Microwave dielectric properties of low-temperature-fired MgNb$_2$O$_6$ ceramics for LTCC applications

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MgNb$_2$O$_6$ ceramics doped with (Li$_2$O–MgO–ZnO–B$_2$O$_3$–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$_2$O$_6$ 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$_2$O$_6$ 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$_2$O$_6$ ceramic doped with 1 wt% LMZBS glass sintered at 925 °C for 5 h, possessed excellent dielectric properties: $\varepsilon_r = 19.7$, $Q\cdot f = 67 839$ GHz, $\tau_f = -41.01$ ppm °C$^{-1}$. Moreover, the favorable chemical compatibility of the MgNb$_2$O$_6$ ceramic with silver electrodes makes it as promising material for low temperature co-fired ceramic (LTCC) applications.

1. Introduction

The forward evolution of electronics, power systems, satellite broadcasting and wireless communication, 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.$^{6,7}$ 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.$^6$ Hence, the aim of the present work is to decrease the sintering temperature of MgNb$_2$O$_6$ 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 Bi$_2$Mo$_2$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 PbO–Bi$_2$O$_3$–B$_2$O$_3$–ZnO–TiO$_2$, B$_2$O$_3$–CuO, Li$_2$O–B$_2$O$_3$–SiO$_2$–CaO–Al$_2$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$_2$O$_6$ ceramic is not easy to obtain, as reported by Liou et al.$^{18}$ Pullar et al.$^{19}$ reported that MgNb$_2$O$_6$ ceramic sintered at 1300 °C for 2 h exhibited remarkable microwave properties: $\varepsilon_r = 19.9$, $Q\cdot f = 79 600$ GHz, $\tau_f = -64.9$ ppm °C$^{-1}$. Tian et al.$^{20}$ reported that MgNb$_2$O$_6$ ceramic were not only successfully sintered at 1050 °C, but also achieved remarkable microwave properties: $\varepsilon_r = 21.5$, $Q\cdot f = 108 000$ GHz, $\tau_f = -44$ ppm °C$^{-1}$ by adding CuO–B$_2$O$_3$ as sintering aid. However, the sintering temperature is still too high.

As known, the synthesis of pure-phase MgNb$_2$O$_6$ ceramic is not easy.$^{21}$ In this work, pure-phase MgNb$_2$O$_6$ 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.$^{22}$ reported that the addition of LMZBS glass decreased the sintering temperature of Li$_2$MgSi$_2$O$_6$ ceramics from 1250 to 875 °C. Besides, the LMZBS glass melts to form a liquid phase and wet the grains of MgNb$_2$O$_6$, thereby promoting the densification of MgNb$_2$O$_6$.$^{23}$ In addition, magnesium oxide in LMZBS glass can compensate for the volatilization of MgO in MgNb$_2$O$_6$, so LMZBS glass plays
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 MgNb₂O₆ ceramics. To our best knowledge, there’s been no relevant report about the co-fired experiment of MgNb₂O₆ ceramics with silver electrodes. In this work, the chemical compatibility of MgNb₂O₆ 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 MgNb₂O₆ ceramics were also studied.

2. Experimental procedures

2.1. Materials preparation

MgNb₂O₆ ceramics were synthesized by solid-state process using high-purity MgO and Nb₂O₅ (all purity > 99.9%) as original materials were. The stoichiometric ratio of MgO and Nb₂O₅ was 1.01 : 1. (The slightly excessive MgO is beneficial to inhibit the production of the secondary phases Mg₄Nb₉O₂ and Nb₂O₅.) 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 MgNb₂O₆ ceramic, and a reasonable extension of the milling time will increase the uniformity of particles and decrease particle size.) Li₂O·MgO·ZnO·B₂O₅·SiO₂ (LMZBS) glass was synthesized by quenching method according to the mol percentage of: Li₂O : MgO : ZnO : B₂O₅ : SiO₂ = 20 : 20 : 20 : 20 : 20 (all purity > 99%). The LMZBS glass 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 MgNb₂O₆ 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 Kα radiation were 40 kV and 30 mA, respectively. Raman spectroscopy was used to analyze (InVia, Renishaw, UK) the crystal structure of MgNb₂O₆ ceramic. The microstructure was studied detailed by scanning electron microscope (SEM, JSM-6490LV; JEOL, Japan). Moreover, the distribution of elements was collected by X-ray spectrometer (EDX, Genesis; EDAX, USA). The dielectric constant (ɛr) and quality factor (Q-f) were calculated by a network analyzer (NS230A, USA) combining the resonant cavity method and the Hakki–Coleman method in TE011 mode. The resonant frequency temperature coefficient (τf) was calculated as follows:

\[ \tau_f = \frac{f_1 - f_2}{f_1 \times (t_2 - t_1)} \]

where \( t_1 = 25 \) °C and \( t_2 = 85 \) °C, corresponding resonance frequencies are \( f_1 \) and \( f_2 \), respectively.

3. Results and discussion

3.1. Crystal structure and phase composition

Fig. 1 indicates the XRD patterns of the MgNb₂O₆ ceramics with different LMZBS additions sintered at 925 °C for 5 h. All the ceramics samples show an orthorhombic columbite structure MgNb₂O₆ 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 MgNb₂O₆ ceramics were formed through slightly excessive MgO in the synthesis process and LMZBS glass had no significant effect on phase composition for MgNb₂O₆ ceramics.

Fig. 2 shows the Raman spectra of MgNb₂O₆ ceramics at 925 °C. Raman spectral is often used to study the crystal structure of materials. According to the symmetry of crystal, the
Raman models are provided by the Bilbao Crystallographic Server for analysis: 

\[ \Gamma_{\text{Raman}} = 13A_g + 13A_u + 14B_{1g} + 14B_{1u} + 13B_{2g} + 13B_{2u} + 14B_{3g} + 14B_{3u} \]

(2)

Theoretically, MgNb₂O₆ 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 NbO₆ octahedron in double chain plane (among them,

Fig. 3 Surface SEM micrographs of MgNb₂O₆–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.

Fig. 4 The grain sizes distribution of MgNb₂O₆–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.\textsuperscript{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 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.\textsuperscript{32} Finally, MgNb_2O_6 ceramic with 1.0 wt% LMZBS glass at 925 °C had the 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.\textsuperscript{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 demonstrates the $Q_f$ value of MgNb$_2$O$_6$ ceramic under different sintering temperatures and different LMZBS amounts. The $Q_f$ value increased firstly until reaching the peak and decreased with the amount of LMZBS glass gradually increasing. Samples with same LMZBS amount got different $Q_f$ at different temperature and we can see that ceramic got the highest $Q_f$ at 925 °C. Besides, for the samples sintered at 925 °C with 1.0 wt% LMZBS glass, the optimal $Q_f$ value was 67 839 GHz. The results demonstrate that 925 °C is the optimization sintering temperature for MgNb$_2$O$_6$ 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. XRD patterns show that there is no second phase, so the influence of secondary phase on $Q_f$ can be excluded. In this work, microwave dielectric loss is mainly affected by apparent density. With the increase of doping amount, the variation in $Q_f$ value are roughly similar to the change of apparent density. This is because the $Q_f$ value is impacted by the density. Therefore, the proper amount of LMZBS glass can effectively improve the $Q_f$ value of MgNb$_2$O$_6$ ceramic, which can make the dielectric ceramics have higher relative density and lower porosity.

Fig. 8 exhibits the $\tau_f$ of MgNb$_2$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, $\tau_f$ value ranged from $-50.7$ ppm °C$^{-1}$ to $-41.01$ ppm °C$^{-1}$. In general, the smaller the $|\tau_f|$, the better the thermal stability of dielectric ceramics. In this work, the phase composition and crystal structure had no significant effect on $\tau_f$ value. Therefore, the change of $\tau_f$ value can be attributed to famous Lichtenecker empirical logarithmic rule:

$$\tau_f = V_1\tau_{f1} + V_1\tau_{f2}$$

Fig. 9 XRD, SEM and EDX analysis of MgNb$_2$O$_6$ 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) | \(\varepsilon_r\) | Q.f (GHz) | \(\tau_r\) (ppm) | Co-fired with Ag | References          |
|--------------|------------|------------------|-------------------|-----------|------------------|------------------|---------------------|
| MgNb2O6      | —          | 1300             | 19.9              | 79 600    | −64.9            | No               | Pullar et al.\textsuperscript{19} |
| MgNb2O6      | B2O3       | 1260             | 21.5              | 115 800   | −48              | No               | Huang et al.\textsuperscript{42}  |
| MgNb2O6      | CuO-B2O3   | 1050             | 21.5              | 108 000   | −44              | No               | Tian Z. Q. et al.\textsuperscript{20} |
| MgNb2O6      | Fe2O3      | 1140             | 20.5              | 70 000    | −49              | No               | Hsu et al.\textsuperscript{43}     |
| MgNb2O6      | LMZBS      | 925              | 19.7              | 67 839    | −41.01           | Yes              | This work            |

where \(V_1\), \(V_2\) and \(\varepsilon_r\), \(\tau_r\) are the volume fractions and \(\tau_r\) values of pure MgNb2O6 and LMZBS, respectively \((V_1 + V_2 = 1)\). On the one hand, \(\tau_r\) value of pure MgNb2O6 ceramic is \(-64.9\) ppm °C\(^{-1}\).\textsuperscript{19} On the other hand, low-melting glass LMZBS have negative \(\tau_r\) value,\textsuperscript{44} which may explain the reason why the \(\tau_r\) value changed slightly. Adding \(\tau_r\) compensation materials have proved to be an effective method to adjust the \(\tau_r\) to near zero. Therefore, in the next step, we may choose the CaTiO\(_3\) (+800 ppm °C\(^{-1}\)) and SrfTiO\(_3\) (+1600 ppm °C\(^{-1}\)) to adjust \(\tau_r\) 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 \(\varepsilon_r\) have similar variation tendency. With the increase of LMZBS amount, \(\tau_r\) value shifted towards positive direction. Particularly, the MgNb2O6-1.0 wt% LMZBS ceramic obtained at 925 °C possessed optimum microwave dielectric characteristics: \(\varepsilon_r = 19.7\), Q.f = 67 839 GHz, \(\tau_r = −41.01\) ppm °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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