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

Rui PENG^a, Yongcheng LU^a, Qin ZHANG^a, Yuanming LAI^b, Guoliang YU^c,
Xiaohui WU^a, Yuanxun LI^{a,d,*}, Hua SU^{a,*}, Huaiwu ZHANG^a

^aState Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

^bSchool of Information Science and Technology, Chengdu University of Technology, Chengdu 610059, China

^cCollege of Information Engineering, China Jiliang University, Hangzhou 310018, China

^dYangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou 313001, China

Received: March 13, 2021; Revised: June 26, 2021; Accepted: July 6, 2021

© The Author(s) 2021.

Abstract: With the support of density functional theory (DFT) calculation, the amelioration of sintering and dielectric properties of the $\text{Mg}_3\text{B}_2\text{O}_6$ (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 ϵ_r , and -56.3 ppm/°C for τ_f .

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

1 Introduction

Materials with low dielectric constant (ϵ_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 $\text{Mg}_3\text{B}_2\text{O}_6$ (MBO) material has excellent dielectric properties, that is, 7 for ϵ_r , 108,000 GHz for $Q \times f$,

* Corresponding authors.

E-mail: Y. Li, liyuanxun@uestc.edu.cn;

H. Su, uestcsh77@163.com

−69 ppm/°C for τ_f , and 97% for relative density sintered at 1350 °C [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 $(\text{Mg}_{1-x}\text{Ni}_x)_3\text{B}_2\text{O}_6$ (MNBO) ceramics in this experiment (x varied from 0.00 to 0.07).

2 Experimental

With 10% B_2O_3 addition for compensation, MgO , NiO , and B_2O_3 powders were premilled for 12 h. The precursor was from Chron Chemicals Co., Ltd., China. The presintering temperature was 1100 °C 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 °C. The crystal phase was determined by X-ray diffraction (XRD, DX-2700, Cu K α 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_T) and 20 °C (f_0) [24].

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

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

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

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 (λ , 1.5406 Å) and factor of shape (K , 0.9) [27].

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

where β_T is the full width at half maximum of XRD data, θ is the diffraction angle, and ε 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), 5.0×10^{-6} eV/atom for system energy, and 0.005 Å for displacement (max). In order to keep the same concentration of the substitution, 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_{Do}) and unsubstituted (E_{Undo}) systems [28]:

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

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 ($Pn\bar{m}n$, No. 58) and JCPDS#15-0537 for $\text{Mg}_2\text{B}_2\text{O}_5$ ($P\bar{1}$, No. 2). No peak intensity variation happened with varying x . The increasing substitution led to a higher angle movement of peaks for MBO and $\text{Mg}_2\text{B}_2\text{O}_5$, 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 $\text{Mg}_2\text{B}_2\text{O}_5$ were almost unchanged (Fig. 2(a)). For the lattice parameters of MBO, a , c , and volume decreased with

increasing x value, and b , α , β , and γ were almost unchanged. As for $\text{Mg}_2\text{B}_2\text{O}_5$, a declined trend could be observed in a , b , c , and volume, the variation trend of α was unobvious, and β and γ 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. 1 (a) XRD patterns of the MNBO ($x = 0.00$ – 0.07) materials sintered at 1175 °C, (b) enlarged peak patterns, and (c) fitted result of the $x = 0.04$ sample sintered at 1175 °C ($R_{\text{wp}} = 7.71\%$, $R_{\text{exp}} = 5.88\%$, and $\chi^2 = 1.71$).

Fig. 2 Molar ratio and lattice parameters of the 1175 °C sintered MBO and $\text{Mg}_2\text{B}_2\text{O}_5$ 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 ε_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, ε_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 ε_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 $\text{Mg}_2\text{B}_2\text{O}_5$ (Eq. (6)) materials were obtained using the

Fig. 3 SEM images of (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.04$, (e) $x = 0.05$, and (f) $x = 0.07$ MNBO materials sintered at 1175 °C; EDS mapping images of (g–j) $x = 0.03$ and (k–n) $x = 0.04$ samples sintered at 1175 °C.

Fig. 4 EDS point result of the $x = 0.04$ sample sintered at 1175 °C.

Bilbao Crystallographic system and DFT calculation, as shown as follows:

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

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

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 MgO_6 and BO_3 . The peaks near 250 cm^{-1} (B_{2u}), 380 cm^{-1} (A_g), 410 cm^{-1} (B_{2u}), 580 cm^{-1} (B_{1u}), and

690 cm^{-1} (B_{3u}) are the external modes of MBO materials, and those near 800 cm^{-1} (B_{1g}) and 920 cm^{-1} (B_{3u}) 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 MgO_6 , and the last two modes are the bending and stretching vibration modes of BO_3 . As to the peaks of $\text{Mg}_2\text{B}_2\text{O}_5$, the peak near 370 cm^{-1} (A_u) is the external mode, and that on the right side is the internal mode. The related vibration atomic group of $\text{Mg}_2\text{B}_2\text{O}_5$ is the same as that of MBO. The peak near 920 cm^{-1} moved to the left

Fig. 5 (a) Relative density and (b–d) dielectric properties of 1150–1200 °C sintered MNBO ($x = 0.00–0.07$) materials at different frequencies, and (e) summary of sintering and dielectric properties of various ceramics.

Fig. 6 (a) Raman spectrum of 1175 °C sintered MNBO ($x = 0.00–0.07$) materials, (b) enlarged peak spectrum, and (c) FWHM of the peak near 920 cm⁻¹.

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 Ni²⁺ 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 MgO₆ and BO₃) before and after nickel substitution is

Fig. 7 (a) Cell of MBO material; symmetry coordinate of the Raman peak near (b) 250 cm^{-1} , (c) 380 cm^{-1} , (d) 410 cm^{-1} , (e) 580 cm^{-1} , (f) 690 cm^{-1} , (g) 800 cm^{-1} , and (h) 920 cm^{-1} .

Fig. 8 (a, b) Bond length and bond population of boron-oxygen before and after nickel substitution, and (c) formation energy of nickel substituted MBO and $\text{Mg}_2\text{B}_2\text{O}_5$.

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 Mg1 and Mg2 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 Mg1 and Mg2 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 $\text{Mg}_2\text{B}_2\text{O}_5$ is depicted in Fig. 8(c). The Mg2 site had relatively lower energy compared with the Mg1 site in MBO and $\text{Mg}_2\text{B}_2\text{O}_5$, indicating that Mg2 had the priority to be occupied. Moreover, the substitution process exhibited the implementation priority in MBO because the formation energy of $\text{Mg}_2\text{B}_2\text{O}_5$ 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 $^{\circ}\text{C}$. 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 $\text{Mg}_2\text{B}_2\text{O}_5$) 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 ϵ_r , and -56.3 ppm/°C for τ_f .

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 61771104 and 62071106), the Jiangxi Innovative Talent Program, and the Sichuan Science and Technology Program (Grant No. 2021JDTD0026).

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40145-021-0515-9>.

References

- [1] Zhou D, Pang LX, Wang DW, *et al.* High quality factor, ultralow sintering temperature $\text{Li}_6\text{B}_4\text{O}_9$ microwave dielectric ceramics with ultralow density for antenna substrates. *ACS Sustain Chem Eng* 2018, **6**: 11138–11143.
- [2] Lei W, Zou ZY, Chen ZH, *et al.* Controllable τ_f value of Barium silicate microwave dielectric ceramics with different Ba/Si ratios. *J Am Ceram Soc* 2018, **101**: 25–30.
- [3] Lai YM, Tang XL, Huang X, *et al.* Phase composition, crystal structure and microwave dielectric properties of $\text{Mg}_{2-x}\text{Cu}_x\text{SiO}_4$ ceramics. *J Eur Ceram Soc* 2018, **38**: 1508–1516.
- [4] Peng R, Li YX, Su H, *et al.* Experiment and calculation: The $\text{Li}(\text{Zn}, \text{Mn})\text{PO}_4$ solid solution ceramics with low dielectric constant, high quality factor, and low densification temperature. *J Alloys Compd* 2020, **842**: 155709.
- [5] Peng R, Li YX, Lu YC, *et al.* High-performance microwave dielectric composite ceramics sintered at low temperature without sintering-aids. *J Alloys Compd* 2020, **831**: 154878.
- [6] Lai YM, Su H, Wang G, *et al.* Improved microwave dielectric properties of $\text{CaMgSi}_2\text{O}_6$ ceramics through CuO doping. *J Alloys Compd* 2019, **772**: 40–48.
- [7] Došler U, Kržmanc MM, Jančar B, *et al.* A high-Q microwave dielectric material based on $\text{Mg}_3\text{B}_2\text{O}_6$. *J Am Ceram Soc* 2010, **93**: 3788–3792.
- [8] Peng R, Li YX, Yu GL, *et al.* Effect of Co^{2+} substitution on the microwave dielectric properties of LiZnPO_4 ceramics. *J Electron Mater* 2018, **47**: 7281–7287.
- [9] Peng R, Lu YC, Tao ZH, *et al.* Improved microwave dielectric properties and sintering behavior of LiZnPO_4 ceramic by Ni^{2+} -ion doping based on first-principle calculation and experiment. *Ceram Int* 2020, **46**: 11021–11032.
- [10] Chen GH, Hou MZ, Bao Y, *et al.* Silver co-firable $\text{Li}_2\text{ZnTi}_3\text{O}_8$ microwave dielectric ceramics with LZB glass additive and TiO_2 dopant. *Int J Appl Ceram Technol* 2013, **10**: 492–501.
- [11] Ma JL, Yang T, Fu ZF, *et al.* Low-fired Mg_2SiO_4 -based dielectric ceramics with temperature stable for LTCC applications. *J Alloys Compd* 2017, **695**: 3198–3201.
- [12] Zhang J, Yue ZX, Luo Y, *et al.* Novel low-firing forsterite-based microwave dielectric for LTCC applications. *J Am Ceram Soc* 2016, **99**: 1122–1124.
- [13] Joseph T, Sebastian MT, Jantunen H, *et al.* Tape casting and dielectric properties of $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ -based ceramic-glass composite for low-temperature co-fired ceramics applications. *Int J Appl Ceram Technol* 2011, **8**: 854–864.
- [14] Vanderbilt D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys Rev B* 1990, **41**: 7892–7895.
- [15] Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Phys Rev B* 1976, **13**: 5188–5192.
- [16] Kohn W, Sham LJ. Self-consistent equations including exchange and correlation effects. *Phys Rev* 1965, **140**: A1133–A1138.
- [17] Hohenberg P, Kohn W. Inhomogeneous electron gas. *Phys Rev* 1964, **136**: B864–B871.
- [18] Perdew JP, Ruzsinszky A, Csonka GI, *et al.* Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys Rev Lett* 2008, **100**: 136406.
- [19] Agbaoye RO, Akinlami JO, Afolabi TA, *et al.* Unraveling the stable phase, high absorption coefficient, optical and mechanical properties of hybrid perovskite $\text{CH}_3\text{NH}_3\text{Pb}_x\text{Mg}_{1-x}\text{I}_3$: Density functional approach. *J Inorg Organomet Polym Mater* 2020, **30**: 299–309.
- [20] Clark SJ, Segall MD, Pickard CJ, *et al.* First principles methods using CASTEP. *Zeitschrift Für Kristallographie Cryst Mater* 2005, **220**: 567–570.
- [21] Hakki BW, Coleman PD. A dielectric resonator method of measuring inductive capacities in the millimeter range. *IRE Trans Microw Theory Tech* 1960, **8**: 402–410.
- [22] Sebastian MT, Jantunen H. Low loss dielectric materials for LTCC applications: A review. *Int Mater Rev* 2008, **53**: 57–90.
- [23] Blackburn J. Solving the double eigenvalue problem: A study of mode matching in arbitrary-layer dielectric resonators. *IEE Proc, Microw Antennas Propag* 2006, **153**: 447–455.
- [24] Peng R, Su H, An D, *et al.* The sintering and dielectric properties modification of $\text{Li}_2\text{MgSiO}_4$ ceramic with Ni^{2+} -ion doping based on calculation and experiment. *J Mater Res Technol* 2020, **9**: 1344–1356.
- [25] Valant M, Suvorov D, Pullar RC, *et al.* A mechanism for low-temperature sintering. *J Eur Ceram Soc* 2006, **26**: 2777–2783.
- [26] Peng R, Li YX, Su H, *et al.* The modification of sintering and microwave dielectric properties of Mn^{2+} doped LiZnPO_4 ceramic. *J Mater Res Technol* 2020, **9**: 4994–5006.
- [27] Zhang Q, Tang XL, Zhong MF, *et al.* Bond characteristics and microwave dielectric properties of high-Q materials in Li-doped $\text{Zn}_3\text{B}_2\text{O}_6$ systems. *J Am Ceram Soc* 2021, **104**: 2102–2115.
- [28] Park SG, Magyari-Köpe B, Nishi Y. Electronic correlation effects in reduced rutile TiO_2 within the LDA + U method. *Phys Rev B* 2010, **82**: 115109.
- [29] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst Sect A* 1976, **32**: 751–767.
- [30] Kim DW, Kim IT, Park B, *et al.* Microwave dielectric properties of $(1-x)\text{Cu}_3\text{Nb}_2\text{O}_8-x\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics. *J*

- Mater Res* 2001, **16**: 1465–1470.
- [31] Ohashi M, Ogawa H, Kan A, *et al.* Microwave dielectric properties of low-temperature sintered $\text{Li}_3\text{AlB}_2\text{O}_6$ ceramic. *J Eur Ceram Soc* 2005, **25**: 2877–2881.
- [32] Kim MH, Lim JB, Kim JC, *et al.* Synthesis of $\text{BaCu}(\text{B}_2\text{O}_5)$ ceramics and their effect on the sintering temperature and microwave dielectric properties of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics. *J Am Ceram Soc* 2006, **89**: 3124–3128.
- [33] Wu XG, Wang H, Chen YH, *et al.* Synthesis and microwave dielectric properties of $\text{Zn}_3\text{B}_2\text{O}_6$ ceramics for substrate application. *J Am Ceram Soc* 2012, **95**: 1793–1795.
- [34] Zhou DX, Sun F, Hu YX, *et al.* Low-temperature sintering and microwave dielectric properties of $\text{Mg}_3\text{B}_2\text{O}_6$ –LMZBS composites. *J Mater Sci: Mater Electron* 2012, **23**: 981–989.
- [35] Dou G, Guo M, Li YX, *et al.* The effect of LMBS glass on the microwave dielectric properties of the $\text{Mg}_3\text{B}_2\text{O}_6$ for LTCC. *J Mater Sci: Mater Electron* 2015, **26**: 4207–4211.
- [36] Došler U, Kržmanc MM, Suvorov D. The synthesis and microwave dielectric properties of $\text{Mg}_3\text{B}_2\text{O}_6$ and $\text{Mg}_2\text{B}_2\text{O}_5$ ceramics. *J Eur Ceram Soc* 2010, **30**: 413–418.
- [37] Chen XY, Zhang WJ, Zalinska B, *et al.* Low sintering temperature microwave dielectric ceramics and composites based on Bi_2O_3 – B_2O_3 . *J Am Ceram Soc* 2012, **95**: 3207–3213.
- [38] Peng R, Li YX, Su H, *et al.* Effect of cobalt-doping on the dielectric properties and densification temperature of $\text{Li}_2\text{MgSiO}_4$ ceramic: Calculation and experiment. *J Alloys Compd* 2020, **827**: 154162.
- [39] Thomas D, Sebastian MT. Temperature-compensated LiMgPO_4 : A new glass-free low-temperature cofired ceramic. *J Am Ceram Soc* 2010, **93**: 3828–3831.
- [40] Cheng ZF, Hu X, Li Y, *et al.* Fabrication and microwave dielectric properties of Mg_2SiO_4 – LiMgPO_4 – TiO_2 composite ceramics. *J Am Ceram Soc* 2016, **99**: 2688–2692.
- [41] Dou G, Zhou DX, Gong SP, *et al.* Low temperature sintering and microwave dielectric properties of $\text{Li}_2\text{ZnSiO}_4$ ceramics with ZB glass. *J Mater Sci: Mater Electron* 2013, **24**: 1601–1607.
- [42] Sasikala TS, Pavithran C, Sebastian MT. Effect of lithium magnesium zinc borosilicate glass addition on densification temperature and dielectric properties of Mg_2SiO_4 ceramics. *J Mater Sci: Mater Electron* 2010, **21**: 141–144.
- [43] Umemura R, Ogawa H, Ohsato H, *et al.* Microwave dielectric properties of low-temperature sintered $\text{Mg}_3(\text{VO}_4)_2$ ceramic. *J Eur Ceram Soc* 2005, **25**: 2865–2870.
- [44] Guo M, Li YX, Dou G, *et al.* A new microwave dielectric ceramics for LTCC applications: $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3$ ceramics. *J Mater Sci: Mater Electron* 2014, **25**: 3712–3715.
- [45] Zhou D, Pang LX, Wang H, *et al.* Phase transition, Raman spectra, infrared spectra, band gap and microwave dielectric properties of low temperature firing $(\text{Na}_{0.5x}\text{Bi}_{1-0.5x})(\text{Mo}_x\text{V}_{1-x})\text{O}_4$ solid solution ceramics with scheelite structures. *J Mater Chem* 2011, **21**: 18412.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.