Abstract: In this study, we predicted and investigated a new light-element compound B-C-N in \(\text{Pm}\) phase, denoted as \(\text{Pm-BCN}\), using density functional theory. \(\text{Pm-BCN}\) is mechanically, dynamically, and thermodynamically stable. The elastic moduli of \(\text{Pm-BCN}\) are larger than those of other B-C-N and light-element compounds, such as \(\text{P2}_{1}/3\) \(\text{BN}\), \(\text{B}_2\text{C}_3\), \(\text{P4}/\text{m}\) \(\text{BN}\), \(\text{Pnc2}\) \(\text{BN}\), and \(\text{dz4}\) \(\text{BN}\). By studying the mechanical anisotropy of elastic moduli, we proved that \(\text{Pm-BCN}\) is a mechanically anisotropic material. In addition, the shear anisotropy factors \(A_2\) and \(A_8\) of \(\text{Pm-BCN}\) are smaller than those of the seven B-C-N compounds mentioned in this paper. \(\text{Pm-BCN}\) is a semiconductor material with an indirect and wide band gap, suggesting that \(\text{Pm-BCN}\) can be applied in microelectronic devices.

Keywords: carbon allotropes; semiconductor material; electronic properties; anisotropy mechanical properties

1. Introduction

Designing new light-element atoms based on boron, carbon, and nitrogen, which easily form strong covalent bonds to form compounds, is an important method of finding new multifunctional materials. New theoretically proposed materials include superhard materials [1–16], direct bandgap materials [17,18], hydrogen and lithium storage materials [19,20], and metal materials that can be used for the preparation of battery cathode materials [1,4,21,22].

Three new carbon allotropes with an orthogonal structure, \(\text{oP-C}_{16}\), \(\text{oP-C}_{20}\), and \(\text{oP-C}_{24}\), were proposed based on first-principles calculations [1], all of which showed metalliclicity. The hardness of \(\text{oP-C}_{16}\), \(\text{oP-C}_{20}\), and \(\text{oP-C}_{24}\) are 47.5, 49.6, and 55.3 GPa, respectively. The ideal shear strengths of \(\text{oP-C}_{16}\), \(\text{oP-C}_{20}\), and \(\text{oP-C}_{24}\) are higher than those of Cu and Fe, and Al. Yu et al. [23] predicted and studied a new \(sp^3\) hybrid BN polymorph, \(\text{Pnc2}\) BN, which showed mechanical and dynamic stability, and found that the elastic properties of \(\text{Pnc2}\) BN are better than those of \(\text{dz4}\) BN. The indirect band gap of \(\text{Pnc2}\) BN calculated using the Heyd–Scuseria–Ernzerhof (HSE06) functional is 3.543 eV, indicating that \(\text{Pnc2}\) BN has semiconductor properties. On the basis of density functional theory (DFT) calculations [24,25], \(m-\text{B}_2\text{C}_3\text{N}_3\) and \(m-\text{B}_2\text{C}_3\text{N}_2\), two new superhard BCN compounds, were designed by Xing et al. [5]. The shear modulus \(B\), bulk modulus \(G\), and Young’s modulus \(E\) of \(m-\text{B}_2\text{C}_3\text{N}_3\) and \(m-\text{B}_2\text{C}_3\text{N}_2\) are 345, 778, and 346, respectively; the \(B\), \(G\), and \(E\) for \(m-\text{B}_2\text{C}_3\text{N}_3\) and \(m-\text{B}_2\text{C}_3\text{N}_2\) are little bit larger than those of \(\text{oC}_6\) \(\text{N}\) [2], \(\text{tC}_6\) \(\text{N}-1\) [2], and \(\text{tC}_6\) \(\text{N}-2\) [2]. Both \(m-\text{B}_2\text{C}_3\text{N}_3\) and \(m-\text{B}_2\text{C}_3\text{N}_2\) are superhard materials because both compounds have a hardness in excess of 40 GPa. The structural properties, anisotropy characteristics, elastic characteristics, and electronic properties, as well as the stability of \(\text{P4}/\text{m}\) \(\text{BN}\) were investigated by Yu et al. [26]. By adopting DFT, Xing et al. established and studied CN and BCN2 compounds with superhard characteristics and a space group of \(\text{C2}/\text{m}\) [4]. The hardness of CN is 58.63 GPa, and it is a semiconductor material, whereas \(\text{BCN}_2\) is metallic. A superhard material, \(l-\text{C}_8\text{B}_2\text{N}_2\), was designed by Zhu et al. [10] and Wang et al. [11]. The bulk modulus...
of t-C₆B₂N₂ was found to be 383.4 [10] and 383.0 GPa [11], and the hardness was 64.7 [10] and 63.2 GPa [11].

In this study, we predicted a BCN polymorph, Pm-BCN, which is mechanically and dynamically stable. We analyzed the structural, mechanical, and electronic characteristics of Pm-BCN through first-principles calculations.

2. Theoretical Methods

On the basis of DFT calculations [24,25], we proposed and investigated a new light-element compound using the Cambridge Serial Total Energy Package (CASTEP) [27]. We adopted the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [28] and local density approximation (LDA) [29] functionals to describe the exchange and correlation potentials. To ensure that the crystal structure of Pm-BCN was optimal, we used Broyden–Fletcher–Goldfarb–Shanno (BFGS) [30] for geometry optimization. The convergence accuracy during optimization was less than 0.001 eV. We described the valence electrons by ultrasoft pseudopotentials [31]. We adopted the Monkhorst–Pack k-points for the k-points separation of 6 × 16 × 7 and found that the plane wave cut-off energy E_{cut-off} is 500 eV for Pm-BCN. For the phonon spectra of Pm-BCN, we used the density functional perturbation theory (DFPT) approach [32], and for the electronic band structures of Pm-BCN, we adopted the HSE06 hybrid functional [33]. In addition, we used the Voigt–Reuss–Hill (VRH) approximations [34–36] to calculate the bulk modulus and shear modulus.

3. Results and Discussion

The crystal structure of Pm-BCN and its structure along the b-axis are shown in Figure 1a,b, respectively. Blue, gray, and purple spheres represent the B, N, and C atoms, respectively. In addition to the common rings such as the 4- and 6-membered rings in the crystal structures of Pm-BCN, two larger rings, a 10- and a 16-membered ring, are present in the crystal structure, the structures of which are depicted in Figure 1c,d. The 4-membered ring consists of one B, one N, and two C atoms; the 6-membered ring consists of one B, one N, and four C atoms; the 10-membered ring consists of three B, three N, and four C atoms. The 16-membered ring consists of five B, five N, and six C atoms. The conventional Pm-BCN cell contains 12 atoms. Because Pm-BCN has a monoclinic system, the crystal structure of Pm-BCN is not symmetrical, and the position of each atom is different. Boron atoms occupy four positions: B1 1a (0.11803, 0.00000, and 0.20845), B3 1a (0.22107, 0.00000, and 0.73817), B10 1b (0.80293, 0.50000, and 0.62435), and B12 1b (0.59805, 0.50000, and 0.04251); nitrogen atoms occupy four positions: N2 1a (0.78254, 0.50000, and 0.74717), N7 1b (0.18971, 0.50000, and 0.61515), N8 1b (0.87536, 0.50000, and 0.36710), and N11 1b (0.40657, 0.50000, and 0.04285); and carbon atoms occupy four positions: C4 1a (0.88003, 0.00000, and 0.20041), C5 1a (0.71892, 0.00000, and 0.1576), C6 1a (0.29294, 0.00000, and 0.01183), and C9 1b (0.11385, 0.50000, and 0.37443). Table 1 shows the crystal lattice parameters of the B-C-N compounds. The crystal lattice parameters of Imm2 BCN and l-4m2 BCN are close to those previously reported [14]; therefore, the crystal lattice parameters of Pm-BCN reported in this manuscript are both convincing and reliable.

The stability of Pm-BCN through phonon spectra (Figure 2a), relative enthalpy (Figure 2b), and elastic parameters. In Figure 2a, no curve appears below zero, so Pm-BCN is dynamically stable. We calculated the formation energies of B-C-N compounds as: \( \Delta H = H_{BCN} - xH_{BN} - yH_{diamond} \). As several B-C-N compounds have an equal number of nitrogen and boron atoms, here, \( x \) is equal to \( z \); \( m, n, \) and \( p \) are the \( B_2C_nN_m \) unit and atom numbers of the conventional cell for B-C-N compounds, c-BN, and diamond. The formation energy of Pm-BCN is 0.7182 eV/atom, which is slightly lower than those of \( o-BC_6N-1, t-BC_6N-2 \), \( B_2C_2N_2-2, B_2C_2N_2-3, B_2C_2N_2-4, \) and \( B_2C_2N_2-5 \) [38]. We found that the Pm-BCN is a metastable phase. Notably, B-C-N compounds with positive formation energies are not unusual [2,4,5,7,8,38].
Figure 1. Crystal structures of Pm-BCN (a), Crystal structures of Pm-BCN along b-axis (b), the 10-membered ring structure (c), and the 16-membered ring structure (d).

Table 1. Crystal lattice parameters of Pm BCN and other B-C-N compounds.

| Material     | a    | b    | c    | \(\beta\) | V    | \(\rho\) |
|--------------|------|------|------|-----------|------|---------|
| Pm BCN       | GGA  | 7.2538 | 2.5387 | 5.4260 | 89.960 | 24.981   |
| 15, x       | LDA  | 7.1697 | 2.5043 | 5.3334 | 89.219 | 23.938   |
| l-C\(_3\)B\(_2\)N\(_2\) | GGA  | 2.5470 | 10.9470 | 17.781 | 3.402  |
| 7.1697       | LDA  | 2.5250 | 10.8540 | 17.092 | 3.539  |
| Imm2 BCN     | GGA  | 2.5451 | 2.5658 | 10.9077 | 17.808 | 3.434  |
| \(\alpha\)  | GGA  | 2.5453 | 2.5658 | 10.9169 | 17.822 |         |
| c           | GGA  | 2.5480 | 2.5690 | 10.9130 | 17.859 |         |
| \(\beta\)   | LDA  | 2.5129 | 2.5313 | 10.7687 | 17.125 | 3.571  |
| 2.5127       | LDA  | 2.5127 | 2.5309 | 10.7659 | 17.212 |         |
| 4m2 BCN      | GGA  | 2.5648 | 10.9948 | 18.081 | 3.382  |
| \(\alpha\)  | GGA  | 2.5641 | 10.9892 | 18.063 |         |
| c           | GGA  | 2.5670 | 11.0020 | 18.124 |         |
| \(\beta\)   | LDA  | 2.5301 | 10.8420 | 17.101 | 3.525  |
| 2.5298       | LDA  | 2.5298 | 10.8396 | 17.343 |         |

\(^a\) [11], \(^b\) [10], \(^c\) [14], \(^d\) [37].

For the monoclinic structure, the Born mechanical stability conditions are [39]:

\[
C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0, [C_{11} + C_{22} + C_{33} + 2 (C_{12} + C_{13} + C_{23})] > 0, (C_{33}C_{55} - C_{35}^2) > 0, (C_{44}C_{66} - C_{46}^2) > 0, (C_{22} + C_{33} - 2C_{23}) > 0, [C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{55}C_{35} - C_{23}^2 - C_{35}^3 - C_{33}C_{55}] > 0, [2(C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})) - [C_{25}^2(C_{22}C_{33} - C_{23}^2) + C_{25}^2(C_{11}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] + C_{55}B] > 0,
\]

and \(B = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 - 2C_{12}C_{13}C_{23} \). Table 2 lists the
\( C_{ij} \) values of \( Pm\)-BCN and other B-C-N compounds. Table 2 shows that the elastic constants of \( Pm\)-BCN determined by LDA are slightly higher than those determined by GGA. All the elastic constants of \( Pm\)-BCN satisfy the above equation for a monoclinic system, proving that \( Pm\)-BCN is mechanically stable. We calculated the \( G \) and \( B \) of B-C-N compounds by using the Voigt–Reuss–Hill approximation [34–36]. The \( B_V \), \( B_R \), \( G_V \), and \( G_R \) are given by [38]:

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

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

\[
B_R = \Delta [(C_{33}C_{55} - C_{35}^2)(C_{11} + C_{22} - 2C_{12}) + (C_{23}C_{35} - C_{25}C_{35})/(2C_{12} - 2C_{11} - C_{23}) + (C_{13}C_{35} - C_{15}C_{35})/(C_{15} - 2C_{25}) + (C_{13}C_{55} - C_{15}C_{55})/(2C_{12} - 2C_{23} - C_{13}) + 2(C_{12}C_{15} - C_{12}C_{25})])^{-1}
\]

\[
G_R = 15 \{4[C_{33}C_{55} - C_{35}^2](A_{11} + C_{12} + C_{13}) + (C_{23}C_{55} - C_{25}C_{35})(A_{11} - C_{12} - C_{23}) + (C_{13}C_{55} - C_{15}C_{55})(A_{15} + C_{12}C_{23} + A)/\Delta + 3[C_{11}C_{22}C_{33} - C_{11}C_{23}C_{12}]^{-1}
\]

\[
A = C_{11}(C_{22}C_{55} - C_{25}^2) - C_{12}(C_{12}C_{55} - C_{15}C_{25}) + C_{15}(C_{12}C_{25} - C_{15}C_{22}) + C_{25}(C_{23}C_{35} + C_{25}C_{33})
\]

\[
C = C_{11}C_{22}C_{33} - C_{11}C_{23}C_{12} - C_{22}C_{13}C_{12} + 2C_{12}C_{13}C_{23}
\]

\[
\Delta = 2[C_{13}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{25}C_{12} - C_{15}C_{23}) + C_{25}C_{35}(C_{13}C_{25} - C_{12}C_{13})]/(C_{13}^2 - C_{12}^2) + 2[C_{11}C_{33} - C_{13}^2] + 2(C_{11}C_{22} - C_{12}^2) + 2(C_{11}C_{23} - C_{12}C_{13}) + 2C_{12}C_{13}C_{23}]
\]

\[
B = (B_V + B_R), G = (G_V + G_R)
\]

Figure 2. Phonon spectra of \( Pm\)-BCN (a) and the relative enthalpies of B-C-N compounds (b).

Young’s modulus \( E \) is calculated by \( E = 9BG/(3B + G) \), and Table 2 lists the calculated elastic moduli of B-C-N compounds. The elastic moduli of \( Pm\)-BCN are less than those of other B-C-N compounds, and larger than those of other light element compounds, such as \( Pnc2 \) BN [25], \( P4/m \) BN [26], \( P2_13 \) BN [40], \( B_2C_3 \) [41], \( d_{z4} \) BN [42], etc.

According to the EAM codes [43], we investigated the anisotropic elastic properties of \( Pm\)-BCN. The \( G_V \), \( G_R \), and \( E \) are illustrated in Figure 3a–e, respectively. The three-dimensional (3D) graphics of \( G \), \( v \), and \( E \) of \( Pm\)-BCN are not regular spheres, as shown in Figure 3. If a material possesses isotropic properties, its 3D diagram should be a regular sphere, and any shape deviating from a sphere indicates anisotropy [44–50]. So, we found that the \( G \), \( v \), and \( E \) of \( Pm\)-BCN exhibit anisotropic elastic properties. The \( G_{\text{max}}/G_{\text{min}} \) and \( E_{\text{max}}/E_{\text{min}} \) ratios are used to characterize the anisotropic elastic properties of \( G \) and \( E \), which are 207.12/75.11 = 2.76 and 755.31/221.89 = 3.40 for \( Pm\)-BCN, respectively. As shown by the \( G_{\text{max}}/G_{\text{min}} \) and \( E_{\text{max}}/E_{\text{min}} \) ratios, the anisotropic elastic properties of \( Pm\)-BCN show that it has a greater shear modulus than \( B_2C_3N_2 \) and \( B_2CN_2 \) [5], but a smaller one than \( BCN_2 \) [4]. \( BCN_2 \) has the largest Young’s modulus among \( Pm\)-BCN, \( B_2C_3N_2 \), and \( B_2CN_2 ; B_2C_3N_2 \) shows the weakest anisotropy in \( E \).
Table 2. Calculated elastic constants (GPa) and elastic moduli (GPa) of Pmca XN, Imm2 BCN, and l-4m2 BCN.

|          | C_{11} | C_{12} | C_{13} | C_{15} | C_{22} | C_{23} | C_{25} | C_{33} | C_{35} | C_{44} | C_{46} | C_{55} | C_{66} | B   | G   | E   |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-----|-----|-----|
| Pm BCN   | 339    | 50     | 184    | 8      | 770    | 48     | 0.4    | 400    | 10     | 194    | 8      | 75     | 189    | 225 | 153 | 374 |
| LDA      | 364    | 61     | 212    | 16     | 829    | 59     | 2      | 405    | 20     | 203    | 12     | 73     | 199    | 245 | 154 | 382 |
| m-B_2C_3N_2 | GGA  | 723    | 97     | 178    | 11     | 936    | 43     | 7      | 871    | 21     | 326    | -2     | 394   | 395   | 351 | 367 | 816 |
| m-B_3CN_3  | GGA  | 684    | 123    | 181    | 21     | 841    | 47     | -7     | 841    | 63     | 304    | 2      | 375   | 387   | 345 | 346 | 778 |
| l-C_8B_2N_2 | GGA  | 987    | 39     | 143    |        |        |        |        |        |        |        |        |        |      |      |     |
| Imm2 BCN  | GGA   | 963    | 23     | 144    | 898    | 141    |        |        |        |        |        |        | 395   | 395   | 457 | 343 | 367 | 394 |
| GGA      | 962    | 22     | 143    | 894    | 140    |        |        |        |        |        |        |        | 400   | 456  | 343 | 365 | 394 | 839 |
| l-4m2 BCN | GGA   | 853    | 45     | 133    | 753    | 377    |        |        |        |        |        |        | 327   | 342  | 358 | 358 |     |     |
| GGA      | 857    | 47     | 135    | 755    | 377    |        |        |        |        |        |        |        | 328   | 345  | 358 | 798 |     |     |

* [5], ^[10], ^[14].

Figure 3. Three-dimensional structure of $G_{\text{max}}$ (a), $G_{\text{min}}$ (b), Poisson’s ratio $\nu_{\text{max}}$ (c), $\nu_{\text{min}}$ (d), and $E$ (e) of Pm-BCN.

For mechanical anisotropy in $G$, the shear anisotropy factor is an index of the mechanical anisotropy of atomic bonding in different shear planes. $A_1$, $A_2$, and $A_3$ represent the shear anisotropic factor for the (100) shear plane between [011] and [010] directions, the (010) shear plane between [011] and [001] directions, and the (001) shear plane between [110] and [010] directions, respectively. $A_1 = 4C_{44} / (C_{11} + C_{33} - 2C_{13})$, $A_1 = 4C_{44} / (C_{22} + C_{33} - 2C_{23})$, $A_3 = 4C_{46} / (C_{11} + C_{22} - 2C_{12})$ [51,52]. The $A_1$, $A_2$, and $A_3$ of carbon allotropes of seven B-C-N compounds are illustrated in Figure 4a. We found that the $A_1$, $A_2$, and $A_3$ of isotropic materials should be one; however, as shown in Figure 4a, the $A_1$ of Pm-BCN is much greater than one, whereas the $A_2$ of Pm-BCN is much lower than one, so Pm-BCN exhibits a larger anisotropy at the (100) and (010) shear plane. Among these seven B-C-N compounds, the (100), (010), and (001) shear planes of l-C_8B_2N_2 show minimal differ-
Anisotropic factors

A1
A2
A3

(a)
Pm
BCN
t-C8B2N2
Imm
2 BCN
I-4m2 BCN BCN
2
B2N2C3
B3N3C

(c) Anisotropic factors

(b)

Linear bulk modulus (GPa)

Pm BCN   t-C8B2N2
 Imm2 BCN  I-4m2 BCN
 BCN2   B2N2C3  
 B3N3C 
Bc A                                             ABa

Figure 4. Anisotropy factor A1, A2, and A3 (a); linear bulk modulus Bα, Bβ, and Bγ (b); Aβα and Aβc (c) for Pm-BCN.

The electronic band structure and the PDOS of Pm-BCN obtained by the HSE06 function are shown in Figure 5, where the dashed line of zero energy (0 eV) indicates the Fermi level (EF). The valence band maximum (VBM) of Pm-BCN is located at Z (0.0, 0.0, 0.5), and its conduction band minimum (CBM) appears at A (0.5, 0.5, 0.0). Pm-BCN has an indirect and wide band gap of 2.458 eV, therefore it is clearly a semiconductor. The PDOS can be divided into three parts: the first region ranges from −23 to −18 eV, the second region ranges from approximately −16 eV to the Fermi level, and the third region ranges approximately from 2.5 to 10 eV. The first region is dominated from the p orbital, which is primarily from the N-s, C-s, and C-p orbitals. The N-p state and C-s orbitals provide a major contribution to the −16 to −12 eV of the second region. From −12 eV to the Fermi level, the distributions of the B-p, C-p, and N-p orbitals are much greater than that of s orbitals. From 2.5 to 10 eV, the distribution of N-p orbitals is slightly smaller than that
of B-p and C-p orbitals. To further understand the chemical bonds, Figure 6 plots the electronic localization function (ELF) of Pm-BCN. ELF is an excellent measure of the strength of covalent bonds. Here, B-C and B-N bonding are strongly covalent, whereas the C-N bonding is weakly covalent. The band decomposed charge densities of VBM and CBM of Pm-BCN are depicted in Figure 6b,c, respectively. The B atom is the main contributor to the CBM; the C atom contributes a small amount to the CBM but is the main contributor to the VBM; and the N atom makes a small contribution to the VBM.

Figure 5. Band structure and the partial density of states (PDOS) of Pm-BCN.

Figure 6. Electronic localization functions (a) and band decomposed charge densities of VBM and CBM (b,c) of Pm-BCN.

4. Conclusions

Based on DFT calculations, in this study, we designed and predicted a new light-element compound, Pm-BCN. First, by analyzing the phonon spectrum, we found that the elastic constants and relative enthalpy of Pm-BCN are theoretically stable. Second, we found that Pm-BCN has an indirect and wide band gap and is a semiconductor material. Third, we showed that the B10 position is the main contributor to the CBM, the C9 position provides a small contribution to the CBM but the main contribution to the VBM, and the N8 position is a minor contributor to the VBM. Finally, we found that the elastic anisotropy in $E$ and the $G$ of Pm-BCN are slightly smaller than those of BCN$_2$ according to $E_{\text{max}}/E_{\text{min}}$ and $G_{\text{max}}/G_{\text{min}}$, whereas the shear anisotropy factor $A_2$ and the anisotropy of $B$ along the $a$
direction with respect to the b direction $A_{3b}$ of $Pm\text{-}BCN$ are smaller than those of $t\text{-}C_8B_2N_2$, $I\text{-}4m2 \text{BCN}$, $Imm2 \text{BCN}$, $B_2N_2C_3$, $BNC_2$, and $B_9N_3C$.

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**References**

1. Fan, Q.; Liu, H.; Jiang, L.; Zhang, W.; Song, Y.; Wei, Q.; Yu, X.; Yun, S. Three-dimensional metallic carbon allotropes with superhardness. *Nanotechnol. Rev.* 2021, 10, 1266–1276. [CrossRef]

2. Gao, Y.; Wu, Y.; Huang, Q.; Ma, M.; Pan, Y.; Xiong, M.; Li, Z.; Zhao, Z.; He, J.; Yu, D. First principles studies of superhard BC6N phases with unexpected 1D metallicity. *Comput. Mater. Sci.* 2018, 148, 157–164. [CrossRef]

3. Fan, Q.; Wu, N.; Yang, R.; Yu, X.; Yun, S. All $sp^2$ hybridization BN polymorphs with wide bandgap. *J. Appl. Phys.* 2022, 131, 055703. [CrossRef]

4. Liu, Y.; Li, X.; Xing, M.; Jin, J. Novel BCN$_2$ and CN compounds in C2/m phase: First-principle calculations. *J. Phys. Chem. Solids* 2021, 158, 110231. [CrossRef]

5. Li, X.; Xing, M. Two novel superhard monoclinic phase of B–C–N compounds. *J. Solid State Chem.* 2020, 292, 121750. [CrossRef]

6. Fan, Q.; Li, C.; Wang, J.; Yu, X.; Yun, S. Stability, mechanical, anisotropic and electronic properties of pO8 carbon: A superhard carbon allotrope in orthorhombic phase. *J. Solid State Chem.* 2021, 294, 121894. [CrossRef]

7. Qu, N.R.; Wu, N.; Li, Y.D.; Li, Z.P.; Gou, H.Y.; Gao, F.M. Surperhard monoclinic BC$_6$N allotropes: First-principles investigations. *Chin. Phys. B* 2019, 28, 096201. [CrossRef]

8. Li, S.; Shi, L. Two novel superhard structures: Monoclinic BC$_3$N. *Physica B* 2020, 584, 412061. [CrossRef]

9. Fan, Q.; Liu, H.; Jiang, L.; Yu, X.; Zhang, W.; Yun, S. Two orthorhombic superhard carbon allotropes: C16 and C24. *Diam. Relat. Mater.* 2021, 116, 108426. [CrossRef]

10. Zhu, H.; Shi, L.; Li, S.; Duan, Y.; Zhang, S.; Xia, W. Effects of hydrostatic pressure and biaxial strains on the elastic and electronic properties of t-C$_8$B$_2$N$_2$. *J. Appl. Phys.* 2018, 123, 135103. [CrossRef]

11. Wang, D.; Shi, R.; Gan, L.H. t-C$_8$B$_2$N$_2$: A potential superhard material. *Chem. Phys. Lett.* 2017, 669, 80–84. [CrossRef]

12. Fan, Q.; Liu, H.; Yang, R.; Yu, X.; Zhang, W.; Yun, S. An orthorhombic superhard carbon allotrope: $Pmaa$ C$_8$. *J. Solid State Chem.* 2021, 300, 122260. [CrossRef]

13. Wang, S.; Oganov, A.R.; Qian, G.; Zhu, Q.; Dong, H.; Dong, X.; Esfahani, M.M.D. Novel superhard B–C–O phases predicted from first principles. *Phys. Chem. Chem. Phys.* 2016, 18, 1859–1863. [CrossRef] [PubMed]

14. Fan, Q.; Wei, Q.; Chai, C.; Zhang, M.; Yan, H.; Zhang, Z.; Zhang, J.; Zhang, D. Elastic and electronic properties of $Imm2$- and $I\text{-}4m2\text{-BCN}$. *Comput. Mater. Sci.* 2015, 97, 6–13. [CrossRef]

15. Fan, Q.; Wei, Q.; Chai, C.; Yan, H.; Zhang, M.; Lin, Z.; Zhang, Z.; Zhang, J.; Zhang, D. Structural, mechanical, and electronic properties of P3m1-BCN. *J. Phys. Chem. Solids* 2015, 79, 89–96. [CrossRef]

16. Li, X.; Xing, M. Novel carbon-rich nitride C$_3$N: A superhard phase in monoclinic symmetry. *Comput. Mater. Sci.* 2019, 158, 170–177. [CrossRef]

17. Xing, M.; Li, X. BC$_2$O in C2/m phase: Light element compound with direct band gaps. *J. Solid State Chem.* 2021, 304, 122590. [CrossRef]

18. Fan, Q.; Wei, Q.; Chai, C.; Yu, X.; Liu, Y.; Zhou, P.; Yan, H.; Zhang, D. First-principles Study of Structural, Elastic, Anisotropic, and Thermodynamic Properties of R3–B$_3$C. *Chin. J. Phys.* 2015, 53, 100601.

19. Fan, Q.; Zhao, Y.; Yu, X.; Song, Y.; Zhang, W.; Yun, S. Physical properties of a novel microporous carbon material. *Diam. Relat. Mater.* 2020, 106, 107831. [CrossRef]

20. Cui, H.J.; Yan, Q.B.; Sheng, X.L.; Wang, D.L.; Zheng, Q.R.; Su, G. The geometric and electronic transitions in body-centered-tetragonal C8: A first principle study. *Carbon* 2017, 120, 89–94. [CrossRef]

21. Xing, M.; Li, X. A porous nanotube network structure of metallic carbon. *Results Phys.* 2021, 28, 104579. [CrossRef]

22. Fan, Q.; Wei, Q.; Chai, C.; Yan, H.; Zhang, M.; Zhang, Z.; Zhang, J.; Zhang, D. Structural, anisotropic and thermodynamic properties of boron carbide: First principles calculations. *Indian J. Pure Ap. Phys.* 2016, 54, 227–235.

23. Yu, X.; Su, R.; He, B. A novel BN Polymorph with ductile manner. *J. Solid State Chem.* 2022, 306, 122794. [CrossRef]

24. Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* 1964, 136, B864. [CrossRef]
