Sintering characteristic, structure, microwave dielectric properties, and compatibility with Ag of novel 3MgO-B$_2$O$_3$-xwt% BaCu(B$_2$O$_4$)$_{y}$wt% H$_3$BO$_3$ ceramics

Haiquan Wang$^{ab}$, Shixuan Li$^a$, Kangguo Wang$^a$, Xi Wang$^a$, HaiLin Zhang$^a$, You Wu$^a$, Xiuli Chen$^a$ and Huanfu Zhou$^a$

$^a$Collaborative Innovation Center for Exploration of Hidden Nonferrous Metal Deposits and Development of New Materials in Guangxi, Key Laboratory of Nonferrous Materials and New Processing Technology, Ministry of Education, School of Materials Science and Engineering, Guilin University of Technology, Guilin, Guangxi, China; $^b$College of Mechanical and Electrical Engineering, Guangdong University of Petrochemical Technology, Maoming, Guangdong Province, China

**ABSTRACT**
In this study, 3MgO-B$_2$O$_3$-xwt%BaCu(B$_2$O$_4$)$_{y}$ wt%H$_3$BO$_3$ (2 ≤ x ≤ 8, 0 ≤ y ≤ 20) ceramics were sintered at the optimum temperature to form Mg$_3$B$_2$O$_6$ and MgO phases. The effects of H$_3$BO$_3$ and BCB on the product characteristics, phase transition, microstructure, and microwave dielectric properties of 3MgO-B$_2$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 the excellent microwave properties with a ε$_r$ of 6.72, $Q$ × f of 83,205 GHz and $\tau_f$ of 65.05 ppm/°C. Besides, the ceramics with x = 8 and y = 5 sintered at 925°C also achieved good microwave dielectric properties with a ε$_r$ of 6.64, $Q$ × f of 78,173 GHz and $\tau_f$ of 57.27 ppm/°C. The sintering temperatures of above both ceramics are 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 the potential candidate materials for microwave ceramics for 5 G technology, provided that $\tau_f$ can be further optimized.

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**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 5 G 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 to 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 MgO-B$_2$O$_3$ system, Zhou et al. [18–20] reported that the sintering temperatures of MgO-xB$_2$O$_3$ ceramics could be reduced by adding BCB. MgO-2B$_2$O$_3$-4 wt%BCB ceramics manufactured at 925°C have the excellent microwave properties, which is a candidate for LTCC components. Based on the above researches, they found that MgO-2B$_2$O$_3$-40 wt%H$_3$BO$_3$-4 wt%BCB and MgO-2B$_2$O$_3$-10 wt%H$_3$BO$_3$-4 wt%BCB manufactured at 900°C and 925°C also had excellent microwave dielectric properties. MgO-rich 3MgO-B$_2$O$_3$ ceramics with good microwave properties have also been of interest to scholars. Dosler reported that Mg$_3$B$_2$O$_6$ ceramics with a grain size of 1000 μm could reach $Q$ × f values up to more than 220,000 GHz [21]. Gu et al. [22] found that pure-phase Mg$_3$B$_2$O$_6$ ceramic could be obtained when the Mg/B molar ratio is 1.2. An appropriate excess of MgO could increase its $Q$ × f value, but it did not contribute to its densification. Kan et al. [23] found that an appropriate amount of B$_2$O$_3$ doping could effectively lower the sintering temperature of this ceramic and improved the dielectric properties of MgO compound. As $x = 0.99, x$MgO–(1- x)B$_2$O$_3$ ceramic sintered at 1,350°C for 4 hours had a $Q$ × 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 (Mg$_{0.8}$Ca$_{0.2}$)$_3$B$_2$O$_6$ ceramics manufactured at 1,250°C showed microwave dielectric properties of ε$_r$ = 6.8, $Q$ × f = 103,556 GHz, and $\tau_f$ = − 34.55 ppm/°C. Furthermore, they [22] also reported that the (Mg$_{0.998}$Sr$_{0.002}$)$_3$B$_2$O$_6$ ceramics

CONTACT Huanfu Zhou zhohuanfu@163.com School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China

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sintered at 1250°C had the excellent microwave properties of $\varepsilon_r = 6.9$, $Q \times f = 110,820$ GHz, and $\tau_f = -32.4$ ppm/°C.

Though 3MgO-B$_2$O$_3$ material system has high $Q \times f$ value, 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 Ni$^{2+}$ can be used as a substitute of Zn$^{2+}$ to optimize the sintering behavior and microwave dielectric properties of Zn$_3$B$_2$O$_6$ ceramics. In addition, they [26] reported that a mixture of Mg$_3$B$_2$O$_6$ and Zn$_3$B$_2$O$_6$ was used to obtain ceramics with excellent dielectric properties at 950°C. Dou et al. [27] investigated that the Mg$_3$B$_2$O$_6$ ceramics with 35% lithium magnesium borosilicate glass sintered at 950°C for 3 h obtained the excellent microwave dielectric properties with $\varepsilon_r = 6.5$, $Q \times f = 21,000$ GHz, and $\tau_f = -49.5$ ppm/°C. Hu et al. [28] found that 55 wt% lithium magnesium zinc borosilicate glass addition could reduce the sintering temperature of Mg$_3$B$_2$O$_6$ ceramics to ~950°C and achieve the excellent microwave dielectric properties with a $\varepsilon_r$ of 6.8, $Q \times f$ of 50,000 GHz, and $\tau_f$ of -64 ppm/°C. Usually, materials (such as H$_3$BO$_3$, CuO, and V$_2$O$_5$) 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 BCB with low melting temperature, good wettability, and microwave dielectric properties could contribute to the densification of Mg$_3$B$_2$O$_6$ ceramics [35–37]. However, it is difficult to obtain pure Mg$_3$B$_2$O$_6$ ceramics because high-temperature sintering will lead to the volatilization of B$_2$O$_3$ [22]. Although some studies have been reported, the relationship between structure and microwave properties of ceramics with addition of BCB and H$_3$BO$_3$ in 3MgO-B$_2$O$_3$ needs to be further investigated.

Figure 1 shows the ternary-phase diagrams of 3MgO-B$_2$O$_3$-BCB-H$_3$BO$_3$ systems. Based on this ternary-phase diagrams, a series of ceramics of 3MgO-B$_2$O$_3$-xwt%BCB-ywt%H$_3$BO$_3$ (where $x = 2, 4, 6, 8; y = 0, 5, 10, 15, 20$) were designed and prepared by a conventional solid state reaction method. The sintering behavior, microstructure, microwave dielectric properties, and compatibility with Ag of ceramics are also reported in detail.

2. Materials and methods

Mg$_3$B$_2$O$_6$ ceramics were prepared by the solid state reaction method. The raw materials were MgO (>98.5%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), H$_3$BO$_3$ (>99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), CuO (>99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and Ba(OH)$_2$·8H$_2$O (>99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The MgO was calcined at 800°C for 2 h to remove water and impurities. Ba(OH)$_2$·8H$_2$O was sieved. After weighing, 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 H$_3$BO$_3$ and 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 with a diameter of 10 mm and a height of ~5 mm under 200 MPa. The resulted samples were sintered in air at 850°C ~ 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
3. Results and discussion

Figure 2 shows the 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.

The bulk density of the sintered samples was measured by Archimedes method. Microwave dielectric properties 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. \( \tau_f \) values were obtained over a temperature range of 25°C to 85°C as shown below.

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

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

Figure 2. 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.

Microscope (SEM, JSM6380-LV SEM, JEOL, Tokyo, Japan). The homogeneous and denser as x value increased. The average grain sizes of the ceramics are approximately 1.88 μm (x = 2, 1050°C), 2.07 μm (x = 4, 1025°C), 1.53 μm (x = 6, 975°C) and 1.81 μm (x = 8, 950°C). In particular, 3MgO-B₂O₃-6 wt% 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-B₂O₃-8 wt% BCB, indicating the critical role played by BCB as a sintering aid.

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

The change of \( Q \times f \) with sintering temperature for 3MgO-B₂O₃-xwt% BCB (x = 2, 4, 6, 8) ceramics is similar to that of bulk density, as shown in (Figure 4). 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 Figure 3. The $Q \times f$ values of $3\text{MgO-}2\text{B}_2\text{O}_3$-$x\text{wt}\%\text{BCB}$ ($x = 2, 4, 6, 8$) ceramics initially increased to the maximum values and then decreased. The optimum sintering

\[\text{(a)} x = 2, 1050°C, \quad \text{(b)} x = 4, 1025°C, \quad \text{(c)} x = 6, 975°C, \quad \text{(d)} x = 8, 950°C.\]
temperature gradually decreased as the x increased from 2 to 8. The optimum Q x f values increased from 73,674 GHz to 99,008 GHz. With further increase of BCB content, the Q x f decreased to 75,222 GHz. The first increase and then decrease of Q x f can be ascribed to the deterioration of quality factor of 3MgO-B2O3 by the addition of excess BCB.

The 3MgO-B2O3-ywt% BCB (x = 2, 4, 6, 8) ceramics showed good overall performance: εr = 6.64–7.36, Q x f = 73,674–99,008 GHz, τf = 73.01 to 59.38 ppm/°C. BCB addition could increase the sintering temperature of 3MgO-B2O3 ceramics from 1,050°C to 950°C. Notably, 3MgO-B2O3-ywt% BCB ceramics sintered at 1,025°C for 4 h exhibited the excellent microwave dielectric properties with a εr of 7.36, Q x f of 99,008 GHz, and a τf of 59.38 ppm/°C. The 3MgO-B2O3-ywt% BCB ceramic sintered at 950°C for 4 h also had the excellent microwave properties with a εr of 6.64, Q x f of 75,222 GHz, and a τf of 64.92 ppm/°C.

Figure 5 exhibits the room-temperature XRD patterns of 3MgO-B2O3-ywt% BCB-ywt% H2BO3 (y = 0, 5, 10, 15, and 20) ceramics sintered at their optimum temperatures. The constituent phases of the ceramics are Mg3B2O6 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 H2BO3 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-ywt% BCB-ywt% H2BO3 (y = 0, 5, 10, 15, and 20).

Figure 6 shows the SEM pictures and grain size distribution of 3MgO-B2O3-ywt% BCB-ywt% H2BO3 (y = 0, 5, 10, 15, and 20) ceramics sintered at their optimum temperatures. The average grain sizes of the ceramics were approximately 1.93 µm (y = 0), 1.64 µm (y = 5), 2.47 µm (y = 10), 1.9 µm (y = 15), and 2.03 µm (y = 20). In particular, the porosity of the ceramic samples became smaller with the increase of H2BO3. The comparison of the grain size of ceramics without and with H2BO3 shows that H2BO3 had an influence on the growth behavior of this ceramics, indicating that the appropriate amount of H2BO3 could 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 H2BO3, thus effectively preventing the volatilization of low melting point B2O3. In addition, H2BO3 compensated for the volatilized B2O3, thus allowing more complete growth of ceramics grains.

Figure 7 illustrates the bulk density of 3MgO-B2O3-ywt% BCB-ywt% H2BO3 (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 increasing the sintering temperature. Further, temperature increase would cause over-sintering of ceramic and resulted in lower density. The bulk density of 3MgO-B2O3-ywt% BCB-ywt% H2BO3 ceramics showed an overall increasing trend with the H2BO3 content increase, which may be attributed to the decrease in porosity, as shown in Figure 5. As y increased from 5 to 15, the bulk density rises from 3.017 g/cm³ to 3.128 g/cm³, indicating that the addition of appropriate H2BO3 could make the ceramic samples sinter more densely. However, with further increasing y value to 20, the bulk density reached the lowest at ρ of 3.04 g/cm³, which is due to the over-sintering by addition of too much H2BO3.

Figure 7 demonstrates the change of τf for 3MgO-B2O3-ywt% BCB-ywt% H2BO3 (0 ≤ y ≤ 20) as a function of the sintering temperature. With the sintering temperature increase, τf first decreased and then increased, which is consistent with the variation of Q x f of ceramics. With the increase of y, the τf first increased and then decreased. When y = 20, the τf of 3MgO-B2O3-ywt% BCB-ywt% H2BO3 ceramics remained stable in the range of ~60.2 to ~53.27 ppm/°C, which allows the microwave electronic components maintaining temperature stability with a nearly zero temperature coefficient of resonance frequency compared to other ceramics.
(Figure 7) displays the εr of 3MgO-B2O3-2 wt%BCB-ywt%H2BO3 (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]. εr first increased to the maximum and then decreased with the increase of temperatures. As shown in Figure 6, the change in εr with temperature is similar to that of Q × f and bulk density. However, as the H2BO3 content increased, the maximum values of dielectric constant for 3MgO-B2O3-2 wt%BCB-ywt%H2BO3 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-B2O3-2 wt%BCB-ywt%H2BO3 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 7) shows the change of Q × f for 3MgO-B2O3-2 wt%BCB-ywt%H2BO3 (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 × f of microwave dielectric ceramics [41–43]. In (Figure 7), the Q × f of 3MgO-B2O3-2 wt%BCB-ywt%H2BO3 (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-B2O3-2 wt%BCB-ywt%H2BO3 (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 × 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 × f of 3MgO-B2O3-2 wt%BCB-ywt%H2BO3 ceramic also reached the maximum value of 113,645 GHz as y 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-xwt%BCB-ywt%H2BO3 (where x = 2, 4, 6, and 8; y = 0, 5, 10, 15, and 20) ceramics.
5, 10, 15, and 20) ceramics. The optimum sintering temperature was decreased with the increase of BCB content when the value of y was constant. Notably, the sintering temperature of 3MgO-B$_2$O$_3$-8 wt%BCB and 3MgO-B$_2$O$_3$-8 wt%BCB-5wt%H$_2$O$_3$ 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-B$_2$O$_3$-8 wt%BCB ceramics are as follows: $\varepsilon_r = 6.47$, $Q \times f = 73,233$ GHz, $\tau_f = -68.52$ ppm/°C. The microwave properties of 3MgO-B$_2$O$_3$-8 wt%BCB-5wt%H$_2$O$_3$ are as follows: $\varepsilon_r = 6.64$, $Q \times f = 78,173$ GHz, and $\tau_f = -57.27$ ppm/°C. In addition, the 3MgO-B$_2$O$_3$-2 wt%BCB-20 wt%H$_2$O$_3$ ceramic sintered at 975°C has the highest quality factor of 113,645 GHz, a $\varepsilon_r$ of 6.67, and a $\tau_f$ of $-53.19$ ppm/°C. As observed by XRD, the increase in H$_2$BO$_3$ content not only decreased the sintering temperature but also enhanced the intensity of the diffraction peak for Mg$_3$B$_2$O$_6$, which indicates that $Q \times f$ increased with the increase of Mg$_3$B$_2$O$_6$ 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-B$_2$O$_3$- xwt%BCB-20 wt%H$_2$BO$_3$.
4. Conclusion

In this study, 3MgO-B₂O₃-xwt%BCB-ywt%H₂BO₃ (where x = 2, 4, 6, and 8; y = 0, 5, 10, 15, and 20) ceramics have been synthesized by the solid state reaction method. When y = 0, the ceramics consist of two phases, namely Mg₃B₂O₆ and MgO. As x increased, the main diffraction peak of MgO phase gradually decreased while the diffraction peak of Mg₃B₂O₆ gradually increased. As x was constant, the diffraction peak intensity of Mg₃B₂O₆ phase increased with the increase of y while the main diffraction peak of MgO phase continuously decreased. H₂BO₃ could effectively stabilize the Mg₃B₂O₆ phase. BCB acted as a grain refinement and reduced the optimum sintering temperature of ceramics from 1,050°C to 950°C. When x = 4 and y = 0, 3MgO-B₂O₃-4 wt%BCB exhibited excellent microwave dielectric properties of εᵣ = 7.36, Q × f = 99,008 GHz, τᵣ = −59.38 ppm/°C. However, excess BCB led to a decrease of microwave dielectric properties. An appropriate amount of H₂BO₃ compensated the boron content of 3MgO-B₂O₃, making 3MgO-B₂O₃ crystal growth more complete and denser. The highest Q × f of 113,645 GHz, εᵣ of 6.67, τᵣ of −53.19 ppm/°C, and ρ of 3.04 g/cm³ of 3MgO-B₂O₃ ceramics 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 εᵣ of 6.72, Q × f of 83,205 GHz, and τᵣ of −65.05 ppm/°C. The ceramic with x = 8, y = 5 sintered at 925°C also achieved good microwave dielectric properties of εᵣ = 6.64, Q × f = 78,173 GHz, and τᵣ = −57.27 ppm/°C. 3MgO-B₂O₃-x wt%BCB-ywt%H₂BO₃ (x = 6, y = 15 or x = 8, y = 5) had excellent microwave dielectric properties and can also be produced at low cost. Both ceramics could be co-fired with Ag, suggesting that they are promising for 5G applications, provided that τᵣ can be further optimized to zero.

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Disclosure statement

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