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ABSTRACT

First principles calculations are performed to investigate the structural, mechanical, electronic, and thermodynamic properties of BeB_2C_2 . Our calculated lattice parameters are in good agreement with the experimental data. Orthorhombic BeB_2C_2 phase is found to be mechanically stable at ambient pressure. The Young's modulus and shear modulus as a function of crystal orientation for the BeB_2C_2 have been systematically investigated. Further mechanical properties demonstrated that BeB_2C_2 is strongly prone to brittle and possesses high Vickers hardness of 26.5–28.6 GPa. Density of states and electron topological analysis show that chemical bonding among Be, B, and C atoms in BeB_2C_2 is a complex mixture of covalent and ionic characters. Based on the quasi-harmonic Debye model, the dependence of Debye temperature, Grüneisen parameter, heat capacity, and thermal expansion coefficient on the temperature and pressure are systematically explored in the whole pressure range from 0 to 20 GPa and temperature range from 0 to 1200 K.

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pounds that were described in the Be–B–C system about 40 years ago. Its structure was first described in 1966 [9], but has only recently been definitely resolved [10]. This was achieved by a combi-

1. Introduction

The chemistry of boron-containing compounds is particularly rich and offers an extremely broad variety of topologies [1]. Physical properties such as superconductivity, hardness, neutron scattering length, and thermoelectricity have made boron-containing compounds attractive to materials research and for applications [2]. The exciting discovery in 2001 that the well-known compound MgB₂ with an unusually high transition temperature ($T_c = 39 \text{ K}$) [3] triggered an enormous interest in compounds with structurally similar features, namely graphite-like layers. In the case of the MB_2C_2 phases (M = alkaline-earth or rare earth metal), for instance, the recent discovery of various potentially interesting properties has revived the interest of the scientific community. The prediction of high temperature superconductivity as high as 120 K in hole doped MgB₂C₂ [4], which containing B-C layers isoelectronic to graphite, fueled the research activities in this field even more. The superconductivity at low temperature has also been reported for YB_2C_2 and LuB_2C_2 as well as the hole-doped Li_xBC (x = 0.5) [5-7]. Although the properties of this family of compounds have been widely investigated, some of their structures are still debated, especially with respect to the position of B atoms versus C atoms (the so-called "coloring problem") [8].

 BeB_2C_2 is the first boride carbide with slipped 6^3 B/C layers as in graphite. This beryllium diboride dicarbide is one of two com-

nation of X-ray power diffractometry on the basis of synchrotron data, and experimental as well as theoretical determination of the energy loss near edge structures (ELNES). DFT calculations have confirmed that the BeB₂C₂ adopts the orthorhombic Pmmn (No. 59, *Z* = 2, *a* = 613.42 pm, *b* = 542.20 pm, and *c* = 469.28 pm) structure. The observed $\eta^1 \eta^6$ – Be coordination by B and C atoms is reminiscent of the $\eta^1 \eta^6$ metal-organic compound [Be(C₅H₅)₂] [11]. Similar to the Li_xBC mentioned above, the superconducting T_c of Be₂B_xC_{1-x} is predicted to increase with boron concentration with a value of 3–8 K at *x* = 0.25 and a plateau of 5–13 K for *x* > 0.4 [12]. Compared to this new determined orthorhombic BeB₂C₂ phase, the high pressure behaviors of the LiBC and MgB₂C₂, both containing B-C layers isoelectronic to graphite, have been investigated in detail in many experimental and theoretically work [13-16]. LiBC was experimentally subjected to very high pressures in a diamond anvil cell [14], which revealed that the crystal structure of LiBC remains stable up to 60 GPa. For MgB₂C₂, a high-pressure orthorhombic Pnnm phase was synthesized and structurally characterized [16]. However, the detailed physical properties, such as elastic constants, electronic properties, and thermodynamic of the BeB₂C₂ are least studied at ambient conditions as well as high pressure and high temperature so far. Therefore, as a novel kind of beryllium boride carbide phase, one might expect excellent physical properties mentioned above. In the present work, using first principles total energy calculations, the electronic properties and bonding scheme of BeB₂C₂ are fully

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discussed. Moreover, the Young's modulus and shear modulus as a function of crystal orientation for BeB_2C_2 have been systematically investigated. The thermodynamic properties, such as the heat capacity, thermal expansion, Grüneisen parameters and so on are investigated by the quasi-harmonic Debye model implemented in Gibbs program [17].

2. Computational methods

The density functional theory (DFT) calculations have been performed within generalized gradient approximation (GGA) [18], as implemented in the Vienna *ab initio* simulation package [19]. The electron and core interactions were included by using the frozencore all-electron projector augmented wave (PAW) method [20], with Be: $1s^22s^2$, B: $2s^22p^1$, and C: $2s^22p^2$ treated as the valence electrons. The convergence tests used a kinetic energy cutoff of 520 eV for the calculations. The special points sampling integration over the Brillouin zone was employed by using the Monkhorst-Pack method [21] with a grid of 0.03 Å⁻¹ to obtain well converged total energy within 1 meV/atom. During the structural optimizations, all forces on atoms were converged to the order of 0.001 eV/Å, and the external stresses were reduced to be less than 0.01 GPa. Crystal orbital Hamiltonian population (COHP) [22] was used for bond analysis, as implemented in the SIESTA package [23]. The elastic constants were calculated from evaluation of stress tensor generated small strain, and the bulk modulus, shear modulus, Young's modulus, and Poisson's ratio were thus derived from the Voigt-Reuss-Hill approximation [24]. The quasi-harmonic Debye model was applied to investigate the lattice thermal expansion and further details of this procedure can be found elsewhere [17,25-26].

3. Results and discussion

3.1. Structural properties

The crystal structure of Pmmn–BeB₂C₂ is shown in Fig. 1. The B/C layers are planar, as shown in Fig. 1a. The Pmmn structure



Fig. 1. Projections of the unit cell of BeB₂C₂ along the crystallographic *a* axis (a), the $\eta^1\eta^6 - Be$ polyhedrons (b), and polyhedral views of the BeB₂C₂ (c). The large, middle, and small spheres represent C, B, and Be atoms, respectively.

consists of a fundamental building block: the $\eta^1 \eta^6 - Be$ polyhedrons (Fig. 1b), which are pointing alternately upward and downward along a-axis (Fig. 1c). To calculate the equilibrium lattice parameters, the total energy is calculated by varying the volume for the Pmmn-BeB₂C₂. The calculated E-V data are fitted to the third-order Birch-Murnaghan equation of state (EOS) [27], and the calculated equilibrium structure constants and bond lengths are listed in Table 1 together with available experimental data for comparison. It is clear that the predicted lattice constants and bond lengths of the Pmmn-BeB₂C₂ are in excellent with those of experimental results in Table 1. This confirms the accuracy and reliability of the computational procedure employed here. In order to provide some insight into the pressure behavior of BeB₂C₂, the pressure dependences of the normalized parameters a/a_0 , b/b_0 , and c/c_0 as a function of pressure for the BeB₂C₂ are calculated, where a_0 , b_0 , and c_0 is its value at T = 0 K 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:

 $a/a_0 = 0.99983 - 3.62 \times 10^{-3}P + 0.32899 \times 10^{-6}P^2$ (1)

$$b/b_0 = 0.99998 - 1.12 \times 10^{-3}P + 7.81124 \times 10^{-6}P^2$$
(2)

$$c/c_0 = 0.99997 - 1.12 \times 10^{-3}P + 7.80587 \times 10^{-6}P^2$$
(3)

It can be clear seen that the compression along the *a*-axis is the largest, and the similar compression behaviors are exhibited along the *b*-axis and *c*-axis in this *Pmmn* structure. This indicates the clear elastic anisotropy of the *Pmmn*-BeB₂C₂.

3.2. Mechanical properties

Recently, Kaner et al. [28] have pointed out that the compounds of beryllium with other light elements (B, C, N, and O) may form alternative superhard materials. Earlier theoretical predictions [29–32] have demonstrated that the $B_{12}N_2Be$, Be_3N_2 , and $BeCN_2$ are potential superhard materials with excellent mechanical properties and high hardness. Therefore, the mechanical properties of this novel beryllium-based compound are highly demanded. By strain-stress method, nine independent zero pressure elastic constants C_{ii} for Pmmn-BeB₂C₂ were calculated in order to check its mechanical stability. Table 2 lists the calculated elastic constants C_{ii} at ambient pressure along with theoretical values of BeCN₂ for comparison. The elastic stability is a necessary condition for a stable crystal. For a stable orthorhombic structure, C_{ij} has to satisfy the elastic stability criteria [33]: $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0$, $(C_{11} + C_{22} - 2C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, and $(C_{22} + C_{33} - 2C_{23}) > 0$. As shown in Table 2, these conditions are clearly satisfied for orthorhombic stability, confirming that *Pmmn*–BeB₂C₂ is mechanically stable. In addition, the calculated results of BeB₂C₂ showed that the elastic constants possess the trend $C_{11} < C_{22} \approx C_{33}$, indicating the anisotropy of the elasticity. The implication of this trend is that the bonding between nearest neighbors along the {100} planes are weaker than that along the {010} and {001} planes, which agree with the pressure dependence of the normalized lattice parameters mentioned above. However, the calculated elastic constants of BeB₂C₂ are smaller than those of BeCN₂, indicating that the Pmmn-BeB₂C₂ may be common hard material.

Like the elastic constants, the bulk modulus, shear modulus, and Young's modulus contain information regarding the hardness of a material with respect to various types of deformation. Bulk modulus *B* measures the resistance of a material to volume changes and provides an estimate of its response to a hydrostatic pressure, shear modulus *G* describes the resistance of a material to shape change, and Young's modulus *E* measures the resistance

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Table 1

Calculated equilibrium lattice parameters, a_0 , b_0 , c_0 , bond length (in Å), and volume V_0 (in Å³ per f.u.) for BeB₂C₂.

	<i>a</i> ₀	b_0	<i>C</i> ₀	Vo	d _{B-C}	$d_{\mathrm{Be-C}}$	d _{B-C}
This work Experimental ^a	6.134 6.134	5.433 5.422	4.701 4.693	39.175 39.021	1.543–1.596 1.544–1.594	1.811–1.971 1.811–1.975	2.021-2.057 2.018-2.068
^a Ref. [10].							

Table 2

Calculated elastic constants C_{ij}, bulk modulus B_H, shear modulus G_H, and Young's modulus E_H in unit of GPa. Also shown are Poisson's ratio v_H and B_H/G_H ratio.

Structure	<i>C</i> ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₁₂	C ₁₃	C ₂₃	B_H	G_H	E_H	v_H	B_H/G_H
Pnnm-BeB ₂ C ₂ CH-BeCN ₂ ^a WU-BeCN ₂ ^a	264 641 741	738 670	741 565 804	305 384 281	73 265	73 361 322	2 101 143	1.5 63	132 206 80	195 321 309	162 302 298	381 689 678	0.175 0.142 0.135	1.203 1.065 1.037

^a Ref. [32].

against uniaxial tensions. These are important parameters for defining the mechanical properties of a material. For engineering applications that make use of single crystals, it is necessary to know the values of bulk modulus, Young's modulus, and shear modulus as a function of crystal orientation. As outlined by Panda et al. [34] and He et al. [35], executing the appropriate coordinate system transformations for the compliances allows the determination of the variation of bulk modulus, Young's moduli, and shear modulus with crystallographic direction, [*uvw*], for a given crystallographic plane, (*hkl*), containing these directions, (i.e., *B*_[*uvw*], *E*_[*uvw*], and *G*_{(*hkl*)[*uvw*]}) are obtained. For orthorhombic BeB₂C₂, the bulk modulus *B* and Young's modulus *E* can be expressed as:

$$B^{-1} = (s_{11} + s_{12} + s_{13})\alpha^2 + (s_{12} + s_{22} + s_{23})\beta^2 + (s_{13} + s_{23} + s_{33})\gamma^2$$
(4)

$$E^{-1} = s_{11}\alpha^4 + s_{22}\beta^4 + s_{33}\gamma^4 + 2s_{12}\alpha^2\beta^2 + 2s_{23}\beta^2\gamma^2 + 2s_{13}\alpha^2\gamma^2 + s_{44}\beta^2\gamma^2 + s_{55}\alpha^2\gamma^2 + s_{66}\alpha^2\beta^2$$
(5)

where α , β , and γ are the direction cosines of [*uvw*] direction, and s_{11} , s_{22} , etc., are elastic compliance constants which are given by Ney [36]. The shear modulus *G* on the (*hkl*) shear plane with shear stress applied along [*uvw*] direction is given by:

$$G^{-1} = 4s_{11}\alpha_1^2\alpha_2^2 + 4s_{22}\beta_1^2\beta_2^2 + 4s_{33}\gamma_1^2\gamma_2^2 + 8s_{12}\alpha_1\alpha_2\beta_1\beta_2 + 8s_{23}\beta_1\beta_2\gamma_1\gamma_2 + 8s_{13}\alpha_1\alpha_2\gamma_1\gamma_2 + s_{44}(\beta_1\gamma_2 + \beta_2\gamma_1)^2 + s_{55}(\alpha_1\gamma_2 + \alpha_2\gamma_1)^2 + s_{66}(\alpha_1\beta_2 + \alpha_2\beta_1)^2$$
(6)

where α_1 , β_1 , γ_1 , α_2 , β_2 , γ_2 are the direction cosines of the [*uvw*] and [*HKL*] directions in the coordinate systems, where the [*HKL*] denotes the vector normal to the (*hkl*) shear plane.

The three-dimensional surface representations showing the variation of the bulk modulus and Young's modulus are plotted in Fig. 2a and b, and the plane projections (*ab* plane and *bc* plane) of the directional dependence of the bulk modulus and Young's modulus are given in Fig. 2c and d for comparison, respectively. It can be clearly seen that BeB₂C₂ exhibit a pronounced anisotropy, with the nonspherical nature in Fig. 2a and b. Moreover, while inplane anisotropy in *bc* plane is nonexistent, a significant in-plane elastic anisotropy in *ab* plane is revealed. In order to have a better understanding of the origin of the changes in Young's modulus along different directions, we have calculated the orientation dependence of Young's modulus when the tensile axis within specific planes. The obtained results for BeB₂C₂ are plotted in Fig. 3a. It can be clear seen that the Young's modulus on the (011) plane is independent of tensile stress direction, which is also in agreement with the results shown in Fig. 2c. For the orientation dependence of

Young's modulus from $[100](\theta = 0^{\circ})$ to $[010](\theta = 90^{\circ})$ on the (001)plane, the BeB₂C₂ possess a maximum of $E_{[010]}$ and a minimum of $E_{[110]}$. For the (010) plane in the Fig. 3a displays the variation of Young's modulus with E_{max} along [001] directions and E_{min} along [101] directions. For the $(1\overline{1}0)$ plane Young's moduli *E* behave again very similar for the directions between [001] and [110] with minima of $E_{[110]}$ and maximum of $E_{[001]}$. Therefore, the ordering of Young's modulus as a function of the principal crystal tensile [*uvw*] for BeB₂C₂ is: $E_{[101]} \approx E_{[110]} < E_{[111]} < E_{[100]} < E_{[001]}$. Meanwhile, the crystallographic characteristics for the shear modulus G are summarized in Fig. 3b. For shear plane (001) with the shear stress direction rotated from [100] to [010], the direction cosines are $\alpha_1 = \cos\theta$, $\beta_1 = \sin\theta$, $\gamma_1 = 0$, $\alpha_2 = \beta_2 = 0$, and $\gamma_2 = 1$, where θ is the angle between the [100] and shear stress direction. From Eq. (6), one can deduce the shear modulus can be expressed as $G^{-1} = s_{55} + (s_{44} - s_{55}) \sin^2 \theta$. For BeB₂C₂, $s_{44} < s_{55}$, the shear modulus is the largest along [010] and the smallest along [001]. When (100) is the shear plane, we rotate the shear stress direction from [001] to [010]. In this case, $\alpha_1 = 0$, $\beta_1 = \sin\theta$, $\gamma_1 = \cos\theta$, $\alpha_2 = 1$, $\beta_2 = \gamma_2 = 0$, then the shear modulus can be obtained as $G^{-1} = s_{55} + s_{55}$ $(s_{66} - s_{55})\sin^2\theta$. Since in our case, $s_{66} = s_{55}$, then $G^{-1} = s_{55}$, which means that within (100) plane, the shear modulus of BeB₂C₂ is nearly independent of the shear stress direction. For the shear plane (010) with the shear stress direction rotated from [001] to [100], $G^{-1} = s_{44} + (s_{66} - s_{44})\sin^2\theta$. Due to $s_{44} < s_{66}$, the shear modulus is the largest along [001] with $G_{(010)[001]} = 305$ GPa and the smallest along [100] with $G_{(010)[100]}$ = 73 GPa. Similarly, the shear modulus within $(1\overline{1}0)$ is also plotted in Fig. 3b with the shear stress direction rotated from [001] to [110]. It can be seen from the Fig. 3b that, the shear modulus is the smallest on the (100) plane and almost independent of shear direction. This means that, (100) plane may be the cleavage plane of Pmmn-BeB₂C₂.

Using the calculated elastic constants C_{ij} , the bulk modulus B_H and shear modulus G_H for the corresponding polycrystalline aggregate are thus determined by the Voig-Reuss-Hill approximation method [24]. In addition, the Young's modulus E_H and Poisson's ratio v_H are obtained in the light of the following equations: E_H = 9- $B_H G_H / (3B_H + G_H)$ and $v_H = (3B_H - 2G_H) / (6B_H + 2G_H)$. The calculated bulk modulus, shear modulus, Young's modulus, and Poisson's ratio are given in Table 2. It can be seen that BeB₂C₂ exhibits a much smaller bulk modulus of 195 GPa than those of BeCN₂, suggesting an low incompressible character. The shear modulus of a material quantifies its resistance to the shear deformation. However, the calculated shear modulus of BeB₂C₂ is 162 GPa, which is also smaller than those of BeCN₂, but larger than the theoretical value of known superhard WB₄ (104 GPa) [37]. 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

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Fig. 2. Three-dimensional surface representations of the bulk modulus (a) and Young's modulus (b) in BeB₂C₂. The plane projections (*ab* plane and *bc* plane) of the directional dependence of the bulk modulus (c) and Young's modulus (d).



Fig. 3. Orientation dependence of the Young's modulus (a) and orientation dependence of the shear modulus (b) in BeB₂C₂.

[38], the ductile behavior is predicted when B/G > 1.75, otherwise the material behaves in a brittle manner. It can be clearly seen in Table 2 that the BeB₂C₂ is strongly prone to brittle with respect to the value of B_H/G_H (1.203), being smaller than 1.75. This is also the case for BeCN₂. Furthermore, the Vickers hardness of BeB₂C₂ is estimated by Šimůnek model [39], in which the hardness of the idea single crystal is assumed to be proportional to the bond strength and to their number in the unit cell. An alternate empirical formula for hardness prediction proposed by Chen et al. [40] was also considered for comparison. According to the Šimůnek model and Chen model, Vickers hardness of BeB₂C₂ is speculated to be 26.5 GPa and 28.6 GPa, respectively, indicating a potentially hard material.

3.3. Electronic properties

In order to elucidate the origin of the mechanical properties of BeB_2C_2 on a fundamental level, we show the calculated total and partial density of states (DOSs) in Fig. 4. As shown in Fig. 4a, the semiconductor nature of BeB₂C₂ is characterized by large energy gap of \sim 0.44 eV, which is in agreement with previous values predicted by the FP-LAPW method within the WIEN2 K codes. [10] Moreover, we could see three groups of states, depicted as I, II, and III in the valence band region. From inspection of its partial DOS curves, Part I and part II are mainly dominated by C-s states mixed with contributions of B-s states. Part III is characterized by a mixture of B-p and C-p states as well as small Be-p states. The electrons of B-s and B-p states have a significant hybridization with C-s and C-p states from the -15 eV up to Fermi level (E_F), signifying the strong B–C covalent bonding nature in B/C layers within bc plane. Moreover, another Be-C and Be-B covalent bonding nature can be seen from their partial DOS profiles from -15 eV to -5 eV, although not as strong as B-C bonds. We have also calculated the crystal orbital Hamilton population (COHP) to investigate the chemical bonding of BeB₂C₂. The COHP analysis,



Fig. 4. Total and partial densities of states of BeB_2C_2 at 0 GPa. The vertical dashed line denotes the Fermi level at zero.

as a partitioning scheme for the band structure energy in terms of the orbital-pair contributions, can provide a quantitative measure of bond strengths. According to the original definition of the COHP, the negative and positive energy regions in the COHP curves correspond to the bonding and antibonding interactions, respectively. The COHP curves of B–C, Be–B, and Be–C bonds for BeB₂C₂ are shown in Fig. 5. It can be seen that B-C interactions are bonding in the energy regions below E_F in Fig. 5a. The Be–B and Be–C interactions are bonding in the energy regions from -15~eV to $\sim -5~\text{eV}$ and turn out to be antibonding in the energy region from $\sim-5~\text{eV}$ to E_{F} . In order to describe the ionic/covalent character quantitatively and more clearly, electron topological analysis [41] are performed. Due to B–C distance in B/C layers is $1.543 \sim 1.596$ Å, which is close to the C–C bond length in diamond (1.55 Å). The properties of the bond critical points (BCPs) of the adjacent B and C atoms in B/C layers were calculated. The B–C bonding has a nature of the shared interaction because the BCP has a negative Laplacian value with large local electron density of $1.160 \sim 1.220$, which is comparable to that of diamond (1.60) [42], indicating that indeed the strong B-C covalent bonding nature. The charge (Q) enclosed within the Bader volume (V) is a good approximation to the total electronic charge of an atom. Based on the calculated data for BeB_2C_2 per f.u. in Table 3, we find that about 1.6465 and 3.5786 electrons transfer from Be and B atoms to C atoms. We thus conclude that the chemical bonding among Be, B, and C atoms in BeB₂C₂ is a complex mixture of covalent and ionic characters.

3.4. Thermodynamic properties

The investigation on the thermodynamic properties of solids at high pressure and high temperature is an interesting topic in the condensed matter physics. Compared to the LiBC and MgB₂C₂, there are very limited theoretical works on the thermodynamic properties for BeB₂C₂ at high pressure and high temperature. The thermal properties of BeB₂C₂ are determined in the temperature range from 0 to 1200 K, where the quasi-harmonic model remains fully valid [10,43]. The pressure effect is investigated in the range of 0-20 GPa. In the quasi-harmonic Debye model, the Debye temperature Θ and the Grüneisen parameter γ are two key quantities. The Debye temperature closely relates to many physical properties of solids, such as specific heat, dynamic properties, and melting temperature. The Grüneisen parameter describes the anharmonic effects in the vibrating lattice, and it has been widely used to characterized and extrapolate the thermodynamic behavior of a material at high pressure and high temperature. The Debye temperature and the Grüneisen parameter at various temperatures (0, 300, 600, and 1200 K) and different pressures (0, 5, 10, 15, and 20 GPa) are listed in Table 4. It is found that, at certain temperature, as pressure increases, Debye temperature Θ increases, and the Grüneisen parameter γ decreases. When the applied temperature increases from 0 to 1200 K, the Debye temperature Θ decreases by 11.33%, 8.57%, 6.90%, 5.75%, and 4.92% at 0, 5, 10, 15, and 20 GPa, respectively. When the applied pressure increases from 0 to 20 GPa, the Grüneisen parameter γ decreases by 15.57%, 15.86%, 16.87%, and 20.62% at 300, 600, 900, and 1200 K, respectively.

Heat capacity belongs to one of the most important thermodynamic properties of solids. It is intimately related to the temperature dependence of fundamental thermodynamic functions, and it is of key importance for linking thermodynamics with microscopic structure and dynamics. The calculated heat capacity at constant pressure C_P and heat capacity at constant volume C_V with the temperature and pressure are shown in Fig. 6. The difference between C_P and C_V is very small at low temperatures (T < 300 K). However, at high temperatures, the C_V approaches a constant value, C_P increases monotonously with increments of the temperature. It is also interesting to note that the values of C_V follow the Debye mod-

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Fig. 5. COHP curves for the B-C (a), Be-B (b), and Be-C (c) interactions in BeB₂C₂. The vertical dashed lines denote the Fermi level.

Table 3

Calculated charge and volumes (Å 3 per f.u.) for BeB_2C_2 according to Bader partitioning.

	Q (Be)	$Q(B \times 2)$	$Q(C \times 2)$	V (Be)	V(B)	V(C)
BeB_2C_2	2.3535	6.4214	17.2265	1.9891	6.3679	30.8183

Table 4

Calculated Debye temperature Θ (in K) and Grüneisen parameter γ of BeB₂C₂ at different pressure and different temperatures.

<i>T</i> (K)	P (GPa)								
	Parameters	0	5	10	15	20			
0	$\Theta \\ \gamma$	1198.9 1.818	1266.0 1.729	1326.4 1.655	1381.5 1.591	1432.3 1.535			
300	$\Theta \\ \gamma$	1191.5 1.829	1260.1 1.736	1321.6 1.660	1377.5 1.595	1429.0 1.539			
600	$\Theta \\ \gamma$	1160.7 1.873	1234.9 1.769	1300.2 1.686	1359.0 1.617	1412.5 1.557			
1200	$\Theta \\ \gamma$	1063.1 2.032	1157.5 1.878	1234.9 1.769	1302.0 1.684	1361.9 1.613			



Fig. 6. Temperature dependences of the heat capacity at different pressures for BeB_2C_2 .



Fig. 7. The temperature dependence of thermal expansion coefficient α of BeB₂C₂ under 0 GPa (a). The pressure dependences of thermal expansion coefficient α of BeB₂C₂ at 600 K. (b).

el at low temperature due to the anharmonic approximations. However, the anharmonic effect on C_V is suppressed and the C_V is close to a constant at sufficient high temperatures, obeying Dulong and Petit's Rule. In a word, one can see that the heat capacity increases with the temperature at the same pressure and decreases with the pressure at the same temperature. The influences of the temperature on the heat capacity are much more significant than that of the pressure on it. The thermal expansion coefficient α dependence on temperature and pressure is presented in Fig. 7. From Fig. 7, we can see that the thermal expansion coefficient α increases quickly with temperature at T < 600 K under 0 GPa, whereas at constant temperature, for instance T = 600 K, it changes linearly with pressure following a gently decreasing trend.

4. Conclusions

Based on the first principles calculations, the structural, mechanical, and electronic, and thermodynamic properties of orthorhombic BeB_2C_2 have been systematically studied. Our calculated lattice parameters are in good agreement with the experimental data. The tensile directional dependences of the Young's modulus *E* have been investigated, and the results show

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 $E_{[101]} \approx E_{[110]} < E_{[111]} < E_{[100]} < E_{[001]}$ for these principal crystal directions. The shear modulus of BeB₂C₂ is the smallest within (100) plane, which may be the cleavage plane of the BeB_2C_2 . The computed mechanical properties suggest that BeB₂C₂ potential hard material with theoretical hardness of 26.5-28.6 GPa. The B-C, Be-C, and Be-B bonds were interpreted as displaying a mixed ionic/covalent character by electronic structure analysis. Moreover, we have demonstrated that the B-C bonds in B/C layers have strong covalency which is comparable to that of C–C in diamond. Using the quasi-harmonic Debye model, the thermodynamic properties including the Debye temperature, Grüneisen parameter, and the heat capacity of BeB₂C₂ are predicted under high pressure and high temperature. We hope that these calculations will be helpful for future experimental works on this technologically important material.

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