sintering behavior and microwave dielectric properties of MgO-2B2O3-xwt%H3BO3-ywt%BCB ceramics

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Abstract

The bulk density, sintering behavior and microwave dielectric properties of MgO-2B2O3 series ceramics synthesized by solid-state reaction method were systematically studied in this paper. X-ray diffraction and microstructural analysis revealed that the as-prepared MgO-2B2O3 ceramics possessed a single-phase structure with rod-like morphology. Through the investigation of the effects of different dosages of H3BO3 and BCB on bulk density, sintering behavior and microwave dielectric properties of MgO-2B2O3 ceramics, the optimum sintering temperature was obtained at an addition of 30wt%H3BO3 and 8wt%BCB and the sintering temperature was reduced to 825 °C. The addition of 40wt %H3BO3 and 4 wt%BCB increased the quality factor $Q\times f$, permittivity $\varepsilon_r$ and temperature coefficient of resonance frequency $\tau_f$ of MgO-2B2O3 to 44,306 GHz, 5.1 and -32 ppm/°C, respectively, meeting the

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criteria of low-temperature co-fired ceramics.

**Keywords:** ceramics; MgO-2B$_2$O$_3$; H$_3$BO$_3$; BCB; Dielectric property

1 **Introduction**

Due to the low manufacturing cost, short development cycle, and potential for miniaturization and incorporation of electronic devices, low-temperature co-fired ceramics (LTCC) is the trend for electronic components manufacture in the wireless communication and broadcasting industry [1-4]. However, most of the high $Q\times f$ dielectric materials are manufactured at high sintering temperatures. High sintering temperatures not only hinder their incorporation with low melting electrode and polymer based substrates but also lead to huge energy consumption and volatile components evaporation. For practical application, LTCC requires not only excellent microwave dielectric properties but also low sintering temperature and good co-fire matching between ceramics and electrodes [5-10]. Materials with low melting point are often added in order to lower the firing temperatures. However, the microwave dielectric properties were lowered by the addition of low melting point materials.

In the past decades, synthesis of $x$MgO-$y$B$_2$O$_3$ ceramic has attracted considerable interest because of its many potential applications in LTCC devices. Davis *et al.* [11] systematically reported the chemistry of MgO-B$_2$O$_3$ binary systems, such as MgO-B$_2$O$_3$, MgO-1/2B$_2$O$_3$ and MgO-1/3B$_2$O$_3$. Nishizuka *et al.* [12] demonstrated that the MgO-$x$B$_2$O$_3$ ($x = 25$ and 33) sintered at low temperatures exhibited remarkable dielectric properties with a $\varepsilon_r$ of ~7 and $Q\times f$ of 79,100-260,100 GHz (@ $x = 33$) and 39,600-310,000 GHz (@ $x = 25$). Zhou *et al.* [13] reported optimal microwave
Dielectric properties could be obtained at sintering temperature as low as 1,100°C with a molecular ratio of MgO:B₂O₃ = 1:1. The resulted ceramics showed excellent microwave dielectric properties with a $\varepsilon_r$ of 5.83, $Q\times f$ of 41,930 GHz and $\tau_f$ of ~62 ppm/°C. According to Zhou’s work, MgO-2B₂O₃-4wt%BaCu(B₂O₅) ceramics possess good microwave dielectric properties, showing promising potential applications in LTCCs [14].

However, the microwave dielectric properties of B₂O₃-rich ceramics in MgO-B₂O₃ binary system (e.g., MgO-2B₂O₃ and MgO-B₂O₃) have not been investigated in detail. In addition, the sintering temperature of MgO-2B₂O₃ ceramics is still too high for LTCC devices [15]. Sintering additives [16-26], ultrafine powders [27-31], and low sintering temperatures materials [32-34] can be used to reduce the sintering temperature of ceramics. However, the preparation of ultrafine powder with low intrinsic sintering temperatures is expensive, complex and hard to be scaled up. By contrast, the sintering temperature of magnesium oxide was effectively reduced by adding appropriate amount of sintering aid [34] such as B₂O₃, H₃BO₃ and BaCu(B₂O₅) (BCB). However, the microwave dielectric properties of MgO-2B₂O₃-xwt%H₃BO₃-ywt%BCB ceramics have not been investigated systematically. This is the objective of this research.

2 Experimental procedure

MgO-2B₂O₃-xwt%H₃BO₃-ywt%BCB ceramics were prepared by solid-state reaction method. MgO (≥98.5%), H₃BO₃ (≥ 99%), Ba(HO)₂·8H₂O (≥99%) and CuO (≥99%) were obtained from Guo-Yao Co., Ltd, Shanghai, China. MgO powders were
pre-calcined at 800 °C for 2 h. The raw materials were weighed according to the molar ratio of MgO:B₂O₃=1:2. The powders were mixed thoroughly in a nylon jar before ball milled for 4 hours. Then, the dried powder mixture was calcined at 800 °C for 4 h. H₃BO₃ and BCB with different mass ratio were added to the calcined powder. The mixture of H₃BO₃, BCB and calcined powder was re-milled for 4 h and pressed into the form of cylinder with a diameter of 10 mm and height of 4-5 mm under a uniaxial pressure of 100 MPa. Subsequently, the samples were sintered for 4 hours at 750-975 °C under air.

Archimedes’ principle was employed to measure the bulk density. X-ray diffractometer (XPERT PRO, PANalytical, Almelo, Netherlands) equipped with Cu Kα radiations was used for structural analysis. Scanning electron microscopy (JSM-6380LV, JEOL, Tokyo, Japan) was used to observe the microstructure of as-fired surfaces. A 300 KHz to 20 GHz Network Analyzer (E5071C, Agilent Co., CA, USA) was used to measure the microwave dielectric properties. The τ₊ values were calculated in the temperature range of 25 °C to 85 °C, as given below:

\[ \tau_+ = \frac{f_T - f_{T_0}}{f_{T_0}(T - T_0)} \times 10^6 \]

Where, \( f_T \) and \( f_{T_0} \) represent the resonant frequencies at 85°C (T) and 25 °C (T₀), respectively.

3 Results and discussion

Figure 1 shows the XRD profiles of MgO-2B₂O₃-10wt%H₃BO₃-ywt%BCB (y = 2, 4, 6 and 8) ceramics sintered at their optimal temperatures. The XRD patterns was
indexed as MgB$_4$O$_7$ (JCPDS card number 00-031-0787), indicating that the addition of H$_3$BO$_3$ and BCB had no effect on the phase structure of ceramics.

SEM images of the MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB (y = 2, 4, 6, and 8) ceramics sintered at optimal temperatures are shown in Figure 2(a-d). It can be seen that the MgO-2B$_2$O$_3$ crystals possessed a rod-like shape and refined with the increase of BCB content. As the BCB content increased to 8 wt %, the MgO-2B$_2$O$_3$ crystals exhibited a glassy phase. Moreover, the porosity increased with the increase of BCB content.

Bulk density, $\varepsilon$, $Q\times f$, and $\tau f$ of the MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB (y = 2, 4, 6 and 8) ceramics sintered at different temperatures are shown in Figure 3. It can be seen that the bulk density initially increased with the increase of sintering temperature except for the sample with 2 wt% BCB which showed a slight decrease as shown in Figure 3 (d). The bulk density change is consistent with the appearance of porosity shown in Figure 2(a)-(d).

When sintering temperature increased from 900 °C to 950 °C, the $Q\times f$ of the MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-2wt%BCB ceramics increased from 25,408 GHz to 33,951 GHz, indicating the change of porosity with the sintering temperature change. The minimum porosity was obtained at 900 °C. However, with further increase of sintering temperature, the $Q\times f$ of MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-2wt%BCB ceramics decreased to 32,541 GHz due to over-firing. The $Q\times f$ of MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB (y = 2, 4, 6 and 8) ceramics first increased and then decreased with the increase of sintering temperatures. The optimum sintering
temperature decreased from 950 °C to 850 °C when BCB content increased from 2 wt% to 8 wt%. The $Q\times f$ reached a maximum of 40,076 GHz when BCB content was 4 wt%, indicating the addition of appropriate amount of BCB reduced the sintering temperature and improved the $Q\times f$ of MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$ ceramics.

Figure 3(b) shows the $\varepsilon_r$ change of MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB ($y = 2, 4, 6$ and 8) ceramics at different temperatures. With the increase of sintering temperature, $\varepsilon_r$ increased for ceramics with 6 wt % and 8 wt % BCB but decreased for ceramics with 2 wt % and 4 wt % BCB, indicating the addition of BCB had a significant effect on the $\varepsilon_r$ of MgO-2B$_2$O$_3$ ceramics.

Figure 3(c) presents the $\tau_f$ at different sintering temperatures, which exhibits a similar trend to $Q\times f$. The $\tau_f$ of MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-2wt%BCB ceramic was -40 ppm/°C when the sintering temperature was 925 °C. Then, the $\tau_f$ value initially increased with the increase of sintering temperature followed by a slight decrease. The $\tau_f$ is affected by the chemical additives and the composition of the ceramic [34, 35]. One should note that the $\tau_f$ of MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB ceramics demonstrated an overall decreasing trend with the increase of BCB content. Meanwhile, sintering temperature decreased with the increase of BCB content, demonstrating its positive effect as a sintering aid. The best ceramics properties with bulk density of 2.409 g/cm$^3$, $Q\times f$ of 40,076 GHz, and $\varepsilon_r$ of -40 ppm/°C were obtained at 4 wt % BCB content and 925 °C.

Figure 4 presents the room-temperature XRD profiles of the MgO-2B$_2$O$_3$-xwt%H$_3$BO$_3$-4wt%BCB ($10 \leq x \leq 40$) ceramics sintered at their optimum
temperatures. XRD results showed that the MgO-2B$_2$O$_3$-xwt\%H$_3$BO$_3$-4wt\%BCB (10≤x≤40) ceramics were crystallized in orthorhombic space group Pbca without impurity phases, indicating the addition of H$_3$BO$_3$ had no negative affect on the phase structure of ceramics.

Figure 5 shows the SEM images of MgO-2B$_2$O$_3$-xwt\%H$_3$BO$_3$-4wt\%BCB (10 ≤ x ≤ 40) ceramics sintered at their optimum temperatures. Distinctly different microstructure was observed for the ceramics with different H$_3$BO$_3$ content. With the increase of H$_3$BO$_3$ content, the MgO-2B$_2$O$_3$-xwt\%H$_3$BO$_3$-4wt\%BCB ceramics achieved denser and more homogeneous microstructure. However, at a H$_3$BO$_3$ content of 40 wt\%, a slight over-burning was observed due to the presence of excessive sintering aid, resulting in abnormal grain growth as shown in Figure 5(d).

Figure 6 shows the bulk density, $\varepsilon_r$, $Q\times f$ and $\tau_f$ of the MgO-2B$_2$O$_3$-xwt\%H$_3$BO$_3$-4wt\%BCB ceramics at different sintering temperatures. The bulk density of ceramics increased initially and then decreased slightly with the increase of H$_3$BO$_3$ content except for the ceramics with 10% H$_3$BO$_3$. The maximum bulk density of MgO-2B$_2$O$_3$-xwt\%H$_3$BO$_3$-4wt\%BCB with 10% H$_3$BO$_3$ was obtained at sintering temperature of 925 °C. However, when H$_3$BO$_3$ increased to 20%~40%, the maximum bulk density was obtained at 900 °C, indicating the addition of H$_3$BO$_3$ as a sintering aid reduced the sintering temperature of ceramics.

In general, the $Q\times f$ of microwave dielectric ceramics is related to the grain size, porosity, densification and secondary phases [36-38]. The $Q\times f$ of MgO-2B$_2$O$_3$-xwt\%H$_3$BO$_3$-4wt\%BCB ceramics increased with the increase of
sintering temperature up to 900 °C and then decreased, showing excellent consistency with the variation of the bulk density. Due to the fact that there was no any secondary phase in MgO-2B2O3-xwt%H3BO3-4wt%BCB ceramics, the \( Q \times f \) was mainly affected by sintering temperature and H3BO3 content, which altered the density and grain size. At a sintering temperature of 850 °C, MgO-2B2O3-10wt%H3BO3-4wt%BCB ceramics showed a significant proportion of pores between grains, resulting in a lower \( Q \times f \). When sintering temperature was 900 °C, denser microstructure of MgO-2B2O3-40wt%H3BO3-4wt%BCB resulted in a maximum \( Q \times f \) of 44,306 GHz, a relative \( \varepsilon_r \) of 5.1 and \( \tau_f \) of -32 ppm/°C.

The dielectric properties depend on relative density, crystal structure, and other phase content [39, 40]. The relative \( \varepsilon_r \) of MgO-2B2O3-xwt%H3BO3-4wt%BCB ceramics was consistent with the change in bulk density. The maximum \( \varepsilon_r \) was found to be 4.81 at a H3BO3 content of 10 wt%. Also, an overall increase in relative \( \varepsilon_r \) was observed for H3BO3-containing ceramics when H3BO3 content increased to 20 wt%, 30 wt% and 40 wt%. Hence, the \( \varepsilon_r \) was influenced by the variation of H3BO3 content, sintering temperature and bulk density.

It is worth emphasizing that the variations of \( \rho \), \( \varepsilon_r \), \( Q \times f \) and \( \tau_f \) values for MgO-2B2O3-xwt%H3BO3-4wt%BCB (x = 10, 20, 30 and 40) are consistent with the change of H3BO3 content. The optimum sintering temperature of MgO-2B2O3-xwt%H3BO3-4wt%BCB ceramics decreased from 925 °C to 900 °C, the \( Q \times f \) increased from 40,076 GHz to 44,306 GHz, the relative \( \varepsilon_r \) increased from 4.81 to 5.11, the \( \tau_f \) increased from -40 ppm/°C to -32 ppm/°C, and the bulk density increased
from 2.460 g/cm$^3$ to 2.463 g/cm$^3$. The increase of H$_3$BO$_3$ content not only lowered the sintering temperature but also improved the microwave dielectric properties of MgO-2B$_2$O$_3$-xwt%H$_3$BO$_3$-4wt%BCB ceramics.

Table 1 tabulates the sintering temperatures and microwave dielectric properties of MgO-2B$_2$O$_3$-xwt%H$_2$BO$_3$-ywt%BCB ceramics at different BCB and H$_3$BO$_3$ content. When the BCB content was fixed, the decrease in sintering temperature was less noticeable with the increase of H$_3$BO$_3$ content. The $\tau_f$ remained stable at around -32 to -62 ppm/$^\circ$C. When H$_3$BO$_3$ content was constant, the increase of BCB content gradually decreased the sintering temperature. The quality factor increased initially and then decreased at higher BCB content. In summary, the addition of BCB and H$_3$BO$_3$ reduced the sintering temperature and increased the quality factor of MgO-2B$_2$O$_3$-xwt%H$_3$BO$_3$-ywt%BCB ceramics, which was ascribed to the growth of MgO-2B$_2$O$_3$ grains. The optimum sintering temperature of the produced ceramics reduced to 825 $^\circ$C, indicating that it can be used as an alternative material for LTCC devices.

4 Conclusions

In summary, MgO-2B$_2$O$_3$-xwt%H$_2$BO$_3$-ywt%BCB ($x = 10, 20, 30, \text{and} 40; y = 2, 4, 6, \text{and} 8$) ceramics were prepared by solid-state method and the influence of H$_3$BO$_3$ and BCB contents on the bulk density, sintering behavior and microwave dielectric properties were systematically investigated. MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB ($y = 2, 4, 6, \text{and} 8$) ceramics consisted of a single-phase MgO-2B$_2$O$_3$ with orthorhombic space group Pbca. The quality factor $Q\times f$ of
MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-ywt%BCB ($y = 2$, 4, 6 and 8) ceramics increased initially and then decreased slightly with the increase of BCB content. The optimal properties of resulted MgO-2B$_2$O$_3$-10wt%H$_3$BO$_3$-4wt%BCB ceramic was $\rho= 2.409$ g/cm$^3$, $Q\times f = 40,076$ GHz, $\varepsilon_r = 5$ and $\tau_f = -45$ ppm/$^\circ$C. In addition, the microwave dielectric properties and sintering temperature of MgO-2B$_2$O$_3$-xwt%H$_3$BO$_3$-4wt%BCB ceramics ($x = 10$, 20, 30, and 40) were improved with the increase of H$_3$BO$_3$ content at 4 wt% BCB. The resulted MgO-2B$_2$O$_3$-40wt%H$_3$BO$_3$-4wt%BCB showed excellent microwave dielectric properties of 5.1, quality factor of 44,306 GHz and $\tau_f$ of -32 ppm/$^\circ$C. The current work presented a novel approach to modify the $\tau_f$ of MgO-B$_2$O$_3$ ceramics, which is highly desirable for microwave equipment and devices.

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References

[1] Sebastian MT, Jantunen H. Low loss dielectric materials for LTCC applications: a review. *Int Mater Rev* 2008, **53**: 57-90.

[2] Zhou HF, Liu XB, Chen XL, et al. ZnLi$_2$/Ti$_4$/O$_6$: A new low loss spinel microwave dielectric ceramic. *J Eur Ceram Soc* 2012, **32**: 261-265.

[3] Zhou D, Guo D, Li WB, et al. Novel temperature stable high-epsilon(r) microwave dielectrics in the Bi$_2$/O$_3$-TiO$_2$-V$_2$/O$_5$ system. *J Mater Chem C* 2016, **4**: 5357-5362.

[4] Zhou D, Pang LX, Wang DW, et al. Novel water-assisting low firing MoO$_3$ microwave dielectric ceramics. *J Eur Ceram Soc* 2019, **39**: 2374-2378.

[5] Dou G, Zhou DX, Guo M, et al. Low-temperature sintered Zn$_2$/SiO$_4$-CaTiO$_3$ ceramics with near-zero temperature coefficient of resonant frequency. *J Alloys Compd* 2012, **513**: 466-473.

[6] Wang KG, Zhou HF, Liu XB, et al. A lithium aluminium borate composite microwave dielectric ceramic with low permittivity, near-zero shrinkage, and low sintering temperature. *J Eur Ceram Soc* 2019, **39**: 1122-1126.

[7] Hughes H, Iddles DM, Reaney IM. Niobate-based microwave dielectrics suitable for third generation mobile phone base stations. *Appl Phys Lett* 2001, **79**: 2952-2954.

[8] Li YX, Li H, Tang B, et al. Microwave dielectric properties of low-fired Li$_2$/ZnTi$_3$/O$_8$-TiO$_2$ composite ceramics with Li$_2$/WO$_4$ addition. *J Mater Sci - Mater Electron* 2015, **26**: 1181-1185.

[9] Hao SZ, Zhou D, Hussain F, et al. Structure, spectral analysis and microwave dielectric properties of novel $x$(NaBi)$_{0.5}$/MoO$_4$-(1-$x$)Bi$_2$/MoO$_4$ ($x=0.2$ similar to 0.8) ceramics with low sintering temperatures. *J Eur Ceram Soc* 2020, **40**: 3569-3576.

[10] Bi JX, Xing CF, Yang CH, et al. Phase composition, microstructure and microwave dielectric properties of rock salt structured Li$_2$/ZrO$_3$-MgO ceramics. *J Eur Ceram Soc* 2018, **38**: 3840-3846.

[11] Davis H M KMA. The system magnesium oxide-moric oxide. *J Am Ceram Soc* 1945, **28**: 97-102.

[12] Nishizuka M, Ogawa H, Kan A, et al. Synthesis and microwave dielectric properties of MgO-$x$/mol%B$_2$/O$_3$ ($x=33$ and 25) ceramics in MgO-B$_2$/O$_3$ system. *Ferroelectrics* 2009, **388**: 101-108.

[13] Fan GC, Zhou HF, Chen XL. Optimized sintering temperature and enhanced microwave dielectric performance of Mg$_2$/B$_2$/O$_5$ ceramic. *J Mater Sci - Mater Electron* 2017, **28**: 818-822.

[14] Zhou HF, Tan XH, Liu XB, et al. Low permittivity MgO-$x$/B$_2$/O$_3$-yBaCu(B$_2$/O$_3$) microwave dielectric ceramics for low temperature co-fired ceramics technology. *J Mater Sci - Mater Electron* 2018, **29**: 18486-18492.

[15] Zhou HF, Tan XH, Wang KG, et al. Microstructure and sintering behavior of low temperature cofired Li$_4$/8Mg$_{4}$/5Ti$_7$/O$_4$ ceramics containing BaCu(B$_2$/O$_3$) and TiO$_2$ and their compatibility with a silver electrode. *RSC Adv* 2017, **7**: 44706-44711.
[16] Guo H-H, Zhou D, Du C, et al. Temperature stable Li$_2$Ti$_{0.75}$(Mg$_{1/3}$Nb$_{2/3}$)$_{0.25}$O$_3$-based microwave dielectric ceramics with low sintering temperature and ultra-low dielectric loss for dielectric resonator antenna applications. J Mater Chem C 2020, 8: 4690-4700.

[17] Iddles DM, Bell AJ, Moulson AJ. Relationships between dopants, microstructure and the microwave dielectric properties of ZrO$_2$-TiO$_2$-SnO$_2$ ceramics. J Mater Sci 1992, 27: 6303-6310.

[18] Wu JM, Huang HL. Microwave properties of zinc, barium and lead borosilicate glasses. J Non-Cryst Solids 1999, 260: 116-124.

[19] Tzou WC, Yang CF, Chen YC, et al. Improvements in the sintering and microwave properties of BiNbO$_4$ microwave ceramics by V$_2$O$_5$ addition. J Eur Ceram Soc 2000, 20: 991-996.

[20] Li EZ, Chen YW, Xiong J, et al. Low-temperature firing and microwave dielectric properties of Ba-Nd-Ti with composite doping Li-B-Si and Ba-Zn-B glasses. J Mater Sci - Mater Electron 2016, 27: 8428-8432.

[21] Kim MH, Lim JB, Kim JC, et al. Synthesis of BaCu(B$_2$O$_5$) ceramics and their effect on the sintering temperature and microwave dielectric properties of Ba(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics. J Am Ceram Soc 2006, 89: 3124-3128.

[22] Huang CL, Weng MH, Lion CT, et al. Low temperature sintering and microwave dielectric properties of Ba$_2$Ti$_9$O$_{20}$ ceramics using glass additions. Mater Res Bull 2000, 35: 2445-2456.

[23] Zhou HF, Wang H, Zhou D, et al. Effect of ZnO and B$_2$O$_3$ on the sintering temperature and microwave dielectric properties of LiNb$_{0.6}$Ti$_{0.3}$O$_3$ ceramics. Mater Chem Phys 2008, 109: 510-514.

[24] Li EZ, Niu N, Wang J, et al. Effect of Li-B-Si glass on the low temperature sintering behaviors and microwave dielectric properties of the Li-modified ss-phase Li$_2$O-Nb$_2$O$_5$-TiO$_2$ ceramics. J Mater Sci - Mater Electron 2015, 26: 3330-3335.

[25] Zhou D, Pang LX, Wang DW, et al. High permittivity and low loss microwave dielectrics suitable for 5G resonators and low temperature co-fired ceramic architecture. J Mater Chem C 2017, 5: 10094-10098.

[26] Pang LX, Zhou D, Qi ZM, et al. Structure-property relationships of low sintering temperature scheelite-structured (1-x)BiVO$_4$-LaNbO$_4$ microwave dielectric ceramics. J Mater Chem C 2017, 5: 2695-2701.

[27] Lu X, Fang B, Zhang S, et al. Decreasing sintering temperature for BCZT lead-free ceramics prepared via hydrothermal route. Funct Mater Lett 2017, 10.

[28] Huang CL, Wang JI, Huang CY. Sintering behavior and microwave dielectric properties of nano alpha-alumina. Mater Lett 2005, 59: 3746-3749.

[29] Bafrooei HB, Feizpour M, Sayyadi-Shahraki A, et al. High-performance ZnTiNb$_2$O$_8$ microwave dielectric ceramics produced from ZnNb$_2$O$_6$-TiO$_2$ nano powders. J Alloys Compd 2020, 834: 9.

[30] Liu F, Liu SJ, Cui XJ, et al. Ordered domains and microwave properties of sub-micron structured Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics obtained by spark plasma sintering. Materials 2019, 12: 11.
[31] Bari M, Taheri-Nassaj E, Taghipour-Armaki H. Role of nano- and micron-sized particles of TiO$_2$ additive on microwave dielectric properties of Li$_2$ZnTi$_3$O$_8$-4wt$\%$ TiO$_2$ ceramics. J Am Ceram Soc 2013, 96: 3737-3741.

[32] Yoon SH, Choi G-K, Kim D-W, et al. Mixture behavior and microwave dielectric properties of (1−x)CaWO$_4_x$TiO$_2$. J Eur Ceram Soc 2007, 27: 3087-3091.

[33] Pan HL, Mao YX, Cheng L, et al. New Li$_3$Ni$_2$NbO$_6$ microwave dielectric ceramics with the orthorhombic structure for LTCC applications. J Alloys Compd 2017, 723: 667-674.

[34] Zhang P, Hao MM, Mao XR, et al. A novel low sintering temperature scheelite-structured CaBiVMoO$_8$ microwave dielectric ceramics. J Alloys Compd 2020, 840: 6.

[35] Ullah B, Lei W, Cao QS, et al. Structure and microwave dielectric behavior of A-site-doped Sr$_{(1-1.5x)}$Ce$_x$TiO$_3$ ceramics system. J Am Ceram Soc 2016, 99: 3286-3292.

[36] Lan XK, Li J, Zou ZY, et al. Lattice structure analysis and optimised microwave dielectric properties of LiAl$_{1-(Zn_{0.5}Si_{0.5})_x}$O$_2$ solid solutions. J Eur Ceram Soc 2019, 39: 2360-2364.

[37] Ferreira VM, Baptista JL. Preparation and microwave dielectric properties of pure and doped magnesium titanate ceramics. Mater Res Bull 1994, 29: 1017-1023.

[38] Lei W, Lu WZ, Wang XC, et al. Effects of CaTiO$_3$ on microstructures and properties of (1-x) ZnAl$_2$O$_4_x$Mg$_3$TiO$_4$ (x=0.1) microwave dielectric ceramics. Int J Inorg Mater 2009, 24: 957-961.

[39] Zhang P, Zhao YG, Li LX. The correlations among bond ionicity, lattice energy and microwave dielectric properties of (Nd$_{1-x}$La$_x$)NbO$_4$ ceramics. Phys Chem Chem Phys 2015, 17: 16692-16698.

[40] Zhao YG, Zhang P. High-Q microwave dielectric ceramics using Zn$_3$Nb$_{1.88}$Ta$_{0.12}$O$_8$ solid solutions. J Alloys Compd 2016, 662: 455-460.
Table 1 Microwave dielectric properties and optimal sintering temperatures of MgO-2B₂O₃-xwt%H₃BO₃-ywt%BCB ceramics.

| Compound                        | S.T. (°C)          | Q × f (GHz) | εᵣ | τᵣ (ppm/°C) |
|---------------------------------|--------------------|-------------|-----|-------------|
| MgO-2B₂O₃-2wt%BCB-10wt%H₃BO₃   | 950°C/4h           | 36,954      | 4.37| -50         |
| MgO-2B₂O₃-2wt%BCB-20wt%H₃BO₃   | 900°C/4h           | 33,591      | 4.44| -35         |
| MgO-2B₂O₃-2wt%BCB-30wt%H₃BO₃   | 900°C/4h           | 37,251      | 4.51| -51         |
| MgO-2B₂O₃-2wt%BCB-40wt%H₃BO₃   | 900°C/4h           | 35,981      | 4.59| -47         |
| MgO-2B₂O₃-4wt%BCB-10wt%H₃BO₃   | 925°C/4h           | 40,076      | 4.81| -40         |
| MgO-2B₂O₃-4wt%BCB-20wt%H₃BO₃   | 900°C/4h           | 42,708      | 5.00| -45         |
| MgO-2B₂O₃-4wt%BCB-30wt%H₃BO₃   | 900°C/4h           | 43,425      | 5.06| -42         |
| MgO-2B₂O₃-4wt%BCB-40wt%H₃BO₃   | 900°C/4h           | 44,306      | 5.10| -32         |
| MgO-2B₂O₃-6wt%BCB-10wt%H₃BO₃   | 850°C/4h           | 37,917      | 5.31| -62         |
| MgO-2B₂O₃-6wt%BCB-20wt%H₃BO₃   | 850°C/4h           | 40,465      | 5.05| -59         |
| MgO-2B₂O₃-6wt%BCB-30wt%H₃BO₃   | 850°C/4h           | 41,477      | 5.07| -38         |
| MgO-2B₂O₃-6wt%BCB-40wt%H₃BO₃   | 800°C/4h           | 37,718      | 5.21| -40         |
| MgO-2B₂O₃-8wt%BCB-10wt%H₃BO₃   | 850°C/4h           | 38,664      | 5.11| -61         |
| MgO-2B₂O₃-8wt%BCB-20wt%H₃BO₃   | 825°C/4h           | 33,985      | 5.28| -60         |
| MgO-2B₂O₃-8wt%BCB-30wt%H₃BO₃   | 825°C/4h           | 34,618      | 5.26| -50         |
Figure Captions:

Fig.1 XRD patterns of MgO-2B2O3-10wt%H3BO3-ywt%BCB (y = 2, 4, 6 and 8) ceramics sintered at their optimal temperatures: (a) y = 2, 950°C, (b) y = 4, 925°C, (c) y = 6, 850°C (d) y = 8, 825°C.

Fig.2 SEM images of MgO-2B2O3-10wt%H3BO3-ywt%BCB ceramics sintered at their optimal temperatures for 4 h: (a) y = 2, 950 °C, (b) y = 4, 925 °C, (c) y = 6, 850 °C, and (d) y = 8, 825 °C.

Fig.3 The variation in bulk density, \( \varepsilon_r \), \( Q\times f \) and \( \tau_f \) values of MgO-2B2O3-10wt%H3BO3-ywt%BCB (y = 2, 4, 6, and8) ceramics after sintering at different temperatures.

Fig.4 XRD patterns of the MgO-2B2O3-xwt%H3BO3-4wt%BCB (10 \( \leq x \leq 40 \)) ceramics sintered at different temperature: (a) \( x = 10 \), 925 °C, (b) \( x = 20 \), 900 °C, (c) \( x = 30 \), 900 °C, and (d) \( x = 40 \), 900 °C.

Fig.5 SEM images of MgO–2B2O3-xwt%H3BO3-4wt%BCB (x = 10, 20, 30 and 40) ceramics sintered at their optimal temperatures: (a) \( x = 10 \), 925 °C, (b) \( x = 20 \), 900 °C, (c) \( x = 30 \), 900 °C, and (d) \( x = 40 \), 900 °C.

Fig.6 The bulk density, relative permittivity, \( Q\times f \) and \( \tau_f \) values of the MgO-2B2O3-xwt%H3BO3(x=10-40)-4wt%BCB ceramics at different sintering temperatures.
FIG. 1
FIG. 2
FIG. 3
FIG. 4
FIG. 5
FIG. 6
