Sintering Characteristic, Structure, Microwave Dielectric Properties and Compatibility with Ag of Novel $3\text{MgO-B}_2\text{O}_3\text{-xwt\% Ba}(\text{CuB}_2)_2\text{O}_5\text{-ywt\% H}_3\text{BO}_3$ Ceramics

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Abstract

In this study, $3\text{MgO-B}_2\text{O}_3\text{-}x\text{wt}\%\text{BCB-}y\text{wt}\%\text{H}_3\text{BO}_3$ ($2 \leq x \leq 8$, $0 \leq y \leq 20$) ceramics were sintered at the optimum temperature to form $\text{Mg}_3\text{B}_2\text{O}_6$ and MgO phases. The effects of H_3BO_3 and BCB on product characteristics, phase transition, microstructure, and microwave properties of $3\text{Mg-B}_2\text{O}_3$ ceramics were investigated. The intensities of diffraction peaks of two phases varied with changing the x and y values. After sintering at 950°C , the ceramics with $x = 6$ and $y = 15$ achieved excellent microwave properties with a ϵ_r of 6.72, $Q \times f$ of 83205 GHz, and τ_f of $-65.05 \text{ ppm}/^\circ\text{C}$. Besides, the ceramic with $x = 8$ and $y = 5$ sintered at 925°C also achieved good microwave dielectric properties with a ϵ_r of 6.64, $Q \times f$ of 78173 GHz, and τ_f of $-57.27 \text{ ppm}/^\circ\text{C}$. The sintering temperatures of above both ceramics are well lower than the melting point of Ag, showing promising applications in low temperature cofired ceramic devices. In particular, these two ceramics can be used as potential candidate materials for microwave ceramics for 5G technology, provided that τ_f can be further optimized.

1. Introduction

In recent years, LTCC technology is widely used in microwave circuits manufacturing and has become the research hot topic for passive component integration [1–7]. In particular, with the emergence of 5G large-scale antenna (Massive MIMO) technology, the number of antennas will increase exponentially. The demand of filters for signal frequency selection and processing will grow with the passage of time, thus the demand for low-temperature co-fired ceramics (LTCC) will also increase significantly [8–13]. LTCC technology requires the dielectrics cofire with high conductivity material electrodes. Because of the low melting point of electrodes (e.g., Ag melting point: 961°C , Al melting point: 660°C), microwave dielectric materials is desired to have low sintering temperatures [14–17].

In the $\text{MgO-B}_2\text{O}_3$ system, Zhou et al [18–20] reported that the sintering temperatures of $\text{MgO-}x\text{B}_2\text{O}_3$ ceramics could be reduced by adding $\text{BaCu(B}_2\text{O}_5\text{)(BCB)}$. $\text{MgO-2B}_2\text{O}_3\text{-4wt}\%\text{BCB}$ ceramics manufactured at 925°C have excellent microwave properties and is a candidate for LTCC components. Based on the above research, they found that $\text{MgO-2B}_2\text{O}_3\text{-40wt}\%\text{H}_3\text{BO}_3\text{-4wt}\%\text{BCB}$ and $\text{MgO-2B}_2\text{O}_3\text{-10wt}\%\text{H}_3\text{BO}_3\text{-4wt}\%\text{BCB}$ manufactured at 900°C and 925°C also had excellent microwave dielectric properties. MgO-rich $3\text{MgO-B}_2\text{O}_3$ ceramics with good microwave properties have also been of interest to scholars. Dosler reported that $\text{Mg}_3\text{B}_2\text{O}_6$ ceramics with a grain size of $1000 \mu\text{m}$ could reach $Q \times f$ values up to more than 220,000 GHz [21]. Gu *et al.* [22] found that pure phase $\text{Mg}_3\text{B}_2\text{O}_6$ ceramic could be obtained when the Mg/B molar ratio is 1.2. An appropriate excess of MgO could increase its $Q \times f$ value, but it did not contribute to its densification. Kan *et al.* [23] found that an appropriate amount of B_2O_3 doping effectively lowered the sintering temperature of this ceramic and improved the dielectric properties of MgO compound. As $x = 0.99$, $x\text{MgO-(1-x)B}_2\text{O}_3$ ceramic sintered at $1,350^\circ\text{C}$ for 4 hours had a $Q \times f$ value of 773,300 GHz. Appropriate ion substitution has been reported to favor densification and dielectric properties of ceramics. For example, Gu *et al.* [24] found that $(\text{Mg}_{0.8}\text{Ca}_{0.2})_3\text{B}_2\text{O}_6$ ceramics manufactured

at 1,250°C showed $\varepsilon_r = 6.8$, $Q \times f = 103556$ GHz, and $\tau_f = -34.5$ ppm/°C. Furthermore, they [22] also reported the excellent microwave properties of $(\text{Mg}_{0.998}\text{Sr}_{0.002})_3\text{B}_2\text{O}_6$ ceramics sintered at 1250°C: $\varepsilon_r = 6.9$, $Q \times f = 110820$ GHz, and $\tau_f = -32.4$ ppm/°C.

Though 3MgO-B₂O₃ material system has high $Q \times f$ values, it is manufactured at high sintering temperatures, which not only hinder their incorporation with low melting electrode and polymer based substrates, but also lead to huge energy consumption and volatile components evaporation. Su et al [25] found that Ni²⁺ can be used as a substitute of Zn²⁺ to optimize the sintering behavior and microwave dielectric properties of Zn₃B₂O₆ ceramics. In addition, they [26] reported that a mixture of Mg₃B₂O₆ and Zn₃B₂O₆ was used to obtain ceramics with excellent dielectric properties at 950 °C. Dou *et al.* [27] investigated the excellent microwave dielectric properties in Mg₃B₂O₆ ceramics with 35% lithium magnesium borosilicate glass sintered at 950°C for 3 h: $\varepsilon_r = 6.5$, $Q \times f = 21000$ GHz, $\tau_f = -49.5$ ppm/°C. Hu *et al.* [28] found that 55 wt% lithium magnesium zinc borosilicate glass addition reduced the sintering temperature of Mg₃B₂O₆ ceramics to ~ 950°C and achieve the excellent microwave dielectric properties with a ε_r of 6.8, $Q \times f$ of 50,000 GHz, and τ_f of -64 ppm/°C. Usually, materials (such as H₃BO₃, CuO, and V₂O₅) with low melting point are often added to lower the sintering temperature for liquid-phase sintering to obtain dense sintered ceramics [29–33]. However, the microwave properties of ceramics doped with low melting point materials are usually much deteriorated [16, 33, 34]. The addition of BaCu(B₂O₅) (BCB) with low melting temperature, good wettability and microwave dielectric properties could contribute to the densification of Mg₃B₂O₆ ceramics [35–37]. However, it is difficult to obtain pure Mg₃B₂O₆ ceramics because high-temperature sintering will lead to the volatilization of B₂O₃ [22]. Although some studies have been reported, the relationship between structure and microwave properties of ceramics with addition of BCB and H₃BO₃ in 3MgO-B₂O₃ needs to be further investigated.

In this study, a series of ceramics of 3MgO-B₂O₃-xwt%BCB-ywt%H₃BO₃ (where $x = 2, 4, 6, 8$; $y = 0, 5, 10, 15, 20$) were prepared by a conventional solid-phase reaction method. The sintering behavior, microstructure, microwave dielectric properties and compatibility with Ag are reported in detail.

2. Experimental

Mg₃B₂O₆ ceramics were prepared by solid-phase method. The raw materials were MgO (> 98.5%), H₃BO₃ (> 99%), CuO (> 99%), and Ba(OH)₂·8H₂O (> 99%). All the raw materials were obtained from Sinopharm, Beijing, China. The MgO was calcined at 800 °C for 2 h to remove water and impurities. Ba(OH)₂·8H₂O was sieved. The raw materials were ball milled with anhydrous ethanol as the medium for 4 h, then dried and sieved. The mixtures were calcined at 800°C for 4 h. The calcined powders mixed with predetermined amount of BCB were subjected to secondary ball milling. 5wt% Polyvinyl alcohol (PVA) was added as the binder to the pellet. The powders were pressed into cylindrical samples having a diameter of 10 mm and a height of ~ 5 mm under 200 MPa. The resulted samples were sintered in air at 850 °C to 1050 °C for 4 h.

An X-ray diffraction spectroscopy (Model X'Pert Pro, PANalytical, Almelo, Netherlands) was used for structure analysis of the specimens. The microstructure of the ceramic surfaces was observed with a scanning electron microscope (SEM, JSM6380-LV SEM, JEOL, Tokyo, Japan). The bulk density of the sintered samples was measured by Archimedes method. Microwave dielectric properties at microwave frequencies were measured using TE01 δ dielectric resonator method and network analyzer (E5071C, Agilent Co., CA, USA) over a frequency range of 300 kHz to 20 GHz at room temperature. τ_f values were obtained over a temperature range of 25 °C to 85 °C as shown below.

$$\tau_f = \frac{f_T - f_{T0}}{f_{T0}(T - T_0)} \times 10^6,$$

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

3. Results And Discussion

As shown in Fig. 1, the XRD patterns of 3MgO-B₂O₃-xwt%BCB ($x = 2, 4, 6, 8$; $y = 0$) ceramics sintered at the optimum temperature. As x increased from 2 to 8, two major phases, indexed as Mg₃B₂O₆ (JCPDS: 75-1807) and MgO, were detected. The diffraction peaks of MgO slowly decreased and that of Mg₃B₂O₆ gradually enhanced with the increase of x , which indicates that with the increase of BCB content, the decrease of sintering temperature and B₂O₃ volatilization will induce the increase of Mg₃B₂O₆ content and decrease of MgO content.

SEM images of 3MgO-B₂O₃-xwt%BCB ($x = 2, 4, 6, 8$) ceramics with optimum sintering temperature are illustrated in Fig. 2. Dense microstructure was observed. The grains gradually became more homogeneous and denser as x -value increased. The average grain sizes of the ceramics are approximately 1.88 μm ($x = 2, 1050^\circ\text{C}$), 2.07 μm ($x = 4, 1025^\circ\text{C}$), 1.53 μm ($x = 6, 975^\circ\text{C}$) and 1.81 μm ($x = 8, 950^\circ\text{C}$). In particular, 3MgO-B₂O₃-6wt% BCB showed variable grain growth and finer grains at 975 °C. This indicates that the addition of appropriate BCB sintering aids can refine the grains. In addition, the sintering temperature of 3MgO-B₂O₃-xwt%BCB ($x = 2, 4, 6, 8$) ceramics gradually decreased with the increase of x value. A grain boundary melting phenomenon appeared in 3MgO-B₂O₃-8wt%BCB, indicating the critical role played by BCB as a sintering aid.

The variation curves of ρ , ε_r , $Q \times f$ and τ_f of 3MgO-B₂O₃-xwt%BCB ($x = 2, 4, 6, 8$) ceramics at different sintering temperature are shown in Fig. 3. As shown in Figs. 3 (a) and (c), the bulk density first increased slightly and then decreased with the increase of the sintering temperature. With changing the sintering temperature, the variation of ε_r is consistent with that of bulk density. The higher the bulk density is, the higher the permittivity is. As x value increased from 2 to 8, the bulk density increased but the value of ε_r decreased, which may be attributed to the addition of BCB with a low ε_r ($\varepsilon_r \sim 7.4$) [35].

The change of $Q \times f$ with sintering temperature for 3MgO-B₂O₃- x wt%BCB ($x = 2, 4, 6, 8$) ceramics is similar to that of bulk density, as shown in Fig. 3(d). The $Q \times f$ is mainly affected by ceramic densification. Higher density leads to a lower porosity and lower losses. A moderate particle size is associated with higher quality factors and lower grain boundary losses [38]. However, desired moderate particle size cannot be obtained for ceramics at lower sintering temperatures. The bulk density of samples first increased and then decreased with the increase of x , indicating that the addition of appropriate amounts of BCB not only decreased the sintering temperature of ceramics but also resulted in denser ceramic, which are consistent with the analysis of the SEM images, as shown in Fig. 2. The $Q \times f$ values of 3MgO-B₂O₃- x wt%BCB ($x = 2, 4, 6, 8$) ceramics initially increased to the maximum and then decreased. The optimum sintering temperature gradually decreased as the x increased from 2 to 8. The optimum $Q \times f$ increased from 73,674 GHz to 99,008 GHz. With further increase of BCB content, the $Q \times f$ decreased to 75,222 GHz. The first increase and then decrease of $Q \times f$ can be ascribed to the deterioration of quality factor of 3MgO-B₂O₃ by the addition of excess BCB.

The 3MgO-B₂O₃- x wt% BCB ($x = 2, 4, 6, 8$) ceramics showed good overall performance: $\varepsilon_r = 6.64 - 7.36$, $Q \times f = 73,674 - 99,008$ GHz, $\tau_f = -73.01$ to -59.38 ppm/°C. BCB addition could reduce the sintering temperature of 3MgO-B₂O₃ ceramics from 1,050°C to 950°C. Notably, 3MgO-B₂O₃-4wt%BCB ceramics sintered at 1,025°C for 4 h exhibited excellent microwave dielectric properties with a ε_r of 7.36, a $Q \times f$ of 99,008 GHz, and a τ_f of -59.38 ppm/°C. The 3MgO-B₂O₃-8wt%BCB ceramic sintered at 950°C for 4 h also exhibited excellent microwave properties with a ε_r of 6.64, a $Q \times f$ of 75222 GHz, and a τ_f of -64.92 ppm/°C.

Figure 4 exhibits the room-temperature XRD patterns of 3MgO-B₂O₃-2wt%BCB- y wt%H₃BO₃ ($y = 0, 5, 10, 15$, and 20) ceramics sintered at their optimum temperatures. The constituent phases of the ceramics are Mg₃B₂O₆ (PDF:038-1475) and MgO complex phases. However, the diffraction peaks of MgO decreased and that of Mg₃B₂O₆ phase increased with the increase of y , indicating that the increase in H₃BO₃ content not only decreased the sintering temperature but also compensated the boron content of 3MgO-B₂O₃ ceramics. Therefore, the content of Mg₃B₂O₆ phase gradually increased, while the content of MgO phase gradually decreased, thereby directly affecting the microwave dielectric properties of 3MgO-B₂O₃-2wt%BCB- y wt%H₃BO₃ ($y = 0, 5, 10, 15$, and 20).

Figure 5 shows the SEM and grain size distribution of 3MgO-B₂O₃-2wt%BCB- y wt%H₃BO₃ ($y = 0, 5, 10, 15$ and 20) ceramics sintered at their optimum temperatures. The images show that the average grain sizes of the ceramics were approximately 1.93 μ m ($y = 0$), 1.64 μ m ($y = 5$), 2.47 μ m ($y = 10$), 1.9 μ m ($y = 15$), and 2.03 μ m ($y = 20$). In particular, the porosity of the ceramic samples became smaller with the increase of H₃BO₃. The comparison of the grain size of ceramics without and with H₃BO₃ shows that H₃BO₃ had an influence on the growth behaviour of this ceramics, showing that the appropriate amount of H₃BO₃ should promote the growth of ceramics. The optimum sintering temperatures of ceramics gradually decreased with the increase of y . The optimum sintering temperatures were 1050°C, 1025°C, 1000°C, 975°C, and 975°C for $y = 0, 5, 10, 15$, and 20, respectively. In particular, the sintering temperature of

ceramics decreased to 975°C ceramics and the ceramics achieved higher densities at $y = 15$. At the same time, the optimum sintering temperature could be reduced with the increase of H_3BO_3 , thus effectively preventing the volatilization of low melting point B_2O_3 . In addition, H_3BO_3 compensated for the volatilized B_2O_3 , thus allowing more complete growth of ceramics grains.

Figure 6(a) illustrates the bulk density of $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ($y = 0, 5, 10, 15$, and 20) ceramics as a function of the sintering temperature. Clearly, the bulk density of ceramic first increased and then decreased with the increase of sintering temperature. This phenomenon indicates that the ceramic was effectively sintered denser initially with the sintering temperature increase. Further temperature increase would cause over-sintering of ceramic and resulted in lower density. The bulk density of $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ($y = 0, 5, 10, 15, 20$) ceramics showed an overall increasing trend with the H_3BO_3 content increase, which may be attributed to the decrease in porosity, as shown in Fig. 5. As y increased from 5 to 15, the bulk density varies from 3.017 g/cm^3 to 3.128 g/cm^3 , indicating that the addition of appropriate H_3BO_3 could make the ceramic samples sintered more densely. However, with further increasing x value to 20, the bulk density reached the lowest at p of 3.04 g/cm^3 , which is due to the over-sintering by addition of too much H_3BO_3 .

Figure 6(b) demonstrates the change of τ_f for $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ($0 \leq y \leq 20$) as a function of temperature. With the sintering temperature increase, τ_f first decreased and then increased, which is consistent with the variation of $Q \times f$ of ceramics. With the increase of y , the τ_f first increased and then decreased from $-94.28 \text{ ppm/}^\circ\text{C}$ to $-53.27 \text{ ppm/}^\circ\text{C}$. When $y = 20$, the τ_f of $3MgO-B_2O_3-2wt\%BCB-20wt\%H_3BO_3$ ceramics remained stable in the range of -60.2 to $-53.27 \text{ ppm/}^\circ\text{C}$, which allows the microwave electronic components maintaining temperature stability with a nearly zero temperature coefficient of resonance frequency compared to other ceramics.

Figure 6(c) displays the ε_r of $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ($y = 0, 5, 10, 15$, and 20) as a function of the sintering temperature. The dielectric constants of ceramic materials are generally closely related to bulk density, phase composition, and crystal structure [39, 40]. ε_r first increased to the maximum and then decreased with the increase of temperatures. As shown in Fig. 6, the change in ε_r with temperature is similar to that of $Q \times f$ and bulk density. However, as the H_3BO_3 content increased, the maximum values of dielectric constant for $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ceramics increased first and then decreased (from 6.95 to 7.05 and then to 6.67), which is similar to that of the bulk density of $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ceramics with sintering temperature. The dielectric constant increased with the increase of bulk density. As the bulk density of ceramic increased, the number of active particles inside the ceramic was relatively high, and the dielectric constant increased and vice versa.

Figure 6(d) shows the change of $Q \times f$ for $3MgO-B_2O_3-2wt\%BCB-ywt\%H_3BO_3$ ($y = 0, 5, 10, 15, 20$) ceramics vs the sintering temperature. In general, grain size, porosity, second phase, and microcracks are the main factors to affect the $Q \times f$ of microwave dielectric ceramics [41–43]. In Fig. 6(d), the $Q \times f$ of $3MgO-B_2O_3-$

2wt%BCB- y wt%H₃BO₃ ($y = 0, 5, 10, 15, 20$) ceramics showed a trend of increasing and then decreasing with the increase of sintering temperature, which is similar to that of the bulk density and relative permittivity. From the analysis of phase structure and microstructure, the microstructure of 3MgO-B₂O₃-2wt%BCB- y wt%H₃BO₃ ($y = 0, 5, 10, 15, 20$) ceramics is clearly relatively denser, and a second phase is present in addition to the main phase 3MgO-B₂O₃. As $y = 15$, the ceramics possessed relatively high $Q \times f$ and maximum density ρ of 3.128 g/cm³. With increasing the y to 20, the optimum sintering temperature was 975°C. Combined with the XRD analysis, it is found that the $Q \times f$ of 3MgO-B₂O₃-2wt%BCB- x wt%H₃BO₃ ceramic also reached the maximum value of 113,645 GHz as x increased. The content of the main phase of the ceramic increases as the content of the second phase MgO in the crystal structure decreases.

Table 1 lists the optimum sintering temperature and microwave dielectric properties of 3MgO-B₂O₃- x wt%BCB- y wt%H₃BO₃ (where $x = 2, 4, 6$, and 8; $y = 0, 5, 10, 15$, and 20) ceramics. The optimum sintering temperature decreased with the increase of BCB content when the value of y was constant. Notably, the sintering temperature of 3MgO-B₂O₃-8wt%BCB and 3MgO-B₂O₃-8wt%BCB-5wt%H₃BO₃ ceramics can be lowered to 925°C (< 961°C, providing the possibility of cofiring with Ag). Both ceramics had high quality factors and low dielectric constants. The microwave dielectric properties of 3MgO-B₂O₃-8wt%BCB are as follows: $\epsilon_r = 6.47$, $Q \times f = 73,233$ GHz, $\tau_f = -68.52$ ppm/°C. The microwave properties of 3MgO-B₂O₃-8wt%BCB-5wt%H₃BO₃ are as follows: $\epsilon_r = 6.64$, $Q \times f = 78,173$ GHz, and $\tau_f = -57.27$ ppm/°C. In addition, the 3MgO-B₂O₃-2wt%BCB-20wt%H₃BO₃ ceramic has the highest quality factor of 113,645 GHz at 975°C, a ϵ_r of 6.67, and a τ_f of -53.19 ppm/°C. As observed by XRD, the increase in H₃BO₃ content not only decreased the sintering temperature but also enhanced the intensity of the diffraction peak for Mg₃B₂O₆, which indicates that $Q \times f$ increased with the increase of Mg₃B₂O₆ content. However, when $y = 20$, the $Q \times f$ decreased with the increase of BCB, indicating that although BCB plays the role as sintering aid, it also deteriorates the microwave dielectric properties of 3MgO-B₂O₃- x wt%BCB-20wt%H₃BO₃.

Table 1
Optimum sintering temperature and microwave dielectric properties of 3MgO-B₂O₃ -
xwt%BCB-ywt%H₃BO₃ ceramics

Compound	S.T. (°C)	Q×f (GHz)	ε _r	τ _f (ppm/°C)
3MgO-B ₂ O ₃ -2wt%BCB	1050 °C	73,674	6.95	-68.38
3MgO-B ₂ O ₃ -4wt%BCB	1025°C	99,008	7.36	-59.38
3MgO-B ₂ O ₃ -6wt%BCB	975°C	69,263	6.78	-73.01
3MgO-B ₂ O ₃ -8wt%BCB	950°C	75,222	6.64	-64.92
3MgO-B ₂ O ₃ -2wt%BCB-5wt%H ₃ BO ₃	1000°C	89,283	7.05	-61.53
3MgO-B ₂ O ₃ -4wt%BCB-5wt%H ₃ BO ₃	975°C	69,055	6.92	-86.84
3MgO-B ₂ O ₃ -6wt%BCB-5wt%H ₃ BO ₃	975°C	80,260	6.65	-57.93
3MgO-B ₂ O ₃ -8wt%BCB-5wt%H ₃ BO ₃	925°C	78,173	6.64	-57.27
3MgO-B ₂ O ₃ -2wt%BCB-10wt%H ₃ BO ₃	1025°C	77,819	7.04	-94.28
3MgO-B ₂ O ₃ -4wt%BCB-10wt%H ₃ BO ₃	1000°C	72,409	6.93	-65.74
3MgO-B ₂ O ₃ -6wt%BCB-10wt%H ₃ BO ₃	950°C	69,740	6.8	-86.99
3MgO-B ₂ O ₃ -8wt%BCB-10wt%H ₃ BO ₃	950°C	58,689	6.95	-62.86
3MgO-B ₂ O ₃ -2wt%BCB-15wt%H ₃ BO ₃	975°C	73,892	9.79	-66.80
3MgO-B ₂ O ₃ -4wt%BCB-15wt%H ₃ BO ₃	975°C	74,136	6.95	-27.46
3MgO-B ₂ O ₃ -6wt%BCB-15wt%H ₃ BO ₃	950°C	83,205	6.72	-65.05
3MgO-B ₂ O ₃ -8wt%BCB-15wt%H ₃ BO ₃	900°C	63,711	6.51	-60.79
3MgO-B ₂ O ₃ -2wt%BCB-20wt%H ₃ BO ₃	975°C	113,645	6.67	-53.19
3MgO-B ₂ O ₃ -4wt%BCB-20wt%H ₃ BO ₃	975°C	81,667	6.55	-50.21
3MgO-B ₂ O ₃ -6wt%BCB-20wt%H ₃ BO ₃	950°C	74,099	6.51	-66.98
3MgO-B ₂ O ₃ -8wt%BCB-20wt%H ₃ BO ₃	950°C	78,401	6.53	-62.85

To investigate whether the 3MgO-B₂O₃-6wt%BCB-15 wt%H₃BO₃ and 3MgO-B₂O₃-8 wt%BCB-5wt%H₃BO₃ ceramics could react with silver electrodes or not, the two calcined powders were mixed with 20 wt% Ag powder and sintered at 950°C and 925°C for 4 hours, respectively. Figure 7 shows the XRD patterns and backscattered electron diagrams of the samples. The XRD shows that Ag was present as a single phase

and the EDS shows that the bright particles in the main ceramic matrix were silver, which further confirms that there is no reaction between the silver and $3\text{MgO-B}_2\text{O}_3\text{-8wt\%BCB-5wt\%H}_3\text{BO}_3$. All these results evidence the potential application of both ceramics in LTCC technology.

4. Conclusion

In this study, $3\text{MgO-B}_2\text{O}_3\text{-}x\text{wt\%BCB-}y\text{wt\%H}_3\text{BO}_3$ (where $x = 2, 4, 6$, and 8 ; $y = 0, 5, 10, 15$, and 20) ceramics was synthesized using solid-phase reaction method. When $y = 0$, the ceramics consist of two phases, namely $\text{Mg}_3\text{B}_2\text{O}_6$ and MgO . As x increased, the main diffraction peak of MgO phase gradually decreased while the diffraction peak of $\text{Mg}_3\text{B}_2\text{O}_6$ gradually increased. As x was constant, the diffraction peak intensity of $\text{Mg}_3\text{B}_2\text{O}_6$ phase increased with the increase of y while the main diffraction peak of MgO phase continuously decreased. H_3BO_3 could effectively stabilize the $\text{Mg}_3\text{B}_2\text{O}_6$ phase. BCB acted as a grain refinement and reduced the optimum sintering temperature of ceramics from $1,050^\circ\text{C}$ to 950°C . When $x = 4$ and $y = 0$, $3\text{MgO-B}_2\text{O}_3\text{-4wt\%BCB}$ exhibited excellent microwave dielectric properties: $\epsilon_r = 7.36$, $Q \times f = 99,008 \text{ GHz}$, $\tau_f = -59.38 \text{ ppm}/^\circ\text{C}$, and $\rho = 2.791 \text{ g/cm}^3$. However, excess BCB led to a decrease of microwave dielectric properties. It was found that an appropriate amount of H_3BO_3 compensated the boron content of $3\text{MgO-B}_2\text{O}_3$, making $3\text{MgO-B}_2\text{O}_3$ crystal growth more complete and denser. The highest $Q \times f$ of $113,645 \text{ GHz}$, ϵ_r of 6.67 , τ_f of $-53.19 \text{ ppm}/^\circ\text{C}$, and ρ of 3.04 g/cm^3 of $3\text{MgO-B}_2\text{O}_3$ ceramic were achieved at 975°C at $x = 2$ and $y = 20$. In particular, comprehensive comparison of the ceramic properties sintered at same low sintering temperature revealed that the ceramics with $x = 6$, $y = 15$ sintered at 950°C achieved good microwave dielectric properties with a ϵ_r of 6.72 , $Q \times f$ of $83,205 \text{ GHz}$, and τ_f of $-65.05 \text{ ppm}/^\circ\text{C}$. The ceramic with $x = 8$, $y = 5$ sintered at 925°C also achieved good microwave dielectric properties ($\epsilon_r = 6.64$, $Q \times f = 78,173 \text{ GHz}$, and $\tau_f = -57.27 \text{ ppm}/^\circ\text{C}$). $3\text{MgO-B}_2\text{O}_3\text{-}x \text{ wt\%BCB-}y \text{ wt\%H}_3\text{BO}_3$ ($x = 6$, $y = 15$ or $x = 8$, $y = 5$) had excellent microwave dielectric properties and can also be produced at low cost. Both ceramics can be co-fired with Ag, suggesting that they are promising for 5G applications, provided that τ_f can be further optimized to zero.

Declarations

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Figures

Figure 1

XRD patterns of 3MgO-B₂O₃-xwt%BCB (x = 2, 4, 6, 8) ceramics sintered at optimum temperatures: (a) x = 2, 1050 °C, (b) x = 4, 1025 °C, (c) x = 6, 975 °C, (d) x = 8, 950 °C.

Figure 2

SEM image of 3MgO-B₂O₃-xwt%BCB (x = 2, 4, 6, 8) ceramics sintered at optimum temperatures: (a) x = 2, 1050 °C, (b) x = 4, 1025 °C, (c) x = 6, 975 °C, (d) x = 8, 950 °C.

Figure 3

Bulk densities and microwave dielectric properties (ϵ_r , $Q \times f$ and τ_f) of the 3MgO-B₂O₃-xwt%BCB (x value ranges from 2 to 8) ceramics at different sintering temperatures (S.T.)

Figure 4

XRD patterns of 3MgO-B₂O₃-2wt%BCB-ywt%H₃BO₃ (y = 0, 5, 10, 15, and 20) ceramics sintered at their optimum temperatures: (a) y = 0, 1050 °C, (b) y = 5, 1025 °C, (c) y = 10, 1000 °C, (d) y = 15, 975°C, (e) y = 20, 975 °C.

Figure 5

SEM images of 3MgO-B₂O₃-2wt%BCB-ywt%H₃BO₃ (y = 0, 5, 10, 15, and 20) ceramics sintered at their optimal temperatures: (a) y = 0, 1050 °C, (b) y = 5, 1025 °C, (c) y = 10, 1000 °C, (d) y = 15, 975 °C, (e) y = 20, 975 °C.

Figure 6

Bulk density, ϵ_r , $Q \times f$, and τ_f of $3\text{MgO-B}_2\text{O}_3\text{-}2\text{wt\%BCB-ywt\%H}_3\text{BO}_3$ ($0 \leq y \leq 20$) ceramics sintered at optimal temperatures as a function of y value.

Figure 7

XRD and SEM results of 3MgO-B₂O₃-xwt%BCB-ywt%H₃BO₃ (x=6,8,y=5,15) ceramics co-fired with silver powder (The inset shows the EDS analysis of a 3MgO-B₂O₃-8wt%BCB-5wt%H₃BO₃ sample co-fired with Ag).