A Reinvestigation of a Superhard Tetragonal $sp^3$ Carbon Allotrope

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Abstract: $\bar{I}4$–carbon was first proposed by Zhang et al., this paper will report regarding this phase of carbon. The present paper reports the structural and elastic properties of the three-dimensional carbon allotrope $\bar{I}4$–carbon using first-principles density functional theory. The related enthalpy, elastic constants, and phonon spectra confirm that the newly-predicted $\bar{I}4$–carbon is thermodynamically, mechanically, and dynamically stable. The calculated mechanical properties indicate that $\bar{I}4$–carbon has a larger bulk modulus (393 GPa), shear modulus (421 GPa), Young’s modulus (931 GPa), and hardness (55.5 GPa), all of which are all slightly larger than those of c-BN. The present results indicate that $\bar{I}4$–carbon is a superhard material and an indirect-band-gap semiconductor. Moreover, $\bar{I}4$–carbon shows a smaller elastic anisotropy in its linear bulk modulus, shear anisotropic factors, universal anisotropic index, and Young’s modulus.

Keywords: elastic properties; anisotropic properties; electronic structure; carbon allotrope

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1. Introduction

The group 14 elements, such as carbon, silicon, and germanium, have attracted much interest and have been extensively studied [1–20]. Carbon is found on the Earth mainly in the form of graphite and diamond. The quest for carbon materials with desired properties is of great interest in both fundamental science and advanced technology. One of the most famous carbon materials is graphene. Recently, some scholars of great research found several carbon allotropes with low-energy metastable structures, such as monoclinic M-carbon [1,2], F-carbon [3], orthorhombic W-carbon [4], Z-carbon [5], H-carbon and S-carbon [6], C-carbon [7], Imma-carbon [8,9], M585-carbon [10], T12-carbon [11], C2/m-16 carbon [12], P2221-carbon [13], and Cco-carbon [14]. We easily found that these carbon allotropes, with low-energy metastable structures with $sp^3$ hybridization, could possibly explain the superhard property of materials. Hardness is an important property that determines many of the technological applications of materials. The mechanical properties of some carbon allotropes (such as T-carbon [21] and Y-carbon [22]) are not excellent, as discussed above, but can be improved through modulation [23,24]. At the moment, there are a multitude of metastable carbon allotropes that have been predicted using the quantum-chemical methods of calculation, e.g., evolutionary metadynamics technique [25–28], and Universal Structure Prediction: Evolutionary Xtallography (USPEX) [29–32], or post-graphite superhard phase synthesized by cold-compressing graphite [33–39]. Compressed graphite appears as an initial material for transition to different superhard phases. An ocean of possible carbon modifications can be obtained by combining four-, five-, six-, seven-, even eight-membered carbon rings. The discussion above of carbon allotropes basically adopts this structure. Wang et al. [40] found a dynamically stable and energetically favourable carbon allotrope, i.e., J-carbon. It has a wider
band gap (5.89 eV within LDA-HSE06) than that of diamond and a larger bulk modulus (395 GPa). Currently, Z-carbon [33, 34] is the most stable and hardest material predicted by the theoretical methods compared with other theoretical structures, but it has not exceeded diamond’s bulk modulus and hardness. The inclusion in the Z-carbon of additional diamond blocks generates another superhard carbon allotrope family, investigated in [41]. Li et al. [42] predicted a new cubic carbon allotrope, namely, C96 carbon. Unfortunately, its mechanical properties are not excellent and it cannot be used as a potential superhard material. Recently, another sp3 carbon allotrope, i.e., diamond nanothread, was synthesized experimentally; Fitzgibbons et al. [43] and Zhan et al. [44] then reported regarding its mechanical properties. These nanothreads show extraordinary properties, such as strength and stiffness, higher than those of sp2 carbon nanotubes.

Moreover, I4–carbon was first predicted in [45]. However, the physical properties, i.e., the structural, mechanical, and electronic properties, of I4–carbon were not studied in [45], nor in other studies. The physical properties of a novel superhard carbon allotrope with tetragonal I4 symmetry (16 atoms/cell) will be detailed in this paper using first-principles calculations.

2. Materials and Methods

The calculations were performed using the density functional theory (DFT) [46, 47] by using the Cambridge Serial Total Energy Package (CASTEP) code [48]. The electron–ionic core interaction was represented using the ultrasoft pseudopotentials [49]. The structural optimizations were conducted using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization [50]. The calculations were performed using the local density approximation (LDA) [51, 52] and generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) [53] exchange correlation potential. The total energy convergence tests showed that convergence to within 1 m\(^{-}\)eV/atom was achieved using the above calculation parameters. The electron and core interactions were included by using the ultrasoft pseudopotentials method, with a plane-wave energy cutoff energy of 400 eV, where 2s2p2 are treated as valence electrons for C. Highly dense k-point [54] sampling with a grid spacing of less than 2\(\pi\) \times 0.025 Å\(^{-}\)1 (7 \times 7 \times 7 for I4–carbon) in the Brillouin zone was used. The self-consistent convergence of the total energy was 5 \times 10^{-6} eV/atom; the maximum force on the atom was 0.01 eV/Å; the maximum ionic displacement was within 5 \times 10^{-4} Å; the maximum stress was within 0.02 GPa.

3. Results and Discussion

3.1. Structural Properties

There is a new tetragonal carbon phase, namely, I4–carbon, which belongs to the I4 space group. The crystal structure of I4–carbon is shown in Figure 1. Different atomic positions are denoted by different colours of spheres. There are five inequivalent carbon atoms in its conventional cell, located at C1: 8g (−0.1219, −0.2709, −0.6225), C2: 8g (0.4044, −0.1809, 0.0492), C3: 8g (0.4812, 0.2514, −0.3772), C4: 2a (0.5000, 0.5000, 0.5000) and C5: 2d (0.0000, 0.5000, 0.7500). The optimized lattice parameters within the GGA and LDA level of I4–carbon at ambient pressure are listed in Table 1. As listed, a = 5.5628 (5.5017) Å and c = 5.5082 (5.4471) Å are within the GGA (LDA) level and c is slightly smaller than a. These lattice parameters are in excellent agreement with the theoretical values predicted by Zhang et al. [45]. The results within GGA are closer to the theoretical values predicted by Zhang et al. [45]; thus, the following discussions use the results of the GGA level. I4–carbon has seven bond lengths, which are also listed in Table 1. Between C1 and C2, C1 and C3, there are two different bond lengths, i.e., 1.5586 and 1.5224 Å, 1.5555 and 1.5207 Å, respectively, within the GGA level. The average bond length of I4–carbon is 1.5510 Å, while it is 1.567 Å and 1.551 Å for C2/m–16 carbon and M carbon, respectively. They are all slightly greater than that of diamond (1.535 Å). The hardness of I4–carbon, C2/m–16 carbon, M carbon, c-BN and diamond is calculated by using Lyakhov and Oganov’s model [55]. The hardness of I4–carbon is 55.5 GPa, which is slightly smaller
than that of C2/m–16 carbon (59.5 GPa) [12] and M carbon (66.6 GPa), approximately half of that of diamond (89.7 GPa), and slightly larger than that of c-BN (49.9 GPa); the hardness of diamond is very close to the result of Ref [55] (91.0 GPa) using the Lyakhov and Oganov’s model. The hardness of I–carbon is 83.0 GPa in Ref [45], the main reason for this situation is that the empirical formula may over or underestimate the value of the material’s hardness. Most researchers agree that “superhard” materials are those with Hv exceeding 40 GPa. Although there are slight differences between the results of the empirical models above, all of them greatly exceed 40 GPa, indicating that I–carbon is a superhard material.

Figure 1. The crystal structure of I–carbon.

Table 1. The calculated lattice parameters (in Å) and bond lengths (in Å) for I–carbon.

| Methods | a   | c   | dc1-c2 | dc1-c3 | dc2-c3 | dc2-c5 | dc3-c4 |
|---------|-----|-----|--------|--------|--------|--------|--------|
| GGA     | 5.5628 | 5.5082 | 1.5586 | 1.5555 | 1.5694 | 1.5871 | 1.5430 |
|         |      |      | 1.5224 | 1.5207 |        |        |        |
| LDA     | 5.5017 | 5.4471 | 1.5435 | 1.5408 | 1.5531 | 1.5683 | 1.5253 |
|         |      |      | 1.5036 | 1.5039 |        |        |        |

3.2. Mechanical Properties

For the tetragonal I–carbon, seven independent elastic constants Cii were determined within the GGA level from the stress of the strained structure with a finite strain. The elastic constants of I–carbon under different pressures are listed in Table 2. From Table 2, one can find that the mechanical stability of I–carbon satisfies Born’s criterion for a tetragonal crystal [56]: Cii > 0, i = 1, 3, 4, 6; C11–C12 > 0; C11 + C33 – 2C13 > 0 and 2(C11 + C12) + C33 + 4C13 > 0, indicating that I–carbon is mechanically stable at 0–100 GPa. Moreover, almost all elastic constants increase with increasing pressure. C11 increases the fastest (dC11/dP = 4.57), followed by C33 (dC33/dP = 4.24); C44 is the slowest (dC44/dP = 0.63). C16 decreases with increasing pressure (dC16/dP = −0.35). Furthermore, it is important to explore the dynamic stability and thermodynamic stability for further experimental synthesis. The phonon spectra and the enthalpies as a function of pressure are shown in Figure 2a–d. Clearly, no imaginary mode is shown in the phonon spectra. This strongly confirms that the I–carbon with the I4 structure is dynamically stable; thus, it is a new metastable phase in the carbon family. The enthalpy of different carbon allotropes is quantified in terms of the following formation enthalpy formula: ΔH = Hcarbon allotropes/n1 – Hdiamond/n2, where n denotes the number of atoms in a conventional cell for carbon allotropes or graphite. As shown in Figure 2c,d, the calculated formation enthalpies of I4–carbon are slightly smaller than those of M-carbon below 32.25 GPa. Bulk modulus B and shear
modulus $G$ are calculated by using the Voigt–Reuss–Hill approximation. It is known that the Voigt bound is obtained by using the average polycrystalline modulus, based on an assumption of uniform strain throughout a polycrystalline, and is the upper limit of the actual effective modulus, while the Reuss bound is obtained by assuming a uniform stress and is the lower limit of the actual effective modulus. The arithmetic average of Voigt and Reuss bounds is referred to as the Voigt–Reuss–Hill approximations. Young’s modulus $E$ and Poisson’s ratio $v$ are obtained using the following equations:

$$E = 9BG/(3B + G), \quad v = (3B - 2G)/(6B + 2G),$$

respectively. The calculated results of elastic modulus for $I^-4$–carbon are also shown in Table 2. The bulk modulus, shear modulus, Poisson’s ratio, and Young’s modulus all increase with increasing pressure. The bulk modulus increases the fastest, while shear modulus increases the slowest, i.e., $dB/dP = 3.30$ and $dG/dP = 0.86$, respectively. Pugh [57] proposed the ratio of bulk to shear modulus ($B/G$) and Lewandowski [58] proposed Poisson’s ratio as indications of a ductile versus brittle characteristic, $B/G > 1.75$ and $v > 0.26$ for a solid material represents ductility, while $B/G < 1.75$ and $v < 0.26$ usually indicate brittleness. From 0 to 100 GPa, $I^-4$–carbon is brittle; namely, the brittleness of $I^-4$–carbon decreases with increasing pressure. Compared with other carbon allotropes (P222$_1$–carbon: 0.872 [13]; C2/m–16 carbon: 0.867 [12]; Imma–carbon: 0.858 [12]; diamond: 0.831 [12]), $I^-4$–carbon (0.933) has the least brittleness at ambient pressure.

![Figure 2. Phonon spectra for $I^-4$–carbon at 0 GPa (a) and 100 GPa (b); enthalpies of $I^-4$–carbon and other carbon allotropes relative to graphite as a function of pressure (c,d).](image-url)
where the unit of pressure is GPa. By fitting using the polynomial, it is clear that the incompressibility of lattice parameter $c$ is slightly larger than that of $a$. Regarding the incompressibility of lattice parameters $a/a_0$ and $c/c_0$, they are very close. The incompressibility of lattice parameter $c$ is slightly better than that of $a$. By fitting the calculated data using the polynomial fitting methods, the following relationships at $0$ GPa and $0$ K are obtained:

$$a/a_0 = 1.96546 \times 10^{-6} P^2 - 7.85386 \times 10^{-4} P + 0.99970$$  \hspace{1cm} (1)$$

$$c/c_0 = 1.93918 \times 10^{-6} P^2 - 7.79164 \times 10^{-4} P + 0.99965$$  \hspace{1cm} (2)$$

where the unit of pressure is GPa. By fitting using the polynomial, it is clear that the incompressibility of lattice parameter $c$ is slightly better than that of $a$.

**Figure 3.** The primitive cell volume $V/V_0$ as a function of pressure for $\text{I}_6$–carbon, $\text{P}2\text{mm}$–carbon, $\text{C}2/m$–16 carbon, $\text{M}$–carbon, $\text{c}$–BN and diamond (a); lattice constants $a/a_0$, $c/c_0$ compression of $\text{I}_6$–carbon as a function of pressure (b).
The defined Debye temperature parameter, which can be interpreted as the temperature at which the highest-frequency mode (and hence every mode) is excited, is of great importance, allowing us to predict the heat capacity at any temperature in an atomic solid. The formula for evaluating the Debye temperature is given by [59]:

$$\Theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{\frac{3}{2}} v_m$$  \hspace{1cm} (3)

where $h$ denotes Planck’s constant, $k_B$ denotes Boltzmann’s constant, $n$ denotes the number of atoms per formula unit, $N_A$ denotes Avogadro’s number, $M$ denotes molar mass, and $\rho$ denotes density. The average sound velocity $v_m$ is described by the following formula:

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_t^2} + \frac{1}{v_l^2} \right) \right]^{-\frac{1}{2}}$$  \hspace{1cm} (4)

The transverse and longitudinal elastic wave velocity, $v_t$ and $v_l$, can be obtained using Navier’s equation, as follows [60]:

$$v_t = \sqrt{\frac{G}{\rho}} \quad \text{and} \quad v_l = \sqrt{\frac{3B + 4G}{3\rho}}$$  \hspace{1cm} (5)

where $B$ and $G$ are the bulk modulus and shear modulus, respectively. Based on Equation (3), the Debye temperature of $\text{I} - \text{carbon}$ $\Theta_D = 2024$ K. The Debye temperature of $\text{I} - \text{carbon}$ as a function of pressure is plotted in Figure 4a. It is found that the Debye temperature increases with increasing pressure. Furthermore, the greater the pressure, the more slowly the Debye temperature increases. The calculated results of the density, Debye temperature, transverse and longitudinal elastic wave velocity $v_t$ and $v_l$, and the mean sound velocity $v_m$ at different pressures are listed in Table 3. The density and $v_t$ increase with increasing pressure. With the increase of pressure, the transverse longitudinal elastic wave velocity $v_t$ shows no monotonic increase or decrease. However, the mean sound velocity $v_m$ increases with increasing pressure from 0 to 80 GPa and decreases with increasing pressure from 80 to 100 GPa. The main reason is that sometimes $v_t$ increases with increasing pressure and sometimes decreases, i.e., there is no law.

![Figure 4](image-url)  \hspace{1cm} \text{Figure 4. Debye temperature (a) and band gap (b) of $\text{I} - \text{carbon}$ as a function of pressure.}
Table 3. The calculated density (ρ, in g/cm$^3$), the longitudinal, transverse, and mean elastic wave velocity ($v_s$, $v_p$, $v_m$, in m/s), and the Debye temperature ($\Theta_D$, in K) for $\overline{I}_4$-carbon.

| P  | $\rho$  | $v_s$ | $v_p$ | $v_m$ | $\Theta_D$ |
|----|---------|-------|-------|-------|-----------|
| 0  | 3.2764  | 17.069| 11,336| 12,398| 2024      |
| 10 | 3.3564  | 17.434| 11,402| 12,503| 2051      |
| 20 | 3.4332  | 17.529| 11,395| 12,513| 2089      |
| 30 | 3.5059  | 17.730| 11,395| 12,513| 2089      |
| 40 | 3.5750  | 17.939| 11,415| 12,549| 2109      |
| 50 | 3.6412  | 18.124| 11,427| 12,589| 2141      |
| 60 | 3.7045  | 18.303| 11,427| 12,589| 2141      |
| 70 | 3.7654  | 18.465| 11,424| 12,598| 2154      |
| 80 | 3.8243  | 18.617| 11,400| 12,594| 2176      |
| 90 | 3.8814  | 18.751| 11,345| 12,547| 2178      |
| 100| 3.9365  | 18.852| 11,345| 12,547| 2178      |

3.3. Anisotropic Properties

It is well known that the anisotropy of elasticity is an important implication in engineering science and crystal physics [61], hence, it is worthwhile to investigate the elastic anisotropy of materials. The shear anisotropic factors provide a measure of $B_a$, $B_b$, and $B_c$, i.e., the bulk modulus along the $a$, $b$, and $c$ axes, respectively, which can be calculated by using the following equations:

$$B_a = \frac{dP}{da} = \frac{\Lambda}{1 + \alpha + \beta}, \quad (6)$$

$$B_b = \frac{dP}{db} = \frac{B_a}{\alpha}, \quad (7)$$

$$B_c = \frac{dP}{dc} = \frac{B_a}{\beta}, \quad (8)$$

$$\Lambda = C_{11} + 2C_{12} + C_{12}a^2 + C_{33}b^2 + 2C_{13}(1 + \alpha), \quad (9)$$

$$\alpha = \frac{(C_{11} - C_{12})}{(C_{22} - C_{12})}, \quad (10)$$

$$\beta = \frac{(C_{22} - C_{12})(C_{11} - C_{12}) - (C_{11} - C_{12})(C_{13} - C_{12})}{(C_{22} - C_{12})(C_{33} - C_{13})}, \quad (11)$$

The calculated $B_a$, $B_b$, and $B_c$ at different pressures are shown in Figure 5a. Due to the lattice constant a being equal to b, the bulk modulus along the $a$-axis is equal to that along the $b$-axis, in other words, $B_a = B_b$. It is clear that $B_a$, $B_b$, and $B_c$ increase with increasing pressure and that $B_a$, $B_b$ (87.69%) increase more than $B_c$ (76.50%). The calculated directional bulk modulus suggests that it is the largest along the $a$-axis and the smallest along the $c$-axis, indicating that the compressibility along the $c$-axis is the smallest, while along the $a$-axis, is the largest. This is in accordance with the relationships between the ratios $a/a_0$, $c/c_0$ and pressure, as shown in Figure 3b. Therefore, the anisotropy of the linear bulk modulus should also be considered. The anisotropy of the bulk modulus along the $a$-axis and $c$-axis with respect to the $b$-axis can be estimated by:

$$A_{B_a} = \frac{B_a}{B_b} \text{ and } A_{B_c} = \frac{B_c}{B_b} \quad (12)$$

The anisotropy factors of the bulk modulus along the $a$-axis and $c$-axis for $\overline{I}_4$-carbon at $T = 0$ K as a function of pressure are shown in Figure 5b. Note that a value of 1.0 indicates elastic isotropy and any departure from 1.0 represents elastic anisotropy. The anisotropy of the bulk modulus along the $a$-axis and $c$-axis with respect to the $b$-axis shows that $A_{B_a}$ is elastic isotropy and $A_{B_c}$ is elastic anisotropy.
After discussing the anisotropy of the bulk modulus, we now discuss the anisotropy of the shear modulus. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. The shear anisotropic factor for the (1 0 0) shear planes between [0 1 1] and [0 1 0] directions and the (0 1 0) shear planes between [1 0 1] and [0 0 1] directions is [62]:

\[
A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}},
\]

(13)

For the (0 1 0) shear planes between [1 0 1] and [0 0 1] directions, it is [60]:

\[
A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}},
\]

(14)

For the (0 0 1) shear planes between [1 1 0] and [0 1 0] directions, it is [60]:

\[
A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}.
\]

(15)

For an isotropic crystal, the factors \(A_1\), \(A_2\), and \(A_3\) are 1.0, while any value smaller or larger than 1.0 is a measure of the elastic anisotropy possessed by the materials. The anisotropy factors of \(\text{I}_\text{I}^2\)–carbon at \(T = 0\) K as a function of pressure are shown in Figure 5c. Due to the symmetry of the crystal structure, \(C_{11} = C_{22}, C_{44} = C_{55}\) and \(C_{13} = C_{23}\); thus, \(A_1 = A_2\). From Figure 5c, \(A_1\) first increases and

Figure 5. Linear bulk modulus \(B_a, B_b, \) and \(B_c\) of \(\text{I}_\text{I}^2\)–carbon at 0 K as a function of pressure (a); anisotropy factors of \(\text{I}_\text{I}^2\)–carbon at 0 K as a function of pressure, (b) \(A_{Bb}\) and \(A_{Bc}\); (c) \(A_1, A_2\) and \(A_3\); (d) \(A_U\).
then decreases with increasing pressure, while \( A_3 \) increases monotonically with increasing pressure. \( \text{I}_4 \)-carbon shows elastic anisotropy in the bulk modulus and shear modulus. The universal anisotropic index \( (A^u = 5G_V/G_R + B_V/B_R - 6) \) combines the shear modulus and bulk modulus to exhibit the anisotropy of the material. The \( A^u \) of \( \text{I}_4 \)-carbon increases with pressure (see Figure 5d), indicating that the anisotropy of \( \text{I}_4 \)-carbon increases with increasing pressure. The \( A^u \) of \( \text{I}_4 \)-carbon is 0.0369, which is smaller than that of \( \text{C}_2/m \)-carbon (0.0766) and \( \text{P}_222_1 \)-carbon (0.0526).

Young’s modulus is not always the same in all orientations of a material; it will change depending on the direction of the force vector. Engineers can use this directional phenomenon to their advantage in creating structures. The directional dependence of the anisotropy in Young’s modulus is calculated by using the Elastic Anisotropy Measures (ELAM) [63,64] code. The 2D representation of Young’s modulus for \( \text{I}_4 \)-carbon in the (001), (010), (100), (111), (00\( \overline{1} \)), and (101) planes is shown in Figure 6a–f, respectively. The black, red, and blue solid curves represent Young’s modulus for \( \text{I}_4 \)-carbon in the (001), (010), (100), (111), (00\( \overline{1} \)), and (101) planes at 0, 50 and 100 GPa, respectively. It is obvious that the anisotropy of Young’s modulus increases with increasing pressure in the (001), (010), (100), (111), (00\( \overline{1} \)), and (101) planes. To investigate the anisotropy of Young’s modulus in detail, we calculate the maximal and minimal values of Young’s modulus for \( \text{I}_4 \)-carbon in the (001), (010), (100), (111), (00\( \overline{1} \)), and (101) planes and for all possible directions, together with the ratio \( E_{\text{max}}/E_{\text{min}} \), which are listed in Table 4.

The conclusion from Table 4 is consistent with the conclusion we obtained from Figure 6, i.e., that the anisotropy of Young’s modulus increases with increasing pressure in the (001), (010), (100), (111), (00\( \overline{1} \)), and (101) planes. Regarding the distribution of Young’s modulus in the (001) plane and (00\( \overline{1} \)) plane, the maximal and minimal values are the same, while in the (010) plane and (100) plane, they are also the same. The (001) plane and (00\( \overline{1} \)) plane exhibit the largest anisotropy of Young’s modulus for \( \text{I}_4 \)-carbon, while the (101) plane exhibits the smallest anisotropy of Young’s modulus. This situation also appears under high pressure. All of the degrees of special plane anisotropy are smaller than the overall performance of the material anisotropy because the minimal value of the entire Young’s modulus was not obtained. The anisotropy of Young’s modulus of \( \text{I}_4 \)-carbon (\( E_{\text{max}}/E_{\text{min}} = 1.133 \)) is slightly smaller than that of \( \text{C}_2/m \)-16 carbon (\( E_{\text{max}}/E_{\text{min}} = 1.275 \)) and \( \text{P}_222_1 \)-carbon (\( E_{\text{max}}/E_{\text{min}} = 1.173 \)). Thus, \( \text{I}_4 \)-carbon shows a smaller elastic anisotropy in its linear bulk modulus, shear anisotropic factors, universal anisotropic index, and Young’s modulus.

### Table 4. The maximum and minimum values of Young’s modulus (in GPa) in different planes and for pressures for \( \text{I}_4 \)-carbon.

| Plane  | \( P \) | Maximum | Minimum | \( E_{\text{max}}/E_{\text{min}} \) |
|--------|--------|---------|---------|-----------------|
| (001)  | 0      | 999     | 887     | 1.126 |
|        | 50     | 1250    | 1054    | 1.186 |
|        | 100    | 1427    | 1168    | 1.222 |
| (010)  | 0      | 998     | 889     | 1.123 |
|        | 50     | 1153    | 1053    | 1.095 |
|        | 100    | 1292    | 1150    | 1.123 |
| (100)  | 0      | 998     | 889     | 1.123 |
|        | 50     | 1153    | 1053    | 1.095 |
|        | 100    | 1292    | 1150    | 1.123 |
| (111)  | 0      | 992     | 888     | 1.117 |
|        | 50     | 1233    | 1045    | 1.180 |
|        | 100    | 1402    | 1139    | 1.231 |
| (00\( \overline{1} \)) | 0      | 999     | 887     | 1.126 |
|        | 50     | 1250    | 1054    | 1.186 |
|        | 100    | 1427    | 1168    | 1.222 |
| (101)  | 0      | 949     | 885     | 1.072 |
|        | 50     | 1160    | 1050    | 1.105 |
|        | 100    | 1298    | 1147    | 1.132 |
| All    | 0      | 999     | 882     | 1.133 |
|        | 50     | 1250    | 1042    | 1.200 |
|        | 100    | 1427    | 1138    | 1.254 |
### 3.4. Electronic Properties

The band structures of $\text{I}_4$–carbon are shown in Figure 7a,b at 0 and 100 GPa, respectively. Semiconductor materials have direct or indirect band gaps. In direct band gap materials, the maximum of the valence band (VBM) and minimum of the conduction band (CBM) occur at the same value of the wave vector, while in indirect band gap materials, they occur for different values of the wave vector. It is obvious that $\text{I}_4$–carbon is an indirect-band-gap and wide-band-gap semiconductor material. The VBM of $\text{I}_4$–carbon is located at the M point (0.500, 0.500, 0.000), while the CBM is located from point (0.000, 0.000, 0.3667) through G (0.000, 0.000, 0.000) to the Z point (0.000, 0.000, 0.500), whether at ambient pressure or under high pressure. From Figure 7a,b, it is shown that the band gap increases with increasing pressure; more details are shown in Figure 4b; the band gap of $\text{I}_4$–carbon increases from 5.19 eV to 5.59 eV. The greater the pressure, the less the band gap increases. To determine the reason why, we calculate the energy values of the CBM and VBM under different pressures. The calculated results are illustrated in Figure 7c. The energy of VBM for $\text{I}_4$–carbon is 7.96 eV at 0 GPa and 10.58 eV at 100 GPa; $\Delta E_{\text{VBM}} = 2.62$ eV. The energy of CBM for $\text{I}_4$–carbon is 13.15 eV at 0 GPa and 16.17 eV at 100 GPa; $\Delta E_{\text{CBM}} = 3.02$ eV. $\Delta E_{\text{CBM}} - \Delta E_{\text{VBM}} = 0.40$ eV, which is the same as with the band gap increase. In other words, as pressure increases, the conduction band and valence band energy will increase, but the energy of the conduction band will increase more than that of the valence band. The partial density of states (PDOS) of five inequivalent carbon atoms in $\text{I}_4$–carbon at 0 and 100 GPa are shown in Figure 8. Figure 8a,c,e,g,i show the partial density of states of five inequivalent carbon atoms at 0 GPa; Figure 8b,d,f,h,j show the partial density of states of five inequivalent carbon atoms at 100 GPa.
No matter the position of the carbon atoms, the partial density of states in the conduction band part is, with increasing pressure intensity, near low energy, and the valence band deviates from the Fermi level. The PDOS in the lower energy part is contributed mainly by the C-2 orbitals, while in the other energy part, is contributed mainly by the C-2s orbitals.

Figure 7. Electronic band structure for the I–carbon at ambient pressure (a) and 100 GPa (b); the calculated energy values of CBM and VBM under different pressures (c).

Figure 8. Cont.
Figure 8. Partial density of state for $\text{I}_4$–carbon; (a,c,e,g,i) are at ambient pressure, while (b,d,f,h,j) are at 100 GPa.

4. Conclusions

In conclusion, the low-energy metastable structures of $\text{I}_4$–carbon have been systematically investigated based on the density functional theory. The related enthalpy, elastic constants and phonon spectra confirm that the newly-predicted $\text{I}_4$–carbon is thermodynamically, mechanically, and dynamically stable. As a potential superhard material for engineering applications, the mechanical properties of $\text{I}_4$–carbon indicate that it is a superhard material. $\text{I}_4$–carbon shows a smaller anisotropy in its linear bulk modulus, shear anisotropic factors, universal anisotropic index, and Young’s modulus. The band structure shows that $\text{I}_4$–carbon is an indirect-band-gap and wide-band-gap semiconductor material. Finally, the calculations of its mechanical properties reveal that $\text{I}_4$–carbon possesses a high bulk and shear modulus as well as a low Poisson’s ratio and $B/G$ ratio (<1.75). Moreover, $\text{I}_4$–carbon has a larger Debye temperature ($\Theta_D = 2024$ K). Due to their wide-band-gap and higher bulk moduli, hardness, they are attractive for semiconductor device applications and superhard material with potential technological and industrial applications.

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