Two B-C-O Compounds: Structural, Mechanical Anisotropy and Electronic Properties under Pressure

Liping Qiao 1,* and Zhao Jin 2

1 Team of Micro & Nano Sensor Technology and Application in High-altitude Regions, Xizang Engineering Laboratory for Water Pollution Control and Ecological Remediation, School of Information Engineering, Xizang Minzu University, Xianyang 712082, China
2 School of Information Engineering, Chang’an University, Xi’an 710064, China; zhaojin@chd.edu.cn
* Correspondence: lpqiao@126.com or lpqiao@xzmu.edu.cn; Tel.: +86-29-3375-5448

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Abstract: The structural, stability, mechanical, elastic anisotropy and electronic properties of two ternary light element compounds, B₂CO₂ and B₆C₂O₅, are systematically investigated. The elastic constants and phonon calculations reveal that B₂CO₂ and B₆C₂O₅ are both mechanically and dynamically stable at ambient pressure, and they can stably exist to a pressure of 20 GPa. Additionally, it is found that B₂CO₂ and B₆C₂O₅ are wide-gap semiconductor materials with indirect energy gaps of 5.66 and 5.24 eV, respectively. The hardness calculations using the Lyakhov-Oganov model show that B₂CO₂ is a potential superhard material. Furthermore, the hardness of B₆C₂O₅ is 29.6 GPa, which is relatively softer and more easily machinable compared to the B₂CO₂ (41.7 GPa). The elastic anisotropy results show that B₆C₂O₅ exhibits a greater anisotropy in the shear modulus, while B₂CO₂ exhibits a greater anisotropy in Young’s modulus at ambient pressure.

Keywords: B-C-O system; stability; mechanical properties; anisotropy; electronic properties

1. Introduction

It has been found that the light elements such as B, C, N, and O can form strong covalently bonded materials that show intrinsic superhard characteristics. A series of new B-C-O compounds with multifunctional properties similar to B₁₃C₂ [1,2], B₆O [2,3], B₄C [3], BC [4,5], B₂C [4,6], B₃C [4,7], B₄C [4], B₅C [4], B₆C [4], B₆C₀ [8,9], and B₇C₂O, B₇C₃O, and B₇C₅O [10], B₄CO [11,12], 2D B-C-O alloys [13], BC₅N [14–19], BCN [20–22], BN [20,23], B₄O [24–26] and CₓNᵧ [27–35] has been designed by the theoretical method. These materials are almost all superhard materials.

Using the developed particle swarm optimization (PSO) algorithm for crystal structure prediction, Wang et al. [4] explored the possible crystal structures of B-C systems that are mechanically and dynamically stable. They found that with the exception of B₄C and B₄C₄, all boron carbides have high shear moduli (more than 240 GPa), indicating their strong resistance to shape change at constant volume. Theoretical Vickers hardness calculations showed that these boron carbides are potential superhard materials because the predicted hardnesses exceed 40 GPa. Zhang et al. [20] designed different kinds of superhard materials using the Crystal structure AnaLysis by Particle Swarm Optimization (CALYPSO) algorithm. They found superhard phases in binary B-N compounds (such as Pct-BN, Pbcn, Z-BN, BC₈-BN, and M-BN) and ternary B-C-N compounds (such as I₄/m2 BCN, Imm2 BCN [21], and P3m1 BCN [22]). Pbcn-BN with an orthorhombic structure was investigated by first-principles calculations by Fan et al. [23], who found that Pbcn-BN has the shear modulus of 316 GPa, bulk modulus of 344 GPa, large Debye temperature of 1734 K, and hardness of 60.1 GPa. Ternary B-C-N compounds I₄/m2 BCN, Imm2 BCN, and P3m1 BCN were investigated by first-principles calculations by Fan et al. [21,22] and were all found to be potential superhard materials. Electronic structure studies showed that BCN materials in the P3m1 and I₄/m2 phases are indirect semiconductors.
with band gaps of 4.10 eV and 0.45 eV, respectively, while the \textit{I\textit{mm}2} phase is a direct semiconductor with a band gap of 2.54 eV.

Recently, Zhang et al. [10] performed extensive structure searches to explore the potential energetically stable $B_2C_2O$ ($x \geq 2$) phases at ambient pressure using the current developed CALYPSO algorithm. $B_2C_2O$, $B_2C_3O$, and $B_2C_5O$ in the tetragonal \textit{I}\textit{41}/\textit{amd}, \textit{I}\textit{4m}2, and \textit{P}4\textit{m}2 phases, respectively, were reported in ref. [10]. The phonon dispersion and formation enthalpy calculations revealed that $B_2C_2O$, $B_2C_3O$, and $B_2C_5O$ are all dynamically stable and can be synthesized at ambient conditions. The hardnesses of $B_2C_2O$, $B_2C_3O$, and $B_2C_5O$ are 57, 62, and 68 GPa using Gao’s model [36], and they are all potential superhard materials. $B_2CO$, a potential superhard material in the B-C-O system, can stably exist in several different phases. $tP4-B_2CO$, with the \textit{P}4\textit{m}2 phase and $tI16-B_2CO$ with the \textit{I}\textit{4}2\textit{d} phase have been reported by Li et al. [9], while $oP8-B_2CO$ with the \textit{Pmc}2\textit{1} phase was systematically investigated by Liu et al. [8] The elastic constants, phonon dispersion spectra and formation enthalpies confirmed the mechanical, dynamical and thermodynamic stabilities, respectively, of $oP8-B_2CO$, $tP4-B_2CO$, and $tI16-B_2CO$. Calculation of the Vickers hardness of $oP8-B_2CO$ shows that $oP8-B_2CO$ is a superhard material, and the Vickers hardness of $oP8-B_2CO$ (47.70 GPa) is much closer to $tP4-B_2CO$ (49.24 GPa) and $tI16-B_2CO$ (49.56 GPa). The band structure calculations illustrate that all $B_2CO$ phases are semiconductor materials with indirect band gaps, and $oP8-B_2CO$ has the widest band gap (3.540 eV), greater than those of $tP4-B_2CO$ (1.658 eV) and $tI16-B_2CO$ (2.988 eV).

$B_2CO_3$, found in the \textit{I}\textit{4} space group, is a novel tetragonal thermodynamically stable phase, and two low-enthalpy metastable compounds ($B_2C_2O_3$ in \textit{P1} phase, $B_2CO_2$ in \textit{C2/m} phase) have been discovered by Wang et al. [12] using the widely used and evolutionary Universal Structure Predictor: Evolutionary Xtallography (USPEX) algorithm. The structural, stability, mechanical, elastic anisotropy and electronic properties of $B_2CO_3$ have been systematically investigated as described in ref. [11,12]. However, the structural, stability, mechanical, and elastic anisotropy properties of $B_2CO_2$ and $B_2C_2O_5$ have not been reported. Therefore, in this work, we systematically investigate the structural, stability, mechanical, elastic anisotropy and electronic properties of $B_2CO_2$ and $B_6C_2O_5$.

2. Theoretical Methods

The calculations were performed using density functional theory with the exchange-correlation functional treated using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [37] and the Perdew-Burke-Ernzerhof for solids (PBEsol) form [38], and with local density approximation (LDA) based on the data of Ceperley and Alder as parameterized by Perdew and Zunger (CA-PZ) [39,40]. The calculations in this work were performed using the Cambridge Serial Total Energy Package (CASTEP) code [41]. Structural optimizations were conducted using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization algorithm [42]. A high-density \textit{k}-point [43] sampling with a grid spacing of less than $2\pi \times 0.025 \text{Å}^{-1}$ (4 $\times$ 16 $\times$ 7 for $B_2CO_2$, 9 $\times$ 9 $\times$ 9 for $B_2CO_5$) in the Brillouin zone was used. The self-consistent convergence criterion for the total energy was $5 \times 10^{-6} \text{eV/atom}$, the maximum force on the atom was 0.01 eV/Å, the maximum ionic displacement was within $5 \times 10^{-4} \text{Å}$ and the maximum stress was within 0.02 GPa. The HSE06 hybrid functional [44] was used for the calculations of electronic structures of $B_2CO_2$ and $B_6C_2O_5$.

3. Results and Discussion

3.1. Structural Properties

The crystal structures of $B_2CO_2$ and $B_6C_2O_5$ are shown in Figure 1a–d, respectively. For the structure shown in Figure 1a, there are two inequivalent oxygen atom positions (O1 in (0.1337, 0.0, 0.0474), red; O2 in (0.9735, 0.5, 0.2763), orange), two inequivalent boron atom positions (B1 in (0.8891, 0.0000, 0.2433), light green; B2 in (0.1298, 0.5000, 0.2027), dark green), and an equivalent carbon atom (C in (0.2497, 0.0000, 0.5855), blue) in $B_2CO_2$. In the structure shown in Figure 1c, each atom occupies a different position in $B_6C_2O_5$ (B in (0.4165, 0.5981, 0.0121), (0.6796, 0.1566, 0.1255), (0.9807, 0.7214,
whereas the volume ratios \( V/V_0 \) of \( \text{B}_2\text{CO}_2 \) and \( \text{B}_6\text{C}_2\text{O}_5 \) are in excellent agreement with the previous report [12], and the calculated lattice parameters of the other B-C-O compounds are also in excellent agreement with the previous report (see Table 1).

The calculated lattice parameters of \( \text{B}_2\text{CO}_2 \), \( \text{B}_6\text{C}_2\text{O}_5 \), and other B-C-O compounds are listed in Table 1. The calculated lattice parameters of \( \text{B}_2\text{CO}_2 \) and \( \text{B}_6\text{C}_2\text{O}_5 \) are in excellent agreement with the previous report [12], and the calculated lattice parameters of the other B-C-O compounds are also in excellent agreement with the previous report (see Table 1).

The relationships among the calculated lattice parameter ratios \( X/X_0 \) (\( a/a_0 \), \( b/b_0 \), \( c/c_0 \)) and lattice volume ratios \( V/V_0 \) of \( \text{B}_2\text{CO}_2 \) and \( \text{B}_6\text{C}_2\text{O}_5 \) and pressure are shown in Figure 2, where \( a_0 \), \( b_0 \), \( c_0 \) and \( V_0 \) are the zero temperature and zero pressure equilibrium lattice constants and lattice volume, respectively. For \( \text{B}_2\text{CO}_2 \), it can be easily seen that the compression of the \( b \)-axis is the most difficult, whereas that of the \( a \)-axis is the easiest. For \( \text{B}_6\text{C}_2\text{O}_5 \), similar to \( \text{B}_2\text{CO}_2 \), the \( b \)-axis is the most difficult to

![Figure 1](image-url)  
Figure 1. Lattice structure of \( \text{B}_2\text{CO}_2 \) (a); and along the [010] direction (b); and lattice structure of \( \text{B}_6\text{C}_2\text{O}_5 \) (c); and along the [001] direction (d).

**Table 1.** Calculated lattice parameters of \( \text{B}_2\text{CO}_2 \), \( \text{B}_6\text{C}_2\text{O}_5 \) and other B-C-O compounds.

| Materials | Source | PBE | PBEsol | CA-PZ |
|-----------|--------|-----|--------|-------|
| \( \text{B}_2\text{CO}_2 \) | This work | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) |
|       | ref. [12] | 9.773 | 2.487 | 5.395 | 90.9 | 9.721 | 2.479 | 5.368 | 90.8 | 9.606 | 2.456 | 5.308 | 90.9 |
| \( \text{B}_6\text{C}_2\text{O}_5 \) | This work | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) |
|       | ref. [12] | 4.503 | 4.536 | 4.557 | 98.1 | 4.479 | 4.526 | 4.508 | 99.3 | 4.278 | 4.474 | 4.457 | 99.3 |
| \( \text{tP4-} \text{B}_2\text{CO} \) | This work | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) |
|       | ref. [9] | 2.656 | 2.656 | 3.678 | 90.0 | 2.648 | 2.648 | 3.656 | 90.0 | 2.618 | 2.623 | 3.619 | 90.0 |
| \( \text{tI6-} \text{B}_2\text{CO} \) | This work | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) |
|       | ref. [9] | 3.722 | 3.722 | 7.493 | 90.0 | 3.702 | 3.702 | 7.515 | 90.0 | 3.664 | 3.670 | 7.394 | 90.0 |
| \( \text{B}_2\text{C}_2\text{O} \) | This work | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) |
|       | ref. [10] | 2.638 | 18.274 | 90.0 | 2.627 | 18.178 | 90.0 | 2.598 | 17.996 | 90.0 |
compress, while the c-axis is the easiest to compress. When the pressure increases, the compression along the b-axis of $B_6C_2O_5$ is much larger than that along the b-axis of $B_2CO_2$. In addition, it is found that the lattice constants $b/b_0$, $c/c_0$ compression of $B_2C_2O_3$ is changed at 10 GPa. This is because the lengths of some bonds decrease strongly along the lattice vector b-axis or the lattice vector c-axis. For example, there are three kinds of B-O bonds along the lattice vector c-axis; the bond lengths of B-O bonds are 1.571 Å (1.553 Å), 1.456 Å (1.459 Å) and 1.561 Å (1.543 Å) at 0 (5) GPa, respectively, and while the lengths of the first and the third bonds suddenly decreased to 1.516 Å and 1.508 Å under 10 GPa, the second bond length suddenly decreased to 1.489 Å under 10 GPa. Under 15 GPa, the first, second and third bond lengths dropped to 1.502 Å, 1.479 Å and 1.497 Å, respectively. From the above discussion, we can see that the abrupt change of the lattice constants $c/c_0$ compression of $B_6C_2O_5$ is due to the sudden decrease of the bond length of the B-O bonds along the lattice vector c-axis. The abrupt changes along the lattice vector b-axis is similar to that due to the abnormal change of the B-C bond length and the B-O bond. Their lattice constants changes show different trends with the pressure, which is related to the crystal structure and atomic composition. $B_2CO_2$ exists in the P1 space group, whereas $B_2CO_2$ is found in the C2/m space group and the P1 space group has the lowest symmetry among the 230 space groups. In Figure 2b, for the lattice volume ratio, we predict that $B_2CO_2$ has better compressive resistance than $B_6C_2O_5$. The results of Figure 2b confirm our prediction. Here, we can also predict that the bulk modulus of $B_2CO_2$ is greater than that of $B_6C_2O_5$.

![Figure 2](image_url)  
**Figure 2.** Lattice constants $a/a_0$, $b/b_0$, $c/c_0$ compression as functions of pressure for $B_2CO_2$ and $B_6C_2O_5$ (a); and primitive cell volume $V/V_0$ for $B_2CO_2$ and $B_6C_2O_5$ (b).

### 3.2. Stability

To demonstrate the dynamical stability of these compound, their phonon spectra are shown in Figure 3. At ambient pressure, there are no virtual frequencies in the entire Brillouin zone, proving that $B_2CO_2$ and $B_6C_2O_5$ are both dynamically stable. When $P = 20$ GPa, there are still no virtual frequencies in the entire Brillouin zone; in other words, $B_2CO_2$ and $B_6C_2O_5$ are still dynamically stable. The calculated elastic constants of $B_2CO_2$ and $B_6C_2O_5$ under different pressures are listed in Table 2. The calculated elastic constants of $B_2CO_2$ and $B_6C_2O_5$ at ambient pressure are in excellent agreement with the previously reported results [12]. There is no doubt that based on the data presented in Table 2, the elastic constants of $B_2CO_2$ and $B_6C_2O_5$ satisfy the mechanical stability criteria [45], indicating that $B_2CO_2$ and $B_6C_2O_5$ are mechanically stable. While dynamical and mechanical stabilities are verified by the phonon spectra and elastic constants, respectively, the formation enthalpy can be used to determine whether the new materials can be synthesized experimentally. Wang et al. have also described the possible synthetic routes of $B_2CO_2$ and $B_6C_2O_5$ in Ref. [12]. With regard to elastic...
constants, compared to other B-C-O compounds, some elastic constants of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ are larger and some are smaller.

![Figure 3. Phonon spectra of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ under different pressures: B$_2$CO$_2$ @ 0 GPa (a); B$_2$CO$_2$ @ 20 GPa (b); B$_6$C$_2$O$_5$ @ 0 GPa (c); and B$_6$C$_2$O$_5$ @ 20 GPa (d).](image)

Table 2. Calculated elastic constants (GPa) and elastic modulus (GPa) of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ under different pressures ($P$; in GPa).

| Materials   | C$_{11}$ | C$_{22}$ | C$_{33}$ | C$_{44}$ | C$_{55}$ | C$_{66}$ | C$_{12}$ | C$_{13}$ | C$_{15}$ | C$_{25}$ | C$_{35}$ | C$_{46}$ | B   | G   | E   |
|-------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|------|------|------|
| B$_2$CO$_2$ |          |          |          |          |          |          |          |          |          |          |          |          |      |      |      |
| 0           | 585      | 784      | 613      | 256      | 213      | 264      | 117      | 65       | 136      | −77      | 13       | 51       | −9   | 287  | 251  | 583  |
| 5           | 622      | 813      | 649      | 267      | 221      | 269      | 125      | 82       | 145      | −81      | 16       | 55       | −10  | 306  | 260  | 608  |
| 10          | 658      | 841      | 686      | 268      | 223      | 279      | 132      | 96       | 157      | −85      | 15       | 57       | −10  | 325  | 267  | 629  |
| 15          | 694      | 872      | 718      | 274      | 226      | 281      | 141      | 110      | 168      | −90      | 16       | 58       | −13  | 344  | 273  | 648  |
| 20          | 723      | 902      | 747      | 260      | 225      | 283      | 150      | 126      | 180      | −95      | 13       | 64       | −18  | 362  | 272  | 653  |
| B$_6$C$_2$O$_5$ |        |          |          |          |          |          |          |          |          |          |          |          |      |      |      |
| 0           | 528      | 519      | 571      | 207      | 170      | 211      | 102      | 40       | 83       | 6        | −0.2     | −72      | −8   | 227  | 203  | 469  |
| 5           | 549      | 547      | 596      | 216      | 163      | 215      | 108      | 35       | 93       | −10      | −1       | −87      | −10  | 234  | 207  | 480  |
| 10          | 640      | 534      | 631      | 233      | 191      | 237      | 131      | 81       | 122      | 26       | 6        | −44      | 5    | 274  | 224  | 528  |
| 15          | 665      | 573      | 665      | 243      | 204      | 245      | 142      | 91       | 133      | 31       | 8        | −49      | 7    | 293  | 234  | 554  |
| 20          | 704      | 613      | 697      | 258      | 210      | 259      | 155      | 104      | 142      | 35       | 11       | −53      | 9    | 312  | 244  | 581  |

|     | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F       | G       | H       | I       | J       | K       | L       | M       | N       | O       | P       | Q       | R       | S       | T       | U       | V       | W       | X       | Y       | Z       | A       | B       | C       | D       | E       | F� 60; 3 Reference [22]; 4 Reference [46].

3.3. Mechanical Properties and Elastic Anisotropy

The primary elastic constants and elastic modulus values of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ as functions of pressure are shown in Figure 4, and the elastic modulus values for B$_2$CO$_2$, B$_6$C$_2$O$_5$ and other B-C-O compounds are also listed in Table 2. Inspection of Figure 4 shows that almost all primary elastic constants and elastic moduli increase with increasing pressure. For B$_2$CO$_2$, the rate of increase of the elastic constants and elastic moduli remains almost constant, while for B$_6$C$_2$O$_5$, the elastic constants and elastic moduli suddenly increase from 5 GPa to 10 GPa, and the rate of increase of elastic constants
and elastic moduli remains almost constant under other pressures. As is well-known, the elastic constant represents the elastic properties of a material. Elastic constants provide a description of the relationship of stress and strain of different directions in an anisotropic medium. The elastic constants also obey Hooke’s law, and strain is proportional to stress, as expressed by Hooke’s law \( F = -kx \), where \( k \) is a constant, called the stiffness coefficient. The stiffness coefficient is a complex physical quantity related to the material itself and the external conditions such as the temperature, so that the changes in the elastic constants for \( B_6C_2O_5 \) observed in Figure 4c are also understandable. The lattice constant changes show different trends with the pressure, which are related to the differences in the crystal structure and atomic composition. \( B_6C_2O_5 \) is found in the \( P1 \) space group, while \( B_2CO_2 \) is found in the \( C2/m \) space group, and the \( P1 \) space group has the lowest symmetry among the 230 space groups. For the \( P1 \) space group, there are 21 independent elastic constants, while for the \( C2/m \) space group, there are only 13 independent elastic constants. The hardnesses of \( B_2CO_2 \) and \( B_6C_2O_5 \) were calculated by Wang et al. [11] using the Chen-Niu model [47] and the Lyakhov-Oganov model [48]. The results show that \( B_2CO_2 \) is a kind of superhard material. The Young’s modulus \( E \) is calculated as: \( E = 9BG/(3B + G) \). The calculated results for Young’s modulus for \( B_2CO_2 \) and \( B_6C_2O_5 \) are also listed in Table 2. The Young’s moduli of \( B_2CO_2 \) and \( B_6C_2O_5 \) increase with pressure, and the increase for \( B_6C_2O_5 \) is greater than that for \( B_2CO_2 \). The increase for \( B_6C_2O_5 \) was 23.88%, almost two times larger than that of \( B_2CO_2 \) (12.01%).

![Figure 4](https://example.com/figure4.jpg)

**Figure 4.** Elastic constants (a) and elastic modulus (b) as functions of pressure for \( B_2CO_2 \); and Elastic constants (c) and elastic modulus (d) as functions of pressure for \( B_6C_2O_5 \).

To analyze the anisotropy of \( B_2CO_2 \) and \( B_6C_2O_5 \) more systematically, the anisotropies of the shear moduli and Young’s moduli of \( B_2CO_2 \) and \( B_6C_2O_5 \) are investigated using the ELAM codes [22,45,49]. To better understand the mechanical and anisotropic properties of \( B_2CO_2 \) and \( B_6C_2O_5 \), 3D surface figures of the shear moduli and Young’s moduli for \( B_2CO_2 \) and \( B_6C_2O_5 \) are shown in Figure 5. The 3D surface figures represent the geometric figure that consists of the maximum or minimum value of the shear modulus or Young’s modulus in all directions of space. The magnitude of the shear modulus or Young’s modulus in all directions can be studied by using plane cutting, and the magnitude of the shear modulus or Young’s modulus in any plane can be represented by a two-dimensional graph.
The 2D representations of the shear modulus and Young’s modulus are shown in Figures 6 and 7, respectively. The 3D figure appears as a spherical shape for an isotropic material, while the deviation from the spherical shape is a measure of the degree of anisotropy [50]. It is clear that the shear and Young’s moduli of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ exhibit different degrees of anisotropy, and the anisotropies of the shear and Young’s moduli of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ increase with as the pressure increases from 0 GPa to 20 GPa. For example, a depression appears on the minimum value surface (green surface) of the shear modulus of B$_2$CO$_2$ at 20 GPa (see Figure 5b), but there is no dent under ambient pressure. In another example, at 20 GPa, a distinct dent appears on the three-dimensional Young’s modulus surface for B$_6$C$_2$O$_5$ (see Figure 5h). Similarly, the indentation on the three-dimensional Young’s modulus surface for B$_6$C$_2$O$_5$ is not so obvious at ambient pressure.

Figure 5. Directional dependence of the shear modulus at 0 GPa (a) and 20 GPa (b), and Young’s modulus at 0 GPa (c) and 20 GPa (d) of B$_2$CO$_2$; and Directional dependence of the shear modulus at 0 GPa (e) and 20 GPa (f), and Young’s modulus at 0 GPa (g) and 20 GPa (h) of B$_6$C$_2$O$_5$.

Figure 6. Cont.
while the minimum value of the shear modulus for $B_{2}CO_{2}$ plane (001) pressure, while under high pressure, the anisotropy of $B_{6}CO_{5}$ decreases first and then increases. The anisotropy of $B_{2}CO_{2}$ in the shear modulus becomes increasingly large. The anisotropy of $B_{6}CO_{5}$ in the shear modulus is larger than that of $B_{2}CO_{2}$ at ambient pressure, while the maximum value of shear modulus for $B_{2}CO_{2}$ increases first and then decreases with pressure, but the maximum values of the shear modulus remain constant in the direction of the x-axis at ambient pressure. According to the geometrical shape of the profile, the anisotropy of $B_{6}CO_{5}$ in the shear modulus is larger than that of $B_{2}CO_{2}$ at ambient pressure, while under high pressure, the anisotropy of $B_{6}CO_{5}$ is smaller than that of $B_{2}CO_{2}$. This can be proved by comparing the ratio of the maximum to the minimum of the shear modulus ($G_{max}/G_{min}$). The maximum and the minimum values of the shear modulus and Young’s modulus for $B_{2}CO_{2}$ and $B_{6}CO_{5}$ are listed in Table 3. The maximum value of shear modulus for $B_{2}CO_{2}$ increases with pressure, while the minimum value of the shear modulus for $B_{2}CO_{2}$ increases first and then decreases with pressure, so that the anisotropy of $B_{2}CO_{2}$ in the shear modulus becomes increasingly large. The anisotropy of $B_{6}CO_{5}$ in the shear modulus decreases first and then increases.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Planar projections of the directional dependence of the shear modulus in $B_{2}CO_{2}$. (a): (001) plane, (b): (010) plane, (c): (100) plane, and (d): (111) plane; and Planar projections of the directional dependence of the shear modulus in $B_{6}CO_{5}$. (e): (001) plane, (f): (010) plane, (g): (100) plane, and (h): (111) plane.

The sectional profiles are constructed on the basis of analysis of the geometrical characteristics of the 3D surfaces of the shear and Young’s moduli of $B_{2}CO_{2}$ and $B_{6}CO_{5}$. Sectional drawings of the shear and Young’s moduli are shown in Figures 6 and 7, respectively. The black, red and cyan lines represent the shear moduli at 0, 10 and 20 GPa, while the dash-dotted line and the solid line represent the shear and Young’s moduli are shown in Figures 6 and 7, respectively. The black, red and cyan lines represent the shear moduli at 0, 10 and 20 GPa, while the dash-dotted line and the solid line represent the shear and Young’s moduli are shown in Figures 6 and 7, respectively.
Young’s modulus appears in the (010) plane. The maximum and minimum values appear in the same plane, whether at ambient pressure or at high pressure. Another interesting phenomenon is that the anisotropy of Young’s modulus at each plane is also different, taking $B_2CO_2$ as an example. The 2D representations of the Young’s moduli of $B_2CO_2$ and $B_6C_2O_5$ in the (001) plane, (010) plane, (100) plane, and (111) plane are displayed in Figure 7a–h, respectively.

Table 3. Calculated the maximum values (in GPa) and minimum values (in GPa) of Young’s modulus and shear modulus and the $X_{\text{max}} / X_{\text{min}}$ ratio for $B_2CO_2$ and $B_6C_2O_5$.

| Materials | $P$ | 0 GPa | 10 GPa | 20 GPa |
|-----------|-----|-------|--------|--------|
|           |     | Max   | Min    | Ratio  | Max   | Min    | Ratio  | Max   | Min    | Ratio  |
| $B_2CO_2$ | $G$ | 309   | 170    | 1.82   | 333   | 177    | 1.88   | 353   | 175    | 2.02   |
|           | $E$ | 734   | 414    | 1.77   | 785   | 446    | 1.76   | 837   | 460    | 1.82   |
| $B_6C_2O_5$ | $G$ | 278   | 140    | 1.96   | 295   | 161    | 1.83   | 321   | 170    | 1.88   |
|           | $E$ | 603   | 345    | 1.75   | 657   | 408    | 1.61   | 717   | 431    | 1.66   |

The 2D representations of the Young’s moduli of $B_2CO_2$ and $B_6C_2O_5$ in the (001) plane ($xy$ plane), (010) plane ($xz$ plane), (100) plane ($yz$ plane) and (111) plane are displayed in Figure 7a–h, respectively. The anisotropy of Young’s modulus at each plane is also different, taking $B_2CO_2$ as an example. The Young’s modulus in the (010) plane ($E_{\text{max}} / E_{\text{min}} = 628$ GPa/414 GPa = 1.52) of $B_2CO_2$ exhibits the largest anisotropy compared to the other planes, while the (100) plane ($E_{\text{max}} / E_{\text{min}} = 734$ GPa/571 GPa = 1.29) exhibits the smallest anisotropy. This result can also be demonstrated by the ratio of the maximum to the minimum of the Young’s modulus at each plane. The maximum values of Young’s modulus for $B_2CO_2$ appear in the (001) plane and (100) plane, while the minimum value of Young’s modulus appears in the (010) plane. The maximum and minimum values appear in the same plane, whether at ambient pressure or at high pressure. Another interesting phenomenon is that the
anisotropy of Young’s modulus in the (001) plane decreases with increasing pressure, and that of the (010) plane increases with increasing pressure, while those of the (100) plane and (111) plane decrease first and then increase. For the whole material, the anisotropies of the Young’s moduli of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ decrease first and then increase. In addition, although the maximum and minimum values appear in the same plane, whether at ambient pressure or at high pressure, the direction is changed. For B$_6$C$_2$O$_5$, the maximum value appears at $\theta = 2.82$, $\phi = 5.93$ (the two angles are used to describe the unit vector, which is fully characterized by the angles $\theta (0, \pi)$, $\phi (0, 2\pi)$, as explained in more detail in Refs. [48,49]) at ambient pressure, where the angle is in radians. While the maximum value appears at $\theta = 1.59$, $\phi = 2.90$ at 10 GPa, for the pressure of 20 GPa, the maximum value appears at $\theta = 1.55$, $\phi = 2.73$. At these three pressures (0 GPa, 10 GPa, 20 GPa), the direction of the minimum appears to be different. However, for B$_2$CO$_2$, the maximum values all appear at $\theta = 1.57$, $\phi = 4.73$, whether at ambient pressure or at high pressure, but the direction of the minimum appears to have changed.

3.4. Electronic Properties

The electronic band structure is a significant physical property of a material that can be used to determine whether the material is a semiconductor, metal, or insulator. The electronic band structures of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ under different pressures are illustrated in Figure 8a–d, respectively. In Figure 8a–d, it is clear that B$_2$CO$_2$ and B$_6$C$_2$O$_5$ are both indirect and wide band gap semiconductor materials with the band gaps of 5.63 and 5.24 eV, respectively. For B$_6$C$_2$O$_5$, the conduction band minimum (CBM) and valence band maximum (VBM) are both located at the Dirac points in the Brillouin zone, the CBM of B$_2$CO$_2$ is also located at the Dirac point in the Brillouin zone, while the VBM of B$_2$CO$_2$ is not at the Dirac point in the Brillouin zone. The CBM and VBM are both located at the Q and F points in the Brillouin zone for B$_6$C$_2$O$_5$, and the CBM of B$_2$CO$_2$ is also located at the V point in the Brillouin zone, while the VBM of B$_2$CO$_2$ is located at ($-0.5000, -0.2143, 0.5000$) along the L-M direction (L: ($-0.5, 0.0, 0.5$); M: ($-0.5, -0.5, 0.5$)) in the Brillouin zone.

The band gaps of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ under different pressures are shown in Figure 8e. The two materials show different trends for the change of the band gap with increasing pressure. The band gap of B$_6$C$_2$O$_5$ increases with pressure, while the band gap of B$_2$CO$_2$ increases and then decreases. The change trend of the band gap of B$_6$C$_2$O$_5$ is similar to that of diamond and c-BN [22]; the band gap of B$_6$C$_2$O$_5$, diamond and c-BN all increase with increasing pressure, but the changes for the band gaps of diamond and c-BN are relatively smooth, and the band gap changes for B$_6$C$_2$O$_5$ are quite abrupt. Then, we investigated the origin of the pressure-driven abrupt increase of the band and the non-monotonic trend of first increase and then decrease of the band gap for B$_6$C$_2$O$_5$ and B$_2$CO$_2$, respectively. We analyzed the trend in the Fermi level and the conduction band minimum with the change of pressure. The relationships between the Fermi level and the conduction band minimum for B$_2$CO$_2$ and B$_6$C$_2$O$_5$ and the pressure are shown in Figure 8f. For the Fermi level and the conduction band minimum of B$_2$CO$_2$ and the conduction band minimum of B$_6$C$_2$O$_5$, the changes are relatively smooth, but the energy at the CBM of B$_6$C$_2$O$_5$ increases abruptly from 0 GPa to 5 GPa and from 5 GPa to 10 GPa. Therefore, the band gaps of B$_6$C$_2$O$_5$ changes abruptly due to the sudden increase in the energy at the CBM leading to a sudden increase of the band gap from 5.309 eV under 5 GPa to 5.549 eV under 10 GPa.

To better understand why the band gap of B$_6$C$_2$O$_5$ becomes larger with increased pressure, we also analyze the density of states of B$_6$C$_2$O$_5$. The densities of states of B$_6$C$_2$O$_5$ under different pressures are shown in Figure 9. Examination of Figure 9a shows that the valence band moves towards low energy, while the conduction band moves towards high energy in the 0–20 GPa range, so that the band gap of B$_6$C$_2$O$_5$ increases with increased pressure. However, as shown in Figure 8e, the Fermi level increases with increased pressure, so, why does the band gap of B$_6$C$_2$O$_5$ increase with the pressure in the 0–20 GPa range? According to Figure 9c, the density of states of the carbon atom almost does not vary with the pressure. Figure 9 b,d shows that, considering the density of states distribution of the oxygen atom, the peak value of the oxygen contribution to the conduction band increases with
the increasing pressure, indicating that for the oxygen atoms under the action of external pressure, the local energy level is higher, resulting in reduced oxygen ions and leading to further changes of the band gap. Further consideration of the B atoms shows that the peak density of states increases with increasing pressure, decreasing the degree of localization of these atoms; however, the decrease in the density of states (from 1.07 state/eV/fu to 0.82 state/eV/fu when the pressure increases from 5 GPa to 10 GPa) is much smaller than the increase in the degree of the O atom localization (from 1.62 state/eV/fu to 3.24 state/eV/fu when the pressure increases from 5 GPa to 10 GPa), so that the results showed that the band gap of B$_6$C$_2$O$_5$ becomes larger.

Figure 8. Band structures of: B$_2$CO$_2$ ((a): 0 GPa; and (b): 20 GPa); and B$_6$C$_2$O$_5$ (c): 0 GPa; and (d): 20 GPa); band gaps as functions of pressure for B$_2$CO$_2$ and B$_6$C$_2$O$_5$ (e); and Fermi level and CBM as functions of pressure for B$_2$CO$_2$ and B$_6$C$_2$O$_5$ (f).
aspects). The changes of the physical properties of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ show different trends with the pressure, and are strongly related to the crystal structure and atomic composition. The origin of band gap increases with increased pressure is explained from the viewpoint of the density of states. In addition, hardness calculations using the Lyakhov-Oganov model show that B$_2$CO$_2$ exhibits a larger anisotropy in the shear modulus, while B$_6$C$_2$O$_5$ exhibits a larger anisotropy in Young’s modulus at ambient pressure.

Another interesting phenomenon is that the anisotropy of the shear modulus of B$_2$CO$_2$ increases with increasing pressure, while the anisotropy of Young’s modulus of B$_2$CO$_2$, and the anisotropy of Young’s modulus and shear modulus along different crystal orientations. The elastic anisotropy results show that B$_6$C$_2$O$_5$ exhibits a larger anisotropy in the shear modulus, while B$_2$CO$_2$ exhibits a larger anisotropy in Young’s modulus at ambient pressure. The electronic band structures are also calculated, showing that B$_2$CO$_2$ and B$_6$C$_2$O$_5$ are wide-gap semiconductor materials with indirect energy gaps of approximately 5.66 and 5.24 eV, respectively. The elastic anisotropy of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ phase has been demonstrated by the Young’s modulus and shear modulus along different crystal orientations. The origin of band gap increases with increased pressure is explained from the viewpoint of the density of states. In addition, hardness calculations using the Lyakhov-Oganov model show that B$_2$CO$_2$ is a potential superhard material.

**4. Conclusions**

Based on first-principles calculations, we have systematically investigated two ternary light element compounds, B$_6$C$_2$O$_5$ and B$_2$CO$_2$. We find that such two $sp^2$ and $sp^3$ hybridized structures could be obtained by other compounds and elements and that these structures are dynamically stable through calculations of the phonon spectra for B$_6$C$_2$O$_5$ and B$_2$CO$_2$. The electronic band structures are also calculated, showing that B$_2$CO$_2$ and B$_6$C$_2$O$_5$ are wide-gap semiconductor materials with indirect energy gaps of approximately 5.66 and 5.24 eV, respectively. The elastic anisotropy of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ phase has been demonstrated by the Young’s modulus and shear modulus along different crystal orientations. The elastic anisotropy results show that B$_6$C$_2$O$_5$ exhibits a larger anisotropy in the shear modulus, while B$_2$CO$_2$ exhibits a larger anisotropy in Young’s modulus at ambient pressure. Another interesting phenomenon is that the anisotropy of the shear modulus of B$_2$CO$_2$ increases with increasing pressure, while the anisotropy of Young’s modulus of B$_2$CO$_2$, and the anisotropy of Young’s modulus and shear modulus along different crystal orientations. The changes of the physical properties of B$_2$CO$_2$ and B$_6$C$_2$O$_5$ exhibit different trends with the pressure, and are strongly related to the crystal structure and atomic composition. The origin of band gap increases with increased pressure is explained from the viewpoint of the density of states. In addition, hardness calculations using the Lyakhov-Oganov model show that B$_2$CO$_2$ is a potential superhard material.

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