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# General Classification of Carbon Allotropes

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## Chapter 2

# Carbon (Graphene/Graphite)

### 2.1 Structures

Carbon is the sixth element of the periodic table with the ground state level  $^3P_0$  and electron configuration  $1s^2 2s^2 2p^2$ , which is hybridized to form  $sp^1$ ,  $sp^2$  and  $sp^3$  chemical bonds between atoms. The general oxidation states (numbers) of carbon in numerous inorganic compounds are (−4) (+4) and (+2); the radii of carbon are:

atomic (metallic, CN = 12)—0.091 nm,  
atomic (van der Waals)—0.170 nm,  
atomic (covalent)—various, see Table 2.1,  
ionic (+4)—0.015 nm (CN = 4) or 0.016 nm (CN = 6);

its electronegativity is 2.55 in Pauling scale, or 2.50 in Allred–Rochow scale. The hybridized  $sp^n$ -bonding ( $1 \leq n \leq 3$ ) differs considerably from common  $s$ - or  $p$ -bonds inherent to other chemical elements of the basic periods. The values of energy characteristics, in particular, specific bond energies (average bond energy per bond order) of carbon–carbon  $sp^n$ -bonds occupy a wide area of intermediate positions between those characteristics of  $s$ - and  $p$ -elements, depending substantially on the hybridisation type of bonding:  $s > sp^3 > sp^2 > sp^1 > p$  (Table 2.1). The electron hybridization predetermines the ability of carbon atoms to arrange numerous compounds with other elements of the periodic table, but also the various allotropes, such as carbyne/carbyte, graphene/graphite and diamond (Table 2.2), which are structured with linear, planar and tetrahedral symmetry, coordination numbers of 2, 3 and 4 and the bond angles of  $180^\circ$ ,  $120^\circ$  and  $109.47^\circ$ , respectively for  $sp^1$ -,  $sp^2$ - and  $sp^3$ -hybridized forms. According to Mendeleev “none of the elements can compete with carbon in ability to form complex structures” [1, 540].

There has been a new wave of interest in carbon materials caused by the recent discoveries in the nanoscience [2, 9–14, 31, 42, 45–53], which has affected all science and engineering fields. Some points of view are developed in literature to classify carbon macro- and nanostructures. In this way, schemes based on hybridization characteristics were suggested by McEnaney [9], Heimann et al. [10],

**Table 2.1** Comparative atomic bonding characteristics of *s*- and *p*-elements of the periodic table [2–9]

Outer electronic configuration	Bond type (examples)	Bond order	Specific bond enthalpy, <sup>a</sup> kJ mol <sup>-1</sup>	Bond length, nm	Covalent atomic radius, nm	Frequency, cm <sup>-1</sup>	Force constant, <sup>b</sup> N/m
<i>s</i>	H–H	1	435	–	–	–	–
<i>sp</i> <sup>3</sup>	Hydrogen molecule						
	C–C	1	369	0.074	0.030	997	3.5
	Diamond			0.154	–		
	<i>sp</i> <sup>3</sup> – <i>sp</i> <sup>3</sup> (6 peripheral atoms in total)			0.153 <sup>c</sup>	0.077		
	<i>sp</i> <sup>3</sup> – <i>sp</i> <sup>2</sup> (5 peripheral atoms in total)			0.151 <sup>c</sup>	–		
<i>sp</i> <sup>2</sup>	<i>sp</i> <sup>3</sup> – <i>sp</i> <sup>1</sup> (4 peripheral atoms in total)			0.149 <sup>c</sup>	–		
	<i>sp</i> <sup>2</sup> – <i>sp</i> <sup>2</sup> (4 peripheral atoms in total)			0.146 <sup>c</sup>	0.073		
	<i>sp</i> <sup>2</sup> – <i>sp</i> <sup>1</sup> (3 peripheral atoms in total)			0.143 <sup>c</sup>	–		
	<i>sp</i> <sup>1</sup> – <i>sp</i> <sup>1</sup> (2 peripheral atoms in total)			0.138 <sup>c</sup>	0.069		
	C=C	1.5	345	–	–	–	–
<i>sp</i> <sup>2</sup> (aromatic)	Graphene			0.142	0.071		
<i>sp</i> <sup>2</sup>	Benzene (4 peripheral atoms in total)			0.140	–		
	C=C	2	306	–	–	1620	9.3
	<i>sp</i> <sup>2</sup> – <i>sp</i> <sup>2</sup> (4 peripheral atoms in total)			0.134 <sup>c</sup>	0.067		
	<i>sp</i> <sup>2</sup> – <i>sp</i> <sup>1</sup> (3 peripheral atoms in total)			0.132 <sup>c</sup>	–		
	<i>sp</i> <sup>1</sup> – <i>sp</i> <sup>1</sup> (2 peripheral atoms in total)			0.128 <sup>c</sup>	0.064		
<i>sp</i> <sup>1</sup>	C≡C	3	279	–	–	2100	15.6
<i>p</i>	Carbyne						
	<i>sp</i> <sup>1</sup> – <i>sp</i> <sup>1</sup> (2 peripheral atoms in total)			0.128	–		
	F–F	1	159	0.121 <sup>c</sup>	–		
	Fluorine molecule			0.141	0.071	–	–

<sup>a</sup> Average bond enthalpy per bond order<sup>b</sup> From infrared absorption and combination scattering spectra data<sup>c</sup> Average values

**Table 2.2** Systematic classification of carbon nano- and macrostructures

Hybridisation types (proposed terms)	Existing (or predicted) structural forms of carbon				References
	Nanostructures		Macrostructures		
	Submolecular	Molecular (mesostructures)	Supramolecular		
$\sigma\text{-}sp^1 + 2\pi$ (carbyne general family)	Short polyyne and polycumulene chains	$\alpha$ - and $\beta$ -Carbyne <sup>a</sup> (methine <sup>b</sup> )	Carbyne nanobundles Carbyne nanorings “Chain armour” structures	Carbyte <sup>c</sup> (carbomite, crystal forms of carbynes and their polytypes)	[9, 10, 15–20]
$(\sigma\text{-}sp^1 + 2\pi) - (\sigma\text{-}sp^2 + \pi)$ or $\sigma\text{-}sp^{1 < n < 2} + (3-n)\pi$ (graphyne intermediate family) <sup>e</sup>	Nanographynes (?) Graphyne nanoribbons (?)	Graphynes Graphdiynes Graphynes-n Supergraphene	Bilayered graphyne Multi-layered graphynes (?)	$\alpha, \beta, \gamma$ -Graphyte <sup>d</sup> (various polytypes) Intermediate graphite (graphene) to carbyte (carbyne) transition phases (?)	[21–29, 53, 179, 187, 694]
$\sigma\text{-}sp^2 + \pi$ (graphene general family)	Nanographenes Graphene nanoribbons	Graphene	Bilayered graphene Multi-layered graphenes Expanded nano-platelets Nanofiber (nanowire, nanorods)	Graphite (H- and R-polymorphs/polytypes) Natural graphite Kish graphite Pyrolytic graphite Expanded (exfoliated) graphite Carbon (graphite) fiber Carbon (graphite) clothes, fabrics and preregs (woven or non-woven)	[11, 30–44, 74–85, 136–138, 676, 694]
$(\sigma\text{-}sp^2 + \pi) - \sigma\text{-}sp^3$ or $\sigma\text{-}sp^{2 < n < 3} + (3-n)\pi$ (fullerene intermediate family) <sup>e</sup>	Nanoclusters of conjugated pentagon and hexagon cycles	Fullerenes (buckminsterfullerene C <sub>60</sub> and other forms in C <sub>2n</sub> series with $n = 10, 12, 13, 14, \dots$ , e.g. C <sub>20</sub> , C <sub>22</sub> , C <sub>24</sub> , C <sub>26</sub> , C <sub>28</sub> , C <sub>30</sub> , C <sub>32</sub> , C <sub>34</sub> , C <sub>36</sub> , C <sub>38</sub> , C <sub>40</sub> , C <sub>42</sub> , C <sub>44</sub> , C <sub>46</sub> , C <sub>48</sub> , C <sub>50</sub> , C <sub>52</sub> , C <sub>54</sub> )	Fullerene rings Fullerene nanotubes Fullerene nanowhiskers (fullerene nanofibers) Nanobeads (“pearl necklace” structures) Fullerene polymers	Fullerites (polymorph forms of fullerene molecular crystals and fullerene polymers) Nanotubular crystals (nanotube yarn) Nanotube lattices	[21, 42, 45–71, 75, 86–167, 649–652, 669–676, 682–688, 694–699]
					(continued)

(continued)

**Table 2.2** (continued)

Hybridisation types (proposed terms)	Existing (or predicted) structural forms of carbon			References
	Nanostructures			
	Submolecular	Molecular (mesostructures)	Supramolecular	
	<p><math>C_{56}</math>, <math>C_{58}</math>, <math>C_{70}</math>, <math>C_{72}</math>, <math>C_{76}</math>, <math>C_{78}</math>, <math>C_{82}</math>, <math>C_{84}</math>, <math>C_{90}</math>, <math>C_{94}</math>, <math>C_{120}</math>, <math>C_{240}</math>, <math>C_{540}</math>, <math>C_{960}</math>, etc.)</p> <p>Single-walled nanotubes (zigzag, arm-chair and intermediate chiral configurations)</p> <p>Capped (closed) single-walled nanotubes</p> <p>Defective single-walled nanotubes</p> <p>Nanotubes (nanoscrolls) with polygonal cross-sections</p> <p>Nanoscrolls (whiskers, "Swiss roll" structures)</p> <p>Nanobarrels</p> <p>Nanocoones</p> <p>Nanodisks</p> <p>Nanobreadsticks</p> <p>Toroids (toroidal cages)</p> <p>Helical nanocoils (coiled cages)</p> <p>Squarographenes</p> <p>Glitter</p>	<p>Hyperfullerenes (multi-walled fullerenes, onion-like fullerenes, "Russian doll" structures)</p> <p>Fullerene intercalated graphite compounds</p> <p>Astralens</p> <p>Double-walled nanotubes</p> <p>Multi-walled nanotubes</p> <p>Capped (closed) multi-walled nanotubes</p> <p>Defective multi-walled nanotubes</p> <p>Nanohorn particles</p> <p>Megatubes</p> <p>Giant nanotubes</p> <p>Supertubes</p> <p>Nanotube bundles (ropes, strands)</p> <p>Nanofiber (nanowire, nanorods)</p> <p>Nanotube lattices</p> <p>Nanobuds</p> <p>Nanopeapods</p> <p>Nanofoams (glitter-like and defected graphene-like networks)</p>	<p>Haeckelites (pentaheptites, octites)</p> <p>Schwarzites</p> <p>Soot</p> <p>Carbon black (channel black, thermal black, lamp black, acetylene black)</p> <p>Defected graphite (armchair prismatic edge dislocations)</p> <p>Defected graphite (zig-zag prismatic edge dislocations)</p> <p>Amorphous carbon</p> <p>Pyrolytic carbon</p> <p>Coke</p> <p>Charcoal</p> <p>Activated carbon</p> <p>Molecular-sieve carbon</p> <p>Carbon (amorphous) fiber</p> <p>Carbon (amorphous) clothes, fabrics, felts, prepregs</p> <p>Aerogel (cryogels, xerogels)</p> <p>Glassy (vitreous) carbon</p> <p>Glassy (vitreous) carbon foam</p> <p>Carbon bead powder (mesocarbon microbeads)</p> <p>Carbide derived carbon</p>	
				(continued)

(continued)

**Table 2.2** (continued)

Hybridisation types (proposed terms)	Existing (or predicted) structural forms of carbon			References	
$\sigma$ - $sp^3$ (diamond general family)	Nanostructures		Macrostructures	[6, 9, 13, 42, 53, 72, 78, 168–177, 666–668]	
	Submolecular	Molecular (mesostructures)	Supramolecular		
	Diamondoids	Nanocrystalline particulate diamond	Ortho-graphite-diamond hybrids		Diamond-like carbon films
	Ultra-nanocrystalline (ultra-dispersed) particulate diamond	Diamond nanorods Diamond nanotubes Diamond nanowhiskers Diamond nanocylinders Diamond nanocones Diamond nanoplatelets	Para-graphite-diamond hybrids Hexagonite (based on barrelene fragment molecules) Haeckelones Schwarzones Ultra-nanocrystalline aggregated diamond Nanocrystalline aggregated diamond Aggregated diamond nanorods (hyperdiamond) Diamond nanofiber (filaments) Ultra-nanocrystalline diamond films Polycrystalline diamond nanopowder Carbide derived diamond-structured carbon		n-diamond (or $\gamma$ -carbon, shock-compressed graphite phase) i-carbon (shock-compressed graphite phase) Intermediate graphite-to-diamond transition phases  Diamond (3C-diamond) single crystal (or polycrystalline) Lonsdaleite (hexagonal diamond, H- and R-polytypes) Hexagonite (cold compressed nanotubes) Diamond D <sub>5</sub> Lonsdaleite L <sub>5</sub> Octacarbon (supercubane, prismane, BC8, ?)

<sup>a</sup> Despite many publications on various carbyne types, the existence of this allotrope has not been universally accepted [73]

<sup>b</sup> According to IUPAC recommendation, the term “methine” has to replace “carbyne”, as the latter one is used to term an organic radical

<sup>c</sup> The term “carbyte” is suggested for carbyne crystal forms by analogy with “graphene–graphite” and “fullerene–fullerite” correlations

<sup>d</sup> The term “graphyte” is suggested for graphyne crystal forms by analogy with “graphene–graphite” and “fullerene–fullerite” correlations

<sup>e</sup>  $\sigma$ - $sp^m$  and  $\sigma$ - $sp^n$  indicate intermediate carbon forms with a non-integer degree of carbon bond hybridization

Inagaki [11], Belenkov [12], Shenderova et al. [13, 78] and Falcao and Wudl [14]. The systematic classification of all the experimentally confirmed and theoretically predicted carbon structures, which is given in Table 2.2, is based mainly on the relative values of the specific bond energies of  $sp^n$ -hybridized carbons as well as carbon phase transformation diagram (see Sect. 2.2). This approach, employing within the overall hierarchy of classified carbon structures from submolecular to macroscopic scales, in accordance to the bonding energy criteria, allows marking out among the variety of carbon structures three general families (with integer degree of hybridisation index  $n$ ):

carbyne general family ( $n = 1$ ), including  $sp^1$ -hybridized ( $\sigma-sp^1 + 2\pi$ ) carbons from nanostructured carbyne to its macrostructural crystalline form “carbyte” (the existence of carbyne (or carbolite) has not been universally accepted; the proposed term for a macrostructural form is given on the basis of analogy with graphene–graphite and fullerene–fullerite correlations);  
 graphene general family ( $n = 2$ ), including  $sp^2$ -hybridized ( $\sigma-sp^2 + \pi$ ) carbons from nanostructured graphene to macrostructural crystalline graphite with its polytypic (hexagonal and rhombohedral) forms;  
 diamond general family ( $n = 3$ ), including  $sp^3$ -hybridized ( $\sigma-sp^3$ ) carbons from various nanostructured diamonds to macrostructural crystalline diamond with its polytypic (cubic and hexagonal) forms.

and two intermediate (or transitional) families (with non-integer degree of hybridisation index  $n$ ):

graphyne intermediate family ( $1 < n < 2$ ), including  $sp^{1<n<2}$ -hybridized ( $\sigma-sp^{1<n<2} + (3 - n)\pi$ ) carbons from nanostructured graphyne (analogue of graphene modified by triple bonds) to macrostructural “graphyte” with various polytypes, which are characterized by the intermediate between carbyne and graphene hybridisation type (currently, hypothetical structures calculated and predicted only theoretically; the proposed term for a macrostructural form is given on the basis of analogy with graphene–graphite and fullerene–fullerite correlations);  
 fullerene intermediate family ( $2 < n < 3$ ), including  $sp^{2<n<3}$ -hybridized ( $\sigma-sp^{2<n<3} + (3 - n)\pi$ ) carbons from numerous species of nanostructured fullerenes and hyperfullerenes, single-walled and multi-walled nanotubes, nanoscrolls, nanobarrels, nanocones and other nanostructures to macrostructural forms, such as fullerites, nanotubular crystals, hypothetical structures of haeckelites and schwarzites, as well as plenty of carbon/carbonaceous products, such as soot, carbon black, so-called “amorphous” carbon, pyrolytic carbon, coke, charcoal, activated carbon, molecular-sieve carbons, glassy carbon, carbide derived carbons, intermediate graphite-to-diamond transition phases, diamond-like carbon films and others, which are characterized by the intermediate between graphene and diamond hybridisation type (mainly, the fullerene family structures can be considered as distorted graphene related structures, where deviation from planarity is occurred because of the partial heptagons and/or pentagons substitution for hexagons in graphene networks; special measures

**Table 2.3** Characteristic and structural features of allotropic, polymorphic and polytypic carbon forms

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
<i>Carbyne Family</i> <sup>a</sup>					
$\alpha$ -Carbyne (methine)	1D carbon polymer with polyyne bonding ( $-C\equiv C-$ ) <sub>n</sub>	Max. length 3.6–4.8 nm, with larger length—degenerate into $\beta$ -carbyne polycumulene chains (predicted theoretically)	–	Extremely unstable	[9–10, 15–20]
$\beta$ -Carbyne (methine)	1D carbon polymer with polycumulene bonding ( $=C=C=$ ) <sub>n</sub>	Chains length 50–250 nm stabilized by impurities and formation of covalent bonds between chains, C–C bond length—0.128 nm (predicted theoretically)	–	Unstable	[9–10, 15–20]
Carbyne nanobundles	Aggregates of various aligned 1D carbon polymers	–	–	–	[9, 11, 16–17]
Carbyne nanorings	Hypothetical 1D and 2D structures (calculated by molecular mechanics and <i>ab initio</i> methods)	Various structures (predicted theoretically)	–	–	[19]
“Chain armour” structures	Hypothetical 3D complex structures of carbyne nanorings (calculated by molecular mechanics and <i>ab initio</i> methods)	Various structures (predicted theoretically)	–	–	[19]
Carbyte	Molecular crystal of $\beta$ -carbyne arranged in hexagonal bundles	Crystal structure—trigonal (rhombohedral), space group— $P\bar{3}m1$ , lattice parameters: $a = b = c = 0.3580$ nm, $\alpha = \beta = \gamma = 118.5^\circ$ , $Z' = 1$ (calculated by molecular mechanics methods)	1.36 <sup>b</sup>	Unstable (predicted)	[20]
Carbyte (carbomite) <sup>d</sup>	Molecular crystal of carbyne chains (C–C bond length—0.133 nm) arranged in hexagonal bundles	Crystal structure—hexagonal, lattice parameters: $a = 1.193$ nm, $c = 1.062$ nm; interchain distance—0.344 nm (XRD)	1.46	–	[18]
<i>Graphyne Family</i>					
Graphynes ( $\alpha$ -graphynes)	Hypothetical flat monolayers of atoms packed into 2D polyhexagonal lattices (basic blocks predicted for graphyne family materials)	C–C bond length—0.1421 nm, C–C (in phenyl rings) bond length—0.1428 nm, C $\equiv$ C bond length—0.1202 nm (calculated by modified neglect of differential overlap (MNDO) quantum chemical method)	–	Stable (predicted)	[22, 53, 694]

(continued)



Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Graphitynes ( $\beta$ - and $\gamma$ -graphynes)	Hypothetical flat monolayers of atoms packed into 2D polyhexagonal lattices, where hexagons are linked through ( $-C \equiv C-$ ) units	—	—	—	[53, 694]
Graphitynes-n	Hypothetical flat monolayers of atoms packed into 2D polyhexagonal lattices, where hexagons are linked by polyyne bonding ( $-C \equiv C-$ ) <sub>n</sub>	—	—	—	[53, 694]
Supergraphene	Hypothetical flat monolayers of atoms packed into distorted 2D hexagonal lattices, where 2/3 of all bonds are replaced by carbyne-like bonding	—	—	—	[694]
6,6-Graphyte (polytype with next-nearest layers eclipsed, like in graphite)	Graphitynes AB-stacked into 3D structures	Crystal structure—monoclinic, space group— $Pn$ , lattice parameters: $a = b = 0.686$ nm, $c = 0.672$ nm, $\gamma = 120^\circ$ , $Z = 24$ (calculated by MNDO quantum chemical method)	1.75	Stable at high temp. (predicted)	[22]
6,6-6-Graphyte (polytype with next-nearest-neighbour layers related by a centre of symmetry)	Graphitynes ABC-stacked into 3D structures	Crystal structure—trigonal, space group— $P(-1)$ , lattice parameters: $a = b = 0.686$ nm, $c = 0.760$ nm, $\alpha = 76.5^\circ$ , $\beta = 117.9^\circ$ , $\gamma = 120^\circ$ , $Z = 24$ (calculated by MNDO quantum chemical method)	1.75	Stable at high temp. (predicted)	[22]
Intermediate graphene-to-carbyne (graphite-to-carbyte) transition phases <i>Graphene Family</i>	?	—	—	At ultra-high temp. and pressures (predicted)	[9, 28, 179, 187]
Nanographenes	2D flat hexagonal carbon atoms ring network with open edges	Average diameter <10 nm	—	—	[30]
Graphene nanoribbons	2D thin strips of graphene or unrolled single-walled carbon nanotubes	Width is less than 50 nm and lengths—below 500 nm	—	—	[30, 74]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Graphene	Flat monolayer of atoms tightly packed into a 2D hexagonal lattice (basic block for all graphene family materials)	C-C bond length—0.142 nm	—	At higher temp. unstable with respect to scrolling	[31–38, 75, 694]
2H-Graphite ( $\alpha$ -carbon, $\alpha$ -Graphite)	Graphenes AB-stacked into 3D structures (main graphite polytype)	Crystal structure—hexagonal, space group— $P6_3/mmc$ , lattice parameters: $a = 0.2464$ nm, $c = 0.6711$ nm, $Z = 4$ , interlayer spacing—0.3356 nm (neutron diffraction, XRD)	2.267	Stable, sublimes at ultra-high temp., binding energy—7.99 eV atom <sup>-1</sup>	[41–43, 76, 676]
1H-Graphite	$\alpha$ -Graphite polytype with A-over-A-stacked graphenes (hypothetical)	—	—	—	[10]
10H-Graphite	$\alpha$ -Graphite polytype	—	—	—	[10]
12H-Graphite	$\alpha$ -Graphite polytype	—	—	—	[10]
3R-Graphite ( $\beta$ -Graphite)	Graphenes ABC-stacked into 3D structures	Crystal structure—trigonal (rhombohedral), space group— $R\bar{3}m$ , lattice parameters: $a = b = c = 0.3635$ nm, $\alpha = \beta = \gamma = 39.49^\circ$ , $Z = 2$ (in hexagonal setting: $a = 0.2456$ nm, $c = 1.0039$ nm, XRD)	2.267	Completely transforms to 2H-graphite ( $\alpha$ -graphite) at temp. 1300–2100 °C	[44, 77]
6R-Graphite	$\beta$ -Graphite polytype	—	—	—	[10]
Natural graphite	Powdered aggregates composed from $\alpha$ - and $\beta$ -graphites with $\beta$ -phase content 7.5–15 %	—	2.20–2.25	—	[42–44]
Kish graphite	Graphite quasi-single crystals	—	—	Stable at high temp.	[11]
Pyrolytic graphite	Highly oriented aggregates of graphenes with some covalent bonding between graphene sheets	Composed from crystallites with deviation from perfect parallel order less than 1 % and apparent size perpendicular to the graphene planes $L_c$ —up to 50–500 nm	2.10–2.25	Stable, sublimes at ultra-high temp.	[10, 42, 136]
Expanded nano-platelets	Nanoparticles consist of small stacks of graphene	Thickness—1–2.5 nm, other linear sizes—ranging from 0.1 to 100 $\mu$ m, increased spacing between graphene layers	—	—	[79–81]
Expanded (exfoliated) graphite	Aggregates of graphene prepared by decomposition of intercalated graphite compounds	Increased spacing between graphene layers	$10^{-3}$ – $10^{-1}$ (powd.) 0.7–1.3 (packed)	Stable, sublimes at ultra-high temp.	[11, 82–83]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Carbon (graphite) fiber	Bundle of graphitic filaments with prevailing alignment of graphene sheets parallel to the fiber axis, needle-shaped voids between crystallites and sheets essentially parallel to the surface	Diameter of filaments—5–8 μm, apparent crystallite thickness $L_c$ —6 nm and sizes $L_a$ —15–50 nm, 2H-graphite lattice parameters: $a = 0.246$ nm, $c = 0.671$ – $0.687$ nm, length-to-diameter ratio >100	1.5–2.2	Stable, sublimates at ultra-high temp.	[8, 42, 84–85, 127, 136–137]
Carbon (graphite) clothes, fabrics and prepreps (woven or non-woven)	(2, 2.5, 3, ...n) D-components made from carbon (graphite) fiber	Variety of structures	—	Stable, sublimates at ultra-high temp.	[8, 84, 136–137]
<i>Fullerene Family</i> Fullerene C <sub>60</sub> (buckminster-fullerene)	Spherical molecule with polyhedral form containing 60 atoms (most abundant)	Truncated icosahedron made of 20 hexagons and 12 pentagons (ratio of pentagon/hexagon rings—0.6) with an atom at the vertices of each polygon and a bond along each polygon edge, each atom is covalently bonded to three others, nucleus-to-nucleus diameter—0.714 nm, C–C bond lengths: between two hexagons—0.1391 nm and between a hexagon and a pentagon—0.1455 nm, pyramidalization angle (obtained from $\pi$ -orbital axis vector analysis)—11.6°	—	Destruction temp. of molecule (in gas phase) >2700 °C	[42, 52, 68, 78, 86–88]
Fullerene C <sub>70</sub>	Spherical molecule with polyhedral form containing 70 atoms	Polyhedron made of 25 hexagons and 12 pentagons (ratio of pentagon/hexagon rings—0.48) with an atom at the vertices of each polygon and a bond along each polygon edge, each atom is covalently bonded to three others, molecule sizes: full height (distance between 2 pentagons in mutually opposite polar areas)—0.780 nm and diameter of equator circle via atomic nuclei—0.694 nm, 8 types of C–C bonds with lengths from 0.137 to 0.147 nm, pyramidalization angle—10.7°	—	Destruction temp. of molecules (in gas phase) >2700 °C	[42, 52, 68, 86–88]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Fullerene C <sub>32</sub>	Spherical molecule with polyhedral form containing 32 atoms	Polyhedron made of hexagons and pentagons (ratio of pentagon/hexagon rings=2)	—	—	[51–52, 68, 78, 86–88]
Fullerene C <sub>28</sub>	Spherical molecule with polyhedral form containing 28 atoms	Polyhedron made of hexagons and pentagons (ratio of pentagon/hexagon rings=3)	—	—	[51–52, 68, 78, 86–88]
Fullerene C <sub>20</sub>	Spherical molecule with polyhedral form containing 20 atoms	Polyhedron made of pentagons (ratio of pentagon/hexagon rings=∞)	—	—	[51–52, 68, 78, 86–88]
Fullerenes in C <sub>2n</sub> -series (buckyballs, carbon cages)	Variety of spherical molecules with polyhedral forms containing 2n (n = 10, 12, 13, 14, 15...) atoms	Various polyhedral structures with pyramidalization angles in the range of 0° (graphene, sp <sup>2</sup> -bonding) to 19.5° (diamond, sp <sup>3</sup> -bonding)	—	—	[42, 51–52, 58, 68, 78, 86–88]
Fullerene rings	Variety of C <sub>2n</sub> -polymerized 2D ring-based structures	... E.g., (C <sub>60</sub> ) <sub>n</sub> -rings with number of members n = 3–8	—	Stable (predicted)	[106]
Fullerene nanotubes	Tubular thin fiber composed of C <sub>2n</sub> molecules or their derivatives	E.g., C <sub>60</sub> - or C <sub>70</sub> -, or C <sub>60</sub> -C <sub>70</sub> -two-component nanotubes with diameter of ~0.24–1.5 μm and length of ~5–60 μm; crystal structure—hexagonal in solvated forms and cubic (face-centred) after losing the contained solvent molecules	—	Stable, decompose in air at temp. >415 °C	[651–652]
Fullerene nanowhiskers (fullerene nanofibers)	Single crystalline nanofibers composed of C <sub>2n</sub> molecules with non-tubular morphologies	E.g., C <sub>60</sub> - or C <sub>70</sub> -nanowhiskers (needle-like crystals) with diameter from 80 nm up to ~1 μm and length from ~1–10 μm up to ~1–10 nm; crystal structure—hexagonal in solvated forms and cubic (face-centred) after losing the contained solvent molecules	—	Stable, decompose in air at temp. >450 °C	[649–650, 652]
Nanobeads (“pearl necklace” structures)	Quasi-1D-structures based on fullerenes, in particular, small fullerenes C <sub>2n</sub> (2n < 60)	Participation of ordinary, double, ternary, etc. chains of carbon atoms bonding vertices, edges and faces of neighbouring fullerenes	—	—	[53]
Fullerene polymers	Variety of C <sub>2n</sub> -polymerized structures such as dimers, trimers,... 1D chains and 2D lattices	E.g., (C <sub>60</sub> ) <sub>n</sub> 2D orthorhombic, tetragonal and hexagonal (rhombohedral) lattices are bonded by the combination of parallel double bonds on adjacent molecules with intermolecular spacing reduced	—	Stable, decompose in air at temp. >470 °C	[55, 90, 91, 652]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Fullerites C <sub>60</sub>	Molecular crystals of C <sub>60</sub> fullerenes and/or C <sub>60</sub> fullerene polymers or 3D C <sub>60</sub> fullerene polymers	Crystal structure—cubic (simple), space group— <i>P4<sub>1</sub>-3</i> , lattice parameter: <i>a</i> = 1.404 nm, <i>Z</i> = 240 (neutron diffraction)	1.729	Stable at lower temp.	[92]
		Crystal structure—cubic (face-centred), space group— <i>Fm<math>\bar{3}</math>m</i> , lattice parameter: <i>a</i> = 1.416 nm, <i>Z</i> = 240 (XRD)	1.686	Stable, melting point >280 °C, sublimates at 530 C°e	[93]
		Crystal structure—cubic (face-centred), space group— <i>Fm<math>\bar{3}</math>-3</i> , lattice parameter: <i>a</i> = 1.426 nm, <i>Z</i> = 240 (electron diffraction)	1.651	Stable, melting point >280 °C, sublimates at 530 C°e	[94]
		Crystal structure—orthorhombic (tetragonal), space group— <i>Ihmm</i> , lattice parameter: <i>a</i> = 0.909 nm, <i>c</i> = 1.495 nm, <i>Z</i> = 120 (calculated)	1.938	Stable under high pressures	[95]
		Crystal structure—orthorhombic (tetragonal), space group— <i>Ihmm</i> , lattice parameter: <i>a</i> = 0.9026 nm, <i>b</i> = 0.9083 nm, <i>c</i> = 1.5077 nm, <i>Z</i> = 120 (XRD)	1.937	—	[96]
Fullerites C <sub>70</sub>	Molecular crystals of C <sub>70</sub> fullerenes and/or C <sub>70</sub> fullerene polymers or 3D C <sub>60</sub> fullerene polymers	Crystal structure—trigonal (rhombohedral), space group— <i>R<math>\bar{3}</math>m</i> , lattice parameters: <i>a</i> = 0.9175 nm, <i>c</i> = 2.4568 nm, <i>Z</i> = 180 (XRD)	2.005	—	[97]
		Crystal structure—tetragonal, space group— <i>P4<sub>2</sub>/mmc</i> , lattice parameter: <i>a</i> = 0.9064 nm, <i>c</i> = 1.5039 nm, <i>Z</i> = 120 (XRD)	1.938	—	[98]
		Crystal structure—orthorhombic, space group— <i>Pmma</i> , lattice parameter: <i>a</i> = 1.0016 nm, <i>b</i> = 1.7349 nm, <i>c</i> = 1.853 nm, <i>Z</i> = 280 (XRD)	1.734	Stable at lower temp.	[99]
		Crystal structure—orthorhombic, space group— <i>Cmcm</i> , lattice parameter: <i>a</i> = 1.7303 nm, <i>b</i> = 0.9990 nm, <i>c</i> = 1.7924 nm, <i>Z</i> = 280 (XRD)	1.802	Stable at lower temp.	[100]
		(continued)			

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Fullerites C <sub>28</sub>	Molecular crystals of C <sub>28</sub> fullerenes and/or C <sub>28</sub> fullerene polymers or 3D C <sub>28</sub> fullerene polymers, including lattices similar to diamond and lonsdaleite (so-called hyperdiamonds and hyperlonsdaleites)	—	1.10 (hyperdiamond)	—	[697]
Self-intercalated fullerites C <sub>28</sub>	Hypothetical 3D C <sub>28</sub> fullerene network formed on the basis of hyperdiamonds, when two similar lattices inserted into one another	—	2.18	—	[697]
Fullerite C <sub>20</sub>	Molecular crystals of C <sub>20</sub> fullerenes and/or C <sub>20</sub> fullerene polymers or 3D C <sub>20</sub> fullerene polymers	Crystal structure—cubic (body-centred), space group— <i>Im</i> (-3), lattice parameter: <i>a</i> = 0.6897 nm, Z = 40 (calculated by density-functional-based tight-binding (DFTB) method)	2.431	—	[101]
Fullerites C <sub>2n</sub>	Molecular crystals of C <sub>2n</sub> fullerenes and/or C <sub>2n</sub> fullerene polymers or 3D C <sub>2n</sub> fullerene polymers	Variety of different structures	—	—	[50, 91, 101]
Hyperfullerenes (multi-walled fullerenes, onion-like fullerenes, buckyonions or “Russian doll” structures)	Spherical nanoparticles based on multiple atomic layers surrounding an initial fullerene core	E.g., C <sub>60</sub> @C <sub>240</sub> , C <sub>60</sub> @C <sub>240</sub> @C <sub>540</sub> , C <sub>60</sub> @C <sub>240</sub> @C <sub>540</sub> @C <sub>1500</sub> , ..., outer diameter—from 10 nm to 1 μm, inner diameter for C <sub>60</sub> —0.7–1.0 nm, interlayer spacing for C <sub>60</sub> @C <sub>240</sub> —0.3524 nm (calculated)	—	—	[50, 68, 78]
Astralens	Polyhedral multi-shell fullerene-like nanoparticles consist of large defect-free flat graphitic faces connected by defective edge regions presumably pentagon-like structured	Particles average size ~40 nm and its graphitic faces sizes ~15 nm (stacking of 20–50 graphene sheets with interlayer spacing ~0.340 nm)	2.1–2.3	—	[57]
Fullerene intercalated graphite compounds	Graphene/C <sub>60</sub> (or C <sub>70</sub> ), (C <sub>60</sub> ) <sub>n</sub> -clusters/graphene systems, where the surface contacts between fullerene “quasi-spheres” and graphene sheets are reduced to “point-like contacts”	For C <sub>60</sub> intercalated graphite compound—interlayer spacing ~1.3 nm (TEM), for (C <sub>60</sub> ) <sub>n</sub> -cluster graphite compound the formation of 2 parallel 7-fullerene monolayers for 2.2–2.7 nm spacing is predicted theoretically	—	—	[698–699]

(continued)

**Table 2.3** (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Single-walled nanotubes (buckytubes, SWCNT)	Cylindrical tube-like molecules with atoms tightly packed into a 2D hexagonal lattice	Molecular diameter—0.43–100 nm (typical—1–10 nm), length: typical—from 50 nm to 1 $\mu$ m and max.—up to centimetre scale, max. length-to-diameter ratio—up to $1.32 \times 10^8$ :1	—	Stable at ultra-high temp.	[58–59, 68, 78, 104–106]
SWCNT capped (closed)	Cylindrical tube-like molecules with atoms tightly packed into a 2D hexagonal lattice with the ends capped by hemispheres of the fullerene structures	—	—	—	[58, 105]
Defective SWCNT	Cylindrical tube-like molecules with the defects in 2D hexagonal lattices (bent and toroidal tube-like structures)	Variety of different forms	—	—	[111]
Double-walled nanotubes (DWCNT)	Assemblies of two concentric cylindrical tube-like molecules with atoms tightly packed into a 2D hexagonal lattice	Outer molecule diameter—3–5 nm, interlayer (intertube) spacing— $\sim 0.39$ nm	—	—	[58]
Multi-walled nanotubes (MWCNT)	Assemblies of several (up to 50 and even more) concentric cylindrical tube-like molecules with atoms tightly packed into a 2D hexagonal lattices	Outer molecule diameter—from 2.5 to 80 nm (the diameter of thinnest armchair (2,2)-type nanotube inside a multi-walled nanotube—0.3 nm), length (typical)—from 10 nm to 1 $\mu$ m, interlayer (intertube) spacing—about 0.34 nm	—	Stable at ultra-high temp.	[58, 68, 78, 103–105]
MWCNT capped (closed)	Assemblies of concentric cylindrical tube-like molecules with atoms tightly packed into a 2D hexagonal lattice with the ends capped by hemispheres of the fullerene structures	—	—	—	[58]
Defective MWCNT	Assemblies of concentric cylindrical tube-like molecules with the defects in 2D hexagonal lattices (bent and L-, Y- and T-branched and helical multi-layered tube-like and bamboo-like structures)	Variety of forms, containing either topological (pentagon-heptagon) defects or structural (discontinuous or cone-shaped walls or bamboo structures)	—	—	[111]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Nanotubes (nanoscrolls) with polygonal cross-sections	1D needle-like molecules or assemblies of these molecules (with non-symmetric 2D hexagonal lattice fringes) shaped as twisted polygons	Outermost diameter of 10–50 nm, while the internal channel diameter varies in the range of 2–10 nm	–	–	[105, 145–147]
Nanobarrels	Imperfect cylindrical nanotubes with barrel-like forms	–	–	–	[53, 71]
Nanohorn particles	Spherical aggregates of capped SWCNTs	With average diameter—80–100 nm (each individual tube with diameter—2–3 nm and cap cone angle of 120°)	–	–	[113–114]
Megatubes	Self-assembled structures formed by branched nanotubes	Exceeding 5 µm in diameter	–	Stable	[89]
Giant nanotubes	Self-assembled knitted structures formed by nanotubes	With average sizes 5 µm in diameter and 100 µm in length	–	Stable	[63]
Supertubes	Hypothetical cylindrical structures built of single-walled nanotube fragments with Y-junctions	–	–	–	[53]
Nanotube bundles (ropes, strands)	Tightly packed aggregates of various aligned SWCNTs or MWCNTs	E.g., a typical bundle of SWCNTs with diameter range from 10 to 20 nm and length—between 10 µm and 1 mm (typical—10–100 µm) consist of 10 to 500 nanotubes, bundles (ropes, strands) are far longer than any individual tube in them	1.3–1.4 (in ropes)	Stable at ultra-high temp.	[78, 104–105, 108]
Nanotube lattices	2D ordered aggregates of various aligned single- or multi-walled nanotubes	Gap between the tubes (with average diameter 1.4 nm)—0.315 nm	–	–	[58, 110]
Nanotubular crystals (nanotube yarn)	Polycrystalline aggregates of various spun nanotube bundles	Length—up to 30 cm	–	Stable at ultra-high temp.	[104–105, 109]
Nanococones	Conical molecules with atoms tightly packed into a 2D polygonal (hexagonal and pentagonal) lattice	Dimensions—up to 1 µm, height and base diameter are of the same order of magnitude, the preferred values of apex angles are approximately 19°, 39°, 60°, 84° and 113°	–	–	[115–118]
Nanodisks	Hypothetical non-spherical (discoidal) molecules formed by cross-linking graphene layers, containing from 44 to 296 atoms	Diameters—from 0.675 nm to 1.952 nm and heights—from 0.307 nm to 0.472 nm (calculated by MM+ molecular mechanics and Hückel semiempirical methods)	–	–	[21]

(continued)



Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Nanobreadsticks	Hypothetical non-spherical (discoidal-tubular) molecules formed by cross-linking graphene layers, adopting different conformations (similar to those in nanotubes) and containing from 148 to 248 atoms	Widths—from 1.078 nm to 1.156 nm, thicknesses—from 0.347 nm to 0.359 nm and lengths—from 1.536 nm to 2.621 nm (calculated by MM+ molecular mechanics and Hückel semiempirical methods)	—	—	[21]
Toroids (toroidal cages)	Giant ring tubular molecules with atoms tightly packed into a 2D hexagonal lattice or 2D hexagonal lattice with inserted pentagons and heptagons into the structures	E.g., series of molecules from C <sub>120</sub> to C <sub>1920</sub> with 10 pentagons and 10 heptagons inserted within the each structure and approximate sizes: outer radii from 0.6 nm to 2.5 nm, inner and transverse radii from 0.25 nm to 1 nm (calculated by molecular dynamics method)	—	Stable	[53, 119–121, 125]
Helical nanocoils (coiled cages)	Giant tubular helical molecules with atoms tightly packed into a 2D hexagonal lattice or 2D hexagonal lattice with inserted pentagons and heptagons into the structures	E.g., derivatives of toroids with similar dimensions (calculated by molecular dynamics method)	—	Stable	[125]
Haackelones, haackelites (pentaheptites, octites)	Hypothetical structures of hexagonal lattice distorted by the equal number of inserted pentagons and heptagons in order to compensate negative and positive curvatures, containing sometimes octagons	—	—	—	[53, 126, 694–696]
Schwarzones, schwarzites	Hypothetical negative curvature structures of hexagonal lattice distorted by the inserted heptagons	Various (predicted)	1.0–1.3 (calc.)	Stable (predicted)	[53, 126]
Squarographenes	Hypothetical structures formed by distorted hexagons and regular squares or by undistorted hexagons and rhombuses	—	—	—	[694]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Nanobuds	Combined (0D + 1D) molecules of fullerenes covalently attached to the outer sidewalls of underlying nanotubes	Two types of fullerene-nanotube bonding: $sp^2$ - and $sp^3$ -hybridized	—	—	[61]
Nanopeapods	Combined (0D + 1D) molecules of fullerenes encapsulated inside nanotubes $C_{2n}$ @SWCNT (e.g. $C_{60}$ , $C_{70}$ , $C_{80}$ , $C_{84}$ )	Orientation of the fullerenes with strong anisotropy is controllable by changing the nanotube radius (on the basis of density-functional theory (DFT) calculations)	—	Stable to 800 °C, at higher temp. transform to bilayered nanotubes	[53, 62]
Nanoscrolls (whiskers, “Swiss roll” structures)	Cylindrical molecules of graphene sheets rolled into scrolls	Molecular dimensions: outermost diameter—up to 80 nm, innermost diameter—1–4 nm, length—0.5–10 $\mu$ m	—	Stable at ultra-high temp.	[60, 68, 75, 123–124]
Nanofiber (nanowire, nanorods)	Cylindrical nanostructures with graphene layers arranged as stacked plates, cones and other configurations	Diameter—less than 0.5 $\mu$ m, length—up to 1 cm	—	Stable at ultra-high temp.	[68, 91, 127–135]
Nanofoam	Low-density (nanoporous) assembly of graphene clusters (nanoplatelets) with negative curvature bonded with each other by $sp^3$ -hybridized atoms and strung together in a loose 3D network	Dimensions of graphene clusters with inclusions of heptagons among the regular hexagonal lattice—about 6 nm ( $\sim$ 4000 atoms)	Very low, up to 0.002–0.010	Stable	[53, 64, 122, 676]
Defected graphite (armchair prismatic edge dislocations)	Distorted graphite structure characterized by formation of wrinkled unbonded graphene layers (well-defined cavities and expansion of interlayer spacing due to the bends of layers)	Structure built from $sp^2$ -hybridized atoms with max. separation between the flat and curled graphene layers— $\sim$ 0.68 nm and min. separation— $\sim$ 0.32 nm; the bent layers perform as spacers in the AA-stacked graphite with spacing of $\sim$ 1 nm	1.62	Very stable with binding energy—7.94 eV atom <sup>-1</sup>	[676]
Defected graphite (zig-zag prismatic edge dislocations)	Distorted graphite structure characterized by the local interconnection of neighboring graphene layers by $sp^3$ -hybridized atoms (reorientation of graphene layers and formation of connected double layers with cavities and loops)	Structure formed by the graphitic stripes connected by $sp^3$ -hybridized atoms with $sp^3$ - $sp^2$ bond length—0.1491 nm; the cavities have a max. height of 0.67 nm, each double layer is repeated with $\sim$ 1 nm distance and min. distance between two graphitic fragments—0.33 nm	1.62	Very stable with binding energy—7.88 eV atom <sup>-1</sup>	[676]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Glitter	Hypothetical 3D structure (3,4-connected atomic net) forming 3D network of interconnected channels constructed from a structural basis constituted by a 1,4-cyclohexadienoid motif (viewed as a plausible model of n-diamond, ?)	Crystal structure—tetragonal, space group— <i>P4<sub>3</sub>/mmc</i> , lattice parameters: $a = b = 0.2560\text{--}0.2564$ nm, $c = 0.5925\text{--}0.6064$ nm, $Z = 6$ (trigonal $sp^2$ -hybridized atoms to tetrahedral $sp^3$ -hybridized atoms ratio—2:1, C—C bond length—0.1510–0.1534 nm, C=C bond length—0.1348–0.1350 nm, DFT and DFTB calculated)	3.00–3.12	Stability is similar to that of diamond (binding energy—7.52 eV atom <sup>-1</sup> )	[673, 676]
Soot	Randomly formed spherical particulates with loose grape-like aggregates (various in origin and contamination), having dominant turbostratic order with graphenes stacked in the manner of roof tiles	Particles with common sizes 10–500 nm consist of small domains—up to 3 nm along the graphene sheets and 2 nm perpendicular to them, interlayer spacing—about 0.344 nm	1.85–2.18	Stable at ultra-high temp.	[42, 58, 136, 138]
Carbon black (channel black, thermal black, lamp black, acetylene black)	Partly crystallized or amorphous spherical particulates (colloids with various origin and contaminations)	Particles with common sizes—10–500 nm, high specific surface area (10–150 m <sup>2</sup> /g) and low apparent density (0.01–0.1 g/cm <sup>3</sup> )	2.04–2.18	Stable at ultra-high temp.	[42, 136, 138]
Amorphous carbon	Structures (including films, porous and contaminated materials) without long-range crystalline order, or having polycrystalline (nanocrystalline) areas distributed by various ways within an amorphous matrix	Deviation of interatomic distances (or interbonding angles) from the perfect graphite crystal is greater than 5 % in both a graphene plane and between graphene planes	1.8–2.1	Stable in some ranges of temp., transforms to crystalline materials	[42, 69, 78, 136, 138]
Pyrolytic carbon	Aggregates of graphenes with covalent bonding between graphene sheets	E.g., material deposited at low temp. composed from crystallites with average dimensions $L_a = 4$ nm, $L_c = 2$ nm and interlayer spacing—more than 0.344 nm	1.1–2.1	Stable, at ultra-high temp. transforms to highly ordered materials	[8, 43, 136]
Coke	Graphene containing products of hydrocarbons pyrolysis (partly contaminated)	Composed from crystallites with $L_c$ —about 5 nm and interlayer spacing—more than 0.344 nm	1.7–2.2	Stable, at ultra-high temp. commonly transforms to highly ordered materials	[42–43, 136, 138–139]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Charcoal	Graphene containing biomorphous products of pyrolysis (porous, contaminated)	Similar to coke	1.5–2.0	Stable, at ultra-high temp. commonly transforms to highly ordered materials	[42, 136, 138]
Activated carbon	Nanoporous assemblies of defective graphene layers	Ratio of pentagons-to-hexagons in the atomic network (estimated by HRTEM for high temp. heat-treated material)—approximately 1:50, average pore diameter—1–5 nm and specific surface area—in the range of 300–2600 m <sup>2</sup> g <sup>-1</sup>	1.4–1.7	Stable	[42, 58, 69, 136, 138, 140]
Molecular-sieve carbon	Nanoporous assemblies of roughly parallel graphene sheets with no 3D crystalline order	Disorientation angles of graphene sheets—up to several degrees, formed from packing imperfection pore structures, consist of relatively wide openings of 0.6–2.0 nm with small ultramicropores of 0.3–0.6 nm (bimodal pore distribution)	1.3–1.8	Stable	[69, 141–144]
Carbon (amorphous) fiber	Bundle of filaments without long-range crystalline order; or having polycrystalline (nanocrystalline) areas distributed by various ways within an amorphous matrix	Various structures	1.4–1.8	Stable at high temp.	[8, 42, 84, 136–137]
Carbon (amorphous) clothes, fabrics, felts and prepregs	(2, 2,5, 3,...n)D-components made from carbon (amorphous) fiber	Various structures	–	Stable at high temp.	[8, 84, 136–137]
Aerogels (cryogels, xerogels)	Assemblies of nanoporous (microporous) spherical nanoparticles formed by defective graphene layers	Particles with diameter of 6–40 nm composed from crystallites with sizes: L <sub>c</sub> of 0.6–0.9 nm and L <sub>a</sub> of 2.5–4.5 nm, interparticulate mesopores with dimensions of 3–15 nm and interior micropores—0.7–1.5 nm, specific surface area—400–1400 m <sup>2</sup> g <sup>-1</sup>	–	Stable at high temp.	[69, 70, 148–150]
Glassy (vitreous) carbon	3D random tough network of 2D hexagonal lattice ribbons tangled and joined with each other	Graphitic ribbon crystallites with dimensions—L <sub>c</sub> of 1.5–3 nm and interlayer spacing—0.360–0.349 nm, total porosity—~30 % with pore diameters of 1 to 3.5 nm (most of the pore entrances—0.4–0.5 nm)	1.4–1.6	Stable at ultra-high temp.	[42, 151–153]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Glassy (vitreous) carbon foam	Cellular (highly porous) structures of 2D hexagonal lattice ribbons networks	Total porosity—97 %, specific surface area—1–2 m <sup>2</sup> g <sup>-1</sup>	~0.05 (bulk), ~1.5 (strut)	Stable at high temp.	[42]
Carbon bead powder (mesocarbon microbeads)	Spherical particles (contaminated by hydrogen) consist of quasi-graphene (planar aromatic compounds) sheets (lamellae) stacked in parallel array	Particle diameters of 1–80 µm, the sheets are arranged perpendicularly along one diameter of a sphere, but curved and normal to the surface with interlayer (interlamellar) spacing—0.346–0.348 nm	1.3–2.2	Stable	[154–156]
Carbide derived carbon	Tunable nanoporous carbons formed by chemically removing metallic or non-metallic elements from carbides and leaving a systematic array of pores	Variety of nanostructures with different parameters	–	–	[71, 157–165]
Diamond-like carbon	Amorphous or semi-crystalline films (partly contaminated by hydrogen) with no lattice long-range order	Broad range of structures (film thickness of 0.1–5 µm) composed of very small crystallites having either tetrahedral or planar threefold local atomic configuration	1.8–2.8	Metastable, convert to graphite at 250–400 °C	[13, 42]
Hexagonite (based on barrelene generating fragment molecules) <sup>f</sup>	Hypothetical 3D structure (3-, 4-connected network) with a large number of derivatives formed by the insertion of 1,4-dimethylene-2,5-cyclohexa-dieneoid organic spacers	Crystal structure—hexagonal, space group— <i>P6<sub>3</sub>/mm</i> , lattice parameters: <i>a</i> = 0.4772 nm, <i>c</i> = 0.4129 nm, <i>Z</i> = 10 (C–C bond length—0.1521 nm, C=C bond length—0.1326 nm, C–C–C trigonal angles—130°, C=C–C trigonal angles—~115°, tetrahedral angles within the cage of barrelene substructures—103°, tetrahedral angles outside the cage of barrelene substructures—115°, calculated and optimized by a DFT algorithm)	2.449	–	[669–671]
Ortho-graphite-diamond hybrids	Hypothetical 3D structure (3-, 4-connected network) with graphene fragments connected with each other in perpendicular directions by <i>sp</i> <sup>3</sup> -bonding	–	–	–	[672]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Para-graphite-diamond hybrids	Hypothetical 3D structure (3-, 4-connected network) with graphene fragments connected with each other in parallel directions by $sp^3$ -bonding	—	—	—	[672]
Intermediate graphite-to-diamond transition phases	Hypothetical 3D structures as progressive intermediates in graphite-to-diamond phase transition	Crystal structure—orthorhombic, space group— <i>Cmmm</i> , lattice parameters: $a = 0.4525$ nm, $b = 0.5334$ nm, $c = 0.5925$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—orthorhombic, space group— <i>Cmme</i> , lattice parameters: $a = 0.4575$ nm, $b = 0.5304$ nm, $c = 0.5635$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—orthorhombic, space group— <i>Pbam</i> , lattice parameters: $a = 0.4048$ nm, $b = 0.4885$ nm, $c = 0.6495$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—orthorhombic, space group— <i>Pcca</i> , lattice parameters: $a = 0.4700$ nm, $b = 0.5978$ nm, $c = 0.4448$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—orthorhombic, space group— <i>Cmmm</i> , lattice parameters: $a = 0.4870$ nm, $b = 0.5565$ nm, $c = 0.4406$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—orthorhombic, space group— <i>Cmme</i> , lattice parameters: $a = 0.4964$ nm, $b = 0.5163$ nm, $c = 0.4387$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—orthorhombic, space group— <i>Pbam</i> , lattice parameters: $a = 0.4127$ nm, $b = 0.4937$ nm, $c = 0.4819$ nm, $Z = 16$ (calculated by molecular mechanics methods) Crystal structure—cubic, space group— <i>Ia<math>\bar{3}</math></i> , lattice parameters: $a = 0.4591$ nm, $Z = 16$ (calculated by molecular mechanics methods)	2.222 2.334 2.484 2.554 2.673 2.839 3.250 3.297	Metastable Metastable Metastable Metastable Metastable Metastable Metastable Metastable	[166] [166] [166] [166] [166] [166] [166] [166]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
i-carbon (shock-compressed graphite phase)	Nanocrystals in intermediate states between graphite and diamond (or glitter modification, ?)	Thin films or spherical particles with diameter of ~25 nm (crystal structure of glitter, ?)	—	—	[675, 682–685]
n-diamond (or $\gamma$ -carbon, shock-compressed graphite phase)	Nanocrystals in intermediate states between graphite and diamond (or glitter modification, ?)	Crystal structure—cubic, space group— $Fm\bar{3}m$ , or crystal structure of glitter, ?	—	—	[170, 674, 682, 684, 686–688]
n-diamond	Hypothetical 3D structure as an intermediate state between rhombohedral graphite and diamond	Crystal structure—trigonal (rhombohedral), space group— $R\bar{3}$ , lattice parameters: $a = b = c = 0.35809$ nm, $Z = 8$ (calculated)	3.474	—	[167]
<i>Diamond Family</i>					
Diamondoids	Hydrogen-terminated molecules	Various shapes with sizes of 1–2 nm	—	—	[72, 677]
Ultra-nanocrystalline (ultra-dispersed)	3D tetrahedral atomic structure in substantially monocrystalline particles (often with multiple twins)	Range of primary particles sizes—2–20 nm, average (or typical) size—4–5 nm, minimal size—1.8 nm, specific surface area—300–400 m <sup>2</sup> /g, crystal structure—cubic with lattice parameter: $a = 0.3573 \pm 0.0005$ nm	3.1–3.4	Stable in some ranges of temp., initial vacuum graphitization temp.—1100–1200 °C	[72, 78]
Ultra-nanocrystalline aggregated diamond	Agglomerates of 3D tetrahedral structured particles	Dimensions of agglomerates—from 40–50 nm to 0.1–1 mm	—	—	[72]
Nanocrystalline particulate diamond	3D tetrahedral atomic structure in monocrystalline particles	Range of smallest fraction sizes—0–50 nm with average size—ca. 25 nm, other fractions—0–100 nm (average size—~50 nm), 0–150 nm and up	—	More stable than graphite nanoparticles being in clusters with less than 10 <sup>4</sup> carbon atoms	[72, 78]
Nanocrystalline aggregated diamond	Polycrystalline agglomerates of 3D tetrahedral structured particles	Average grain size—~20 nm	—	—	[72]
Diamond nanorods	1D form of 3D tetrahedral atomic structure	Diameter of 5–200 nm, length—up to 1–10 $\mu$ m	—	—	[72, 78]
Aggregated diamond nanorods (hyperdiamond)	Assembly of interconnected diamond nanorods	Nanorods with diameters of 5–20 nm and lengths of ~1 $\mu$ m	3.526	—	[168–169]
Diamond nanotubes	1D form of 3D tetrahedral atomic structure	Diameter of 50–160 nm	—	—	[72]

(continued)

Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Diamond nanowhiskers	1D form of 3D tetrahedral atomic structure	Diameter of 10–60 nm, length—~ 300 nm	—	—	[72]
Diamond nanocylinders	1D forms of nanodiamond with circular, triangular or squared cross-sections	Diameter—up to 600 nm, length—~ 5 nm	—	—	[72]
Diamond nanocones	1D form of 3D tetrahedral atomic structure	Diameters at base—0.1–1 $\mu$ m	—	—	[72]
Diamond nanofiber (filaments)	1D form of polycrystalline ultra-dispersed diamond	Diameter of 0.1–1 $\mu$ m, length of 2–3 $\mu$ m, average grain size <10 nm	—	—	[72, 78]
Diamond nanoplatelets	2D form of 3D tetrahedral atomic structure with triangular and parallelogram shapes	Thickness ranges from 20 to 70 nm and length—0.1–10 $\mu$ m	—	—	[72]
Ultra-nanocrystalline diamond films	3D form of polycrystalline ultra-dispersed diamond with grain boundaries formed by <i>sp</i> <sup>2</sup> -hybridized atoms	Average grain size—2–5 nm, grain boundaries width—0.2–0.4 nm	—	—	[72]
Polycrystalline diamond nanopowder	3D form of polycrystalline ultra-dispersed diamond	Grain sizes with bimodal distribution—1–4 nm and 10–160 nm	—	—	[72]
Carbide derived diamond-structured carbon	Wide variety of nanoporous diamond polytype structures formed by chemically removing non-metallic elements from carbides	Grain sizes—5–10 nm	—	—	[71–72, 78, 170–171]
Diamond (3C-diamond, $\beta$ -carbon) single crystal (or polycrystalline)	Giant molecule with atoms tightly packed into a 3D tetrahedral lattice (or assemblies of grains with similar structure)	Crystal structure—cubic, space group— <i>Fd<math>\bar{3}</math>m</i> , lattice parameter: <i>a</i> = 0.35667 nm, <i>Z</i> = 8 (C-C bond length—0.1545 nm, XRD)	3.516	Thermodynamically unstable with respect to graphite with a negative free-energy change of 2.88 kJ mol <sup>-1</sup> at standard conditions	[9, 42, 58, 172]
Lonsdaleite (2H-diamond, $\gamma$ -carbon)	Diamond polytype	Crystal structure—hexagonal, space group— <i>P6<sub>3</sub>/mmc</i> , lattice parameters: <i>a</i> = 0.25221 nm, <i>c</i> = 0.41186 nm, <i>Z</i> = 4 (XRD)	3.521	—	[42, 166, 172]
Lonsdaleite (4H-diamond)	Diamond polytype	Crystal structure—hexagonal, space group— <i>P6<sub>3</sub>/mmc</i> , lattice parameters: <i>a</i> = 0.25221 nm, <i>c</i> = 0.82371 nm, <i>Z</i> = 8 (XRD)	3.521	—	[42, 166, 172]

(continued)



Table 2.3 (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Lonsdaleite (6H-diamond)	Diamond polytype	Crystal structure—hexagonal, space group— $P6_3/mmc$ , lattice parameters: $a = 0.25221$ nm, $c = 1.23557$ nm, $Z = 12$ (XRD)	3.521	—	[42, 172]
Lonsdaleite (8H-diamond)	Diamond polytype	Crystal structure—hexagonal, space group— $P6_3/mmc$ , lattice parameters: $a = 0.25221$ nm, $c = 1.64743$ nm, $Z = 16$ (XRD)	3.521	—	[10, 42, 172]
Lonsdaleite (10H-diamond)	Diamond polytype	—	—	—	[42]
Lonsdaleite (12H-diamond)	Diamond polytype	—	—	—	[10]
Lonsdaleite (16H-diamond)	Diamond polytype	—	—	—	[10]
Lonsdaleite (20H-diamond)	Diamond polytype	—	—	—	[10]
Lonsdaleite (15R-diamond)	Diamond polytype	Crystal structure—trigonal (rhombohedral), space group— $R\bar{3}m$ , lattice parameters: $a = 0.25221$ nm, $c = 3.08893$ nm, $Z = 30$ (XRD)	3.521	—	[172]
Lonsdaleite (21R-diamond)	Diamond polytype	Crystal structure—trigonal (rhombohedral), space group— $R\bar{3}m$ , lattice parameters: $a = 0.25221$ nm, $c = 4.3245$ nm, $Z = 42$ (XRD)	3.521	—	[172]
Hexagonite (cold compressed nanotubes) <sup>f</sup>	Super-hard phase	Crystal structure—hexagonal, space group— $P6_3/mc$ , lattice parameters: $a = 0.2496$ nm, $c = 0.4123$ nm, $Z = 4$ (interlayer spacing—0.21 nm, C-C bond length—0.143 nm, electron diffraction, XRD) The ratio of pentagon/hexagon rings is going up to 9	3.65 (or 3.6 ± 0.2) <sup>g</sup>	Quenched from ~75 GPa, preserved at room conditions	[668]
Diamond D <sub>5</sub>	Hypothetical diamond-like networks consisting mostly of pentagon rings	—	—	More stable than C <sub>60</sub> (calculated)	[666–667]

(continued)

**Table 2.3** (continued)

Form	Character	Structure parameters (at ambient conditions)	Density, g cm <sup>-3</sup>	Thermal stability	References
Lonsdaleite L <sub>5</sub>	Hypothetical lonsdaleite-like networks consisting mostly of pentagon rings	The ratio of pentagon/hexagon rings is going up to 9	–	More stable than C <sub>60</sub> (calculated)	[666–667]
Octacarbon (supercubane, prismane, BC8)	High-temp. modification of diamond (?)	Crystal structure—cubic (body-centred), space group— <i>Im</i> (-3), lattice parameter: <i>a</i> = 0.428 nm, Z = 16 (electron diffraction and calculated by molecular mechanics methods)	4.1	Stable at ultra-high temp. and pressures	[166, 176–177, 187, 189]
		Crystal structure—cubic (body-centred), space group— <i>Ia</i> l(-3), lattice parameter: <i>a</i> = 0.4293 nm, Z = 16 (calculated by molecular mechanics methods)	4.03	–	[166, 173–175, 187, 189]

<sup>a</sup> Concerning the carbyne family, see notes *a-c* to Table 2.2<sup>b</sup> Calculated on the basis of data [20]<sup>c</sup> Number of formula units per lattice<sup>d</sup> Some other forms have been reported in literature [9]<sup>e</sup> Data available in literature are controversial [112]<sup>f</sup> Not to be confused with the inorganic mineral structure and some trademark names<sup>g</sup> Average (reduced) density due to possibly amorphous carbon on the grain boundaries

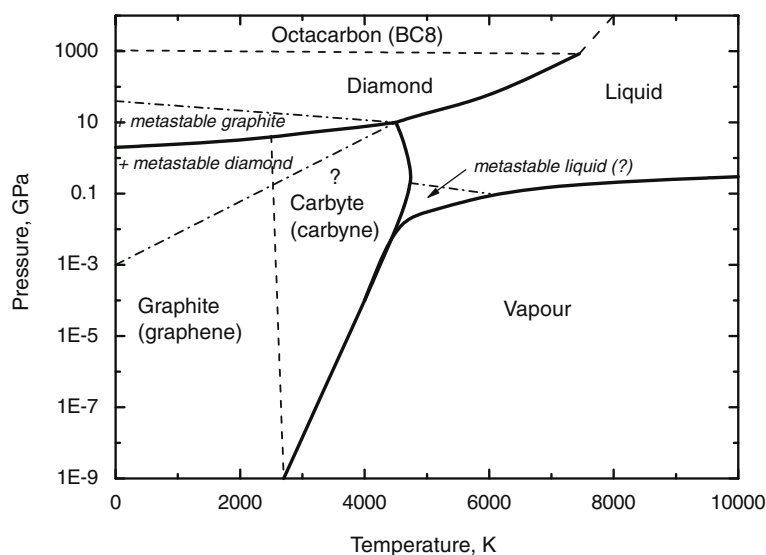
termed pyramidalization angle and/or curvature are used for evaluation of nonplanarity (deviation from graphene plane geometry) in fullerene family structures),

which differ in the  $sp^n$ -hybridisation ( $1 \leq n \leq 3$ ) types of carbon structures.

The main structural characteristics, including crystal lattice parameters and densities, and relative thermal stabilities of the various carbon allotropic, polymorphic and polytypic forms, grouped under family headings within the overall hierarchy from submolecular to macrostructural scales, are summarized in Table 2.3.

## 2.2 Thermal Properties

2H-graphite (or  $\alpha$ -graphite) is the most stable thermodynamically form of carbon under standard conditions, so its standard enthalpy of formation (at 298.15 K)  $\Delta H_{f,298}^\circ$  is zero, similar to those characteristics for all other chemical elements. The generalized phase and transition diagram of carbon based on several main sources [28, 176–190, 535–538] is given in Fig. 2.1. In the region of moderate pressures, this variant of carbon phase diagram assumes the sequence of transformations with temperature (energy) increase from  $sp^3$  (diamond) through  $sp^2$  (graphite/graphene) to  $sp^1$  (carbyte/carbyne), which is corresponding to the specific bond energy approach established for the carbon structures classification previously (see Sect. 2.1). The general thermodynamic properties of carbon (graphite) are summarized in Table 2.4.



**Fig. 2.1** The generalized phase and transformation diagram of carbon according to the several main sources [28, 176–190, 535–538]