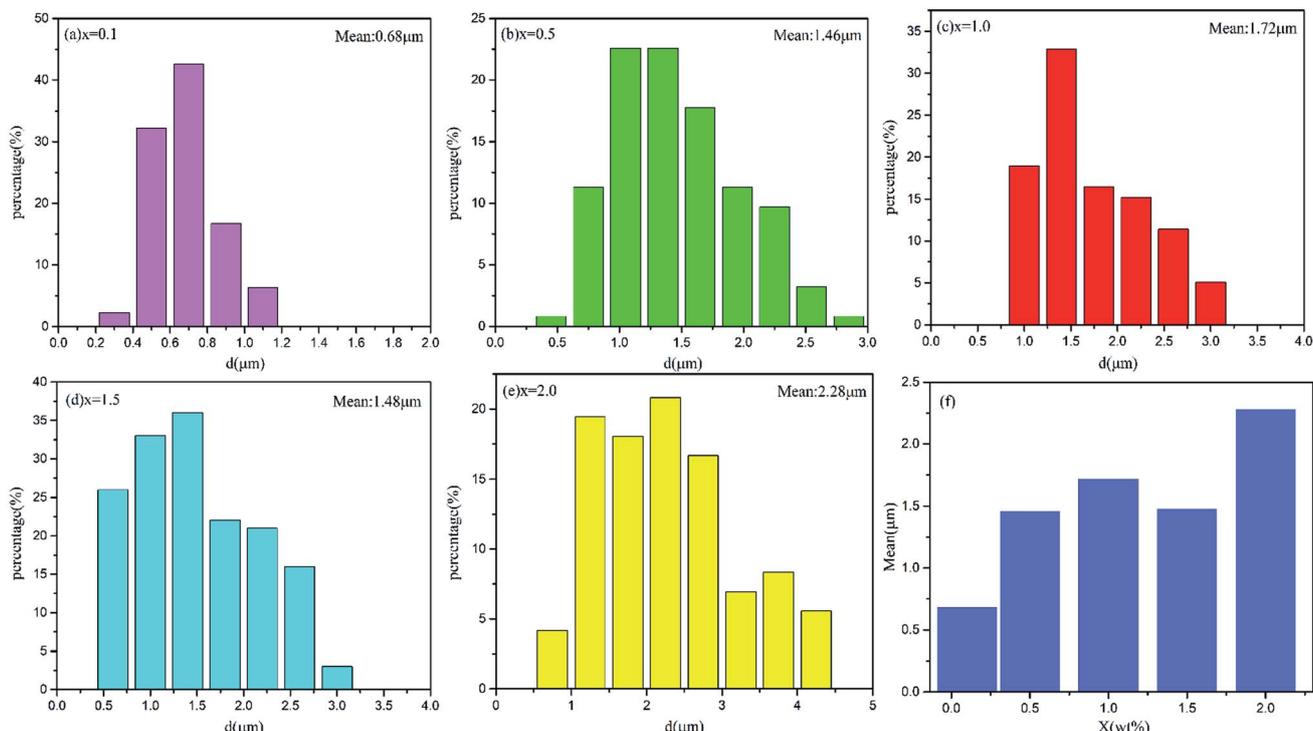


Fig. 4 The grain sizes distribution of $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ($x = 0.1, 0.5, 1.0, 1.5$ and 2.0) ceramics sintered at 925°C . (a–e) Grain sizes distribution, (f) mean grain size.



Ot represents an oxygen atom linked to a Nb atom and two Mg atoms), this is consistent with the Raman spectrum reported by Y. C. You *et al.*³¹ It can be observed from Fig. 2 that no new Raman peak appears. By comparing the position of Raman peak, it is found that the additions of LMZBS have no influence on Raman spectrum.

3.2. Microstructure analysis

Fig. 3 and 4 show the SEM diagram and distribution of grain sizes of MgNb_2O_6 ceramics sintered at 925 °C. LMZBS glass has a remarkable influence on the average grain size and density of MgNb_2O_6 ceramics. In Fig. 3a, it can be intuitively seen that the grains are loose and irregular, and the average grain size was 0.68 μm , which is related to low amount of LMZBS glass. With the amount of LMZBS glass increasing, the grains started to grow, as shown in Fig. 3b. When the doping amount reaches 1 wt%, uniform and dense microstructure with clear grain boundaries could be observed. The average grain size reached to 1.72 μm and there was barely any hole. Because an appropriate amount of LMZBS glass will melt to form a liquid phase during sintering, which will make the grains of ceramic moist and thus promote the densification of ceramics. Nevertheless, with the further increase of doping amount, the grain grew abnormally and the average size of the grain is 1.48 μm . From Fig. 3e, abnormal grains growth can be obviously observed. The average grain size increased to 2.28 μm , and the grain boundary was indistinct, which may deteriorate the microwave dielectric characteristics. These results show that the proper amount of LMZBS glass can increase relative density and decrease porosity.

3.3. Dielectric characteristics analysis

Fig. 5 shows the apparent density of MgNb_2O_6 ceramic with different doping amounts at different sintering temperatures. When the doping amount ranged from 0.1 wt% to 1.0 wt%, the density increased under same sintering temperature.³² Finally, MgNb_2O_6 ceramic with 1.0 wt% LMZBS glass at 925 °C had the

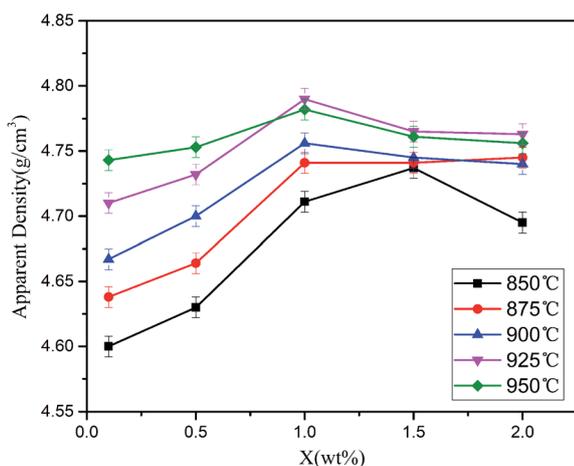


Fig. 5 Apparent densities of $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ($0.1 \leq x \leq 2.0$) ceramics sintered at different temperatures.

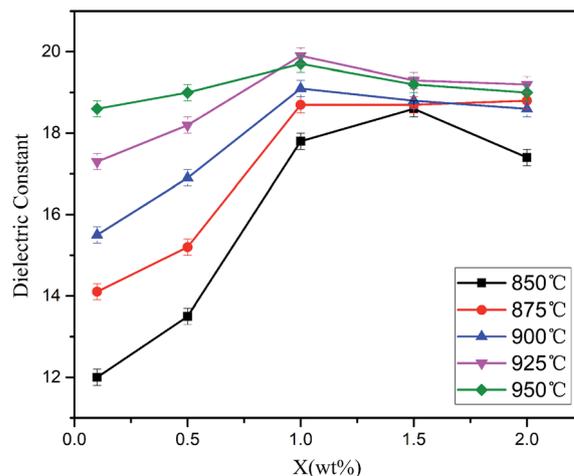


Fig. 6 The dielectric constant of $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ($0.1 \leq x \leq 2.0$) ceramics sintered at various temperatures for 5 h.

highest apparent density. This is attributed to the increase in liquid phase. However, with the further increase of the doping amount, the apparent density decreased slightly. This was because the excessive LMZBS addition led to excessive liquid phase, resulting in abnormal grain growth and porosity, which eventually led to the decrease in the density of MgNb_2O_6 ceramic.

According to Fig. 6, it can be observed that when the doping amount is in the range of 0.1 wt% to 1.0 wt%, the dielectric constant is related to the doping proportion exhibiting a similar tendency as the apparent density. As known, second phase, molecular volume, structural characteristics, density and ionic polarizability affect the dielectric constant.^{33,34} As shown in Fig. 1, there is no impurity in the ceramic system, so the influence of the second phase on the dielectric constant can be excluded. In this paper, apparent density is the primary factor impacting the dielectric constant. High density means low porosity and large dielectric constant. Therefore, dielectric constant is related to the density.

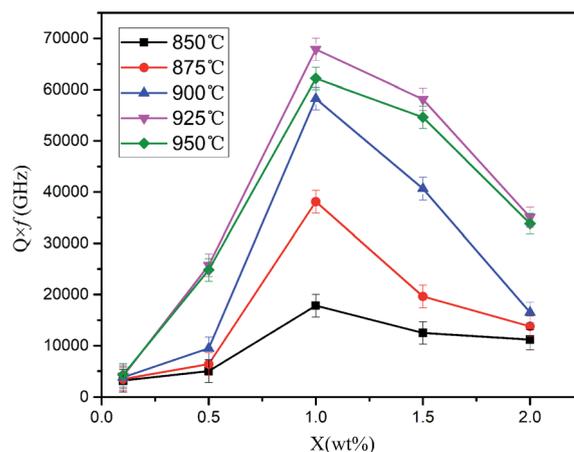


Fig. 7 The $Q \times f$ values of $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ($0.1 \leq x \leq 2.0$) ceramics sintered at various temperatures.



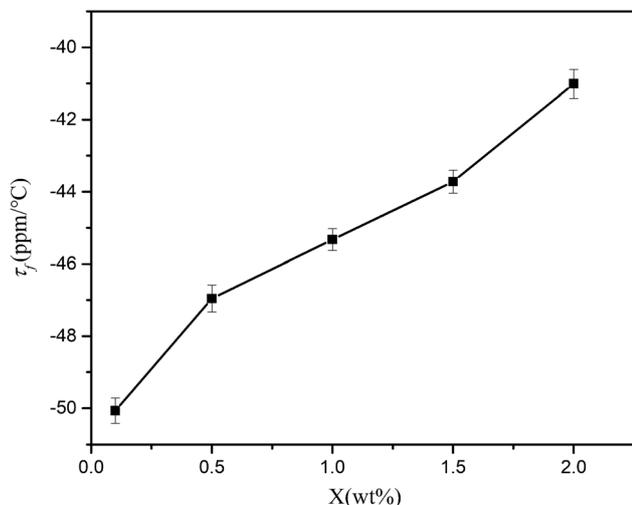


Fig. 8 τ_f values for the $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ceramics sintered at 925 °C.

Fig. 7 demonstrates the $Q \cdot f$ value of MgNb_2O_6 ceramic under different sintering temperatures and different LMZBS amounts. The $Q \cdot f$ value increased firstly until reaching the peak and decreased with the amount of LMZBS glass gradually increasing. Samples with same LMZBS amount got different $Q \cdot f$ at different temperature and we can see that ceramic got the highest $Q \cdot f$ at 925 °C. Besides, for the samples sintered at 925 °C with 1.0 wt% LMZBS glass, the optimal $Q \cdot f$ value was 67 839 GHz. The results demonstrate that 925 °C is the optimization

sintering temperature for MgNb_2O_6 ceramic in terms of densification and dielectric performance. In general, the dielectric loss is mainly composed of two modules: internal loss and external loss. Among them, the intrinsic loss is difficult to avoid, because it is the inherent nature of the material. However, external losses are affected by various factors, including second phase, porosity, grain boundaries, average grain size, and microstructure defects, *etc.*^{35,36} XRD patterns show that there is no second phase, so the influence of secondary phase on $Q \cdot f$ can be excluded. In this work, microwave dielectric loss is mainly affected by apparent density. With the increase of doping amount, the variation in $Q \cdot f$ value are roughly similar to the change of apparent density. This is because the $Q \cdot f$ value is impacted by the density.^{37,38} Therefore, the proper amount of LMZBS glass can effectively improve the $Q \cdot f$ value of MgNb_2O_6 ceramic, which can make the dielectric ceramics have higher relative density and lower porosity.

Fig. 8 exhibits the τ_f of $\text{MgNb}_2\text{O}_6-x$ wt% LMZBS ($x = 0.1, 0.5, 1.0, 1.5$ and 2.0) ceramics at optimal temperatures. It can be found that with the increase of glass addition, τ_f value ranged from $-50.7 \text{ ppm } ^\circ\text{C}^{-1}$ to $-41.01 \text{ ppm } ^\circ\text{C}^{-1}$. In general, the smaller the $|\tau_f|$, the better the thermal stability of dielectric ceramics.³⁹ In this work, the phase composition and crystal structure had no significant effect on τ_f value. Therefore, the change of τ_f value can be attributed to famous Lichtenecker empirical logarithmic rule:⁴⁰

$$\tau_f = V_1\tau_{f_1} + V_2\tau_{f_2} \quad (3)$$

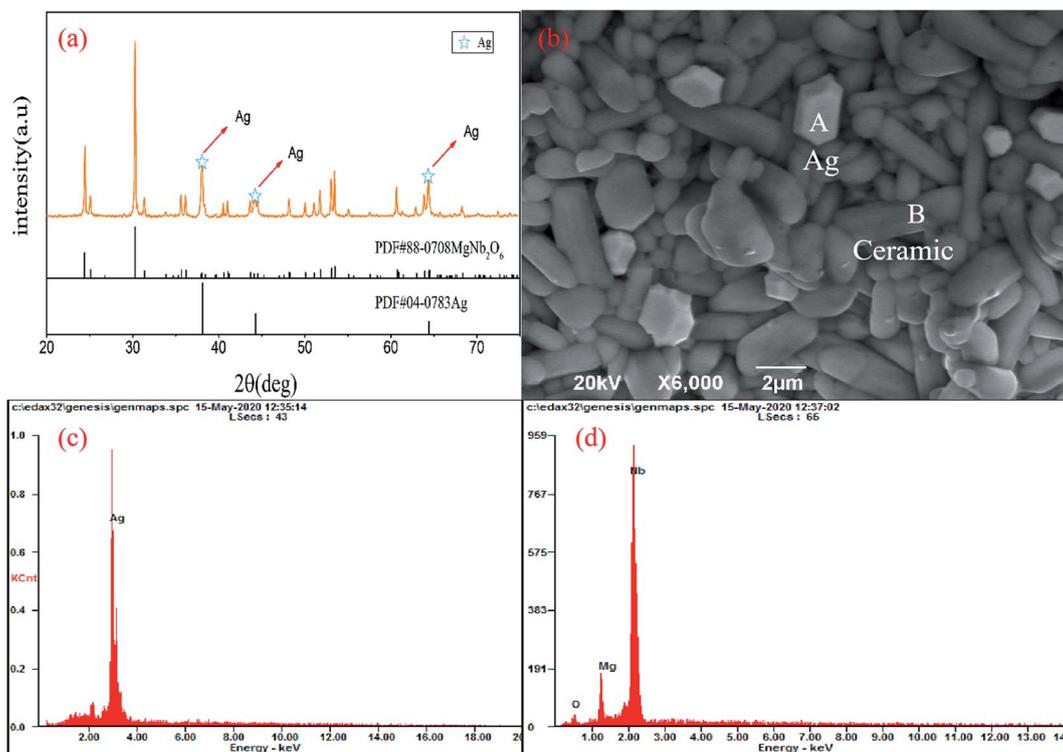


Fig. 9 XRD, SEM and EDX analysis of MgNb_2O_6 ceramics doped with 1.0 wt% LMZBS and co-fired with 20 wt% Ag at 925 °C for 5 h. (a) XRD pattern, (b) back scattered electron images, (c) EDX analysis on A spot, and (d) EDX analysis on B spot.



Table 1 Comparison of microwave dielectric properties among MgNb₂O₆ ceramics

Material	Dopant	Temperature (°C)	ϵ_r	Q·f (GHz)	τ_f (ppm)	Co-fired with Ag	References
MgNb ₂ O ₆	—	1300	19.9	79 600	−64.9	No	Pullar <i>et al.</i> ¹⁹
MgNb ₂ O ₆	B ₂ O ₃	1260	21.5	115 800	−48	No	Huang <i>et al.</i> ⁴²
MgNb ₂ O ₆	CuO–B ₂ O ₃	1050	21.5	108 000	−44	No	Tian Z. Q. <i>et al.</i> ²⁰
MgNb ₂ O ₆	Fe ₂ O ₃	1140	20.5	70 000	−49	No	Hsu <i>et al.</i> ⁴³
MgNb ₂ O ₆	LMZBS	925	19.7	67 839	−41.01	Yes	This work

where V_1 , V_2 and τ_{f_1} , τ_{f_2} are the volume fractions and τ_f values of pure MgNb₂O₆ and LMZBS, respectively ($V_1 + V_2 = 1$). On the one hand, τ_f value of pure MgNb₂O₆ ceramic is $-64.9 \text{ ppm } ^\circ\text{C}^{-1}$.¹⁹ On the other hand, low-melting glass LMZBS have negative τ_f value,⁴¹ which may explain the reason why the τ_f value changed slightly. Adding τ_f compensation materials have proved to be an effective method to adjust the τ_f to near zero. Therefore, in the next step, we may choose the CaTiO₃ (+800 ppm $^\circ\text{C}^{-1}$) and SrTiO₃ (+1600 ppm $^\circ\text{C}^{-1}$) to adjust τ_f for the MgNb₂O₆ ceramic.

It is imperative to research the chemical compatibility of the MgNb₂O₆ ceramics with silver for practical LTCC applications. Fig. 9a exhibits the XRD pattern of the 1.0 wt% LMZBS-doped MgNb₂O₆ ceramics co-fired with 20 wt% Ag powders sintered at 925 °C. No chemical reaction occurred between MgNb₂O₆ ceramics and Ag. Fig. 9b–d show the back scattered electron images and elements distribution of the fracture surface. The EDX analysis proves that there is no reaction between ceramic and silver. The whole experimental results confirm that the 1.0 wt% LMZBS-doped MgNb₂O₆ ceramic can be compatible with Ag. Besides, the comparison between this work and previous literature is listed in Table 1. It can be observed that the MgNb₂O₆ ceramics doped with LMZBS exhibited chemical compatibility with silver electrodes without deteriorating microwave dielectric properties, which makes MgNb₂O₆ ceramics as promising material for LTCC applications.

4. Conclusions

MgNb₂O₆ ceramics doped with LMZBS glass were prepared by solid phase reaction process. The effects of LMZBS amount on the phase composition, microstructure, grain growth, apparent density, chemical compatibility with Ag and microwave properties of ceramics were studied. Raman spectra and XRD demonstrate single columbite MgNb₂O₆ phase. The scanning electron microscope (SEM) results indicated that the homogeneous and dense microstructure appeared at 925 °C. The relative density and ϵ_r have similar variation tendency. With the increase of LMZBS amount, τ_f value shifted towards positive direction. Particularly, the MgNb₂O₆–1.0 wt% LMZBS ceramic obtained at 925 °C possessed optimum microwave dielectric characteristics: $\epsilon_r = 19.7$, $Q \cdot f = 67\,839 \text{ GHz}$, $\tau_f = -41.01 \text{ ppm } ^\circ\text{C}^{-1}$. Meanwhile, XRD pattern and EDX elements analysis proved that the MgNb₂O₆ ceramic showed excellent chemical compatibility with Ag, which confirmed the applicability of MgNb₂O₆ ceramic in LTCC.

Conflicts of interest

There are no conflicts to declare.

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