Pressure effect of the mechanical, electronics and thermodynamic properties of Mg–B compounds

A first-principles investigations

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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 varied slightly and decreased with an increase in the pressure. The Debye temperature $\Theta_D$ 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 thermal expansion coefficient $\alpha$ were both obtained on the basis of Debye model under increased pressure from 0 to 40 GPa and increased temperatures. This paper brings a convenient understanding of the magnesium–boron alloys.

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 the 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 investigate the 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 vapourisation 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, Alapati et al.$^4$ calculated the lattice parameters of Mg–B compounds using the first principle based on the density functional theory (DFT). The elastic constants, mechanical properties, bond structure, and electronic properties of MgB$_4$ at 0 GPa were investigated by Ozisik$^{20}$. Furthermore, the heat capacity and the thermal expansion of MgB$_2$ at 0 GPa was predicted by Saengdeejing$^{21}$. The thermodynamic properties of Mg–B compounds and Al–Mg–B films were also investigated by using ab initio calculations and CALPHAD methods$^{22,23}$. So far, the
The most effective method to obtain the hexagonal phase MgB$_2$ is the high-pressure and high-temperature growth by using different kinds of solvents, and the external pressures and higher temperature may promote the reaction of Mg–B compounds. 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 MgB$_2$, MgB$_4$, and MgB$_7$ under pressure from 0 to 40 GPa were investigated by using DFT calculation. The thermal expansion coefficient, Debye temperature, heat capacity, and other thermodynamic properties were theoretically studied for determining the pressure and temperature dependence of Mg–B compounds.

### Computational methodology

In this study, all the calculated results were obtained by using the first-principle method through the Vienna ab initio simulation package (VASP) codes. PBE (Perdew–Burke–Ernzerhof) in GGA (generalized gradient approximation) was performed to expound the exchange-correction function and calculate the self-consistent electronic density. All the calculations in the current study were considered Mg $3p^63s^2$ and B $2s^22p^1$ as the valence electrons. To obtain an accurate calculated results, the cut-off energy $E_{\text{cutoff}}$ was set to 500 eV. Moreover, the Brillouin-zone sampling mesh for the Monkhorst–Pack k-point for MgB$_2$, MgB$_4$, and MgB$_7$ 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 $\sigma$ 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 $1.0 \times 10^{-5}$ eV/atom.

### Results and discussions

#### Structural stability

The optimised crystal texture of Mg–B compounds is shown in Fig. 1, and the corresponding calculated crystal parameters of the Mg–B compounds at 0 GPa are tabulated in Table 1. 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.

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

\[ P(V) = \frac{3}{2} \frac{B_0}{K_0} \left( \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right) \]

where $P$ is the pressure, $V$ is the volume, $B_0$ is the bulk modulus, and $K_0$ is the pressure derivative of the bulk modulus.
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.

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 Fig. 3. Moreover, the $P(V)$ curves were calculated by using the equilibrium thermodynamic relation as follows:

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

$$B_0 = -V \left\{ \left( \frac{dP}{dV} \right)_{V=0} \right\} = V_0 \left( \frac{d^2E(V)}{dV^2} \right)_{V=0} \hspace{1cm} (2)$$

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.

$$B'_0 = -\frac{d}{dP} \left( \frac{dP}{dV} \right)_{P=0}$$

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 Fig. 3. Moreover, the $P(V)$ curves were calculated by using the equilibrium thermodynamic relation as follows:

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

The volume ratio $V/V_0$ of the three Mg–B compounds decreased with an increase in the pressure, as shown in Fig. 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 to 40 GPa ranged in the following order: $\text{MgB}_2 < \text{MgB}_4 < \text{MgB}_7$. That is, $\text{MgB}_7$ was harder to compress under the same applied pressure, as it had the highest value of $V/V_0$ among the three Mg–B compounds. Furthermore, $\text{MgB}_2$ was the most sensitive to the pressure–volume relationship.
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 \((C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55}, \text{and } C_{66})\) elastic constants for the orthorhombic crystals of \(\text{MgB}_4\) and \(\text{MgB}_7\), and six elastic constants \((C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, \text{and } C_{66})\) for the hexagonal crystal of \(\text{MgB}_2\). 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:

For the hexagonal (\(\text{MgB}_2\)) crystal:

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

(4)

For the orthorhombic (\(\text{MgB}_4\) and \(\text{MgB}_7\)) crystal:

\[
C_{ii} > 0, \quad i = 1 \sim 6, \quad C_{11} + C_{22} > 2C_{12}, \quad C_{11} + C_{33} > 2C_{13}, \quad C_{22} + C_{33} > 2C_{23}, \quad C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0
\]  

(5)

The influence of the applied pressure from 0 to 40 GPa on the calculated elastic constants for the Mg–B compounds is displayed in Fig. 4. As shown in Fig. 4, the entries in the elastic tensor \(C_{ii}\) 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 \(\text{MgB}_2\) and \(\text{MgB}_7\) is higher 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 \(\text{MgB}_2\) and \(\text{MgB}_7\). Similarly, the \(C_{12}\) of \(\text{MgB}_4\) with the largest elastic constant indicated that the \(y\)-axis had the highest deformation resistance for \(\text{MgB}_4\). According to the existing literature, the values of \(C_{44}, C_{55}, \text{and } C_{66}\) are always used to represent the ability of compounds to resist shear deformation. Therefore, \(\text{MgB}_7\) had higher values of \(C_{44}\) and \(C_{66}\) than the other two Mg–B compounds, according to Fig. 4, which implied that \(\text{MgB}_7\) had the highest resistance ability for the shear deformation.

Generally, the elastic modulus contained \(B, G, \text{and } E\) could be subsequently obtained by using the VRH (Voigt–Reuss–Hill) approximation, after the elastic constants \(C_{ij}\) were obtained. The calculation equations are given by Ref. 39,40:

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

(6)

For the hexagonal crystal:

\[
B_V = \frac{2}{9} \left( C_{11} + C_{12} + 2C_{13} + \frac{1}{2} C_{33} \right)
\]  

(7)
Figure 5. Elastic modulus (B, G, and E) of Mg–B compounds various from different pressure.

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

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

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

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

For an orthorhombic crystal:

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

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

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

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

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

As displayed in Fig. 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 the resistance to deformation was Ref.44. Simultaneously, we found that MgB₂ had a stronger capacity to resist volume deformation and had higher hardness, as it had the highest values of the elastic moduli than others at a constant pressure. From Fig. 5, we inferred that the volume deformation resistance ability under a pressure from 0 to 30 GPa deferred to the following increased order: MgB₂ < MgB₄ < MgB₇. Nevertheless, the ability to resist to the volume change of MgB₂ was stronger than others under pressures of 30–40 GPa, and it’s G and E were larger than that of MgB₇’s. Therefore, it would be inaccurate to predict the hardness of MgB₂ and MgB₄.

In general, the B/G ratio and Poisson’s ratio \( \nu \) can be used to explain the ductility and brittleness of Mg–B compounds. Figure 6 presents the relation between the B/G ratio and Poisson’s ratio of Mg–B compounds under changed pressure. Poisson’s ratio \( \nu \) can be calculated as follows:

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

The B/G ratio and \( \nu \) were proposed to describe the brittle or ductile of materials, when the values were 1.75 and 0.26, respectively. As shown in Fig. 6, the Poisson’s ratio \( \nu \) and B/G ratio of MgB₂ were 0.267 and 1.80 at 30 GPa, and 0.277 and 1.91 at 40 GPa, respectively. Thus, MgB₂ 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: MgB$_7$ < MgB$_4$ < MgB$_2$. Moreover, all the B/G ratios and $\nu$ values increased with an increase in the pressure, which indicates that the ductility could be improved by increasing the applied pressure on the Mg–B compounds.

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$^{44}$:

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

As shown in Fig. 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: MgB$_7$ > MgB$_4$ > MgB$_2$, 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 Fig. 5, we can summarized 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$^{45}$:

$$A^U = 5\frac{G_V}{G_G} + \frac{B_V}{B_B} - 6$$  \hspace{1cm} (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$_7$ 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: MgB$_2$ < MgB$_7$ < MgB$_4$.

**Electronic properties.** 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 Fig. 8. Figure 8a,b,c shows 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 Fig. 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$_7$. Figure 8d,e,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.

**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 $\Theta_D$ 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. 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 0.80 a to 1.20 a 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:

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

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}$$

where $v_m$, $v_s$, and $v_l$ represent the average wave velocity and the shear and longitudinal sound velocities, respectively; $\hbar$ is Planck’s constant; $k_B$ is Boltzmann’s constant; $n$ is the total number of atoms; $N_A$ is Avogadro’s number; $\rho$ is the density; and M is the molecular weight. As shown in Fig. 9, the $\Theta_D$ 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

![Figure 7. Variation of micro-hardness at various pressures.](image_url)

| 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  |
200 K. Simultaneously, the ΘD of the Mg–B compounds from low to high could be rowed as the following order: MgB2 < MgB4 < MgB7, when all the compounds were under the same temperature and pressure conditions.

Figure 10 shows the temperature and pressure dependence of the volumetric 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

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

Figure 9. Debye temperature of Mg–B compounds under various pressure and temperature.
T3 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 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:

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

\[
C_P = \frac{\pi^2 K_B^2 D_J T^3}{3} + \frac{12\pi^4 R n T^3}{5\theta_D}, \quad \gamma = \frac{\pi^2 K_B^2 D_J}{3}, \quad \beta = \frac{12\pi^4 R n}{5\theta_D}
\]

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 Fig. 11. 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 Fig. 11, we inferred that the heat capacity of MgB7 was higher than that of MgB4 and MgB2, indicating the stronger ability of release and absorption energy of MgB7.

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/V0 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 0 to 40 GPa. The additional pressure on MgB2, MgB4 and MgB7 can improve it's B, G, and E, which rowed as the following order: MgB2 < MgB4 < MgB7, but these properties of MgB2 is more excellent than that of MgB4 when the pressure reach to 30 GPa. Besides, a ductile conversion behavior at 30GPa is found in the process of increasing the pressure for MgB4.

(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: MgB7 > MgB4 > MgB2. Conversely, the calculated elastic anisotropy could be ranked as following order: MgB7 < MgB4 < MgB2.

(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 MgB2, MgB4 and MgB7, respectively. There has no phase transformation under the rising external pressure. From the band structure, the MgB7 and the MgB4 shows semiconductor properties, but MgB2 presents excellent conductivity characteristic.

(5) The Debye temperature of all Mg–B compounds reduce with an increase temperature from 0 to 1400 K but increase with an increase pressure from 0 to 40 GPa. 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.

**Data availability**
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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**Figure 11.** Pressure and temperature dependence of heat capacity $C_V$, $C_P$ of Mg–B compounds.
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Competing interests
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Additional information
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