Pressure Effect of the Mechanical, Electronics and Thermodynamic Properties of Mg-B Compounds: A First-Principles Investigation

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Pressure effect of the mechanical, electronics and thermodynamic properties of Mg-B compounds: A first-principles investigation

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Abstract: First principle calculations were performed to investigate the structural, mechanical, electronic properties, and thermodynamic properties of three binary Mg-B compounds under pressure, by using the first principle method. The results implied that the structural parameters and the mechanical properties of the Mg-B compounds without pressure are well matched with the obtainable theoretically simulated values and experimental data. The obtained pressure–volume and energy–volume revealed that the three Mg-B compounds were mechanically stable, and the volume variation decreases with an increase in the boron content. The shear and volume deformation resistance indicated that the elastic constant C_{ij} and bulk modulus B increased when the pressure increased up to 40 GPa, and that MgB_7 had the strongest capacity to resist shear and volume deformation at zero pressure, which indicated the highest hardness. Meanwhile, MgB_4 exhibited a ductility transformation behaviour at 30 GPa, and MgB_2 and MgB_7 displayed a brittle nature under all the considered pressure conditions. The anisotropy of the three Mg-B compounds under pressure were arranged as follows: $MgB_4 > MgB_2 > MgB_7$. Moreover, the total density of states (TDOS) varied slightly and decreased with an increase in the pressure. The Debye temperature Θ_D of the Mg-B compounds gradually increased with an increase in the pressure and the boron content. The temperature and pressure dependence of the heat capacity and the linear thermal expansion coefficient α were both obtained on the basis of Debye model under increased pressure from 0 GPa to 40 GPa and increased temperatures. This paper brings a convenient understanding of the magnesium-boron alloys.

Keywords: First principle; Mg-B compounds; Anisotropy; Mechanical and electronic properties; Thermodynamic properties

1. Introduction

Magnesium boride alloys (MgB_2 , MgB_4 , and MgB_7) as desirable compounds play an important role in many fields due to their remarkable conductivity, excellent ductility, and high hardness [1–3]. Usually, boron-rich magnesium alloys have excellent material characteristics such as mechanical properties and stability [4–5]. Moreover, MgB_2 has been widely introduced into magnesium alloys for reinforcement and grain refinement [6–7], because of the chemical substitution and the crystal growth of substituted MgB_2 [8–11]. Therefore, increasing attention has been paid to the investigation of magnesium boride alloys in many academic fields.

Superconductors of magnesium diboride were reported first by Akimitsu [12] in 2001. Since then, magnesium boride systems have been extensively studied through theoretical simulations and experimental analyses [13–15]. The intermediate phases of Mg-B alloys, which include MgB_2 , MgB_4 , and MgB_7 , were found through the continued investigation of the Mg-B binary phase diagram using the CALPHAD method based on experimental data [16–17]. Furthermore, Brutti *et al.* [18] studied the vaporisation behaviour of MgB_2 and MgB_4 by the Knudsen effusion-mass spectrometry

technique. Wenzel *et al.* [19] predicted the crystal system and the lattice parameters of Mg-B compounds by using the electron probe micro analysis (EPMA) and X-ray diffraction (XRD) analytical approaches. Moreover, the lattice parameters of Mg-B compounds were calculated using the first principle based on the density functional theory (DFT) by Alapati *et al.* [20]. The elastic constants, mechanical properties, bond structure, and electronic properties of MgB₇ at 0 GPa were investigated by Ozisik [21]. Furthermore, the heat capacity and the thermal expansion of MgB₂ at 0 GPa was predicted via DFT calculations by Saengdeejing [22]. The thermodynamic properties of Mg-B compounds and Al-Mg-B films were also investigated by using *ab initio* calculations and CALPHAD methods [23–24]. Nevertheless, the structural stability of Mg-B compounds under thermodynamic conditions have not been reported as yet. Moreover, the crystal structure, electronic properties, thermodynamic properties, and mechanical properties of Mg-B compounds at different pressure and temperature have not been studied.

Assuredly, the above mentioned experimental studies have evidenced that the properties of Mg-B compounds can be calculated using DFT for establishing the trends of stability through the cohesive energies and the trends of charge transfers onto boron. Therefore, in the current article, the structural, mechanism, electronic, and anisotropic properties of MgB₂, MgB₄, and MgB₇ under pressure from 0 to 40 GPa were investigated by using the VASP (Vienna Ab-initio Simulation Package) codes. The linear thermal expansion coefficient, Debye temperature, heat capacity, and other thermodynamic properties were entirely studied theoretically for determining the pressure and temperature dependence of Mg-B compounds.

2. Computational methodology

In this study, all the calculated results were obtained using the first-principle method through the Vienna *ab initio* simulation package (VASP) [25] codes. PBE (Perdew-Burke-Ernzerhof) [27] in GGA (generalized gradient approximation) was performed to expound the exchange-correction function [26] and calculate the self-consistent electronic density. All the calculations in the current study considered Mg 3p⁶3s² and B 2s²2p¹ as the valence electrons. To obtain an accurate calculated results, the cut-off energy E_{cut} was set to 500 eV. Moreover, the Brillouin-zone sampling mesh for the Monkhorst-Pack [28] k-point for MgB₂, MgB₄, and MgB₇ was set to $19 \times 19 \times 14$, $9 \times 11 \times 7$, and $8 \times 8 \times 8$, respectively, due to the k-mesh was forced to be centred on the gamma point. Besides, the σ value of the first-order Methfessel-Paxton smearing was set to 0.2 eV, the convergence threshold of the self-consistent field was set to 1.0×10^{-5} eV/atom. Generally, the band gap calculated by GGA is lower than that of experimental results, but the relative value is still very accurate. Thus, GGA as an effective approximation method is used to calculated the electronic properties and band structure.

3. Results and discussions

3.1. Structural stability

The optimised crystal texture of Mg-B compounds is shown in Figure 1, and the corresponding calculated crystal parameters of the Mg-B compounds at 0 GPa are tabulated in Table 1 [29–31]. As listed in Table 1, the simulated crystal structure parameters considered in this study matched well with the reported literature data from the experimental and theoretical calculations, which verified the reasonability of the Mg-B compound models.

Figure 1. Optimised crystal structures of Mg-B compounds: (a) MgB₂; (b) MgB₄; (c) MgB₇.

Table 1. The simulated structure parameter of Mg-B compounds contained lattice constant (Å), bulk modulus B_0 , and its derivative B'_0 .

Phase	Compositi on (at% B)	Magnesium site	Space group	Unit cell lattice parameter (Å)			B_0 (GPa)	B'_0	reference
				a	b	c			
MgB ₂	66.7	1a(0, 0, 0)	P6/mm m	3.07	3.07	3.53	151.7	3.54	This work
				3.08	3.08	3.52	157.0	3.50	cal[29-30]
MgB ₄	80	4c(0.25, 0.546, 0.362)	Pnma	5.49	4.4	7.42	158.3	3.10	This work
				5.45	4.43	7.47			cal[31]
MgB ₇	87.5	4c(0, 0.5, 0)	Imma	10.47	5.97	8.11	198.2	3.56	This work
				10.48	5.97	8.12	206.5		cal[21]

The energy–volume $E(V)$ relation curves at zero absolute temperature were obtained using the first-principle method, as shown in Figure 2. All the energy–volume data were fitted to the Birch-Murnaghan model as follows [32]:

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (1)$$

where B_0 is the bulk modulus, B'_0 is the first pressure derivative of the bulk modulus, and V_0 is the equilibrium volume.

$$B_0 = -V \left(\frac{dP}{dV} \right)_{P=0} = V_0 \left(\frac{d^2E(V)}{d^2V} \right)_{V_0} \quad B'_0 = - \left(\frac{dB}{dP} \right)_{P=0} \quad (2)$$

The functional pressure–volume $P(V)$ data were obtained after the fitting of the $E(V)$ curves to the Birch-Murnaghan model; therefore, the $P(V)$ curves displayed the relationship between the structural change and the pressure increase with a step of 10 GPa, as shown in Figure 3. Moreover, the $P(V)$ curves were calculated by using the equilibrium thermodynamic relation as follows [33]:

$$P(V) = \frac{3}{2} B_0 \left(\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right) \left(1 + \frac{3}{4} (B'_0 - 4) \left(\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right) \right) \quad (3)$$

Figure 2. Variation between energy and volume of Mg-B compounds.

Figure 3 . Volume ratio and pressure relation of Mg-B compounds with an interval of 10GPa.

The volume ratio V/V_0 of the three Mg-B compounds decreased with an increase in the pressure, as shown in Figure 3, which was in agreement with the general rules. Moreover, the value of V/V_0 of the Mg-B compounds under the same pressure from 10 GPa to 40 GPa ranged in the following order: $MgB_7 < MgB_4 < MgB_2$. That is, MgB_7 was harder to compress under the same applied pressure, as it had the lowest value of V/V_0 among the three Mg-B compounds; furthermore, MgB_2 was the most sensitive to the pressure–volume relationship.

3.2. Mechanical properties

The elastic constants (C_{ij}) of the crystal as an indispensable parameter played an important role in characterising the mechanical behaviours, because it contains a significant mechanical information under various pressures. There were nine (C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} , and C_{66}) elastic constants for the orthorhombic crystals of MgB_4 and MgB_7 , and six elastic constants (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66}) for the hexagonal crystal of MgB_2 . Table 2 shown the simulated elastic constants and other elastic parameters of the Mg-B compounds; they were in agreement with the reference data. Moreover, the mechanical stability criterion of the hexagonal and orthorhombic structures of the Mg-B compounds is listed below:

Table 2. Elastic constants C_{ij} (GPa) and elastic moduli B, G, and E (GPa) of Mg-B compounds at 0 GPa along with the reported data.

Phase	Species	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}	B	G	E
MgB_2	Present	419.8		253.6	53.2	41.5		184.3	64.6		151.7	116.2	276.1
	Cal[30]	432.0		254.3	61.0	41.0		185.1	71.3		157.0	116.9	277.6
MgB_4	Present	231.4	289.6	493.5	22.8	162.9	41.3	96.8	108.6	173.5	158.3	112.4	272.7
MgB_7	Present	536.5	530.6	500.3	60.8	42.1	45.1	194.3	221.3	248.7	205.8	225.9	496.2
	Cal[21]	539	527.7	496.9	61.1	42.4	44.8	195.1	220.6	250.1	206.5	226.6	497.7

For the hexagonal (MgB_2) crystal [34]:

$$C_{44} > 0, C_{11} > |C_{12}|, (C_{11} + 2C_{12})C_{33} - 2C_{13}^2 > 0 \quad (4)$$

For the orthorhombic (MgB_4 and MgB_7) crystal [35]:

$$C_{ii} > 0, i = 1 \sim 6, C_{11} + C_{22} > 2C_{12}, C_{11} + C_{33} > 2C_{13}$$

$$C_{22} + C_{33} > 2C_{23}, C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0 \quad (5)$$

The influence of the applied pressure from 0 GPa to 40 GPa on the calculated elastic constants for the Mg-B compounds is displayed in Figure 4. As shown in Figure 4, the entries in the elastic tensor C_{ij} increased with an increase in pressure in the range from 0 to 40 GPa, and when the pressure reached to 40 GPa, all the elastic constants are well matched with the criterion of mechanical stability. Moreover, the deformation resistance of MgB_2 and MgB_7 is highest in the x-axis direction than in that of the other axes; this might be attributed to the fact that the largest elastic constant of C_{11} was observed for MgB_2 and MgB_7 . Similarly, the C_{22} of MgB_4 with the largest elastic constant indicated that the y-axis had the highest deformation resistance for MgB_4 . According to the existing literature [36], the values of C_{44} , C_{55} , and C_{66} are always used to represent the ability of compounds to resist shear deformation. Therefore, MgB_7 had higher values of C_{44} and C_{66} than the other two Mg-B compounds, according to Figure 4, which implied that MgB_7 had the highest resistance ability for the shear deformation.

Figure 4. Pressure dependence of the elastic constants of the three Mg-B compounds.

Generally, the elastic modulus contained B, G, and E could be subsequently obtained by using the VRH (Voigt-Reuss-Hill) approximation [37], after the elastic constants C_{ij} were obtained. The calculation equations are given by [38–39]:

$$B_H = \frac{1}{2}(B_V + B_R) \quad G_H = \frac{1}{2}(G_V + G_R) \quad E = \frac{9BG}{3B + G} \quad (6)$$

For the hexagonal crystal:

$$B_V = \frac{2}{9} \left(C_{11} + C_{12} + 2C_{13} + \frac{1}{2}C_{33} \right) \quad (7)$$

$$G_V = \frac{1}{15} (2C_{11} + C_{33} - C_{12} - 2C_{13}) + \frac{1}{5} (2C_{44} + C_{66}) \quad (8)$$

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} - 4C_{13} + 2C_{33}} \quad (9)$$

$$G_R = \frac{5C^2 C_{44} C_{66}}{2[3B_V C_{44} C_{66} + C^2(C_{44} + C_{66})]} \quad (10)$$

$$C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2 \quad (11)$$

For an orthorhombic crystal:

$$B_V = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] \quad (12)$$

$$G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})] \quad (13)$$

$$B_R = \Delta/[C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12}(2C_{23} - C_{12}) + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})] \quad (14)$$

$$G_R = 15\{4[C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12} - C_{12}^2(C_{23} + C_{12}) - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})]/\Delta + 3\left(\frac{1}{C_{44}} + \frac{1}{C_{55}} + \frac{1}{C_{66}}\right)\} \quad (15)$$

$$\Delta = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{22} - C_{12}^2) \quad (16)$$

As displayed in Figure 5, the elastic moduli consisting of bulk modulus B, shear modulus G, and Young's modulus E increased linearly with an increase in the pressure, which indicated that the resistance to the volume deformation increased. From the reports, we inferred that the higher the bulk modulus was, the better was the resistance to deformation [40]. Simultaneously, we found that MgB₇ had a stronger capacity to resist volume deformation and had higher hardness, as it had the highest values of the elastic moduli than the others at a constant pressure. From Figure 5, we inferred that the volume deformation resistance ability under a pressure from 0 GPa to 30 GPa deferred to the following increased order: MgB₂ < MgB₄ < MgB₇. Nevertheless, the ability resist to the volume change of MgB₂ was stronger than others under pressures of 30–40 GPa, and its G and E were larger than MgB₄'s. Therefore, it would be inaccurate to predict the hardness of MgB₂ and MgB₄.

Figure 5. Elastic modulus (B, G, and E) of Mg-B compounds various from different pressure.

In general, the B/G ratio and Poisson's ratio ν can be used to explain the ductility and the brittleness of Mg-B compounds [41–42]. Figure 6 presents the relation between the B/G ratio and

Poisson's ratio of Mg-B compounds under changed pressure. Poisson's ratio ν can be calculated as follows:

$$\nu = \frac{3B - 2G}{6B + 2G} \quad (17)$$

The B/G ratio and ν were proposed to describe the brittle or ductile of materials, when the values were 1.75 and 0.26, respectively. As shown in Figure 6, the Poisson's ratio ν and B/G ratio of MgB_4 were 0.267 and 1.80 at 30 GPa and 0.277 and 1.91 at 40 GPa, respectively. Thus, MgB_4 showed ductile behaviour under pressures of 30–40 GPa, but brittle behaviour at 0–30 GPa, illustrating that the ductile transition for MgB_4 occurred when the pressure increased to 30 GPa. Nevertheless, MgB_2 and MgB_7 displayed a brittle nature, and the brittleness of Mg-B compounds could be ranked in the following order: $\text{MgB}_4 < \text{MgB}_2 < \text{MgB}_7$. Moreover, all the B/G ratios and ν values increased with an increase in the pressure, indicating that the ductility could be improved by increasing the applied pressure on the Mg-B compounds.

Figure 6. Pressures dependence of the B/G ratio and Poisson's ratio ν .

The hardness H is an important parameter to measure the structure and mechanical properties, which can be calculated by using the following semi-empirical law [43]:

$$H = \frac{(1 - 2\nu)E}{6(1 + \nu)} = \frac{G * E}{9B} \quad (18)$$

Figure 7. Variation of micro-hardness at various pressures.

As shown in Figure 7, the hardness of Mg-B compounds increased with an increase in the external pressure, and the values of hardness could be rowed as the following order: $\text{MgB}_7 > \text{MgB}_2 > \text{MgB}_4$, which implied that MgB_7 had the highest hardness; this finding matched well with the above mentioned results. On the basis of a comparison with Figure 5, we can summarised that the effects of G and E on the hardness was greater than B.

Elastic anisotropy plays an important role in crack behaviour and phase transformations, and its formula is defined as follows [44]:

$$A^U = 5 \frac{G_v}{G_R} + \frac{B_v}{B_R} - 6 \quad (19)$$

As listed in Table 3, all the predicted values of A_U were greater than zero, which implied that all the three Mg-B compounds were anisotropic materials. Moreover, the values of A_U of MgB_4 increased with an increase in the applied pressure, indicating that the anisotropy of MgB_4 was enhanced by the increase in the applied pressure. Moreover, the elastic anisotropy of MgB_4 was more sensitive to pressure according to the increase in the values of A_U , and the anisotropy from low to high could be ranked in the following order: $\text{MgB}_7 < \text{MgB}_2 < \text{MgB}_4$.

Table 3. Universal anisotropy A_U of Mg-B binary compounds at external pressure.

Universal anisotropy	Pressure (GPa)	MgB_2	MgB_4	MgB_7
A^U (GPa)	0	1.231	1.865	0.153
	10	0.910	1.987	0.131
	20	0.690	2.151	0.118
	30	0.466	2.236	0.108
	40	0.393	2.362	0.104

3.3. Electronic properties and band structure

To determine the effects of pressure on the mechanical properties and gain in-depth knowledge of the electronic structure of Mg-B compounds, the partial density of states (PDOS) and the total density of states (TDOS) under various pressures are shown in Figure 8. Figures 8(a), 8(b), and 8(c) show that the MgB_2 presented many peak point near the Fermi level, this indicated that MgB_2 exhibited its special electrical conductivity, but the Fermi level of MgB_4 and MgB_7 are both in the range of zero DOS value, which implied that MgB_4 and MgB_7 may present semiconductor or insulator characteristics. Moreover, the primary bond peaks near the Fermi level were mainly occupied by the B 2p states and Mg 3p states for MgB_2 , MgB_4 , and MgB_7 . It can be seen from the Figure 8, the DOS values of MgB_4 and MgB_7 at the Fermi level are all above 0, which implies that both of MgB_4 and MgB_7 also present metallic properties. However, for the MgB_7 , the valence band from 2.0 to 5.0 eV, Mg-p band contributes less than the Mg-s band near the Fermi level, The s-p hybridization between the B and Mg atoms forms covalent bonding for MgB_7 . Figures 8(d), 8(e), and 8(f) only depict the TDOS of the Mg-B compounds at 0 GPa, 20 GPa, and 40 GPa, to demonstrate the regularity of TDOS for Mg-B compounds under various pressures. They show that there was a slight decrease in TDOS with an increase in the external pressure, which indicated that there was no structural phase transformation and small interaction potentials changed because of the decrease in the atomic distance under pressure. These figures also display the structural stability and the various electronic characteristics of Mg-B compounds under applied pressure.

Figure 8. Density of states of Mg-B compounds, (a), (b), and (c) are partial density of states for MgB₂, MgB₄, and MgB₇, respectively; (d), (e), and (f) are total density of states under various pressures for MgB₂, MgB₄, and MgB₇, respectively.

3.4. Thermodynamic properties

The quasi-harmonic Debye model of the phonon density of states was implemented in this part of the study to investigate the thermodynamic behaviours of the Mg-B compounds under pressure, namely the heat capacity C_v , C_p , the linear thermal expansion coefficient, and the Debye temperature Θ_D of the Mg-B compounds. The above-obtained $E(V)$ curves, as important input data for numerical minimisation programs in this model, were used to obtain more thermodynamical information of the Mg-B compounds [45–46]. Moreover, the vibrational thermodynamic properties were obtained at a designated temperature in the quasi-harmonic Debye model; this might be attributed to the consideration of the vibrational contribution for the internal energy. To improve the calculated precision of the thermodynamic behaviours, the 21 volume points from 0.90a to 1.10a of the calculated energy–volume were implied.

The Debye temperature of the Mg-B compounds was calculated from the average sound velocity by using the following formula [47]:

$$\Theta D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m$$

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad v_s = \sqrt{\frac{G}{\rho}} \quad v_l = \sqrt{\frac{3B+4G}{3\rho}} \quad (20)$$

where v_m , v_s , and v_l represent the average wave velocity and the shear and longitudinal sound velocities, respectively; h is Planck's constant; k_B is Boltzmann's constant; n is the total number of atoms; N_A is Avogadro's number; ρ is the density; and M is the molecular weight. As shown in Figure 9, the ΘD of the Mg-B compounds increased with an increase in the pressure and remained almost constant from 0 to 200 K but linearly decreased after 200 K. Simultaneously, the ΘD of the Mg-B compounds from low to high could be rowed as the following order: $\text{MgB}_2 < \text{MgB}_4 < \text{MgB}_7$, when all the compounds were under the same temperature and pressure conditions.

Figure 9. Debye temperature of Mg-B compounds under various pressure and temperature.

Figure 10 shows the temperature and pressure dependence of the linear thermal expansion coefficient α of the Mg-B compounds. The thermal expansion coefficient is defined as $\alpha = \frac{1}{V} \frac{\partial V}{\partial T}$, and the thermal expansion coefficient α increased with an increase in the pressure and the temperature. Although α was linear with T^3 in the range from 0 to 300 K, α presented a gradual growth rate and changed gently when the temperature exceeded 300 K, which implied that the main thermal expansion of the Mg-B compounds occurred in the low-temperature region. In addition, α presented a decreasing tendency when the pressure increased to 40 GPa at a constant temperature. Meanwhile, the impact strength of pressure on the linear thermal expansion coefficient increased when the pressure was above 20 GPa.

The heat capacity are estimated by using Debye temperature and electronic structures of Mg-B compounds, which defined as follows:

$$C_v = 3nk \left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right]$$

$$C_p = \frac{\pi^2 K_B^2 D_f T}{3} + \frac{12\pi^4 R n T^3}{5\theta_D^3}, \quad \gamma = \frac{\pi^2 K_B^2 D_f}{3}, \quad \beta = \frac{12\pi^4 R n}{5\theta_D^3}$$

Where γ and β are the electronic and phonon contributions to the specific heat respectively.

The temperature and the pressure dependence of the isochoric heat capacity (C_V) and the isobaric heat capacity (C_P) of the Mg-B compounds are displayed in Figure 10. When the temperature was below 300 K, the variation of C_V and C_P exhibited an obvious and sharp rise; this subordinated Debye's law. However, C_P and C_V were likely to continue to increase and remained constant after 300 K, respectively, due to the C_V abided by the Dulong-Petit limit under high temperature conditions. Moreover, both the isochoric heat capacity (C_V) and the isobaric heat capacity (C_P) decreased with an increase in the pressure. Thus, from Figure 11, we inferred that the heat capacity of MgB_7 was higher than that of MgB_4 and MgB_2 , indicating the stronger ability of release and absorption energy of MgB_7 .

Figure 10. Linear thermal expansion coefficient of Mg-B compounds as function of pressure and temperature.

Figure 11. Pressure and temperature dependence of heat capacity C_V , C_P of Mg-B compounds.

4. Conclusion

In this investigation, the structural, mechanical, electronic, and thermodynamic properties of Mg-B compounds were studied by using density functional theory; the conclusions of this paper can be summarized as follows:

- (1) The simulated elastic constants and elastic modulus through first-principle method are well coincided with the experimental values and theoretical calculations. The ratio of V/V_0 decreased with an increase in the external pressure and increased with an increase in the boron content.
- (2) The three Mg-B compounds are mechanically stable from 0GPa to 40GPa. The additional pressure on MgB_2 , MgB_4 , and MgB_7 can improve its B, G, and E, which rowed as the following order: $\text{MgB}_2 < \text{MgB}_4 < \text{MgB}_7$, but these properties of MgB_2 is more excellent than that of MgB_4 when the pressure reach to 30GPa. Besides, a ductile conversion behavior at 30GPa is found in the process of increasing the pressure for MgB_4 .
- (3) The hardness of three Mg-B compounds enhanced with the increased pressure, the hardness of Mg-B compounds could be rowed as following order: $\text{MgB}_7 > \text{MgB}_2 > \text{MgB}_4$. Conversely, the calculated elastic anisotropy could be ranked as following order: $\text{MgB}_7 < \text{MgB}_2 < \text{MgB}_4$.
- (4) From the results the total density of states(TDOS) and the partial density of states (PDOS), the main orbital hybridizations of Mg-B compounds are B p and Mg d orbitals, B p and Mg s orbitals and B p and Mg p orbitals for MgB_2 , MgB_4 and MgB_7 , respectively. There has no phase transformation under the rising external pressure. From the band structure, the MgB_7 and the MgB_4 shows semiconductor properties, but MgB_2 presents excellent conductivity characteristic.
- (5) The Debye temperature of all Mg-B compounds reduce with an increase temperature from 0 to 1400K but increase with an increase pressure from 0 to 40GPa. The linear thermal expansion coefficient α increase linearly with an increase temperature and pressure, while it present a sharp increase when the pressure is rising up to 40GPa. The results of the isochoric heat capacity (C_V) and the isobaric heat capacity (C_P) increase gradually with an increase temperature, while the C_V remain unchanged at higher temperature due to followed the Dulong-Petit limit.

Compliance with Ethical Standards

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Author Contributions statement

Guowei Zhang and Chao Xu: Conceptualization, Methodology, Software, Hong Xu and Yuhong Zhao: Visualization and Supervision. Ying Dong: Editing. Fenger Sun and Xiaoyan Ren: Investigation. Mingjie Wang: Writing- Reviewing, Investigation and Editing.

Competing Interests information

Author Mingjie Wang, Guowei Zhang, Hong Xu, Ying Dong, Fenger Sun, Xiaoyan Ren, Yizheng Fu and Yuhong Zhao has both received research grants from North university of china. We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, the authors declare that they have no conflict of interest.

Data Availability Statement

Some or all data, models, or code generated or used during the study are proprietary or confidential in nature and may only be provided with restrictions .

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Figures

Figure 1

Optimised crystal structures of Mg-B compounds: (a) MgB₂; (b) MgB₄; (c) MgB₇.

Figure 2

Variation between energy and volume of Mg-B compounds.

Figure 3

Volume ratio and pressure relation of Mg-B compounds with an interval of 10GPa.

Figure 4

Pressure dependence of the elastic constants of the three Mg-B compounds.

Figure 5

Elastic modulus (B, G, and E) of Mg-B compounds various from different pressure.

Figure 6

Pressures dependence of the B/G ratio and Poisson's ratio ν .

Figure 7

Variation of micro-hardness at various pressures.

Figure 8

Density of states of Mg-B compounds, (a), (b), and (c) are partial density of states for MgB_2 , MgB_4 , and MgB_7 , respectively; (d), (e), and (f) are total density of states under various pressures for MgB_2 , MgB_4 , and MgB_7 , respectively.

Figure 9

Debye temperature of Mg-B compounds under various pressure and temperature.

Figure 10

Linear thermal expansion coefficient of Mg-B compounds as function of pressure and temperature.

Figure 11

Pressure and temperature dependence of heat capacity C_V , C_P of Mg-B compounds.