C2/c-C32: A New Superhard \( sp^3 \) Carbon Allotrope with Direct Band Gap

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A new monoclinic carbon crystal with the space group \( C2/c \) was uncovered; its unit cell comprises 32 carbon (C32) atoms. This full \( sp^3 \)-bonded carbon phase is dynamically and mechanically stable. The results show that \( C2/c-C32 \) has excellent mechanical properties, with its shear modulus and Vickers hardness being 343 and 56 GPa, respectively. Based on the elastic anisotropic calculations, \( C2/c-C32 \) is confirmed to be an anisotropic material. Notably, \( C2/c-C32 \) has a direct band gap structure with a band gap of 2.50 eV.

1. Introduction

Carbon is one of the most versatile elements in nature and displays a broad range of physical and chemical properties. In particular, carbon allotropes have unique structural, electronic, and mechanical properties, owing to which they have gained considerable research attention and are desirable for various applications. Superhard materials, such as diamond and cubic boron nitride (c-BN), have been extensively studied for their potential application in cutting and polishing tools. Finding new carbon allotropes with high hardness has become a subject of great concern. Hundreds of superhard carbon allotropes with cubic [1–3], hexagonal [4], orthorhombic [5–7], and tetragonal [8, 9] symmetry are collected in the SACADA database [10]. In addition, some superhard monoclinic allotropes, such as V-carbon [11], \( P2/m-C54 \) [12], \( M585 \)-carbon [13], \( M10 \)-carbon [14], \( M \)-carbon [15], monoclinic \( C12 \) [16], and \( P2_1/m \)-carbon [17], have been proposed. Most carbon allotropes are semiconductors, while some carbon allotropes are metallic [5, 18–20]. For example, diamond is a semiconductor with a wide indirect band gap of 5.4 eV. Recently, carbon allotropes with direct band gap have been discovered. Fan et al. [7] proposed an orthorhombic carbon allotrope, \( Ima2-C32 \), with a direct band gap of 2.926 eV. Based on high-throughput calculations, Wei et al. [21] found seven direct band-gap carbon allotropes that exhibit superhardness, four of which (G21, G90, G117, and G223) show monoclinic symmetry. In the present work, a crystal structure predicting technique was used to find more superhard carbon allotropes with a direct band gap. As a result, a new superhard carbon allotrope, \( C2/c-C32 \), was proposed that possesses a direct band gap, making it a promising material for electronic and optoelectronic applications.

2. Computational details

Research on new carbon allotropes is based on a particle swarm optimization algorithm implemented in the CALYPSO code [22–24], which has been successfully applied to structural prediction [25–29]. All first-principles calculations were performed in the framework of density functional theory (DFT) [30, 31] as implemented in the VASP code [32], and electron interactions were described using the generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [33]. In order to describe the ion–electron interactions, the projected augmented wave (PAW) method was used [34]. An energy cut-off value of 800 eV and a \( \Gamma \)-centered
of this structure are a = 8.636 Å, b = 4.605 Å, c = 5.089 Å, and \( \beta = 86.2^\circ \). The Wyckoff positions occupied by carbon atoms are C1 8f (0.0324, 0.1123, 0.0974), C2 8f (0.4587, 0.8834, 0.03352), C3 8f (0.2885, 0.1520, 0.6092), and C4 8f (0.2100, 0.1123, 0.0974), C2 8f (0.4587, 0.8834, 0.03352). The crystal structure shown in Fig. 1 indicates that all carbon atoms in C2/c-C32 are \( sp^3 \)-bonded. The average bond length of the C–C bonds is 1.567 Å. Compared to the bond length of a diamond (1.544 Å), it can be concluded that the C–C bond length of C2/c-C32 is very close to that of a diamond. So, one can expect that C2/c-C32 is also a superhard material. The C2/c-C32 phonon spectrum was calculated to verify the stability of C2/c-C32 (Fig. 2). No negative frequency was observed in the entire Brillouin zone, indicating that C2/c-C32 is dynamically stable.

The elastic constants were calculated for C2/c-C32 to verify its mechanical stability. The results are listed in Table I. For comparison, the elastic constants of diamond and other monoclinic carbon materials are also shown in Table I. From the elastic constants, one can obtain that all eigenvalues of the elastic constants matrix are positive, thus indicating the mechanical stability of C2/c-C32. Additionally, the C11 constant of C2/c-C32 is almost the same as that of diamond, indicating high incompressibility of C2/c-C32 along the \( x \) direction. Using the Voigt–Reuss–Hill approximation \[37\], the shear modulus \( G \) and the bulk modulus \( B \) of C2/c-C32 were calculated, and the results were listed in Table II, which also presents a comparison with the values of other monoclinic carbon phases and diamond. The Poisson’s ratio \( v \) and Young’s modulus \( E \) can be obtained \[40\] by

\[
v = \frac{3B - 2G}{2(3B + G)} \quad (1)
\]
and

\[
E = \frac{9BG}{(3B + G)} \quad (2)
\]

The calculated \( B \), \( E \), and \( G \) of C2/c-C32 are 355 GPa, 780 GPa, and 343 GPa, respectively, which are slightly higher than those of \( P2/m-C54 \) (345 GPa, 754 GPa, and 332 GPa, respectively). The \( B/G \) ratio of C2/c-C32 is 1.03, which is lower than the critical value of 1.75. This means that C2/c-C32 is a brittle material. High elastic constants and elastic moduli indicate high hardness. The hardness of C2/c-C32 was calculated using Chen’s model \[38\]. The calculated hardness of C2/c-C32 and other carbon phases is shown in Table II. As can be seen, the C2/c-C32 hardness value is 56 GPa, indicating the superhardness of C2/c-C32. The directional dependence of Young’s modulus of C2/c-C32 is illustrated in Fig. 3. As shown in the figure, the shape of the directional dependence of Young’s modulus is not a sphere, which indicates

3. Results and discussion

In the process of structure search using the CALYPSO software, we set the number of carbon atoms of a structure to be \( \simeq 20–40 \), limited the symmetry in the monoclinic system, and set the number of structures in each generation to 40. A total of 40 generations were searched. We successfully searched several previous structures, e.g., M-carbon. Additionally, a new structure having a C2/c space group was obtained. A unit cell of this structure contains 32 carbon atoms. Moreover, the lattice parameters of this structure are \( a = 8.636 \) Å, \( b = 4.605 \) Å, \( c = 5.089 \) Å, and \( \beta = 86.2^\circ \). The high-symmetry points in the reciprocal space associated with energy band structure and phonon dispersion were at the \( Z (0.0 0.0 0.5) \), \( \Gamma (0.0 0.5 0.0) \), \( \Lambda (0.5 0.5 0.0) \), \( \Delta (0.5 0.0 0.5) \), \( E (0.5 0.5 0.5) \) and \( C (0.0 0.5 0.5) \) points. The Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional \[36\] was used for a more accurate calculation of the band structure. The stress–strain calculation of the band structure. The stress–strain method was used to calculate the elastic constants, and the elastic moduli were obtained using Voigt–Reuss–Hill approximation \[37\]. The Vickers hardness was estimated using Chen’s model \[38\]. The phonon spectra were calculated by the Phonopy code \[39\].

![Fig. 1. Crystal structure of C2/c-C32.](image)

![Fig. 2. Phonon spectra of C2/c-C32.](image)
Table I: Elastic constants $C_{ij}$ [in GPa] of $C2/c$-C32 and other monoclinic carbon allotropes.

<table>
<thead>
<tr>
<th>Phases</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{15}$</th>
<th>$C_{25}$</th>
<th>$C_{35}$</th>
<th>$C_{46}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C2/c$-C32</td>
<td>1053</td>
<td>943</td>
<td>655</td>
<td>270</td>
<td>277</td>
<td>451</td>
<td>83</td>
<td>75</td>
<td>140</td>
<td>−7</td>
<td>33</td>
<td>−15</td>
</tr>
<tr>
<td>diamond [16]</td>
<td>1054</td>
<td>561</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P2_1/m$-C54 [12]</td>
<td>910</td>
<td>830</td>
<td>728</td>
<td>276</td>
<td>364</td>
<td>333</td>
<td>84</td>
<td>45</td>
<td>192</td>
<td>26</td>
<td>−55</td>
<td>21</td>
</tr>
<tr>
<td>$V$-carbon [12]</td>
<td>1089</td>
<td>1104</td>
<td>1033</td>
<td>508</td>
<td>466</td>
<td>447</td>
<td>40</td>
<td>87</td>
<td>98</td>
<td>−31</td>
<td>−27</td>
<td>−7</td>
</tr>
<tr>
<td>monoclinic C12 [16]</td>
<td>572</td>
<td>1048</td>
<td>951</td>
<td>343</td>
<td>311</td>
<td>173</td>
<td>84</td>
<td>152</td>
<td>116</td>
<td>67</td>
<td>−62</td>
<td>−167</td>
</tr>
<tr>
<td>$P2_1/m$-carbon [17]</td>
<td>1006</td>
<td>1080</td>
<td>1046</td>
<td>522</td>
<td>420</td>
<td>397</td>
<td>34</td>
<td>109</td>
<td>87</td>
<td>72</td>
<td>−28</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 3. Directional dependence of Young’s modulus of $C2/c$-C32.

Table II: Bulk modulus $B$ [in GPa], shear modulus $G$ (in GPa), Young’s modulus $E$ [in GPa], $B/G$ ratio, Poisson’s ratio $v$, and hardness $H$ [in GPa] of $C2/c$-C32 and other monoclinic carbon allotropes.

<table>
<thead>
<tr>
<th>Phases</th>
<th>$B$</th>
<th>$G$</th>
<th>$E$</th>
<th>$B/G$</th>
<th>$v$</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C2/c$-C32</td>
<td>355</td>
<td>343</td>
<td>780</td>
<td>1.03</td>
<td>0.13</td>
<td>56</td>
</tr>
<tr>
<td>diamond [16]</td>
<td>431</td>
<td>522</td>
<td>1116</td>
<td>0.83</td>
<td>0.07</td>
<td>90</td>
</tr>
<tr>
<td>$P2_1/m$-C54 [12]</td>
<td>345</td>
<td>332</td>
<td>754</td>
<td>1.04</td>
<td></td>
<td>54</td>
</tr>
<tr>
<td>monoclinic C12 [16]</td>
<td>351</td>
<td>277</td>
<td>657</td>
<td>1.27</td>
<td>0.19</td>
<td>67</td>
</tr>
<tr>
<td>$P2_1/m$-carbon [17]</td>
<td>398</td>
<td>457</td>
<td>991</td>
<td>0.87</td>
<td>0.08</td>
<td>82</td>
</tr>
</tbody>
</table>

In summary, a new all-$sp^3$-hybridized superhard carbon phase $C2/c$-C32 with a band gap of 2.50 eV was proposed in this study, and its structural stability and mechanical anisotropy were examined. Our calculated results show that $C2/c$-C32 can be stable at ambient pressure. $C2/c$-C32 exhibited a hardness of 56 GPa and a direct bandgap of 2.50 eV. Our study extended the family of carbon allotropes that exhibit superhardness and a direct band gap. Further experimental studies are needed to verify their properties and explore their potential applications.

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References


