CONFERENCES AND SYMPOSIA

Nontraditional synthesis of nano- and microcrystal diamonds under high static pressures

E A Ekimov, M V Kondrin

DOI: https://doi.org/10.3367/UFNe.2018.04.038375

Contents

1.	Introduction	199
2.	Methane or molecular hydrogen?	200
3.	Nanodiamonds from graphitized carbon materials	201
4.	Synthesis of nano- and microcrystal diamonds from hydrocarbons	201
5.	Conclusion	206
	References	206

<u>Abstract.</u> Diamond synthesis from organic materials under high pressure performed for the first time more than half a century ago is now in high demand to fit the needs of nanoelectronics and biomedicine due to the possibility of obtaining nanodiamonds of high structural perfection. The Institute for High Pressure Physics, RAS, being a pioneer in diamond synthesis in metallic solutions and unconventional media, is a recognized leader in the promotion of new trends in the synthesis of nanodiamonds free from metallic impurities. In this short review, we consider the most likely scenario of hydrocarbon carbonization with the formation of nano- and microcrystal diamonds.

Keywords: diamonds, synthesis, high pressure, organic compounds, nanodiamonds

1. Introduction

The first synthesis of nano- and microcrystal diamonds from organic matter under high static pressures and temperatures was accomplished by R Wentorf [1] more than half a century ago. By that time, nanodiamond detonation synthesis from explosive decomposition products had been reported, and nanodiamond synthesis under static conditions did not arouse great practical interest [2]. Today, the great demand for doped diamond nanocrystals of high structural perfection for use in nanoelectronics and biomedicine as luminescent biomarkers, single-photon sources for quantum computation, sensors for measuring local temperatures and magnetic fields has revived attention to the high-pressure synthesis of nanodiamonds from organic materials [3–5].

E A Ekimov, M V Kondrin Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences,

Kaluzhskoe shosse 14, 108840 Troitsk, Moscow, Russian Federation E-mail: ekimov@hppi.troitsk.ru, mkondrin@hppi.troitsk.ru

Received 2 July 2018 Uspekhi Fizicheskikh Nauk **189** (2) 208–216 (2019) DOI: https://doi.org/10.3367/UFNr.2018.04.038375 Translated by Yu V Morozov The thermodynamically stable conditions of the synthesis imply the potential to produce structurally perfect diamonds under high pressure and temperature. For example, the first single-photon emitters with extremely narrow individual spectral lines close to the lifetime limit in the excited state were obtained using high-pressure synthesis [6]. On the one hand, synthesis from organic materials was shown to lower the potential barrier for diamond formation; on the other hand, it allowed avoiding metallic impurities and inclusions inevitable for traditional diamond synthesis in carbon solutions based on transition metals (Fe, Co, N, etc.) [7, 8]. Unlike diamonds obtained under metastable conditions in hydrogen-containing plasma by chemical vapor deposition (CVD) [9], those synthesized under high pressures and temperatures are free from hydrogen admixtures [10, 11].

Studies on diamond synthesis from organic materials have until recently been scarce and fragmentary. The lack of understanding about mechanisms of nucleation and growth of diamond crystals from organic substances seriously hampers progress in large-scale nanodiamond synthesis. This situation partly originates from the difficulty of the problem in question, which dictates the necessity to consider a number of issues, such as the behavior of organic compounds of various structures and chemical compositions at high pressures and temperatures; their phase and structural transformations accompanied by polymerization, bond saturation, and hydration; decomposition pathways; and mechanisms of structural changes in the carbon phases being formed.

Investigations into the behavior of organic matter under high pressure were initiated at the Vereshchagin Institute for High Pressure Physics (IHPP), Russian Academy of Sciences (Troitsk, Moscow), by E N Yakovlev in the 1980s in the context of experimental simulation of thermally stable diamond formation processes in nature and industry [12, 13]. Thenceforth, the range of interests extended considerably to include the production of doped diamonds from organic materials of more complicated chemical compositions and the search for new nontraditional growth media [14–17]. Nowadays, IHPP, being a recognized leader in the promotion of innovative trends in the synthesis of nanodiamonds from unconventional precursors, is engaged in research aimed at developing the physicochemical principles of large-scale production of high-quality doped nanodiamonds.

Our analysis of the literature data was focused on several problems pertaining to the creation of nano- and microdiamonds from organic materials under high pressures and temperatures. The answer to the central question (what is the end product of hydrocarbon decomposition: hydrogen or methane?) would help in understanding mechanisms of carbonization and diamond formation. Also, the question is important in itself, because the answer would provide an insight into the geochemical processes happening deep in Earth's mantle and leading to abiogenic oil synthesis [18] and pyrolytic hydrocarbon decomposition under high pressure [19]. Consideration of the peculiarities of nanodiamond synthesis from graphitized carbon materials in the absence of special growth media may give a due to the most probable mechanism of diamond nanocrystal formation during carbonization. We shall also discuss certain specific features of diamond synthesis from organic materials pointing towards approaches to the solution to the problem of large-scale synthesis of doped nanodiamonds with reference to the most important results obtained by IHPP researchers.

2. Methane or molecular hydrogen?

An essential prerequisite for the synthesis of diamonds from hydrocarbons is elucidation of their stability and decomposition pathways at high pressures and temperatures. These issues remain poorly explored, and relevant publications not infrequently contain controversial data on the final products of hydrocarbon decomposition at high pressures and temperatures. Temperature appears to be the key parameter influencing the course of the reaction. The problem can be somewhat narrowed to clear up whether methane or molecular hydrogen is the end product of hydrocarbon decomposition.

It is easy to show that hydrocarbon decomposition into methane and diamond is energetically more favorable at low temperatures and relatively small pressures (< 10 GPa). In the case of a short-duration synthesis, a cell can supposedly be hydrogen-terminated, because molecular hydrogen simply fails to leave it. Let us consider a hydrocarbon with the relative concentration C:H = 1:z and energy of C-C, C-H, and H-H bonds of 346, 411, and 432 kJ mol⁻¹, respectively. Two scenarios are conceivable: the reaction produces either hydrogen or methane. Then, for a single CH_z structural unit, the end products are

$$\frac{z}{2} H_2 + C, \qquad (1)$$

$$\frac{z}{4} CH_4 + \left(1 - \frac{z}{4}\right)C. \qquad (2)$$

In a diamond, there are two C–C bonds per atom, as is easy to see, because a covalent bond can be marked by its center so that the bonds are in the octahedral position 16c, i.e., their number is twice that of the atoms. Then, the total bond energy for the former equation is lower than for the latter at any z value. By way of example, for C:H = 1:1, these two values are 908 and 930 kJ mol⁻¹, respectively. According to [18], the conclusion that any heavy hydrocarbon tends toward methane-carbon equilibrium at low enough pressures is confirmed by "a century of petrochemical engineering practice." However, these values prove to be rather close; due to this, taking account of enthalpic and entropic contributions at high pressures and temperatures can readily change the pyrolytic decomposition of hydrocarbons.

The key evidence for solving this problem could be provided by a study of hydrocarbon (first and foremost, methane) stability at high pressures and temperatures. In this case, however, experimental data are patchy and contradictory. The formation of molecular hydrogen from hydrocarbons was observed in static experiments on methane decomposition in diamond anvils [20–23] and in shock-wave experiments [24] with different hydrocarbons.

A common feature of these experiments is the rather high pressures (> 13 GPa) and temperatures (above 2000 K). The products of pyrolytic methane decomposition are either hydrogen and diamond [21] with an admixture of heavier hydrocarbons, or hydrogen and higher alkanes [22, 23] $(CH_4 \rightarrow 1/x(C_xH_y) + (2 - y/(2x))H_2)$. At the same time, the study of methane behavior [25] in the range from the melting curve to diamond formation temperatures (T = 4000 K) revealed signs of methane dimerization to ethane starting from temperatures slightly higher than 1100 K (methane melting temperature at 10 < P < 80 GPa), whereas intense polymerization occurred at temperatures of > 1800 K. Traces of hydrogen were altogether absent, although it should have been a by-product of methane polymerization; for example, the Raman mode corresponding to hydrogen molecule stretching was not recorded (just as in Ref. [20] where P = 19 GPa, T = 2000 - 3000 K). It was argued in Ref. [24] that parts of Hugoniot adiabats in the high pressure region can be adequately described on the assumption that pyrolysis products of different hydrocarbons are molecular hydrogen and diamond. At the same time, the absence of a portion corresponding to pyrolytic decomposition-related phase transition on Hugoniot adiabats obtained on alkane polymers (polyethylene, etc.) questions the validity of this inference. A likely alternative explanation of the observed phenomena is that relatively low temperatures (1500-2000 K) at high enough pressures (20-30 GPa) do not lead to hydrocarbon decomposition; rather, it is a mere change in the type of the $sp^2 - sp^3$ bond in hydrocarbon chains that causes abnormalities on shock adiabats.

References [19, 26] report basic research on hydrocarbon stability at high pressure and temperature. The thermodynamic calculations in [26] give evidence that an anthracenegraphite mixture is converted into methane and hydrogen at moderate temperatures T = 1500-1700 K and pressures P = 5.7 GPa. In this case, the excess carbon is released in the form of carbon as in Ref. [26], where the authors observed the growth of diamond grains added to the starting mixture. Because the temperature in these experiments and calculations was rather low and the entropic contribution to the free energy relatively small, these findings agree on the whole with the above estimates.

Hydrocarbon stability at higher temperatures is a far more interesting matter. It was analyzed by the firstprinciples molecular dynamics method in [19], where methane stability under a pressure of 4–8 GPa was compared at 1000 and 2000 K. The result was shown to be virtually independent of pressure and could be extrapolated to its values up to 20 GPa. Calculations for higher temperatures (4000 K) gave unambiguous evidence of heavy alkane formation under these conditions.

This finding is in excellent agreement with experimental data of Hirai et al. [25] and Benedetti et al. [20]. On the other hand, molecular dynamics methods proved inapplicable at low temperatures when the calculation time did not allow the monitoring of the phase transition. In this case, the analysis was performed by comparing free methane energy with that of an ethane-molecular hydrogen mixture. The data thus obtained indicate that methane remains stable at 1000 K, whereas the ethane-molecular hydrogen mixture is energetically more favorable at 2000 K. The analysis has demonstrated that the key factor responsible for the phase transition is the additional vibrational entropic term of ethane, amounting to 53 kJ mol⁻¹ of methane. Other contributions (translational and rotational) to entropy comparable to vibrational ones in terms of magnitude remain virtually unaltered for both methane and ethane-hydrogen mixtures (in Ref. [19], all components were considered in the fluid phase). These facts should be borne in mind when extrapolating the calculated data to higher pressures and/or other phase transformation products (e.g., diamond), because only the vibrational contribution to entropy needs to be taken into account for solids. In such a case, methane may happen to be energetically more favorable by virtue of a greater energy contribution to the Gibbs potential.

The above review of the literature shows that the hydrocarbon stability problem is still a long way from being solved, while the available experimental data are fragmentary and contradictory. Moreover, they need to be analyzed with due regard for possible catalytic effects related to details of the reaction cell and its open/closed nature for molecular hydrogen. The absence of hydrogen in decomposition products [20, 25] could be attributed to its escape from the reaction volume. Also, results can be radically different in the graphite stability region and in that of low temperatures and pressures. A recent study [27] showed that pyrolysis of benzene and other polyaromatic substances with the liberation of hydrogen and graphitized carbon begins at temperatures below 1000 K and pressures up to 8 GPa, at variance with the data from [28, 29], where benzene polymerization and dispersed graphite hydration yielding graphane (hydrographite) occurred in the same P-T region. In all probability, this discrepancy arises first and foremost from different constructions of the experimental cell (a teflon capsule in one case [27] and a copper or noble metal capsule in two others [28, 29]).

3. Nanodiamonds from graphitized carbon materials

Studies on direct graphite-to-diamond transformation under high pressure have been carried out without carbon solvents. They showed that diamonds more readily form in graphitized carbon materials with a disordered structure than in perfect graphite due to the presence of pre-existing nuclei in the former [1]. Diamonds smaller than 1 μ m in size were synthesized at a pressure of 10–14 GPa and temperature above 1300 °C. The idea to prepare diamonds from amorphous carbon was further developed in Refs [30–32]. Because diamond formation onset temperature decreased with a degree of disorder in the structure of graphite-like materials [30, 32], it was conjectured that diamond nucleation occurs largely in difficult-to-graphitize carbon clusters with sp³hybridized carbon. The diamonds thus obtained were less than 100 nm in size. For structurally perfect graphite, the diamond formation mechanism includes a two-step martensitic transformation of graphite to lonsdaleite (dense carbon with a hexagonal structure) with its subsequent diffuse conversion into diamond [33]. For amorphous or structurally disordered carbon, graphitization (i.e., perfect graphite formation) is not an indispensable prerequisite for diamond formation; in this case, diffuse rearrangement of difficult-to-graphitize clusters with sp³-hybridized carbon into diamond is thought to take place [34]. In general, the low diffusion mobility of carbon atoms with covalent bonds in the solid phase is responsible for the size of the nanocrystals being limited to 5–30 nm [33, 34].

Compact specimens of polycrystalline nanodiamonds with perfect physico-mechanical properties have so far been synthesized from graphitized carbon materials for engineering and instrumentation facilities [35]. Preparation of individual crystals from structurally disordered carbon remains to be accomplished, even though examples of boron-doped polycrystalline nanodiamond synthesis have already been reported in Refs [36, 37]. The relatively slow transformation of graphitized carbon materials into nanodiamonds taking minutes under 9-15 GPa of pressure and a temperature of 1300-1900 °C [34] is an encouraging circumstance in the context of further development of technologies for controlled synthesis of individual nanocrystals. Dopantcontaining disordered carbon materials can be used to produce diamond nanocrystals with optically active vacancy-impurity centers, such as Sn-V [38, 39], Pb-V [40], or rare-earth elements [41], that are difficult to create in conventional CVD [42] and high-pressure high-temperature (HPHT) [43] growth processes. It is believed that diamond doping by elements with low chemical affinity to carbon (Sn, Pb) is easier to accomplish in the absence of competing admixtures [39].

4. Synthesis of nano- and microcrystal diamonds from hydrocarbons

Reduction of the potential barrier for diamond formation from hydrocarbons instead of direct graphite transition to diamond allows diminishing parameters of the synthesis and employing the existing HPHT technologies for the mass production of nanodiamonds. Another advantage of hydrocarbon-based synthesis is the possibility of varying the diamond crystal size from a few nanometers to hundreds of micrometers due to high carbon diffusivity in hydrogencontaining growth media. Structurally perfect crystals with the unique optical characteristics of silicon [6, 44], nitrogen [44], and germanium [45–47] impurity centers were obtained from hydrocarbons in the presence of doping elements. Diamonds with GeV centers promising for quantum applications were used to study the influence of isotope substitution of the carbon matrix and impurity on the fine structure of zero-phonon line and phonon replicas of vacancy-impurity defects in absorption and photoluminescence [46, 47]. It was shown that the nature of isotopic shifts in isotope ${}^{12}C/{}^{13}C$ substitution of the matrix is related to energy variations in a purely electronic transition; in the case of isotope substitution of an impurity, it is related to a change in the curvature of its vibrational potential in the ground and excited states (Fig. 1) [46].

Because most optical property studies have been carried out using microcrystalline diamonds with only a small fraction of nanocrystals, large-scale synthesis of nanodia-



Figure 1. Illustration of optical effects due to the difference between potential surface curvatures in the ground and excited states of an impurity atom [46, 47]. (a) Difference in side bands (solid curve) of the zero-phonon line of GeV-center (2.059 eV) in absorption (right) and luminescence (left). (b) Large isotopic shift of zero-phonon line Z_{1-4} caused by substitution of carbon atoms is also mainly due to the difference between potential surface curvatures in the ground and excited states.



Figure 2. (a) Size distribution of boron-doped nanodiamonds prepared from 9-BBN at 1550 K and 8–9 GPa. The size of the nanodiamonds was determined from measurements of dynamic light scattering in water (b–d). TEM bright-field images of nanocrystals. (b) Thick and thin arrows indicate nanodiamonds and nanographite, respectively. The inset shows an electronogram with the rings corresponding to reflections from diamond (111) and (220) planes. (c, d) Diamond nanocrystals viewed along the [110] zone axis [48].

monds has thus far been performed in few experiments [48–50]. It is therefore premature to characterize the technological level in this sphere. Nevertheless, the successful large-scale synthesis of impurity-free boron-doped nanodiamonds from the organoboron compound 9-borabicyclo[3.3.1]noane dimer or 9-BBN (MF: $C_{16}H_{30}B_2$) [48, 49] (Figs 2 and 3) and adamantane [50] (Fig. 4) at pressures of 8–9 GPa and temperatures of 1000–1400 °C gives hope that this problem will be solved in the near future.

Let us consider several key issues pertaining to the production of nano- and microcrystalline diamonds from hydrocarbons that should be taken into account in the development of technologies for the large-scale synthesis of nanodiamonds under high static pressure.

The studies by Wentorf [1] and Onodera [31, 51] demonstrated the influence of the structure of hydrocarbons on their behavior at high temperatures and pressures. Specifically, Wentorf [1] distinguished two temperature



Figure 3. Raman scattering spectra (a) and photoluminescence spectra (b) of boron-doped nanodiamonds (1550 K) and microcrystals (1950 K) [48].

regimes of diamond formation, depending on the hydrocarbon structure. Diamonds from saturated hydrocarbons were obtained at temperatures of around 1300 °C, while graphite formed from aromatic hydrocarbons under these conditions converted into diamond at 2000 °C. In was shown in [31, 51] that in the 'low-temperature regime' synthesis from hydrocarbons with the bridge-like structure of sp³-hybridized carbon under pressures below 10 GPa yielded nanodiamonds tens of nanometers in size. It was assumed by analogy with nanodiamond synthesis from graphitized carbon materials that the nucleation of diamond crystals occurs in the difficultto-graphitize sp³-hybridized carbon clusters formed during hydrocarbon carbonization. The limited size of the resultant crystals (tens of nanometers) and its weak dependence on the duration of the experiment at temperatures of up to 1300-1400 °C suggest the diffusional character of solid phase transformations. It should be borne in mind that low-temperature synthesis is associated not only with diffusive rearrangement in the solid phase but also with carbon recrystallization in the fluid phase with the formation of perfect graphite [52-54], whereas 'catalytic' properties of the growth medium influencing graphite transformation into diamond are manifested at temperatures above 1300-1400 °C [26, 50]. Clearly, temperature-dependent peculiarities of carbon recrystallization are directly related to the height of potential barriers for the formation of graphite and diamond nuclei in the presence of hydrogen (methane).

It follows from the above that competing processes of diffuse rearrangement in the solid phase and carbon recrystallization in the fluid phase determine what is formed from saturated nanocarbons with the bridged structure at 'pre-critical' temperatures of synthesis. Here, as in the synthesis of microcrystalline diamonds from aromatic hydrocarbons, pressure plays an important role. Sustainable nanodiamond synthesis appears to occur at pressures above 8-9 GPa [49, 50], although certain authors report its observation at 6 GPa [51]. In the 'high temperature regime', nanodiamonds formed at low temperatures complete their growth, and new crystals are nucleated from carbon-oversaturated hydrogen-containing growth media, including those on existing graphene substrates (Fig. 5). The most probable scenario (see Section 2) with carbon transport leading to diamond formation can be described in



Figure 4. (a, b) TEM bright-field images of nanocrystals synthesized from adamantane at 8–9 GPa and 1600 K. Inset in Fig. a is an electronogram with three diffraction rings: (111), (220), and (311). Dashed lines in Fig. b enclose diamond crystals. Inset: diamond crystal with perfect structure along [110] axis [48].



Figure 5. Microphotographs of diamond (a) and graphite (b) prepared from adamantane at 8–9 GPa and 1700–1900 K

terms of the following reactions:

$$CH_4 + C(sp^2) \rightarrow C_y H_y,$$
 (3)

$$C_x H_v \to C H_4 + C(sp^3) \tag{4}$$

or

$$C(sp^2) + H_2 \to CH_4, \qquad (5)$$

$$CH_4 \to C(sp^3) + H_2. \tag{6}$$

Because a methane decomposition reaction under a pressure less than 10 GPa is unlikely, carbon transport is fairly well described by Eqns (3), (4), e.g., with the formation of ethane C_2H_6 or ethylene C_2H_2 . Ethane formation from methane was observed in diamond anvil experiments where hydrogen was not found [19, 25].

Results of earlier experiments carried out at IHPP with the participation of Voronov [52, 53] and later investigations into the behavior of hydrocarbons under high pressure involving Davydov [55, 56] are in conflict with the data from Wentorf and Onodera. The IHPP research failed to demonstrate the influence of molecular structure on the temperature at the onset of carbonization and diamond synthesis from hydrocarbons; the diamonds formed as microcrystals at 1000-1300 °C when Wentorf and Onodera obtained nanodiamonds and graphite. It was proposed to use the decomposition of methane-intercalated graphite (an intermediate product of hydrocarbon carbonization) to produce microcrystal diamonds. The difference in the results of precursor experiments was attributed to the influence of kinetic factors due to the higher transparency for hydrogen of the graphite capsule than that of the metal capsules used in nanodiamond production.

We think that the most plausible explanation for the lowtemperature of diamond microcrystal synthesis can be its inaccurate measurement of temperature and a change in the growth medium composition as a result of methane and hydrogen interaction with the material of the CaCO₃ container. For example, the synthesis of diamond microcrystals in aqueous carbonate solutions occurred at temperatures below 1200 °C [57], whereas in a purely hydrogen medium their sustainable formation was observed only at temperatures above 1300–1400 °C [26, 50]. To recall, the mechanism of diamond synthesis from methane-intercalated graphite is rather the incorrect interpretation of the role of methane formed in the carbonization process.



Figure 6. X-ray diffractograms demonstrating the evolution of the phase composition of specimens obtained from 9-BBN (a, b) and $C_{27}H_{33}B$ trimesitylborane (c) under heating at the pressure 8–9 GPa.



Figure 7. Transmission electron microscopic study of a sample obtained from 9-BBN at 1520 K and 8–9 GPa: (a, b) bright-field images, D—diamond, G—graphite. (c) Electronogram of the sample: D(311), D(220), D (111), G(002), and BC_x—diamond (D), graphite (G), and boron carbide (BC_x) diffraction rings, respectively.



Figure 8. Characteristic micro-crystals (a) and submicro-crystals (b) of diamonds obtained from 9-BBN at 1900 K and 8-9 GPa.

The 'intercalation' mechanism fails to account for the characteristic crystal growth patterns observed in experiment. Early IHPP studies measuring a decrease in naphthalene and adamantane sample mass have led to the conclusion of the unquestionable value of further investigations in this area of hydrocarbon decomposition yielding methane rather than hydrogen as previously thought [54]. Another important achievement was the identification of the hydrocarbon carbonization stages at 8 GPa, as exemplified by naphthalene and adamantane. At temperatures up to 300 °C, the formation of amorphous states without a change in the composition was observed, a two-phase disordered carbonmethane system formed in the range from 450 to 700 °C, and perfect graphite crystallized at 700-1000 °C [52, 53]. The disordered carbon phase appears to retain some amount of hydrogen as an admixture stabilizing sp³-carbon clusters [55].

The mechanism of nanodiamond formation from organic compounds postulated by Onodera [31] was confirmed in recent IHPP-based investigations of nanodiamond synthesis from 9-BBN [49], adamantane [50], and a mixture of naphthalene with fluorinated graphite [58]. In all three cases, the nanodiamond synthesis was attributable to the formation of structurally disordered difficult-to-graphitize nanocarbon clusters during the decomposition of organic substances. The

best illustration of nanodiamond synthesis from disordered carbon was presented in the article by Ekimov et al. [49] devoted to the influence of the ab initio structure of boroncontaining hydrocarbons on diamond synthesis. Nanodiamonds were obtained at 800-1400 °C only from compounds with the bridged skeleton structure, whereas aromatic hydrocarbons yielded only graphite under the same conditions (Fig. 6). A distinctive feature of the carbonization of a compound with the bridge-like structure was the formation of the disordered carbon phase stable at temperatures of up to 1250–1400 °C. The evolution of the sample composition upon heating deduced from X-ray diffraction measurement data gives evidence that it is in this phase that nanodiamonds nucleate and grow (Figs 6 and 7). The formation of diamond microcrystals at temperatures above 1400-1600 °C was observed using both aromatic hydrocarbons and compounds with the bridged structure (Fig. 8).

Unfortunately, it is impossible today to tell what bridgelike structured compounds are suitable for nanodiamond synthesis under pressures below that at which the direct transition of graphitized carbon materials occurs (11 GPa [59, 60]). For example, it is more difficult to obtain nanodiamonds from adamantane than from 9-BBN, despite the fact that the carbon skeleton of the former is nothing more than an element of the diamond lattice. At the same time, the influence of additional chemical elements (especially those making up part of carbon cycles—heteroatoms) on the carbonization of organic compounds is difficult to predict; they may have a multidirectional effect on diamond crystal nucleation and growth that awaits elucidation. For example, the presence of boron atoms in the carbon cycle appears to favor carbonization with the formation of sp³-hybridized carbon clusters and nanodiamonds [49]. On the contrary, nitrogen stimulates graphite crystallization and hinders diamond synthesis [1]; oxygen decreases its temperature and promotes the growth of microcrystals in the aqueous fluid solution being formed [61].

5. Conclusion

An analysis of publications in the literature suggests the possibility of large-scale nanodiamond synthesis under high static pressure. It is shown that the formation of nanodiamonds from structurally disordered carbon materials and hydrocarbons with a bridge-like skeleton structure, as well as from mixtures of organic compounds yielding difficult-to-graphitize carbon clusters (precursors of nanodiamond nucleation), constitutes the most promising option for the synthesis of nanodiamonds. The most probable mechanism of diamond synthesis from hydrocarbons is their pyrolysis with the liberation of methane, which facilitates a transition from sp²-hybridized carbon to its sp³-hybridized form.

Acknowledgements

The authors are grateful to V V Brazhkin for his interest and support. This research benefited from grant funding by the Russian Foundation for Basic Research in the framework of projects 17-52-50075 and 16-02-01120.

References

- 1. Wentorf R H (Jr.) J. Phys. Chem. 69 3063 (1965)
- Danilenko V V Phys. Solid State 46 595 (2004); Fiz. Tverd. Tela 46 581 (2004)
- 3. Pezzagna S et al. New J. Phys. 13 035024 (2011)
- 4. Aharonovich I et al. Rep. Prog. Phys. 74 076501 (2011)
- Ekimov E A, Kondrin M V Phys. Usp. 60 539 (2017); Usp. Fiz. Nauk 187 577 (2017)
- 6. Jantzen U et al. New J. Phys. 18 073036 (2016)
- 7. Sumiya H et al. J. Cryst. Growth 178 485 (1997)
- Kiflawi I, Kanda H, Lawson S C Diamond Related Mater. 11 204 (2002)
- 9. Charles S J et al. Phys. Status Solidi A 201 2473 (2004)
- 10. Field J E (Ed.) *The Properties of Natural and Synthetic Diamond* (London: Academic Press, 1992)
- 11. Zaitsev A M Optical Properties of Diamond. A Data Handbook (Berlin: Springer, 2001)
- 12. Yakovlev E N, Voronov O A Almazy Sverkhtverd. Mater. (7) 1 (1982)
- Yakovlev E N, Voronov O A, Rakhmanina A V Sverkhtverd. Mater. (4) 8 (1984)
- 14. Yakovlev E N et al. Zh. Fiz. Khim. 59 1517 (1985)
- Astakhov M, Ziganshina R, Shalimov M Izv. Vyssh. Uchebn. Zaved. Chern. Metallurg. (3) 15 (1993)
- Voronov O A, Rakhmanina A V Inorg. Mater. 29 533 (1993); Neorg. Mater. 29 623 (1993)
- Voronov O A et al. "Sposob sinteza legirovannykh almazov" ("Method for synthesis of doped diamonds"), Author's certificate SU1345581A (1985)
- 18. Kenney J F et al. Proc. Natl. Acad. Sci. USA 99 10976 (2002)
- 19. Spanu L et al. Proc. Natl. Acad. Sci. USA 108 6843 (2011)
- 20. Benedetti L R et al. Science 286 100 (1999)

- 21. Zerr A et al. High Press. Res. 26 23 (2006)
- Kolesnikov A, Kutcherov V G, Goncharov A F Nature Geosci. 2 566 (2009)
- 23. Lobanov S S et al. Nature Commun. 4 2446 (2013)
- 24. Ree F H J. Chem. Phys. 70 974 (1979)
- 25. Hirai H et al. Phys. Earth Planet. Interiors 174 242 (2009)
- 26. Sokol A G et al. Diamond Related Mater. 10 2131 (2001)
- 27. Chanyshev A D et al. Cryst. Growth Des. 18 3016 (2018)
- 28. Kondrin M V et al. CrystEngComm 19 958 (2017)
- 29. Antonov V E et al. *Carbon* **100** 465 (2016)
- 30. Onodera A, Higashi K, Irie Y J. Mater. Sci. 23 422 (1988)
- Onodera A, Suito K, in Science and Technology of High Pressure. Proc. of the Intern. Conf. on High Pressure Sciene and Technology, AIRAPT-17, Honolulu, Hawaii, 25 – 30 July, 1999 (Eds M H Manghnani, W J Nellis, M F Nicol) (Hyderabad: Univ. Press, 2000)
- 32. Higashi K, Onodera A Physica B 139-140 813 (1986)
- 33. Sumiya H et al. J. Mater. Sci. 39 445 (2004)
- 34. Le Guillou C et al. Carbon 45 636 (2007)
- 35. Sumiya H, Harano K, Irifune T Rev. Sci. Instrum. 79 056102 (2008)
- 36. Shatskiy A et al. *Rev. Sci. Instrum.* **80** 023907 (2009)
- 37. Sumiya H et al. Diamond Related Mater. 70 7 (2016)
- 38. Iwasaki T et al. Phys. Rev. Lett. 119 253601 (2017)
- Ekimov E A, Lyapin S G, Kondrin M V Diamond Related Mater. 87 223 (2018)
- 40. Trusheim M E et al. Phys. Rev. B 99 075430 (2019)
- 41. Magyar A et al. Nature Commun. 5 3523 (2014)
- 42. Sedov V S et al. Diamond Related Mater. 72 47 (2017)
- 43. Ekimov E A et al. *Mater. Lett.* **193** 130 (2017)
- 44. Davydov V A et al. *JETP Lett.* **99** 585 (2014); *Pis'ma Zh. Eksp. Teor. Fiz.* **99** 673 (2014)
- 45. Ekimov E A et al. *JETP Lett.* **102** 701 (2015); *Pis'ma Zh. Eksp. Teor. Fiz.* **102** 811 (2015)
- 46. Ekimov E A et al. Phys. Rev. B 95 094113 (2017)
- 47. Ekimov E A et al. Phys. Rev. B 97 045206 (2018)
- 48. Ekimov E A et al. Adv. Mater. 27 5518 (2015)
- 49. Ekimov E et al. Phys. Status Solidi A 213 2582 (2016)
- 50. Ekimov E A et al. ChemNanoMat 4 269 (2018)
- Onodera A, Suito K, Morigami Y Proc. Jpn. Acad. B 68 167 (1992)
 Voronov O A, Bakhmanina A V Inorg. Mater. 33 375 (1997): Neorg.
- Voronov O A, Rakhmanina A V Inorg. Mater. 33 375 (1997); Neorg. Mater. 33 735 (1997)
- Voronov O A, Rakhmanina A V Inorg. Mater. 28 1113 (1992); Neorg. Mater. 28 1408 (1992)
- 54. Voronov O A et al. Dokl. Akad. Nauk SSSR 274 100 (1984)
- 55. Davydov V A et al. Carbon 42 261 (2004)
- 56. Davydov V A et al. Carbon 44 2015 (2006)
- 57. Pal'yanov Yu N et al. Nature 400 417 (1999)
- 58. Davydov V A et al. Carbon 90 231 (2015)
- 59. Bundy F P J. Chem. Phys. 38 631 (1963)
- 60. Sumiya H SEI Tech. Rev. (74) 15 (2012)
- 61. Kondrina K M et al. Diamond Related Mater. 83 190 (2018)