First-principles study of elastic and thermodynamic properties of orthorhombic OsB$_4$ under high pressure

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**ABSTRACT**

The first-principles study on the elastic properties, elastic anisotropy and thermodynamic properties of the orthorhombic OsB$_4$ is reported using density functional theory method with the ultrasoft pseudo-potential scheme in the frame of the generalized gradient approximation. The calculated equilibrium parameters are in good agreement with the available theoretical data. A complete elastic tensor and crystal anisotropies of the ultra-incompressible OsB$_4$ are determined in the pressure range of 0–50 GPa. By the elastic stability criteria, it is predicted that the orthorhombic OsB$_4$ is stable below 50 GPa. By using the quasi-harmonic Debye model, the heat capacity, the coefficient of thermal expansion, and the Grüneisen parameter of OsB$_4$ are also successfully obtained in the present work.

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1. Introduction

Transition metal borides have attracted considerable attentions from both theoretical and experimental studies due to their chemically inert and extreme hardness as well as high thermal and electrical conductivity [1]. Recently, Kaner et al. have suggested that the introduction of light and covalent-bond-forming elements (B, C, N, and O) into the transition metal (TM) lattices with highly valence-electron density is expected to have profound influences on their chemical, mechanical, and electronic properties [2–4]. Based on this prospect, recent design of new intrinsically potential superhard materials ($H_p \geq 40$ GPa) has concentrated on light element TM compounds with high elastic moduli, in particular the 4d and 5d TM compounds [5–8]. Following the first synthesized ultra-incompressible material OsB$_2$ [3], extensive experimental and theoretical investigations have been carried out for other TM borides in view of their synthesis is more straightforward. Nowadays, some TM borides such as WB$_4$, ReB$_2$, WB$_2$, RhB$_{1.15}$, and IrB$_{1.35}$ has been synthesized and were proposed to be superhard with claimed hardness of $\sim$40 GPa [9–12]. Among these superhard TM borides, WB$_4$ has the largest B contents reported hitherto. WB$_4$ exhibits a unique three-dimensional boron covalent bonding network which consisted of in-plane honeycomb B sublattice and out-of-plane B$_2$ dimer. This is responsible for its high hardness [13].

Up to now, the structures of osmium borides with various stoichiometries (OsB$_8$, Os$_3$B$_4$, and OsB$_6$) have been synthesized and some related mechanical properties were also investigated. The obtained results indicated that they are all only hard materials. However, a promising material, osmium tetraboride (OsB$_4$) within WB$_4$-type structure, was proposed to be superhard with claimed hardness of 46.2 GPa but with a much low shear modulus of 52 GPa through first-principles calculations [13]. Recently, Zhang et al. [14] proposed an orthorhombic $Pmnm$ structure for OsB$_4$, which is energetically much superior to the WB$_4$-type structure. This $Pmnm$ structure consists of irregular OsB$_{10}$ dodecahedrons connected by edges and is stable against decompression into a mixture of Os and B at ambient pressure. The elastic and electronic properties of this orthorhombic structure are also explored at ambient conditions. However, to our knowledge, the investigations on its elastic and thermodynamic properties of the orthorhombic OsB$_4$ under pressures are least studied. Especially, the comprehensive analysis of elastic characteristics (elastic constants, bulk and shear modulus, etc.) under pressures can provide a deeper insight into the response of the crystal to external forces, and obviously play an important
role in determining the strength and hardness of materials. Moreover, it is essential for many practical applications, such as load deflection, thermoelastic stress, fracture toughness, anisotropic character of the bonding, and structural stability [15]. The physical properties under pressures and temperatures have important guiding significances to accelerate the synthesis of OsB₄ and other TM borides.

Here, the aim of this paper is to perform a theoretical investigation of structural, elastic and thermodynamic properties of OsB₄ within orthorhombic Pnma structure under pressures up to 50 GPa by first-principles calculations. The elastic properties of orthorhombic OsB₄ under high pressure are investigated for the first time, from which the elastic anisotropy are also determined. In order to further investigate the OsB₄, the thermodynamic properties, such as the heat capacity, thermal expansion, Gruneisen parameters and so on are determined by the Debye model.

2. Computational methodology

2.1. Total energy electronic structure calculations

In the present work, density functional theory calculations are performed with plane-wave ultrasoft pseudopotential [16] using the generalized gradient approximation with the Perdew–Wang functional [17] as implemented in the CASTEP code [18]. The ionic cores are represented by ultrasoft pseudopotentials for B and Os atoms. The B: 2s²p¹ and Os: 4p⁶5d⁶6s² electrons are explicitly treated as valence electrons. The electronic wave functions are expanded in plane-wave basis set with cutoff energy of 540 eV, and the special points sampling integration over the Brillouin zone was employed by using the Monkhorst–Pack method with a grid of 0.03 Å⁻¹. The total energy was well converged within 1 meV/atom and this set of parameters assures the maximum force is 0.01 eV/Å, the maximum stress is 0.02 GPa.

2.2. Elastic properties

The elastic constants are defined by means of a Taylor expansion of the total energy, \( E(V, \delta) \), for the system with respect to a small strain \( \delta \) of the lattice primitive cell volume \( V \). The energy of a strained system is expressed as follows [19]

\[
E(V, \delta) = E(V_0, 0) + V_0 \left( \sum_{i} \tau_{i} \delta_{i} + \frac{1}{2} C_{ij} \delta_{i} \delta_{j} \right),
\]

where \( E(V_0, 0) \) is the energy of the unstrained system with equilibrium volume \( V_0 \); \( \tau_{i} \) is an element in the stress tensor; and \( \delta_{i} \) is a factor to take care of Voigt index. It is known, there are nine independent components of the elastic tensor for the orthorhombic structure OsB₄, i.e. C₁₁, C₁₂, C₁₃, C₂₂, C₂₃, C₃₃, C₄₄, C₅₅, and C₆₆.

For the specific case of orthorhombic OsB₄ phase, the isotropic Reuss shear modulus \( G_R \) and the Voigt shear modulus \( G_V \) are [20–22]

\[
G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})},
\]

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

and the isotropic Reuss bulk modulus \( B_R \) and the Voigt bulk modulus \( B_V \) are defined as

\[
B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})},
\]

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

In Eqs. (2) and (4), the \( S_i \) are elastic compliance constants. The arithmetic average of the Voigt and the Reuss bounds is called the Voigt–Reuss–Hill (VRH) average and is commonly used to estimate elastic moduli of polycrystals. Hence, The VRH averages for shear modulus (\( G \)) and bulk modulus (\( B \)) are \( G = (G_R + G_V)/2 \) and \( B = (B_R + B_V)/2 \). The Young’s modulus, \( E \), and Poisson’s ratio, \( \nu \), are given by \( E = (9BG)/(3B + G) \) and \( \nu = (3B - 2G)/(2B + 2G) \).

The Debye temperature can be calculated from the elastic constants using the average sound velocity \( v_m \), by the following equation [23]

\[
\Theta_D = \frac{h}{k} \frac{3n}{4\pi} \left( \frac{M}{N_A} \right)^{\frac{1}{3}} v_m,
\]

where \( h \) is Planck’s constant, \( k \) is Boltzmann’s constant, \( N_A \) is Avogadro’s number, \( n \) is the number of atoms per formula unit, \( M \) is the molecular mass per formula unit, and \( \rho \) is the density. The average sound velocity \( v_m \) is given by

\[
v_m = \left[ \frac{1}{3} \left( \frac{1}{\nu_l^2} + \frac{1}{\nu_t^2} \right) \right]^{\frac{1}{2}},
\]

where \( \nu_l \) and \( \nu_t \) are the transverse and longitudinal elastic wave velocity of the polycrystalline materials and are given by Navier’s equation [24].

2.3. Thermodynamic properties

The investigations on the thermodynamic properties of the orthorhombic OsB₄ under high temperature and pressure are determined by the quasi-harmonic Debye model [25], in which the phononic effect is considered. However, it should be noted that the Debye model of phonon density of states is essentially a linear extrapolation of the sound speed of acoustic branches but not optical branches in order to get density states. In fact, the thermodynamic properties of the crystal can be obtained by treating the lattice vibrations as quantized (phonons). However, this model is very computationally quick and easy, which has been successfully applied to predict the thermodynamic properties of some materials [26–28]. The model has been described in detail elsewhere [25], here, we give only a brief description as follows:

In the quasi-harmonic Debye model, the non-equilibrium Gibbs function \( G'(V; P, T) \) is taken in the form of

\[
G'(V; P, T) = E(V) + PV + A_{vib}(\Theta(V); T),
\]

where \( E(V) \) is the total energy, \( PV \) corresponds to the constant hydrostatic pressure condition, \( \Theta(V) \) is the Debye temperature, and the vibrational contribution \( A_{vib} \) can be written as

\[
A_{vib}(\Theta(V); T) = nkT \frac{9}{8T} \frac{\Theta}{T} \left[ 3\ln \left( 1 - e^{-\Theta/T} \right) - \frac{\Theta}{T} \right],
\]

here \( D(\Theta/T) \) represents the Debye integral, \( n \) is the number of atoms per formula unit. For an isotropic solid, \( \Theta \) is expressed as

\[
\Theta = h \left( \frac{6\pi^2}{3N_A} \nu(M/n) \right)^{1/3} f(\sigma) \sqrt{\frac{B_S}{kT M}},
\]

where \( V, M, n, f(\sigma) \) is the molar volume, molar mass, the number of atom per formula unit, and a scaling function that depend on Poisson’s ratio of the isotropic solid, respectively. The \( B_S \) is the
adiabatic bulk modulus, which is equal to the isothermal bulk modulus $B_T$ in the Debye model, leading to the following equation:

$$B_S = B_T = V \left( \frac{d^2E}{dV^2} \right)$$  \hspace{1cm} (11)

where $E$ is the total energy of the crystal at 0 K.

Therefore, the non-equilibrium Gibbs function $G^*$ as a function of $(V; P, T)$ can be minimized with respect to volume $V$ as

$$\left( \frac{\partial G^*(V; P, T)}{\partial V} \right)_{P, T} = 0.$$  \hspace{1cm} (12)

By solving Eq. (12), one can get the thermal equation of state (EOS) $V(P, T)$. The heat capacity $C_V$, $C_p$ and the thermal expansion $\alpha$ are expressed as is given by

$$C_V = 3nk \left[ 4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right],$$  \hspace{1cm} (13)

$$C_p = C_V(1 + \alpha \gamma T),$$  \hspace{1cm} (14)

$$\alpha = \frac{\gamma C_V}{B_T V},$$  \hspace{1cm} (15)

where $\gamma$ is the Grüneisen parameter defined as

$$\gamma = -\frac{\text{d} \ln \Theta(V)}{\text{d} \ln V}.$$  \hspace{1cm} (16)

### 3. Results and discussion

#### 3.1. Structural properties

The crystal structure of the OsB$_4$ with Pmmn space group is shown in Fig. 1. To calculate the equilibrium lattice constants and bulk modulus, the total energy is calculated by varying the volume for the Pmmn-OsB$_4$. The calculated $E$–$V$ data are fitted to the third-order Birch–Murnaghan equation of state (EOS) [29], and the calculated equilibrium structure parameters, bulk modulus, and its pressure derivative are tabulated Table 1 together with other theoretical results for comparison. It is clear that our results agree well with the recent work from the Ref. 14 using PAW + GGA method, and the mismatch of lattice parameter is within 0.3%. Furthermore, the pressure dependence of the normalized parameters $a/a_0$, $b/b_0$, and $c/c_0$ as a function of pressure for the Pmmn-OsB$_4$ is exhibited in Fig. 2, where $a_0$, $b_0$, and $c_0$ is its value at $T = 0$ K.

<table>
<thead>
<tr>
<th>Source</th>
<th>$a_0$ (Å)</th>
<th>$b_0$ (Å)</th>
<th>$c_0$ (Å)</th>
<th>$V_0$ (Å$^3$/f.u.)</th>
<th>$b_0$ (GPa)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>7.106</td>
<td>2.888</td>
<td>4.015</td>
<td>82.199</td>
<td>291</td>
<td>4.327</td>
</tr>
<tr>
<td>Theoretical*</td>
<td>7.119</td>
<td>2.896</td>
<td>4.015</td>
<td>82.776</td>
<td>293</td>
<td>4.119</td>
</tr>
</tbody>
</table>

* Ref. [14].

Table 1

And $P = 0$ GPa. By fitting the calculated data with least squares method, we obtained their relationships at the temperature of 0 K as the following relations:

$$\frac{a}{a_0} = 0.99985 - 0.8438 \times 10^{-3}P + 3.65293 \times 10^{-6}P^2$$  \hspace{1cm} (17)

$$\frac{b}{b_0} = 0.99991 - 1.34 \times 10^{-3}P + 5.86437 \times 10^{-6}P^2$$  \hspace{1cm} (18)

$$\frac{c}{c_0} = 0.99979 - 1.05 \times 10^{-3}P + 4.45302 \times 10^{-6}P^2$$  \hspace{1cm} (19)

It can be clear seen that the compression along the $b$-axis is the largest, and the smallest compression is exhibited along the $a$-axis. This indicates the clear elastic anisotropy of the Pmmn-OsB$_4$. The smallest compression along the $a$-axis can be attributed to the strong covalent B–B bonding in B layers and B–Os bonding in B0s10 dodecahedron along $a$-axis that has been clarified in our previous work [14].

#### 3.2. Elastic properties

The nine independent elastic constants of the Pmmn-OsB$_4$ using stress–strain relation derived from the method described above and listed in Table 2. It is shown that our results are in good agreement with data reported in Ref. [14] at 0 K and 0 GPa. Under high pressure, the elastic constants $C_{ij}$ increase monotonically with pressure (Fig. 3). Relatively, the slopes for $C_{44}$ and $C_{66}$ are slower when one carefully checks the augmental interval of these elastic

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Fig. 1. Crystal structure of the Pmmn-OsB$_4$. The large and small spheres represent Os and B atoms, respectively.

Fig. 2. The normalized parameters $a/a_0$, $b/b_0$, $c/c_0$ as a function of the pressure for the Pmmn-OsB$_4$. 

constants. Moreover, these nine independent elastic constants \( C_{ij} \) of the \( Pmmn\)-OsB\(_4\) still satisfy the well-known Born stability criteria [30] up to 50 GPa. As shown in Table 2, the calculated elastic moduli also increase monotonically with pressure as expected. The ratio between the bulk and the shear modulus \( B/G \) are used to predict the brittle or ductile behavior of materials. According to the Pugh criterion [31], the ductile behavior is predicted when \( B/G > 1.75 \), otherwise the material behaves in a brittle manner. As shown in Table 2, the ration of \( B/G \) in the \( Pmmn\)-OsB\(_4\) increases with pressure and reaches nearly 1.75 at 50 GPa. The results indicate that the \( Pmmn\)-OsB\(_4\) is prone to brittleness below 50 GPa, and is strongly prone to ductility above 50 GPa. Such a phenomenon was also found in other transition metal borides [33,34]. Debye temperature correlates with many physical properties of materials, such as specific heat, elastic constants, and melting temperature. The Debye temperatures are predicted deriving from elastic constants under pressures and the result at 0 GPa for the \( Pmmn\)-OsB\(_4\) is 781 K, which is close to that of the known intra-incompressible OsB\(_2\) (780 K) [32].

The elastic anisotropy of crystals can exert great effects on the properties of physical mechanism, such as anisotropic plastic deformation, crack behavior, and elastic instability. Hence, it is important to calculate elastic anisotropy in order to improve its mechanical durability [19]. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. The shear anisotropic factor for the \( \{100\} \) shear planes between the \( \langle011\rangle \) and \( \langle010\rangle \) direction is:

\[
A_1 = 4C_{44} \left( \frac{1}{C_{11} + C_{33} - 2C_{13}} \right). \tag{20}
\]

For the \( \{010\} \) shear planes between the \( \langle010\rangle \) and \( \langle001\rangle \) directions it is

\[
A_2 = 4C_{55} \left( \frac{1}{C_{22} + C_{33} - 2C_{23}} \right), \tag{21}
\]

and for the \( \{001\} \) shear planes between the \( \langle110\rangle \) and \( \langle010\rangle \) directions it is

\[
A_3 = 4C_{66} \left( \frac{1}{C_{11} + C_{22} - 2C_{12}} \right). \tag{22}
\]

For an isotropic crystal the factors \( A_1, A_2, \) and \( A_3 \) must be 1.0, while any value smaller or greater than 1.0 is a measure of the degree of elastic anisotropy. Moreover, for the orthorhombic crystal, the elastic anisotropy which arises from the anisotropy of linear bulk modulus was also considered in addition to the shear anisotropy. The directional bulk modulus along different crystallographic axes can be defined as \( B_i = (1/dP/di)(i = a, b, \) and \( c) \) in Ref. [19].

Using the relations mentioned above, the parameters about elastic anisotropy are calculated and shown in Table 3. It is clear that the \( Pmmn\)-OsB\(_4\) is elastic anisotropic. The shear anisotropy results indicate that the elastic anisotropy for \( \{010\} \) shear planes between the \( \langle011\rangle \) and \( \langle001\rangle \) directions is close to that of the \( \{001\} \) shear planes between the \( \langle110\rangle \) and \( \langle010\rangle \) directions, but larger than that of the \( \{100\} \) shear planes between the \( \langle011\rangle \) and \( \langle010\rangle \) directions. The smaller shear anisotropy within \( \{100\} \) shear planes can be explained by the orderly manner of BOs\(_n\) dodecahedrons along \( \{001\} \) directions. This result also demonstrates that the \( \{010\} \) and \( \{001\} \) shear planes are easier to be cleavage planes among these principal planes. Moreover, it can be seen that the \( A_1 \) remains nearly invariant on the whole, \( A_2 \) increases with increasing pressure, and \( A_3 \) decrease with increasing pressure. Meanwhile, it is interesting to note that the directional bulk modulus \( B_0 \) along the \( a \)-axis is largest when compared to the \( B_0 \) and \( B_c \), which is in agreement with the pressure dependence of the normalized lattice parameters (see Fig. 2). However, this result is not consistent with the calculated elastic constants values of \( C_{11} \) and \( C_{33} \) (see Table 2). This differentia can be explained by the definition of the directional bulk modulus which is proportional to both lattice parameters and the pressure dependence of the lattice parameters. The lattice constant \( a \) is almost 1.8 times larger than \( c \) for the \( Pmmn\)-OsB\(_4\), although the elastic \( C_{33} \) is little larger than \( C_{11} \).

An illustrative way of describing the elastic anisotropy is a three-dimensional surface representation showing the variation of elastic modulus with crystallographic direction. This directional dependence of the Young’s modulus \( E \) for orthorhombic crystal is given by [19]:

\[
1 \quad E = \frac{l_1^2 S_{11} + l_2^2 S_{22} + l_3^2 S_{33} + 2l_1^2 l_2 S_{12} + 2l_1^2 l_3 S_{13} + 2l_2^2 l_3 S_{23}}{l_1^2 S_{66} + l_1^2 S_{44} + l_1^2 S_{55}} \tag{23}
\]

where \( S_{ij} \) are the elastic compliance constants and \( l_1, l_2, \) and \( l_3 \) are the direction cosines. Fig. 4 illustrate the directional dependence of the \( Pmmn\)-OsB\(_4\) in the elastic modulus calculated using the

| Table 2 | Calculated elastic constants \( C_{ij} \), bulk modulus \( B \), shear modulus \( G \), Young’s modulus \( E \) in unit of GPa of the \( Pmmn\)-OsB\(_4\). Also shown are \( B/G \) ratio and Debye temperature \( \Theta \) under pressure. |
|---|---|---|---|---|---|---|---|---|
| \( P \) | \( C_{11} \) | \( C_{12} \) | \( C_{13} \) | \( C_{22} \) | \( C_{23} \) | \( C_{33} \) | \( B \) | \( G \) | \( E \) | \( B/G \) | \( \Theta \) |
| 0° | 612 | 576 | 630 | 152 | 349 | 178 | 128 | 245 | 51 | 294 | 218 | 524 | 1.34 |
| 0 | 605 | 583 | 632 | 149 | 347 | 177 | 127 | 247 | 48 | 293 | 217 | 522 | 1.35 | 781 |
| 10 | 670 | 648 | 702 | 159 | 382 | 188 | 155 | 290 | 69 | 335 | 233 | 567 | 1.44 | 807 |
| 20 | 729 | 710 | 765 | 167 | 413 | 198 | 182 | 329 | 89 | 375 | 248 | 610 | 1.51 | 829 |
| 30 | 875 | 768 | 825 | 174 | 441 | 207 | 210 | 368 | 110 | 414 | 260 | 645 | 1.59 | 847 |
| 40 | 937 | 825 | 880 | 179 | 468 | 219 | 238 | 408 | 130 | 450 | 273 | 681 | 1.65 | 865 |
| 50 | 887 | 878 | 932 | 184 | 493 | 223 | 264 | 444 | 154 | 487 | 282 | 709 | 1.73 | 877 |

*Ref. [14].

| Table 3 | Calculated anisotropy factors \( A_1 \), \( A_2 \), and \( A_3 \) and the directional bulk modulus \( B_0, B_1, B_3 \) in GPa of the \( Pmmn\)-OsB\(_4\) under pressure. |
|---|---|---|---|---|---|---|---|---|---|
| \( P \) | \( B_0 \) | \( B_1 \) | \( B_2 \) | \( A_1 \) | \( A_2 \) | \( A_3 \) |
| 0 | 1118 | 700.3 | 889.4 | 0.802 | 1.240 | 0.758 |
| 10 | 1284.2 | 798.3 | 1020.7 | 0.803 | 1.261 | 0.746 |
| 20 | 1436.6 | 892.8 | 1139.6 | 0.799 | 1.274 | 0.737 |
| 30 | 1588.9 | 984.4 | 1254.8 | 0.798 | 1.296 | 0.731 |
| 40 | 1742.2 | 1074.3 | 1362.3 | 0.791 | 1.296 | 0.739 |
| 50 | 1877.6 | 1161.2 | 1478.8 | 0.790 | 1.313 | 0.722 |
compliance constants computed from the present calculation. The projection of the Young’s modulus along $ab$, $ac$, and $bc$ planes are also shown in Fig. 4. It can be seen that Fig. 4(a) shows a large deviation from a spherical shape and hence one can conclude that the $Pmmm$-$OsB_4$ exhibit a high degree of anisotropy. As expected, the $Pmmm$-$OsB_4$ keeps it strong elastic anisotropy along different planes with the increasing pressure as shown in Fig. 4(b) and (c).

3.3. Thermodynamics properties

The thermodynamic properties of the $Pmmm$-$OsB_4$ are determined in the temperature range from 0 K to 1800 K where the quasi-harmonic model remains fully valid, meanwhile, the pressure effect is studied in the range 0–50 GPa. The temperature-dependent behavior of the calculated constant pressure heat capacity $C_P$ and constant volume heat capacity $C_V$ at various pressures $P$ are shown in Fig. 5. It clearly shows that the difference between $C_P$ and $C_V$ is very small at low temperatures ($<400$ K), meanwhile, the $C_P$ and $C_V$ increase rapidly with pressure that this is due to the anharmonic approximations of the Debye model. However, the anharmonic effect on $C_V$ is suppressed at high temperatures, and the $C_V$ approaches a constant value called as Dulong–Petit limit ($C_V (T) \sim 3R$ for mono atomic solids) and the $C_P$ still increases monotonously with increments of the temperature. In addition, one can also see that both the $C_P$ and $C_V$ increase with the temperature at the given pressure and decrease with the pressure at the given temperature, the influences of the temperature on the heat capacity are much more significant than that of the pressure on them.

The pressures and temperatures’ dependences of the thermal expansion coefficient $\alpha$ for the $Pmmm$-$OsB_4$ are also illustrated in Fig. 6. It is shown that the expansion coefficient $\alpha$ increases sharply at low temperatures especially at 0 GPa and gradually reaches to
a linear increase at high temperature in Fig. 6(b). The variations of thermal expansion coefficient with pressures become gentle. At a given temperature, the thermal expansion coefficient decreases strongly with pressures and remains very smoothly at high temperatures and high pressures. It can be found that the thermal expansion coefficient $\alpha$ converges to a constant value at high temperatures and pressures. These results are in accordance with the results of the Debye theory which applied to many kinds of materials.

The Grüneisen parameter could describe the alteration in vibration of a crystal lattice based on the increase or decrease in volume as a result of temperature change. Recently, it has been widely used to characterize and extrapolate the thermodynamic properties of materials at high pressures and high temperatures such as the temperature dependence of phonon frequencies and line-widths. Grüneisen parameter [35] is dominated by lower-frequency transverse modes at low temperatures. In Fig. 7, we have plotted the Grüneisen parameter $\gamma$ of the $Pmmm$-OsB$_4$ at

**Fig. 6.** Pressure (a) and temperature (b) dependence of the thermal expansion coefficient $\alpha$ for the $Pmmm$-OsB$_4$.

**Fig. 7.** Pressure (a) and temperature (b) dependence of the Grüneisen parameter $\gamma$ for the $Pmmm$-OsB$_4$. 
various temperatures and pressures. It can be observed that the $\gamma$ decreases dramatically with pressure at given temperature in Fig. 7(a). Meanwhile, at higher temperatures, the $\gamma$ decreases more rapidly with the increasing pressure. As shown in Fig. 7(b), at fixed pressure ($T > 600$ K), the $\gamma$ increases monotonously with temperature. These results are due to the fact that the effect of temperature on the Grüneisen parameter $\gamma$ is not as significant as that of pressure, and there will be a large thermal expansion at a low pressure.

4. Conclusion

In summary, the structural, elastic, and thermodynamic properties of the ultra-incompressible orthorhombic $Pmmn$ structure of OsB$_4$ under pressures have been predicted by first-principles calculations in combination with the quasi-harmonic Debye model. The obtained results of the ground state structural properties and equation of state are in good agreement with previous theoretical calculations. The elastic constants $C_{ij}$, polycrystalline aggregate elastic moduli, Debye temperature, and the elastic anisotropies of the $Pmmn$-OsB$_4$ under high pressures are also predicted for the first time. The results indicated that the $Pmmn$-OsB$_4$ is prone to brittleness below 50 GPa and exhibits larger elastic anisotropy with increasing pressure. In addition, some basic thermodynamical quantities such as the heat capacity ($C_V$ and $C_P$), thermal expansion coefficient $\alpha$, and Grüneisen parameter $\gamma$ are calculated systematically based on the quasi-harmonic Debye model at the pressure of 0–50 GPa and temperature of 0–1800 K, and the results are also interpreted. We hope that our results will stimulate further experimental and theoretical works on this technologically material in the future.

Acknowledgments

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