$C2/c$-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.

topics: carbon, superhard materials, mechanical properties

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 Γ-centered
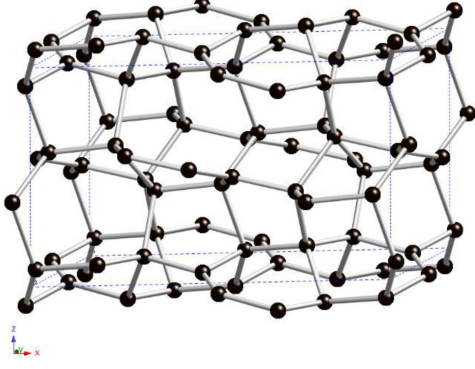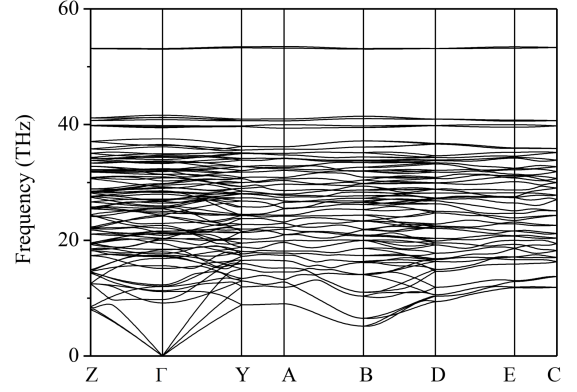
Fig. 1. Crystal structure of $C2/c$-C32.

Fig. 2. Phonon spectra of $C2/c$–C32.

grid of $6 \times 11 \times 10$ k-point mesh [35] were used for the ionic relaxation and electronic self-consistent iteration. 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), Γ (0.0 0.0 0.0), Y (0.0 0.5 0.0), A (0.5 0.5 0.0), B (0.5 0.0 0.0), D (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 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].

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 β = 86.2°. 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, 0.8433, 0.616859). 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 C_{11} 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–Ruess–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

$$v = \frac{3B - 2G}{2(3B + G)} \tag{1}$$

and

$$E = \frac{9BG}{(3B + G)}. \tag{2}$$

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

TABLE I

Elastic constants C_{ij} [in GPa] of $C2/c$-C32 and other monoclinic carbon allotropes.

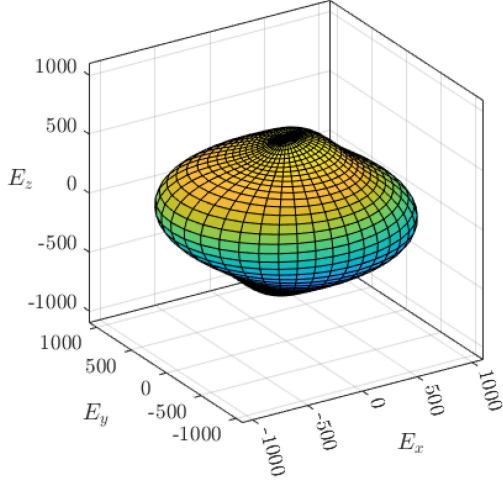| Phases	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}
$C2/c$-C32	1053	943	655	270	277	451	83	75	140	−75	−7	33	−15
diamond [16]	1054			561			120						
$P2/m$-C54 [12]	910	830	728	276	364	333	84	45	192	26	−55	21	20
V-carbon [12]	1089	1104	1033	508	466	447	40	87	98	−31	−27	−7	−52
monoclinic C12 [16]	572	1048	951	343	311	173	84	152	116	67	−62	−167	−102
$P2_1/m$-carbon [17]	1006	1080	1046	522	420	397	34	109	87	72	−28	12	−15

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.

Phases	B	G	E	B/G	v	H
$C2/c$-C32	355	343	780	1.03	0.13	56
diamond [16]	431	522	1116	0.83	0.07	90
$P2/m$-C54 [12]	345	332	754	1.04		54
monoclinic C12 [16]	351	277	657	1.27	0.19	67
$P2_1/m$-carbon [17]	398	457	991	0.87	0.08	82

the anisotropy characteristic of $C2/c$-C32. The universal anisotropy index A^U [41] of $C2/c$-C32 is 0.42. The maximum of Young's modulus value of $C2/c$-C32 is 1067 GPa, whereas the minimum of Young's modulus is 577 GPa. The ratio of $E_{\max}/E_{\min}$ is 1.85.

The calculation of the electronic band structure revealed that $C2/c$-C32 is a direct semiconductor with bandgaps of 1.54 and 2.50 eV at the PBE and HSE06 levels, respectively. Both the valence-band maximum and the conduction-band minimum are at the A (0.5 0.5 0.0) point. The direct band gap of $C2/c$-C32 is almost the same as that of C72 (1.52 eV at PBE) and lower than those of other direct band gap carbon phases (see Fig. 4), e.g., Z-CABA-carbon (4.2 eV at PBE) [42], $Fmmm$-C80
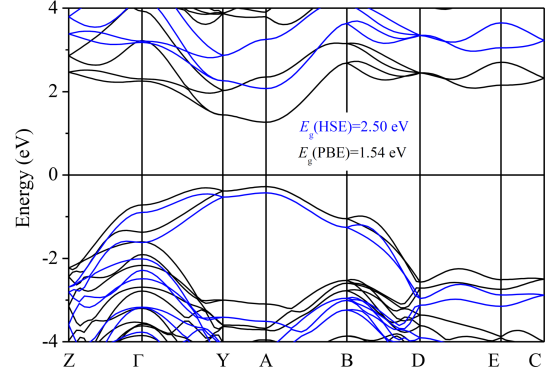

Fig. 4. Band structure of $C2/c$-C32 at the PBE (black lines) and HSE06 (blue lines) level.

(4.11 eV at HSE06) [6], and P-carbon (3.52 eV at HSE) [43].

4. Conclusions

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.

Acknowledgments

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