Amelioration of sintering and multi-frequency dielectric properties of Mg$_3$B$_2$O$_6$: A mechanism study of nickel substitution using DFT calculation

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Abstract: With the support of density functional theory (DFT) calculation, the amelioration of sintering and dielectric properties of the Mg$_3$B$_2$O$_6$ (MBO) ceramic was realized through the substitution of magnesium with nickel. The TE-mode cylindrical cavity method was used to measure the dielectric properties at different frequencies. The thermo-mechanical analysis and simultaneous thermal analysis were used to characterize the chemical and mechanical properties. The phase composition was determined through the X-ray diffraction (XRD) and Raman spectrum. The microstructure was investigated using the scanning electron microscopy (SEM). Magnesium substitution with nickel (4 mol%) could ionize the B–O bond of BO$_3$, modify the vibration mode, improve the order degree, densify the microstructure, decrease the intrinsic densification temperature, and ameliorate the dielectric properties of the MBO ceramics. The maximum values were achieved for the ceramics with 4 mol% nickel and sintered at 1175 °C, that is, 97.2% for relative density, 72,600 GHz (10 GHz), 75,600 GHz (11.4 GHz), and 92,200 GHz (15 GHz) for $Q \times f$, 7.1 (10 GHz), 7.01 (11.4 GHz), and 6.91 (15 GHz) for $\varepsilon_r$, and $-56.3$ ppm/°C for $\tau_f$.

Keywords: borate; density functional theory (DFT); low dielectric constant; dielectric properties

1 Introduction

Materials with low dielectric constant ($\varepsilon_r$) and high quality factor ($Q \times f$) have been widely applied in the communication field, such as a base station, to maintain the quality and delay of digital signals [1,2]. Such materials usually have a relatively high sintering temperature, which is unsuitable for the technology of low-temperature cofired ceramics (LTCC) [3–6]. The Mg$_3$B$_2$O$_6$ (MBO) material has excellent dielectric properties, that is, 7 for $\varepsilon_r$, 108,000 GHz for $Q \times f$,
−69 ppm/℃ for $\tau_f$, and 97% for relative density sintered at 1350 ℃ [7]. Moreover, the oxide related to MBO is cheap, and a module fabricated using MBO could be equipped with a high added value. However, its sintering temperature is excessively high to meet the requirement of LTCC. The substitution of equivalence ions with different (ones with close) ionic radius and polarizability (e.g., Mg$^{2+}$ with Co$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$) is an effective method to lower the intrinsic densification temperature, but the influence mechanism has not been discussed in detail [3,8–13]. Therefore, we speculate that the moderate substitution of Mg$^{2+}$ with Ni$^{2+}$ could lower the densification temperature of MBO, and the first-principles calculation was considered to explore the amelioration mechanism [14–20].

The frequency stability of dielectric property is a key factor for the material used to fabricate a module with wide working bandwidth. Nevertheless, the recently reported dielectric properties at microwave frequency are mostly obtained at a specific frequency by the Hakki–Coleman method, which could not obtain the dielectric property of a material at different frequencies by only one sample [21,22]. The resonance peak of some materials is also unobvious, which means that the dielectric properties could not be measured using the Hakki–Coleman method. The TE-mode cylindrical cavity method could obtain the frequency characteristics of a material without the making of different samples, and it avoids the risk of missing the resonance peak [23]. Thus, this method was used to measure the dielectric properties at different frequencies, and the solid-state reaction method was used to synthesise (Mg$_{1-x}$Ni$_x$)$_3$B$_2$O$_6$ (MNBO) ceramics in this experiment ($x$ varied from 0.00 to 0.07).

## 2 Experimental

With 10% B$_2$O$_3$ addition for compensation, MgO, NiO, and B$_2$O$_3$ powders were premilled for 12 h. The precursor was from Chron Chemicals Co., Ltd., China. The presintering temperature was 1100 ℃ for 4 h, and the obtained powders were milled again for 12 h. A 5% polyvinyl alcohol binder was used to shape these remilled powders into cylinders with a size of 6 mm in radius and thickness. The calcination temperature for the shaped sample was 1150–1200 ℃. The crystal phase was determined by X-ray diffraction (XRD, DX-2700, Cu Kα radiation 1.54184 Å, 10°–110°, 0.01 (°)/step, 30 min/sample). The refined XRD data were obtained through the Rietveld refinement. The grain distribution was determined by scanning electron microscopy (SEM; FEI Versa3D, USA), and the quantitative analysis was realized by energy-dispersive X-ray spectroscopy (EDS; Ametek OCTANE Plus, USA). The TE-mode cylindrical cavity method and the R & S network analyser (ZNB40, 9 kHz–40 GHz, Germany) were used to measure the dielectric performance at different frequencies [23]. The chemical and mechanical performance with increasing temperature was evaluated using a thermo-mechanical analyser (Mettler2+, air, 2, 5, 10, and 15 K-min$^{-1}$, Switzerland) and a simultaneous thermal analyser (Mettler3+, air, 2 K-min$^{-1}$, Switzerland). The thermal stability of dielectric performance was quantified using Eq. (1) through the resonant frequency at 80 ($f_0$) and 20 ℃ ($f_f$) [24].

$$\tau_f = \frac{f_f - f_0}{f_0(T - T_0)} \times 10^6$$  (1)

The sintering performance (activation energy, $E_a$) was quantified using Eq. (2) through the heating rate ($k$) and sintering temperature ($T$) [25].

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln z$$  (2)

where $R$ and $z$ are the gas constant and Arrhenius constant, respectively. The Archimedes drainage method was used to measure the sample density [26]. The crystallite size ($D$) was quantified using the Williamson–Hall (W–H) method through the wavelength of radiation ($\lambda$, 1.5406 Å) and factor of shape ($K$, 0.9) [27].

$$\beta_f \cos \theta = \frac{K \lambda}{D} + 4\varepsilon \sin \theta$$  (3)

where $\beta_f$ is the full width at half maximum of XRD data, $\theta$ is the diffraction angle, and $\varepsilon$ is the slope of fitted line.

DFT-related (DFT: density functional theory) calculation was performed using the Cambridge Serial Total Energy Package, and the interplay of ions and electrons was determined using the Vanderbilt ultrasoft pseudopotential. The interplay of exchange correlation was analysed using the Perdew–Burke–Ernzerhof algorithm, and the vibration property was evaluated using the linear response standard. The valence electron was 2p$^6$3s$^2$ (magnesium), 3d$^8$4s$^2$ (nickel), 2s$^2$2p$^1$ (boron), and 2s$^2$2p$^4$ (oxygen), and crystal optimisation was realised through the Broyden–Fletcher–Goldfarb–Shanno algorithm. After testing, the related convergence
threshold values were 380 eV for energy cutoff, $3 \times 2 \times 3$ for k-point mesh, 0.005 eV/Å for force (max), 0.005 GPa for stress (max), $5.0 \times 10^{-6}$ eV/atom for system energy, and 0.005 Å for displacement (max). In order to keep the same concentration of the substitution-ion, a supercell ($2 \times 2 \times 1$) was constructed to explore the substitution property of crystal. The priority of occupation was quantified through Eq. (4) by the energy of substituted ($E_{\text{Do}}$) and unsubstituted ($E_{\text{Undo}}$) systems [28]:

$$\Delta E = E_{\text{Do}} - E_{\text{Undo}} - \sum_i k_i p_i$$  \hspace{1cm} (4)

where $p_i$ is the chemical potential, and $k_i$ is the unite of coefficient.

3 Results and discussion

Figures 1(a) and 1(b) show the XRD patterns of 0.00–0.07 samples sintered at 1175 °C. Two phases emerged at this sintering setting, that is, JCPDS#38-1475 for MBO ($Pmnm$, No. 58) and JCPDS#15-0537 for Mg$_2$B$_2$O$_5$ ($P\bar{T}$, No. 2). No peak intensity variation happened with varying $x$. The increasing substitution led to a higher angle movement of peaks for MBO and Mg$_2$B$_2$O$_5$, corresponding to the shrinkage of crystal volume. The relatively smaller ionic radius of Ni$^{2+}$ (0.69 Å) compared with that of Mg$^{2+}$ (0.72 Å) should be responsible for such shrinkage [29]. To obtain the detailed lattice parameters, refinement was done for all raw data, as illustrated in Figs. 1(c) and 2. The fitted result and convergence parameters (Table S1 in the Electronic Supplementary Material (ESM)) were satisfactory, and the fractions of MBO and Mg$_2$B$_2$O$_5$ were almost unchanged (Fig. 2(a)). For the lattice parameters of MBO, $a$, $c$, and volume decreased with increasing $x$ value, and $b$, $\alpha$, $\beta$, and $\gamma$ were almost unchanged. As for Mg$_2$B$_2$O$_5$, a declined trend could be observed in $a$, $b$, $c$, and volume, the variation trend of $\alpha$ was unobvious, and $\beta$ and $\gamma$ increased with the intensified ion substitution. The variation in cell volume was consistent with the conclusion from XRD pattern. According to the W–H plots, the calculated crystallite size ($D$) varies from 58 to 66 nm pointing to the minimal influence of lattice distortion at the substitution of Mg atoms with Ni ones (see Fig. S1 and Table S1 in the ESM).

The microstructure of the 1175 °C sintered MNBO samples is presented in Figs. 3(a)–3(f). The grain of the Ni-clean sample was small, and some pores could be observed obviously. The Ni addition resulted in the expansion of grain size accompanied by the disappearance of pores. Melting grain and boundary emerged with the over addition of nickel, and some trapped pores were generated in the 0.07 sample. The densest microstructure was that of the 0.04 sample. The distribution of element composition was quantified through EDS mapping, which could be observed in Figs. 3(g)–3(n). The measurable elements included oxygen, magnesium, and nickel, and boron was over the accuracy of detection. The distribution of all elements was even, and the mole ratio of grain for the 0.04 sample was obtained through the EDS point (Fig. 4). In consideration of the measurement error of equipment, the mole ratio of oxygen, magnesium, and nickel is consistent with that of MNBO as $x = 0.04$. The EDS result verified the discussion regarding the phase formation.

The density and dielectric properties of 1150–1200 °C sintered MNBO at different frequencies are presented in Figs. 5(a)–5(d). The value of relative density, quality factor, and dielectric constant indicated a para-curve.
Fig. 2  Molar ratio and lattice parameters of the 1175 °C sintered MBO and Mg2B2O5 materials.

trend, and the summit was obtained as $x = 0.04$ sintered at 1175 °C, that is, 97.2% for relative density; 72,600 GHz at 10 GHz, 75,600 GHz at 11.4 GHz, and 92,200 GHz at 15 GHz for $Q \times f$; 7.1 at 10 GHz, 7.01 at 11.4 GHz, and 6.91 at 15 GHz for $\varepsilon_r$. The variation tendency of the relative density is the same as that of microstructure discussed above. $Q \times f$ of all samples at a relatively low frequency was smaller than that at a relatively high frequency, and the dielectric loss increased with increasing frequency. By contrast, $\varepsilon_r$ decreased with increasing frequency. The temperature coefficient of resonant frequency for the 0.04 (1175 °C) sample was $-56.3$ ppm/°C. The lowered intrinsic sintering temperature, caused by crystal distortion, should be the incentive for the increasing stage of density. The worsening density should be attributed to the oversintering. With the unobvious variation in phase ratio, the alteration of dielectric properties of MNBO was dominated by the variation in sample density, which played an extrinsic role. The decreased cell volume also influenced the increased $\varepsilon_r$ to some extent because the theoretical dielectric constant was dominated by the crystal volume and total polarizability of atoms [30]. Figure 5(e) presents the comparison of sintering and dielectric properties of different ceramics, and the materials obtained in this study have excellent dielectric performance [5,7–9,31–44]. Therefore, a moderate nickel substitution could improve the dielectric properties of the MBO ceramic and lower its intrinsic densification temperature.

The Raman spectra were obtained to explore the variation in vibration mode, as depicted in Figs. 6(a) and 6(b). The vibration modes of MBO (Eq. (5)) and Mg2B2O5 (Eq. (6)) materials were obtained using the
Bilbao Crystallographic system and DFT calculation, as shown as follows:

$$\Gamma_{\text{Optic}} = 8A_g(R) + 7A_u(R) + 8B_g(R) + 6B_{1u}(IR) + 7B_{2g}(R) + 10B_{2u}(IR) + 7B_{1g}(R) + 10B_{3u}(IR)$$ (5)

$$\Gamma_{\text{Optic}} = 27A_g(R) + 24A_u(IR)$$ (6)

where R is the abbreviation of the Raman mode, and IR is the abbreviation of the infrared mode. Figure 7(a) is the crystal structure of MBO, and the atomic groups include MgO₆ and BO₃. The peaks near 250 cm⁻¹ (B₂g), 380 cm⁻¹ (A₂g), 410 cm⁻¹ (B₁u), 580 cm⁻¹ (B₁u), and 690 cm⁻¹ (B₂u) are the external modes of MBO materials, and those near 800 cm⁻¹ (B₁u) and 920 cm⁻¹ (B₁u) are the internal modes of MBO materials. Figures 7(b)–7(h) are the symmetry coordinate of the Raman peak mentioned above for MBO. The first five modes are the rotational and translational modes of MgO₆, and the last two modes are the bending and stretching vibration modes of BO₃. As to the peaks of Mg₂B₂O₅, the peak near 370 cm⁻¹ (A₁u) is the external mode, and that on the right side is the internal mode. The related vibration atomic group of Mg₂B₂O₅ is the same as that of MBO. The peak near 920 cm⁻¹ moved to the left...
with increasing $x$, indicating that the lattice distortion was strengthened with increasing substitution degree. The intensity of 920 cm$^{-1}$ peak varied with varying $x$, that is, increasing firstly and decreasing subsequently. Its full width at half maximum (FWHM) was extracted (Fig. 6(c)). The FWHM showed a saddle trend, and the lowest point was 16.75 cm$^{-1}$ at $x = 0.04$. The order degree of a crystal is inverse about FWHM, and a high FWHM corresponds to a low order degree. Accordingly, a moderate substitution amount of Ni$^{2+}$ could ameliorate the order degree of MBO material, and oversubstitution would worsen it [45]. The improved order degree should be another incentive (intrinsic factor) for the amelioration of $Q \times f$. The bond property of boron–oxygen (where oxygen is shared by MgO$_6$ and BO$_3$) before and after nickel substitution is
presented in Figs. 8(a) and 8(b) to explore the variation in the Raman spectrum in detail. L, P, B, A, and E are the abbreviations of length, population, before substitution, after substitution, and experiment, respectively. Two kinds of Mg site were available to be occupied in MBO. The bond length increased and the bond population decreased in BO$_3$ after Mg$_1$ and Mg$_2$ site substitution, which phenomenon is the same as our previous study of LiZnPO$_4$ [26]. The variation trend of bond length from experiment is the same as that from calculation, indicating that the substitution of magnesium with nickel happened in both Mg$_1$ and Mg$_2$ sites. The decreased bond population corresponded to the depletion of covalency, and the increased length of boron–oxygen corresponded to the expansion of BO$_3$. Hence, the variation in the Raman peak near 920 cm$^{-1}$ was the result of the ionisation and expansion of BO$_3$ caused by nickel substitution. The formation energy of substituted MBO and Mg$_2$B$_2$O$_5$ is depicted in Fig. 8(c). The Mg$_2$ site had relatively lower energy compared with the Mg$_1$ site in MBO and Mg$_2$B$_2$O$_5$, indicating that Mg$_2$ had the priority to be occupied. Moreover, the substitution process exhibited the implementation priority in MBO because the formation energy of Mg$_2$B$_2$O$_5$ was generally larger than that of MBO.

The variation in sintering properties for the nickel-substituted MBO was further researched through TG, DSC, and TMA (Figs. 9(a)–9(c)). Four obvious gradations of weight loss are presented in the TG curve. The volatilisation of water was responsible for the first gradation near 150 °C. The continued water volatilisation and the predecomposition of boric acid were responsible
Fig. 9  (a) TG, (b) DSC, (c) TMA, and (d) activation energy of the samples with $x = 0.00, 0.04$, and $0.07$.

for the second gradation near 300 °C. The continued decomposition of boric acid and the preformation of MNBO were the reasons for the third gradation of weight loss. The further weight loss over 500 °C was minimal, which was relevant to the continued phase formation of MNBO and boron volatilisation. The peaks in DSC curve correspond to the weight loss in TG curve. The shift point in TG, DSC, and TMA curves moved to a lower temperature obviously with increasing level of substitution. Besides, the amelioration of sintering properties was quantified using $E_a$ (Fig. 9(d) and Fig. S2 in the ESM). The substitution could lower $E_a$ from 1721 ± 100 to 1457 ± 87 kJ/mol for 4% nickel substitution, and 1304 ± 95 kJ/mol for 7% nickel substitution. The ionised B–O bond in BO$_3$, corresponding to decreasing bond population, was responsible for the variation in activation energy. Hence, the sintering performance of the MBO material could be ameliorated by the moderate substitution of magnesium with nickel, and the intrinsic densification temperature could be lowered from 1350 to 1175 °C.

4 Conclusions

With the support of DFT calculation, the amelioration of sintering and dielectric properties of the MBO ceramic was realised through the substitution of magnesium with nickel, and a two-phase (MBO and Mg$_2$B$_2$O$_5$) material system was obtained. The TE-mode cylindrical cavity method was used to measure the dielectric properties at different frequencies, and the symmetry coordinate of different Raman peaks was elaborated. Nickel substitution (4 mol%) could ionise the B–O bond of BO$_3$, modify the vibration mode, improve the order degree, densify the microstructure, decrease the intrinsic densification temperature, and ameliorate the dielectric properties of the MBO ceramic. The summit values were obtained during 4 mol% nickel substitution and sintered at 1175 °C, that is, 97.2% for relative density, 72,600 GHz (10 GHz), 75,600 GHz (11.4 GHz), and 92,200 GHz (15 GHz) for $Q \times f$, 7.1 (10 GHz), 7.01 (11.4 GHz), and 6.91 (15 GHz) for $\varepsilon_r$, and $-56.3$ ppm/°C for $\tau_f$.

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Electronic Supplementary Material

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