Acta Scientific Applied Physics

Volume 3 Issue 1 January 2023

Research Article

Novel Ultrahard Carbon Allotrope C_5 with Mixed sp^2/sp^3 Carbon Hybridizations. Crystal chemistry and First Principles Investigations

Samir F Matar*

Lebanese German University (LGU), Sahel-Alma, Jounieh, Lebanon

***Corresponding Author:** Samir F Matar, Lebanese German University (LGU), Sahel-Alma, Jounieh, Lebanon. **Email:** sfm68@hotmail.com

Received: November 28, 2022

Published: December 06, 2022

Abstract

From crystal chemistry rationale and first principles investigations, novel tetragonal carbon allotrope C_5 with mixed sp^2/sp^3–like carbon sites hybridizations is identified as cohesive and stable both dynamically and mechanically with metallic behavior. Charge density distribution is localized at tetrahedral C-sp^3 and delocalized with π-like electrons between trigonal C-sp^2 leading to metallic like electronic behavior. The anisotropic structure resulting from vertically aligned C=C (ethene –like) along the tetragonal c-axis provides large C_{33} elastic constant and high Vickers hardness with a magnitude slightly below diamond. The properties of novel simple allotrope should help assessing nanodiamonds with mixed sp^2/sp^3 C investigated in different fields of materials as electrochemical ones.

Keywords: Diamond; Hardness; Phonons; DFT; Crystal Chemistry

Introduction

Diamond is recognized as the hardest material [1]. In last decades large research efforts were devoted to identifying novel allotropes of carbon close to diamond using modern materials research methodologies as CALYPSO [2]. In view of the large number of claimed stoichiometries and structures, a database: SACADA was built regrouping all known carbon allotropes to help researchers and to avoid erroneous claims of existing systems [3].

Recently published body centered tetragonal BCT C_4 (Figure 1a) was proposed in space group I-4m2 as one of the simplest three-dimensional (3D) carbon networks with ultra-hard properties [4]. It was then found out that by considering the primitive cell, C_4 had the same topology as cubic diamond using TopCryst crystallography package [5] with "dia" -for diamond- topology as categorized for several chemical compounds in Reticular Chemistry Structure Resource (RCSR) Database [6]. Nevertheless, with its simplicity BCT C_4 can be used as seed-template for other original chemical compounds as shown herein. Starting from C_4, novel tetragonal C_5 is built through crystal chemistry followed by full geometry relaxations using calculations based on the quantum mechanics density functional theory DFT [7]. Analyzed through TopCryst crystallography program, the fully geometry relaxed structure of C_5 was found to be in original uncategorized topology within RCSR Database [6]. The novel allotrope found cohesive and stable both mechanically and dynamically is characterized with large hardness magnitude slightly below diamond. Furthermore, C_5 has mixed carbon hybridization sp^2 and sp^3. Such stoichiometry and chemical behavior were reported in recent literature for so-called cubic 'pentadiamond', qualified as a novel allotrope with high mechanical properties close to diamond; but the paper was later retracted due to calculation errors on the mechanical properties admitted by the authors [8]. The relevance of mixed carbon hybridization is in the change of the mechanical properties of the hardest material, diamond, and of its electronic insulating structure.

The relevance of mixed carbon hybridization bringing changes of the electronic structure of insulating diamond by inducing metallic-like behavior. Such modifications lead to applications in materials science. As a matter of fact, mixed C(sp^2)/C(sp^3) were identi-

fied in nanodiamonds, arising large interest in different fields of materials investigations as electrochemical ones recently exposed by Zhai., *et al*. [9]. The presently proposed original Pentacarbon is meant to serve as a model illustrating the observed electronic, mechanical, and dynamic behaviors at an elementary scale of small cluster made of 3 C(sp^3) and 2 C(sp^2).

Computational framework

The search for the ground state structures goes through protocols of geometry optimizations calculations onto the ground state characterized by minimal energies. The iterative computations were performed using DFT-based plane-wave Vienna Ab initio Simulation Package (VASP) [10,11]. For the atomic potentials, the projector augmented wave (PAW) method was used [11,12]. DFT exchange and correlation effects (XC) were treated locally at the same level with a generalized gradient approximation scheme (GGA) [13]. The relaxation of the atoms onto ground state geometry was done applying a conjugate-gradient algorithm [14]. A tetrahedron method [15] with corrections made with Methfessel-Paxton scheme [16] was applied for geometry optimization and energy calculations, respectively. A special *k*point sampling [17] was applied for approximating the reciprocal space Brillouin-zone (BZ) integrals. For better reliability, the optimization of the structural parameters was carried out along with successive self-consistent cycles with increasing mesh until the forces on atoms were less than 0.02 eV/Å and the stress components below 0.003 eV/$Å^3$.

The mechanical stabilities and hardness were inferred from the calculations of the elastic constants. Furthermore, the phonon dispersion band structures were calculated to verify the dynamic stability of the novel carbon allotropes. The phonon modes were computed considering the harmonic approximation through finite displacements of the atoms around their equilibrium positions to obtain the forces from the summation over the different configurations. The phonon dispersion curves along the direction of the Brillouin zone were subsequently obtained using "Phonopy" interface code based on Python language [18].

The electronic band structures and density of states were obtained with the full-potential augmented spherical wave ASW method based on DFT using the same GGA scheme as above [19].

	C_4 [4] I-4m2, N°119	C_3 P-4m2, N°115	C_5 P-4m2, N°115
a	2.527	2.521	2.4786
c	3.574	3.402	5.0279
C1(tet.).	(2a) 0, 0, 0	(1a) 0, 0, 0	(1a) 0, 0, 0
C2(tet.)	(2d) ½, 0, ¼	(2g) ½, 0, z z= 0.237	(2g) ½, 0, z z= 0.187
C(trig.)	-	-	(2f) ½, ½, z z= 0.646
Volume ($Å^3$)	22.82	21.63	30.89
$d_{C1(tet.)-C2(tet.)}$	1.55	1.50	1.55
$d_{C2(tet.)-C2(trig.)}$	-	-	1.50
$d_{C(trig)-C(trig.)}$	-	-	1.46
E_{total}.	-36.36	-21.58	-43.26
$E_{coh./at.}$	-2.49	-0.59	-2.05

Table 1: Tetragonal carbon crystal structure parameters: C_4, C_3, and C_5. Lattice constants and distances are in units of Å (Vol. $Å^3$). Energies are in eV.

Crystal chemistry and characteristics of C_5

Body center tetragonal C_4 structure (Figure 1a) consists of two distinct carbon sites with 2-atoms occupancy: C1 at the corner and body center positions developing *C4* tetrahedra with C2 positioned at the faces (Table 1a). We highlight that all lattice parameters of the structures in Table 1 result from unconstrained geometry optimizations to the energy ground states. The removal of the body center carbon breaks the body-center symmetry and leads to C_3 where tetrahedra are at the 8 corners forming a two-dimensional like stacking along c-tetragonal direction (Figure 1b). Such modification leads to a lowering of symmetry and the space group shifts from I-4m2, N°119 down to P-4m2, N°115. The second column of Table 1 shows C_3 crystal parameters with the Wyckoff positions. Both types of carbon atoms are labeled C1(tet) and C2(tet) in so far that they produce tetrahedral carbon. Expectedly, the volume and the interatomic distance decrease with the removal of one carbon. The last lines present the total energy and the atom averaged cohesive energies. From the cohesive energy there is a large destabilization of the diamond-like structure upon removal of central carbon to create C_3 that can be used as template to devise novel allotropes.

It needs to be noted that despite the small magnitude cohesive energy (Table 1) -versus the other allotropes in Table 1, C_3 was found mechanically and dynamically stable from the sets of elastic constants and phonons band structures respectively, as detailed in the development of the paper.

Consequently, the following scheme is presented:
C_3 "receives"

- One extra carbon to make C_4, already investigated [4],
- C-C pair to make C_5 (shown in Figure 1c),
- One additional carbon atom at cell center, based on C_5, to make C_6 introducing tricarbon entity, not developed upon here, and published as a structure in CCDC [20].

The major difference between C_4 and C_5 is that whereas in C_4 the central carbon is tetrahedral C(tet) completing the diamond-like structure as discussed above, the two additional carbon atoms are labeled C(trig); with "trig" standing for trigonal carbon shown with white spheres in Figure 1c. Alike C_3, the new allotrope C_5 belongs to P-4m2, N°115 space group. The C-C interatomic distances are within range of C_4 (diamond-like) and smaller magnitudes are observed for $d(C_{trig}\text{-}C_{trig})$ =1.47 Å. Beside C-C single bonds for C(tet)-C(tet), we are in presence of additional double C=C bond, thus characterizing pentacarbon C_5 with sp^2/sp^3 carbon hybridizations. The atom averaged cohesive energy is significantly larger than in C_3 with a magnitude close to C_4.

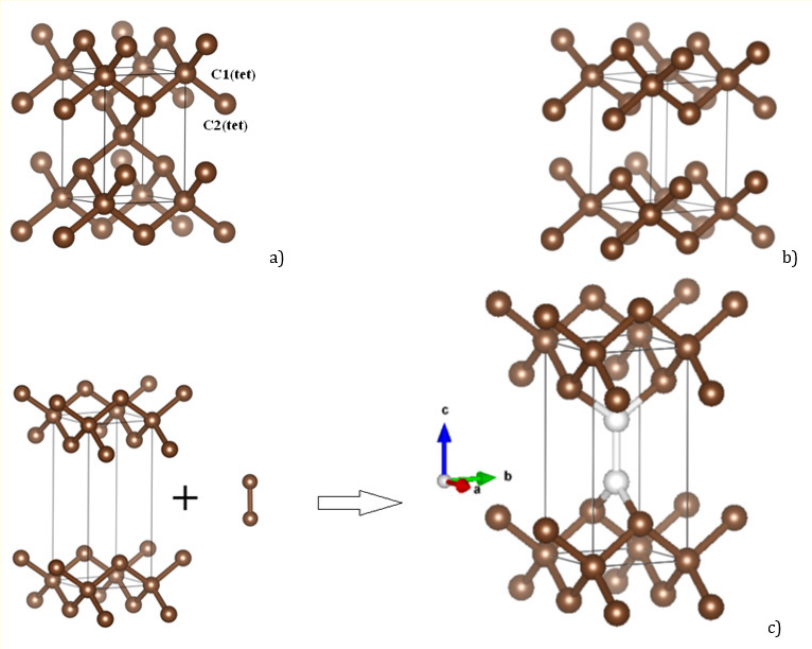

Figure 1: Sketches of the crystal structures with schematics of transformations (cf. text). a) C_4, b) C_3, and c) C_5 White spheres represent trigonal carbon pair.

Charge density projections

Further qualitative illustration of the different types of hybridizations is obtained from the projections of the charge densities around and between atoms. Figure 2 presents the projections shown with yellow volumes. Upon crossing crystal plane, charge density slices with red color are shown indicating strong charge localizations.

In C_4 (Figure 2a) the sp^3-type hybridization expected for C(tet) is clearly observed especially on central carbon with the yellow volumes taking the shape of a tetrahedron, and alike diamond, C_4 is a perfectly covalent chemical system. Upon removal of central carbon producing C_3 with only C(tet) -cf. Table 1, the charge density is modified especially for the carbon atoms pointing towards the empty space as it is exhibited by the larger red area versus C_4.

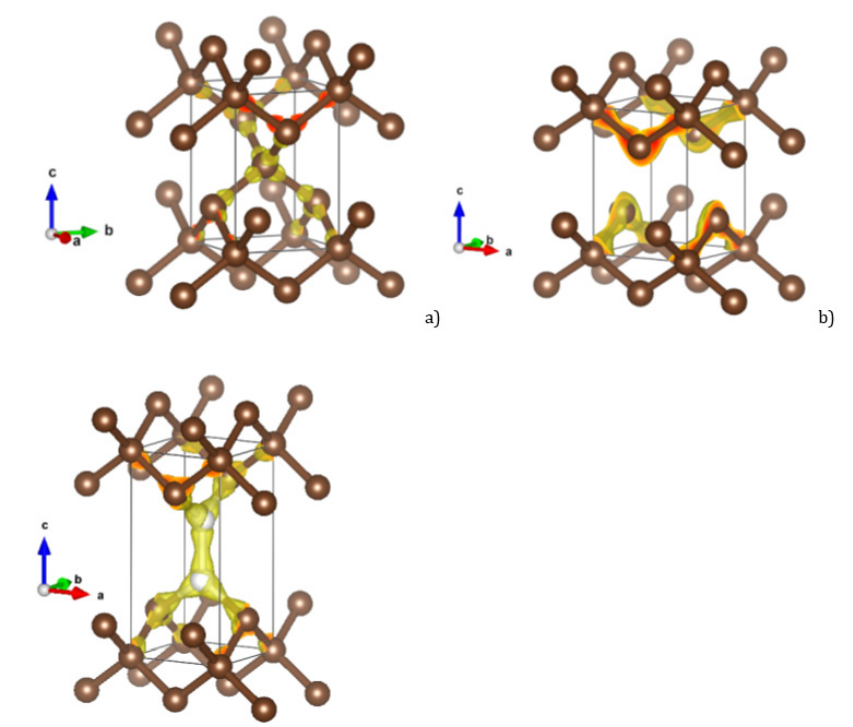

Figure 2: Charge density projections (yellow volumes) in a) C_4, b) C_3, and c) C_5. White spheres represent trigonal C=C (ethene-like) carbon pair.

Larger changes are observed in C_5 (Figure 2c) where the charge density is skewed towards the ethene-like C=C pair of C(trig) white spheres. The charge density in no more homogeneously distributed as in covalent C_4, and less pronounced red color is observed letting suggest a polar-covalent behavior normally found in a compound with different constituents' electronegativities such as boron nitride.

Therefore, we are presented with a decrease of the covalence from $C_4 \rightarrow C_5$ brought by the introduction of trigonal carbon.

Mechanical properties from elastic constants

The investigation of mechanical properties was based on the calculations of the elastic properties determined by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship. Most compounds are polycrystalline, and generally considered as randomly oriented single crystalline grains. Consequently, on a large scale, such materials can be considered as statistically isotropic. They are then fully described by bulk (B) and shear (G) moduli obtained by averaging the single-crystal elastic constants. The method used here is Voigt's [21], based on a uniform strain. The calculated sets of elastic constants are given in Table 2; the elastic constants of C_4 [6] are reported for the sake of comparison. While most elastic constants of C_4 are larger than in C_5, it can be noted that C_{33} magnitude is larger in C_5, concomitantly with aligned trigonal C-C along the c-tetragonal axis (cf. Figure 1c).

The elastic constants of C_3 exhibit a relatively large magnitude for in-plane C_{11} and much smaller magnitude for C_{33} relevant to inter-planes, i.e., along tetragonal c-direction. Both largest C_{ii} (C_{11} and C_{33}) are smaller than the corresponding values in C_5. Indeed, the system describing C_3 is more relevant to two-dimensional 2D letting it receive interstitials as schematized in Section 3, and hence leading to 3D C_4, C_5 and C_6 etc. All magnitudes of the other C_{ij} are very small letting expect a soft material. However, it will be shown

that C_3 is dynamically valid from the calculations of positive phonon frequencies in next section.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B_{Voigt}	G_{Voigt}
C_4 [4]	1147	28	126	1050	461	559	434	574
C_5	922	21	112	1192	217	370	390	430
C_3	696	20	33	155	10	5	191	115

Table 2: Calculated elastic constants and bulk B_V and shear G_V moduli. All values are in GPa units.

All C_{ij} (i=j and i≠j) values are positive and their combinations obey rules pertaining to the mechanical stability of the chemical system.

C_{ii} (i =1, 3, 4, 6) > 0; $C_{11} > C_{12}$, $C_{11} + C_{33} - 2C_{13} > 0$;
and $2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0$.

The equations providing the bulk B_V and shear G_V moduli are as follows for the tetragonal system [22]:

$$B_{Voigt}^{tetr.} = 1/9\ (2C_{11} + C_{33} + 2C_{12} + 4C_{13});$$

and

$$G_{Voigt}^{tetr.} = 1/15\ (2C_{11} + C_{12} + 2\,C_{33} - 2C_{13} + 6C_{44} + 3C_{66}).$$

C_4 has the largest B_V and G_V, close to the accepted values for diamond B_V =445 GPa and G_V = 550 GPa [1]. The corresponding B_V and G_V magnitudes in C_5 are slightly smaller but they remain high, oppositely to C_3 which shows much smaller B_V and G_V magnitudes versus C_5.

Vickers hardness (H_V) was predicted using three theoretical models of hardness [23-25]. The thermodynamic model (T) [23] is based on thermodynamic properties and crystal structure, while Mazhnik-Oganov (MO) [24] model uses the elastic properties. Lyakhov-Oganov (LO) approach [25] considers topology of the crystal structure, strength of covalent bonding, degree of ionicity and directionality. The fracture toughness (K_{Ic}) was evaluated within MO model [24].

The results are summarized in Table 3 presenting Vickers hardness calculated using the different theoretical models and other mechanical properties such as shear modulus (G), Young's modulus (E), the Poisson's ratio (ν) and fracture toughness (K_{Ic}). The hardness of tet.C_4 shows expectedly close magnitude to

	HV			B_V	G_V	E^*	ν^*	K_{Ic}
	T [23]	LO [24]	MO [25]					
C_4	97	89	110	434	574	1195	0.041	6.4
C_5	89	81	76	390	414	917	0.108	5.1
C_3	––	26	13	191	115	287	0.249	2.0
Diamond	98	90	100	445 [1]	530 [1]	1138	0.074	6.4

Table 3: Mechanical properties of carbon allotropes: Vickers hardness (H_V), bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν). All values are in GPa (Giga Pascal) unit. Fracture toughness (K_{Ic}) is in MPa·m^{½}.

*E and ν values calculated using isotropic approximation.

diamond using the three models as discussed in the introduction highlighting the close relationship of C_4 with diamond. Turning to C_3 low hardness magnitudes are identified with both LO and MO model while the thermodynamic model was found to provide unreliable values; nevertheless, with H_V = 15 GPa tet-C_3 is described as a soft material. Lastly for tet-C_5 the thermodynamic model provides the highest hardness magnitude versus LO and LO models; all values are lower than in tet-C_4 or diamond due to the mixed valence carbon sites leading to less covalence than in ideal diamond. Concomitantly the fracture toughness: K_{Ic}(tet-C_5) = 5.1 MPa·m^{½} is found smaller than calculated for diamond with K_{Ic} = 6.4 MPa·m^{½}. Lastly E and ν calculated with the isotropic approximation show lower magnitudes than diamond. Consequently, the novel pentacarbon allotrope can be considered as prospective ultra-hard material showing interesting mixed carbon hybridization.

Dynamic properties from the phonons

Another criterion of stability is obtained from the phonons defined as quanta of vibrations; their energy is quantized through the Planck constant 'h' used in its reduced form ħ (ħ = h/2π) giving with the wave number ω the phonons energy: E = ħω. Besides the novel allotropes C_3 and C_5 the phonon band structures of C_4 [4] are shown for the sake of comparison. Figure 3 shows the phonon bands.

Along the horizontal direction, the bands run along the main lines of the tetragonal Brillouin zone (reciprocal k- space). The vertical direction shows the frequencies given in units of terahertz (THz). Since no negative frequency magnitudes are observed, ex-

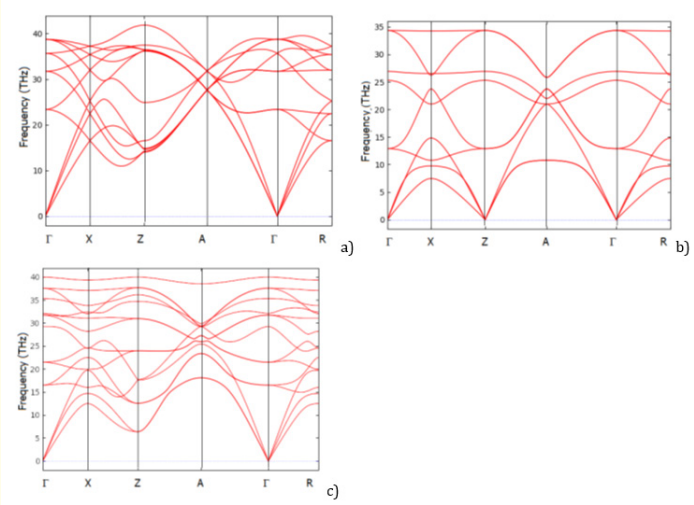

Figure 3: Phonons band structures of a) C_4 [4], b) C_3, and c) C_5.

pectedly for C_4, but also for C_3 and C_5, all structures are considered as dynamically stable. There are 3N-3 optical modes found at higher energy than three acoustic modes that start from zero energy ($\omega = 0$) at the Γ point, center of the Brillouin Zone, up to a few Terahertz. They correspond to the lattice rigid translation modes of the crystal (two transverse and one longitudinal). The remaining bands correspond to the optic modes and culminating at $\omega \sim 40$ THz in C_4 and C_5, a magnitude observed for diamond by Raman spectroscopy [26], and only up to 34 in less stable C_3 (cf. Table 1). The phonons show the closeness of C_5 to C_4 regarding dynamic stability.

Electronic band structures and density of states

Using the crystal parameters in Table 1, the electronic band structures were obtained using the all-electrons DFT-based augmented spherical method (ASW) [19] and shown in Figure 4. The bands develop along the main directions of the primitive tetragonal Brillouin zones. For diamond-like insulating C_4 (Figure 4a) the energy level along the vertical line is with respect to the top of the valence band (VB), E_V. As a specific character of diamond, the band gap of C_4 is indirect along k_z between Γ_{VB} and Z_{CB} with a magnitude close to 5 eV. Oppositely, C_3 (Figure 4b) and C_5 (Figure 4c) behave as metals with bands crossing the Fermi level E_F.

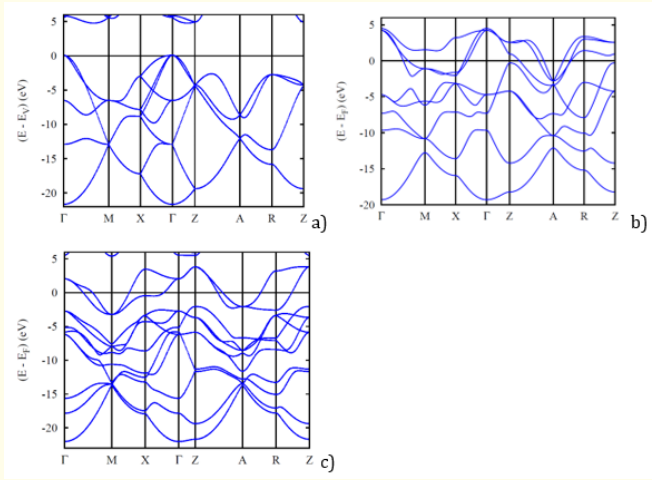

Figure 4: Electronic band structures of a) C_4 [4], b) C_3, c) C_5.

Concluding Note and Prospective

With novel C_5 we are presented with a simple stoichiometry metallic material showing original occurrence of mixed sp^2-sp^3 -like carbon hybridizations, characterized by ultra-hardness close to diamond. The practical interest in such electronic systems is their presence in nanostructures of hybrid diamond/C(sp^2) inves-

tigated in the domain of electrochemistry, for instance.

As prospective work, extended 3D carbon networks are being examined to reduce the amount of C(sp^2) to highlight further doping effect of diamond-like structures.

Acknowledgments

I am grateful to Dr Vladimir Solozhenko Directeur de Recherche at CNRS-Paris for exchanges and his expertise in discussing hardness along different models.

Author Statement

I declare that conceptualizations, calculations, and analyses are all mine and I have no conflict of interest with any other work or colleagues.

Bibliography

1. VV Brazhkin and VL Solozhenko. "Myths about new ultrahard phases: Why materials that are significantly superior to diamond in elastic moduli and hardness are impossible". *Journal of Applied Physics* 125, 130901 (2019).

2. Shuang Shuang Zhang., *et al*. "Discovery of superhard materials via CALYPSO methodology". *Chinese Physics B* 28 (2019): 106104.

3. R Hoffmann., *et al*. "Homo Citans and Carbon Allotropes: For an Ethics of Citation". *Angewandte Chemie* 55 (2016): 10962-10976. and SACADA database (Samara Carbon Allotrope Database). www.sacada.info.

4. SF Matar., *et al*. "The simplest dense carbon allotrope: Ultrahard body centered tetragonal C4". *Journal of Solid State Chemistry* 314 (2022): 123424.

5. AP Shevchenko., *et al*. "Topological representations of crystal structures: generation, analysis, and implementation in the TopCryst system". *Science and Technology of Advanced Materials: Methods* 2.1 (2022): 250-265.

6. O'Keeffe M., *et al*. "The reticular chemistry structure resource (RCSR) database of, and symbols for, crystal nets. *Acc. Chem. Res*., , 41, 1782-1789 (2008).

7. P Hohenberg and W Kohn. "Inhomogeneous electron gas". *Physical Review B* 136 (1964): 864-871.

8. Y Fujii., *et al*. "Pentadiamond: A Hard Carbon Allotrope of a Pentagonal Network of sp2 and sp3 C Atoms. *Physical Review Letters* 125 (2020): 016001 and Retraction: *Physical Review Letters* 125 (2020): 079901 (2020).

9. Zhaofeng Zhai., *et al*. "Progress in electrochemistry of hybrid diamond/sp2-C nanostructures". *Current Opinion in Electrochemistry* 32 (2022): 100884.

10. G Kresse and J Furthmüller. "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set". *Physical Review B* 54 (1996): 11169.

11. G Kresse and J Joubert. "From ultrasoft pseudopotentials to the projector augmented wave". *Physical Review B* 59 (1999): 1758-1775.

12. PE Blöchl. "Projector augmented wave method". *Physical Review B* 50 (1994): 17953-17979.

13. J Perdew., *et al*. "The Generalized Gradient Approximation made simple". *Physical Review Letter* 77 (1996): 3865-3868.

14. WH Press., *et al*. "Numerical Recipes". 2nd ed. Cambridge University Press: New York, USA, (1986).

15. PE Blöchl., *et al*. "Improved tetrahedron method for Brillouin-zone integrations". *Physical Review B* 49 (1994): 16223-16233.

16. M Methfessel and AT Paxton. "High-precision sampling for Brillouin-zone integration in metals". *Physical Review B* 40 (1989): 3616-3621.

17. HJ Monkhorst and JD Pack. "Special k-points for Brillouin Zone integration". *Physical Review B* 13 (1976): 5188-5192.

18. A Togo and I Tanaka. "First principles phonon calculations in materials science". *Scripta Materialia* 108 (2015): 1-5.

19. V Eyert. "Basic notions and applications of the augmented spherical wave method". *International Journal of Quantum Chemistry* 77 (2000): 1007-1031.

20. SF Matar. CCDC 2208344: (Refcode NEQHUQ; name C6POLr) (2022).

21. W Voigt. "Über die Beziehung zwischen den beiden Elasticitätsconstanten isotroper Körper". *Annals of Physics* 274 (1889): 573-587.

22. DC Wallace. "Thermodynamics of crystals". New York, USA: John Wiley and Sons (1972).

23. VA Mukhanov., *et al*. "The interrelation between hardness and compressibility of substances and their structure and thermodynamic properties". *Journal of Superhard Materials* 30 (2008): 368-378.

24. E Mazhnik and AR Oganov. "A model of hardness and fracture toughness of solids". *Journal of Applied Physics* 126 (2019): 125109.

25. AO Lyakhov and AR Oganov. "Evolutionary search for superhard materials: Methodology and applications to forms of carbon and TiO2". *Physical Review B* 84 (2011): 092103.

26. RS Krishnan. "Raman spectrum of diamond". *Nature* 155 (1945): 171.