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o-C₂₄₀: a new sp³-dominated allotrope of carbon

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Abstract

We report a new allotrope of carbon predicted from first principles simulations. This allotrope is formed in a simulated conversion of two-dimensional polymeric C₆₀ precursor subjected to uniaxial compression at high temperature. The structure is made up of 240 carbon atoms in an orthorhombic unit cell (termed as o-C₂₄₀) having a mixed sp²/sp³ hybridization with the ratio of about 1:5. o-C₂₄₀ is stable at ambient condition and exhibits superior mechanical performance including optimum Vickers hardness (45 GPa) and fracture toughness (4.10 MPa m^{1/3}), outperforming most of widely used hard ceramics. The electronic structure reveals semiconducting ground state with an indirect band gap of 1.72 eV. The simple reaction pathway could accelerate discovery of this allotrope in laboratory, and the simultaneous occurrence of high fracture toughness, superhardness and semiconductivity is expected to find applications for this material.

Keywords: carbon allotropes, hardness, theoretical materials prediction, density functional theory

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon exists in various forms such as graphite, lonsdaleite, diamond, fullerenes, nanotubes, and amorphous carbon owing to its ability to form sp²- and sp³-hybridized bonds, thereby giving it a wide range of structural and electronic properties. On this account, search for new allotropes of carbon remains active for several decades [1–4]. Cubic diamond (c-diamond) is the hardest known naturally occurring material, due to its strong sp³ bonds and rigid tetragonal network. Graphite has even stronger sp² bonds and therefore it is the most stable form of carbon, but the weak interaction between the layers makes it soft, and easily separable. Due to the bonding difference, converting graphite to diamond requires high temperature and high pressure (to overcome the large activation barrier) [5, 6]. Finding new allotropes of carbon means to modify

the bonding environment of carbon using extreme physical stimuli to achieve bonding conversion. The sp³ bonding is associated with high stiffness and good thermodynamic properties, while sp² is responsible for ultrasoft compressibility, narrow band gap up to complete metallicity. For example, molecular dynamics simulation shows that carbon nanotubes (CNT) with uniform chirality can be converted to a pristine sp³ phase made up of only C4 square at 20 GPa [7]. Carbon nano-onions (concentric graphitic shells) have been converted to diamond by controlled nano-twinning, which turns out to be even harder than natural diamond [8].

Carbon allotropes with mixed sp²/sp³ atoms are often obtained in the conversion; amorphous carbon is a good example. Some of these mixed phases possess interesting properties such as optimum combination of strength, hardness, elasticity, and tunable electronic properties that make them fit for applications in device fabrication. There has been series

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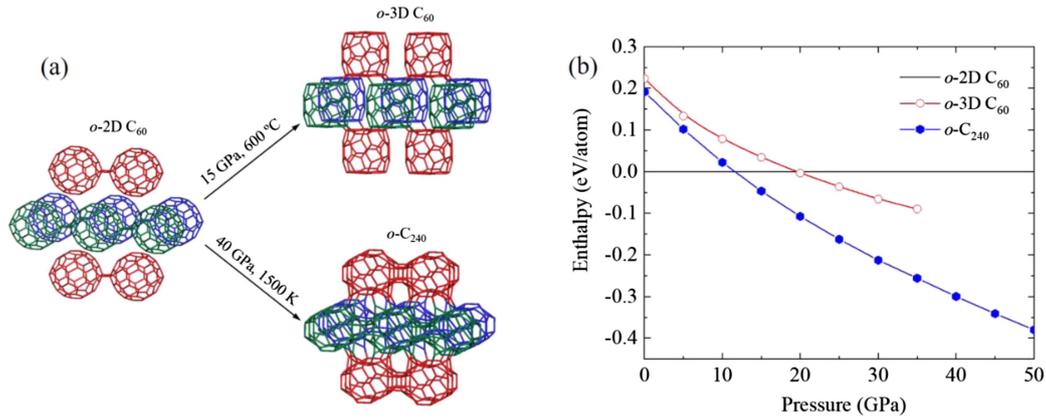


Figure 1. (a) Thermal conversion pathways for precursor o-2D C₆₀ to o-3D C₆₀ [28] and to o-C₂₄₀ (this work). C₆₀ units are colored to highlights the stacking patterns. (b) Calculated enthalpies as functions of pressure for o-C₂₄₀, o-3D C₆₀ and o-2D C₆₀. The enthalpy of the precursor o-2D C₆₀ is used as the reference enthalpy.

of work to synthesize mixed sp²/sp³ forms of carbon using controlled compression of pure sp² carbons. For example, intermediate hybridizations have been reported in fullerenes [9], CNTs [10], and amorphous carbon [11]. For fullerenes, experiment combined with theory has realized the polymerized forms of solid C₆₀ under pressure, reported to contain large numbers of both sp² and sp³ bonds [12]. Collapsed fullerene has also been studied [13] and was found to yield a fine blend of sp²-graphite-like and sp³-diamond-like amorphous carbon as a result of restructuring heterogeneity developed during the pressure quenching. Such collapsed phase exhibits high hardness and remarkable elastic strength despite having low compressive strength. Carbon-based clathrates composed of host cages have also been explored [14]. These clathrates showed prospect in that they could exhibit strength while being lightweight and could also offer tunable properties by carefully choosing the guest atoms.

Albeit the notable success, experimental discovery of new carbon allotropes is time-consuming and has a high cost. Synthesizing metastable carbon requires many trial and error to explore the thermodynamic pathways. To this end, theory-led structure search becomes essential. The search is more feasible than ever due to the fast advancement of first principles methods [15, 16] and exponential rise in computing power over time. In this paper, we report a new superhard allotrope of carbon (o-C₂₄₀) predicted from first principles. This allotrope is formed in a simulated conversion of two-dimensional (2D) polymeric C₆₀ at high pressure and high temperature conditions. The structure has a mixed sp²/sp³ phase with the sp² carbon to sp³ carbon ratio of about 1:5. The new allotrope is calculated to have optimum fracture toughness and to be both superhard and semiconducting, which could find applications in adsorption, photocatalysis, and high frequency electronic devices.

2. Computational method

All calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [17] with a cut-off energy of 500 eV and a projector augmented wave (PAW) potential [18], with the Perdew–Burke–Ernzerhof (PBE) functional [19]. The self-

consistent field (SCF) and electronic structure calculations were performed using a dense *k*-point grid with a spacing of $2\pi \times 0.02 \text{ \AA}^{-1}$. The electron localization function (ELF) [20] and charge density were calculated with an $80 \times 80 \times 80$ FFT grid. The dynamic stability calculation was carried out within the density functional perturbation theory (DFPT) [21] as implemented within the VASP with a *q*-point mesh of size $3 \times 3 \times 3$. The conversion of polymeric C₆₀ under high temperature and high-pressure conditions was simulated using the density functional-based metadynamics method [22]. Each metastep consists of a first-principles molecular dynamics simulation in a canonical (NVT) ensemble for a simulation time of 0.8 ps. The history-dependent potential well was constructed in the simulations using Gaussians with a width $\delta s = 15 (\text{kbar} \cdot \text{A}^3)^{1/2}$ and height $W = 225 \text{ kbar} \cdot \text{A}^3$. To accelerate the conversion, the system was pressurized non-hydrostatically, with additional 10% anisotropic stress loaded on the *c*-axis. A recent modification of the metadynamics method [23] was used to load the uniaxial stresses to the simulation cell. The molecular dynamics components were carried out using a dense *k*-point grid with a spacing of $2\pi \times 0.08 \text{ \AA}^{-1}$.

3. Results and discussion

3.1. Transition pathway

Several polymeric C₆₀ forms have been reported in literature, produced via high-temperature and high-pressure synthesis [24–26]. We choose the orthorhombic 2D C₆₀ (o-2D C₆₀) polymer characterized by Chen and Yamanaka [27] as the precursor for high-pressure conversion in this work. The o-2D C₆₀ was obtained under a pressure of 2.5 GPa at 500 °C and annealed to ambient conditions. The 2D polymerization in this structure is realized by covalent linking of neighboring C₆₀ units via [2 + 2] cycloaddition which then form the (001) plane. Each C₆₀ unit on the plane has four first neighbors, each connected by two σ bonds. To accommodate the inter-unit bonds, the carbon atoms at the connections adopt sp³ hybridization, which results in a 52:8 sp² to sp³ ratio. The polymerized layers are stacked along in *ABA* sequence by van der Waals forces. The plane *B* has identical geometry, but translated by $[a/2, b/2, c/2]$, i.e., to the body center, so that all C₆₀ units are occupying

Table 1. Optimized structural parameters of o-C₂₄₀ phase at ambient conditions.

SG	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Site	Fractional atomic coordinates		
					<i>x</i>	<i>y</i>	<i>z</i>
<i>Pmmm</i>	13.25	14.74	8.581	8 <i>a</i>	0.184	0.805	0.337
				8 <i>a</i>	0.183	0.306	0.336
				8 <i>a</i>	0.090	0.854	0.406
				8 <i>a</i>	0.090	0.355	0.406
				8 <i>a</i>	0.061	0.943	0.299
				8 <i>a</i>	0.062	0.444	0.301
				8 <i>a</i>	0.173	0.829	0.166
				8 <i>a</i>	0.170	0.330	0.164
				8 <i>a</i>	0.280	0.840	0.411
				8 <i>a</i>	0.278	0.340	0.410
				8 <i>a</i>	0.109	0.912	0.144
				8 <i>a</i>	0.110	0.416	0.145
				8 <i>a</i>	0.684	0.055	0.835
				8 <i>a</i>	0.683	0.555	0.836
				8 <i>a</i>	0.590	0.104	0.906
				8 <i>a</i>	0.590	0.604	0.906
				8 <i>a</i>	0.562	0.194	0.802
				8 <i>a</i>	0.562	0.694	0.802
				8 <i>a</i>	0.669	0.080	0.664
				8 <i>a</i>	0.668	0.580	0.664
				8 <i>a</i>	0.779	0.090	0.910
				8 <i>a</i>	0.778	0.590	0.910
				8 <i>a</i>	0.610	0.166	0.645
				8 <i>a</i>	0.610	0.666	0.646
				8 <i>a</i>	0.157	0.750	0.077
				4 <i>w</i>	0.654	0.000	0.576
				4 <i>x</i>	0.652	0.500	0.576
				4 <i>u</i>	0.000	0.795	0.634
				4 <i>u</i>	0.000	0.296	0.633
				4 <i>v</i>	0.500	0.046	0.133
				4 <i>v</i>	0.500	0.546	0.133
				4 <i>y</i>	0.050	0.911	0.000
4 <i>y</i>	0.057	0.445	0.000				
4 <i>z</i>	0.557	0.195	0.500				
4 <i>z</i>	0.557	0.695	0.500				

the interstitial voids of the first plane (A) (figure 1(a)). The o-2D C₆₀ has the *Immm* space group. In a previous study [28], Yamanaka *et al*, synthesized an orthorhombic 3D C₆₀ polymer (o-3D C₆₀) by a topotactic conversion of o-2D C₆₀ at a pressure of 15 GPa and 600 °C. In o-3D C₆₀, the C₆₀ units are distorted significantly to cuboids. Each cuboid is corner-linked to eight cuboid neighbors via [3 + 3] cycloaddition by 16 σ bonds. The 16 atoms at the corners adopt sp³ hybridization, resulting in a 44:16 sp² to sp³ ratio. The o-3D C₆₀ has a clathrate-like carbon framework, while robust in bonding; it has sizable voids inside and between cuboids. In the present study, we compress o-2D C₆₀ to 40 GPa and 1500 K using metadynamics simulation. Additional 10% uniaxial stress is loaded along the [001] direction to squeeze the van der Waals space between the planes and increase the conversion efficiency.

3.2. Crystal structure and dynamical stability of the o-C₂₄₀ structure

After the conversion, the C₆₀ units lost molecular identities and all fused together to a 3D structure. New bonds are developed

between and within the initial C₆₀ units via sp³ hybridization, changing the ratio of sp² carbon to sp³ carbon to 9:51. Since this structure is not a C₆₀ polymer anymore, we term it using the number of atoms in the unit cell, o-C₂₄₀. The o-C₂₄₀ has an orthorhombic cell with space group *Pmmm*. The optimized structural parameters at 0 GPa are presented in table 1. At ambient conditions, the o-C₂₄₀ has a density of 2.86 g cm⁻³, significantly denser than graphite, but lower than diamond (3.55 g cm⁻³). The enthalpies of the o-2D C₆₀ (precursor), o-3D C₆₀ and o-C₂₄₀ phases are compared in figure 1(b) from 0 GPa up to 50 GPa. The o-2D C₆₀ is found to be the lowest enthalpy phase up to 11.5 GPa while the o-C₂₄₀ phase is such from 11.5 GPa to above. The o-3D C₆₀ phase is more stable than the precursor above 20 GPa. Thus, the o-C₂₄₀ is the energetically favorable high-pressure phase in the conversion, which provides a synthesis route for future experiment.

The structure of o-C₂₄₀ features five basic types of carbon rings: C3, C4, C5, C6 and C8 (figure 2), and three types of bonding: single (between 2 sp³ atoms), double (between 2 sp² atoms), and mixed (between 1 sp² and 1 sp³ atoms). The

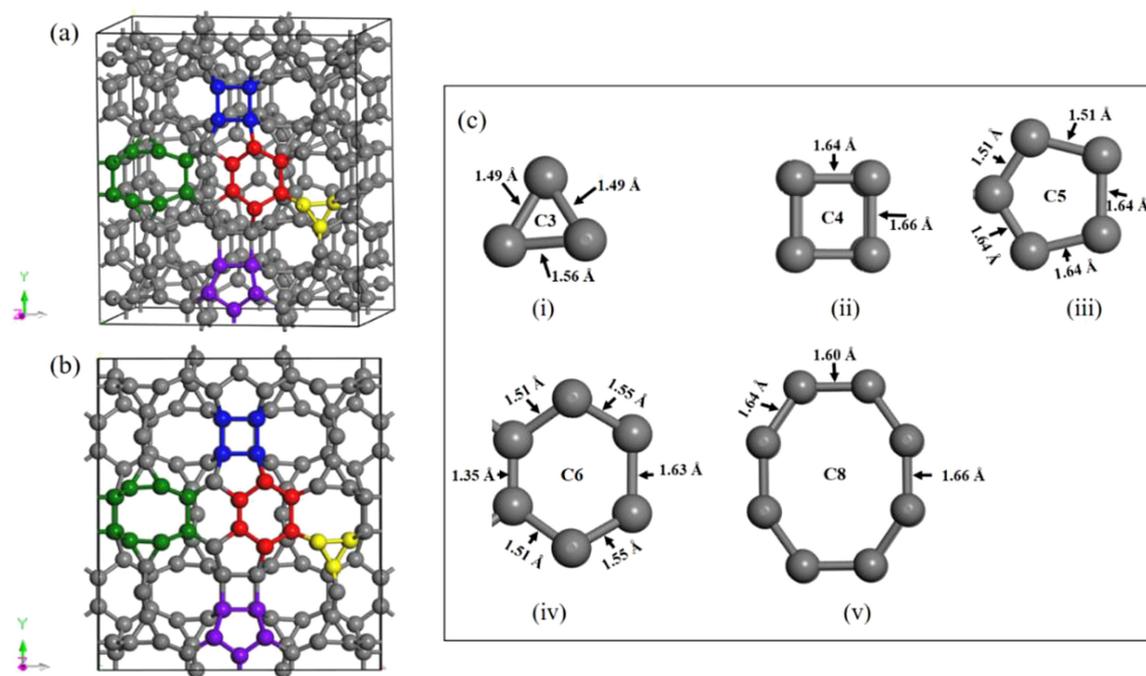


Figure 2. (a) Three-dimensional and (b) two-dimensional views of the crystal structure of the o-C₂₄₀ phase at ambient conditions. Structure is shown in one unit cell. Colors are used to highlight various carbon rings in the structure. (c) Unique carbon rings that characterize the o-C₂₄₀ structure.

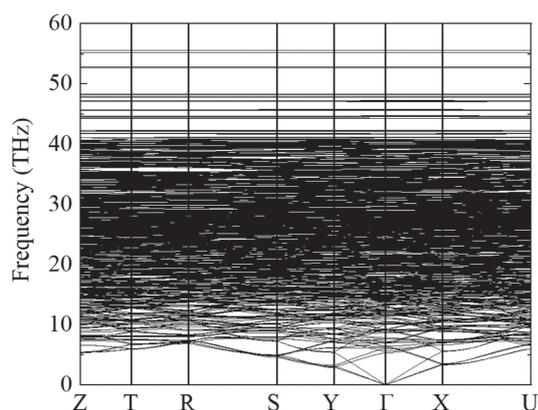


Figure 3. Calculated phonon dispersion relations of the o-C₂₄₀ structure at 0 GPa.

single bonds have various bond lengths between 1.55 Å to 1.66 Å, which are longer than the sp³ bonds in diamond (1.54 Å). The double bonds have the bond length range of 1.31 Å to 1.35 Å, shorter than the sp² bonds in both graphite (1.42 Å) and C₆₀ molecule (1.40–1.44 Å). The mixed bonds are in the range of 1.41–1.51 Å. The notable deviation of the bond lengths compared to standard sp³ (diamond) and sp² (graphite) bonds reveals that the bonding topology in o-C₂₄₀ are largely distorted. The formation of o-C₂₄₀ is a consequence of the competition between sp² and sp³ bonding. The domination of sp³ carbon improves the bonding-dependent properties toward diamond. The dynamic stability of the o-C₂₄₀ structure are assessed at 0 GPa. The absence of imaginary frequencies throughout the entire Brillouin zone (BZ) as shown

in figure 3 reveals that the o-C₂₄₀ structure is dynamically stable and quench recoverable in an event of high temperature-high pressure (HTHP) synthesis. The phonon band structure exhibits gaps in the range of optical modes between 40 THz and 56 THz. Analysis of the Γ point phonon reveals that bands in this region are triply degenerate. Thus, these modes may be used as a signature for the o-C₂₄₀ identification during synthesis.

3.3. Electronic properties of the o-C₂₄₀ structure

The calculated electronic band structure shows that o-C₂₄₀ is semiconducting in nature (figure 4(a)) with an indirect band gap of 1.72 eV. The band gap of o-C₂₄₀ is small compare to other high-pressure allotropes of carbon such as S-carbon, H-carbon [29], protomene [30], F-carbon [31] and D-carbon [32]. The electronic density of states projected to orbital (figure 4(b)) reveals that the C p-states lie at the valence band maximum (VBM) and the conduction band minimum (CBM) for the o-C₂₄₀. The bonding in each of the ring structures that made up the o-C₂₄₀ structure is analyzed using electron localization function. The ELF can help identify places in a structure where localization of electron (covalent bonds or lone pairs) are located. The C3 ring is made up of two distinct C–C bond lengths: 1 single bond at 1.56 Å and 2 mixed bonds at 1.49 Å. It has an σ - π -hybrid trigonal planar geometry similar to cyclopropane (C₃H₃), with an angle strain that causes an orbital overlap outside the C–C lines. The C6 ring has four distinct C–C bond lengths: three single bonds (1.55 Å \times 2 and 1.63 Å), one double bond (1.35 Å) and two mixed bonds (1.51 Å). The C6 ring has the geometry similar to benzene

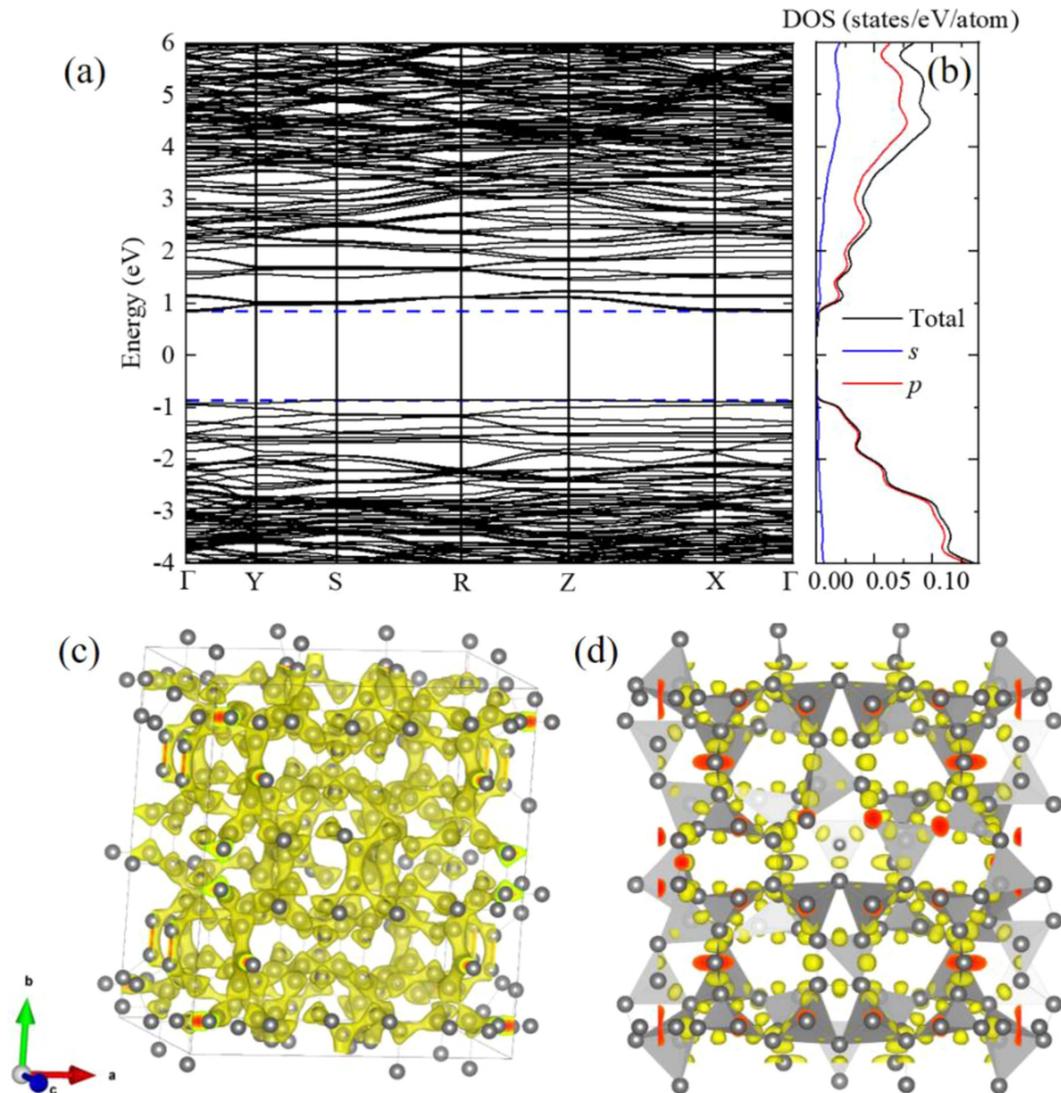


Figure 4. (a) Electronic band structure of $o\text{-C}_{240}$. (b) Total and projected electronic density of states of $o\text{-C}_{240}$. (c) Charge density distribution for $o\text{-C}_{240}$. (d) Electron localization function for $o\text{-C}_{240}$. The ELF isosurface is drawn with an isovalue of 0.85 to reveal all bonding and lone pairs.

(C_6H_6) but with puckered plane due to insufficient π electrons for aromaticity. The C5 ring is such that connects two C6 rings which is the only reminiscence of the C_{60} structure. The C4 and C8 rings are both made of single bonds, which exhibit unpolarized σ -bonds with electrons localized mid-way between each C–C pair. Polymerization of C_{60} is known to induce large increase in its electrical conductivity. The $o\text{-2D}$ C_{60} has highly anisotropic conductivity, in which the in-plane conductivity is similar to a metal, while the out-of-plane conductivity is semiconductor-like [33]. The 2D conductivity is attributed to the sp^2 bonding and delocalized π -electrons on the polymer plane. However, in the $o\text{-C}_{240}$, the dominance of sp^3 bonding in a 3D extended framework means that majority of the π -electrons become localized and converted to σ -bonds, making the $o\text{-C}_{240}$ to attain a semiconducting state. The band gap in the $o\text{-C}_{240}$ (1.72 eV) is halfway between narrow-gap-semiconducting and insulating state (strictly judging by the size of the band gap) but could, in principle, be doped toward

an extrinsic semiconductor when applied in the fabrication of devices.

3.4. Elastic properties and hardness of $o\text{-C}_{240}$

The mechanical properties of $o\text{-C}_{240}$ are evaluated to compare with other superhard materials [34–40]. The elastic constants are the determining factors for both elastic and mechanical stability of a material. Thus, we examined the mechanical stability of $o\text{-C}_{240}$ by calculating its elastic constants. The results are listed in table 2. The $o\text{-C}_{240}$ is characterized by nine independent elastic constants components. The results are found to satisfy the criteria for mechanical stability of an orthorhombic crystal system [41]. Furthermore, the C_{ij} matrix for the $o\text{-C}_{240}$ is symmetric and has all-positive eigenvalues, revealing its elastic stability. The bulk (B), shear (G) and Young's (E) moduli are measures of a material's intrinsic response to different kinds of deformations. B measures a material's volumetric elasticity and its response to isotropic compression;

Table 2. Calculated elastic constants C_{ij} (in GPa) for the o-C₂₄₀ compared with other carbon allotropes.

	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
o-C ₂₄₀	728	787	817	258	249	227	103	67	74
c-diamond ^a	1076			577			125		
C ₆₄ ^b	598		677	254		107	43	108	
oC ₂₀ ^c	794	760	979	405	251	261	112	61	75

^aRef [39].^bRef [36].^cRef [40].**Table 3.** Calculated mechanical properties of o-C₂₄₀ compared with c-diamond and other superhard materials. Numbers without superscripts are present results. Numbers with superscripts are previously reported in literature. Numbers with primed superscripts are estimations using VRH model fed with the data reported in literature.

Properties	Material			
	c-diamond	o-C ₂₄₀	C ₆₄	B ₆ O
B (GPa)	457 (443 ^a)	313	264 ^c	222 ^d
G (GPa)	536 (535 ^a)	281	217 ^c	204 ^d
E (GPa)	1156 (1144 ^{a'})	649	510 ^c	468 ^{d'}
Poisson ratio	0.079 (0.069 ^{a'})	0.154	0.18 ^c	0.15 ^{d'}
H_v (GPa)	92 (92 ^b)	45	34 ^{c'}	38 ^{d'} 45 ^e

^aRef [34].^bRef [35].^cRef [36].^dRef [37].^eRef [38].

G represents a material's tendency to shear under an opposing stress, while E is a measure of the stiffness of a material in the linear elasticity regime of a uniaxial deformation. The Poisson ratio (ν), on the other hand, is a measure of the expansion of a material in directions perpendicular to the direction of compression. The B and G were calculated for o-C₂₄₀ and compared with c-diamond, C₆₄ and B₆O in table 3. The bulk moduli reveal that o-C₂₄₀ is more compressible than c-diamond, but less compressible than C₆₄ and B₆O. The E and ν were estimated using the Voigt–Reuss–Hill (VRH) approximation [42], i.e., $E = [9BG/(3B + G)]$ and $\nu = [(3B - 2G)/2(3B + G)]$. The o-C₂₄₀ exhibits a large E of 649 GPa, indicating that it is stiffer than C₆₄ and B₆O, but less stiff compared to c-diamond and c-BN. The Pugh's ratio (B/G) of the o-C₂₄₀ indicates that it is a brittle material. The calculated ν shows that while c-diamond is more covalent than the o-C₂₄₀, the o-C₂₄₀ structure is more covalent than the C₆₄ and the graphite is already close to being a metallic material [43].

Hardness is the extent to which a solid resists both elastic and plastic deformations. As a commonly used metrics, Vickers hardness (H_v) is hinged on the fact that the hardness

of a crystal is proportional to the number of covalent bonds per unit volume and the bond strengths in the crystal. Hard materials will have H_v value up to 40 GPa and superhard materials will have H_v value greater than 40 GPa. Another point to note about hardness is that it depends strongly on the creation and motion of dislocations which is an effect of plastic deformation. We have calculated the H_v of the o-C₂₄₀ structure using the Chen *et al* [44] model and compared it to other superhard materials (table 3). Using this model, we correctly reproduced the Vickers hardness of c-diamond, which establishes the validity of this model for sp³ dominated carbon materials. The calculated H_v of the o-C₂₄₀ is 45 GPa indicating that it is a superhard material. Significantly, the hardness of o-C₂₄₀ is close to or exceeds some synthesized superhard materials, i.e., B₄C (38 GPa) [45], B₆O (45 GPa) [38], and WB₅ (45 GPa) [46]. This is expected from the coexistence of the sp² and sp³ bonding inherent in the o-C₂₄₀, since there is a strong correlation between the hardness of a carbon allotrope and the sp²/sp³ ratio. The 1:5 sp²/sp³ ratio makes o-C₂₄₀ a superhard material while maintaining a semiconducting state, which could find versatile applications in industry. Fracture toughness (K_{IC}) is another important mechanical property of a material that shows how resistive it is to a propagating crack. An optimum combination of hardness and fracture toughness is desirable, which both diamond and tungsten carbide (WC) seems to lack. We calculated the K_{IC} of the o-C₂₄₀ structure using the Niu *et al* [47] empirical model to be 4.10 MPa m^{1/2}, similar to the value reported for c-BC₂N ($K_{IC} = 4.5$ MPa m^{1/2}) [45]. Such a K_{IC} value is indicative of high yield at critical strain, suggesting that the o-C₂₄₀ is ductile. The relatively high K_{IC} of o-C₂₄₀ exceeds the recently found or widely used hard ceramics, e.g., γ -B, B₆O and B₄C [47], which suggests great potential for technological applications.

4. Conclusion

In summary, we report a new allotrope of carbon obtained in simulated thermal conversion of orthorhombic 2D C₆₀ polymer at 30 GPa and 1500 K. The new allotrope has an orthorhombic $Pmmm$ symmetry with a unit cell containing 240 carbon atoms (o-C₂₄₀). The structure has a sp²/sp³ mixed 3D network, in which the sp² carbon to sp³ carbon ratio is 9:51. The o-C₂₄₀ is characterized to be a superhard material with a calculated Vickers hardness of 45 GPa, close to that of B₆O and WB₅. It has a semiconducting ground state with an

indirect band gap of 1.72 eV. The o-C₂₄₀ also possess fracture toughness of 4.10 MPa m^{1/3}, superior to most of hard ceramics widely used in industry. The mixing of the sp²/sp³ bonding in favor of sp³ gives the o-C₂₄₀ superior mechanical and electronic properties compared to other competitive allotropes previously predicted.

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