

Investigation of Various Carbon Modifications by Means of Raman Spectroscopy

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Abstract

The investigation of natural substances with a high carbon content (CS), as well as natural and synthetic crystal modifications of carbon including diamonds, graphites, fullerenes, has been carried out by means of Raman light scattering. It has been shown that the major constituent of CS is graphite with various ordering degree. Along with crystal graphite phase (sp^2 hybridization of carbon), ultrafine graphite is also present, as well as the amorphous phase with the elements of sp^2 hybridization of carbon. The possibility to use the parameters of Raman spectra of impact diamonds as a type-morphous index is demonstrated with the samples from Popigay and Karsk astroblemes as an example.

INTRODUCTION

The studies of natural modifications of carbon, including diamond, graphite, linear carbon polymorphs (carbines) and fullerenes that have been discovered recently in natural samples [1, 2], are of interest for the solution of a series of genetic problems, search tasks [3–6] and technologies. The interest to the studies of rocks with a high carbonization degree is connected both with the discovery of diamond crystals in these rocks and the determination of the conditions for mobilization, transport and re-deposition (in different forms) of primarily scattered magmatic carbon [5]. The present work deals with the studies of carbonaceous substances (CS) in carbon-containing rocks [4, 5, 7], impact diamonds formed as a result of impact metamorphism from graphite and carbon [3] and, for comparison, some synthetic crystalline modifications of carbon. Raman light scattering (RS) has been used as the instrument in this study. For complicated polycrystalline

natural samples, RS allows to obtain the data on the composition and defect content of the structures, on the presence of stresses and on the dimensions of particles [2, 8–10].

THE SUBJECT AND METHODS OF INVESTIGATION

The studied samples include carbonaceous material of ultrabasic rocks from ophiolitic complex within the East Sayan, extracted by fractioning of the insoluble organic substance [4] at the Geological Institute, SB RAS (samples I, II), impact diamonds formed from graphite as a result of impact metamorphism in the Popigay crater (Taimyr) and from carbon-containing substances *via* graphitization of the initial structure from the Karsk crater (the Polar Urals). We also studied the synthetic turbostratic graphite obtained from anthracite under *PT*-action under the conditions providing the synthesis of diamond crystals with the size of 50–100 Å (sample III), as well as C_{60} syn-

thesized at the Boreskov Institute of Catalysis, SB RAS.

X-ray analysis of the samples I and II of carbon-containing material of ultrabasic rocks revealed the presence of reflections characteristic of the crystal graphite structure. According to X-ray structural data, impact diamond samples were translucent polycrystalline aggregates of diamond grains with a low content of lonsdaylite.

For the synthetic graphite III, we observed the elements of structural ordering (Fig. 1). The image was taken with the help of electron microscope at the resolution of 1.4 Å with respect to lines. The sample was prepared by mechanical comminution and deposition of perforated carbon substrates fixed on standard copper grids.

Raman spectra were recorded with a Ramanor U1000 spectrometer. Excitation was 514.5 nm radiation of Ar⁺ laser. Recording was carried out in photon count regime in the geometry of 90° scattering. The sample orientation was arbitrary. The samples were used either without any special preparation or after pressing in KBr tablets in order to decrease heating. The weighed sample was 8 mg. In order to avoid nonuniform heating of nonhomogeneous polycrystalline samples, the exciting radiation ($W = 100$ mW) was focused by a cylindrical lens which allowed to project the exciting radiation as a spot 100 μm in diameter. The working width of the slit was up to 80 μm. This soft recording regime allows to analyse the scattering

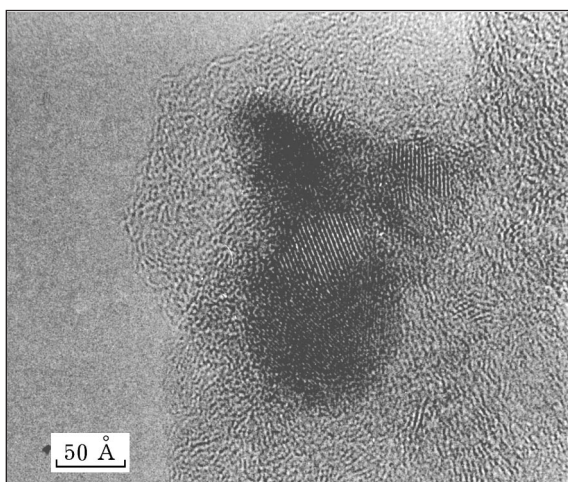


Fig. 1. High-resolution electron microscopic image of turbostratic graphite (JEM-2010, resolution 1.4 Å with respect to line).

from the sample region under investigation which was under quasiequilibrium conditions.

CHARACTERISTICS OF OPTICAL VIBRATIONAL SPECTRA OF CRYSTAL CARBON

Diamond is the major high-pressure carbon phase which belongs to the cubic syngony O_h^7 , $z = 2$ and exhibits RS-active triple-degenerated optical vibration F_{2g} (1332 cm^{-1}). No active phonone modes are observed in IR spectrum [8].

Graphite. Monocrystalline graphite belongs to the D_{6h}^4 , $z = 4$ space group (sp. gr.) and has 9 optical vibration modes with $k = 0$. Among them, two modes of B_{1g} symmetry are inactive and one is active in IR (A_{2u} , E_{1u}); two modes of the E_{2g} symmetry are active in RS ($1580, 42\text{ cm}^{-1}$) [9].

Fullerene. C_{60} is a closed polyhedron composed of carbon atoms. It is icosahedron of the I_h group with 60 equivalent three-bonded apexes. The sp. gr. is O_h^5 , $z = 4$. All the RS-active $2A_g + 8H_g$ and IR-active $4F_u$ vibrations are observed in vibration spectra [10]. The most intensive band is 1470 cm^{-1} [2, 10].

RESULTS AND DISCUSSION

RS spectra of the samples under investigation are shown in Figs. 2–5. A substantially broadened band of the main fundamental vibration of impact diamonds with the frequency $\nu \approx 1332\text{ cm}^{-1}$ is observed against the strong background of luminescence (see Figs. 2 and 3, b). The constituents of the overall spectrum originating from different physical phenomena differ in their parameters (half-width, line shape) which allows to separate the spectrum recorded experimentally into the Raman spectrum and luminescence spectrum [11].

The disintegration of the spectra of impact diamonds showed that the experimental contour is composed of three overlapping bands at the frequencies of 1324, 1329.5 and 1336 cm^{-1} (Karsk samples) and 1326, 1331, 1336 cm^{-1} (Popigay samples) (see Fig. 3, a).

The appearance of additional bands in the region of fundamental vibration can be explained by the presence of stress [8, 12] and dimensional effect [13, 14].

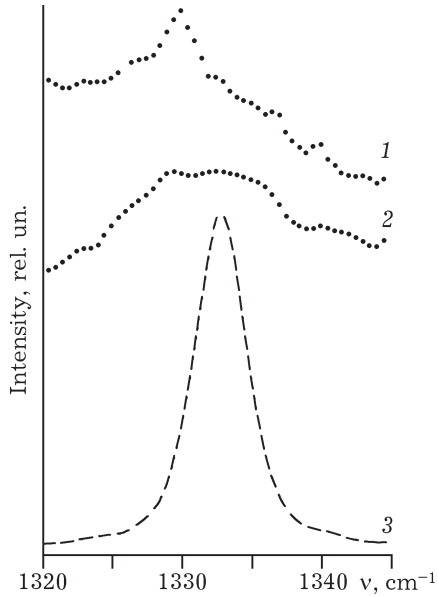


Fig. 2. Raman spectra of impact diamonds from the Karsk (1) and Popigay (2) astroblemes and monocrystalline kimberlite diamond (3).

There are three optical phonons with the symmetry F_{2g} (longitudinal LO and transverse TO_1 and TO_2 for monocrystalline diamond without stress. These phonons are degenerate and have one and the same frequency $\nu = 1332 \text{ cm}^{-1}$ corresponding to the centre of Brillouin zone ($k=0$) (see Fig. 2). Under pressure, the cubic symmetry of diamond decreases and the degeneration of the main fundamental vibration is drawn off. Depending on the kind of applied pressure (hydrostatic or single-axle) and its direction, a shift to shorter wavelengths can be observed together with the splitting of the main fundamental vibration of diamond. The relation between frequency shift and stress has been considered in a series of experimental and theoretical studies [8, 12].

The reason of the high-frequency splitting $\Delta\nu = 4 \text{ cm}^{-1}$ is most likely connected with the existence of residual stresses (deformations) induced by shock wave in the crystal grains of impact diamonds. It seems impossible to estimate the direction of deformations for the studied polycrystalline samples. However, a general estimate according to the equations $\delta\nu_{[100]} = 0.073 \text{ cm}^{-1}/\text{kbar}$ and $\delta\nu_{[111]} = 0.22 \text{ cm}^{-1}/\text{kbar}$ [8] gives the residual stress of 20–50 kbar for diamond. This value is not in contradiction with the conclusions of [3] concerning the Popigay and Karsk astroblemes.

Low-frequency shift can be explained on the basis of the theory involving the influence of the dimensional effect [13, 14]: Raman spectrum would be determined by optical phonons not only from the Brillouin zone centre ($k=0$) but also a substantial contribution would be made by the phonons with $k \neq 0$.

The shape of RS line of diamond was determined in [15] taking into account the dimensional effect.

Using theoretical dependencies of shift and broadening of RS bands on diamond crystallite size [15], it can be concluded that the samples under investigation contain diamond grains smaller than 50 \AA which is confirmed by the calculations made in [14]. Besides, the existence of nanostructures in these samples is confirmed by the observation of a band at 1150 cm^{-1} (see insertion in Fig. 3, b) which is attributed to the phonon of the edge of Brillouin zone [16].

The influence of dimensional effect is also the reason why additional bands appear in the region of fundamental vibration of graphite [9, 17]. Along with the basic band of crystal graphite at $\approx 1580 \text{ cm}^{-1}$ (G-band), Raman spectra of samples I, II, III (see Figs. 4 and 5) contain two

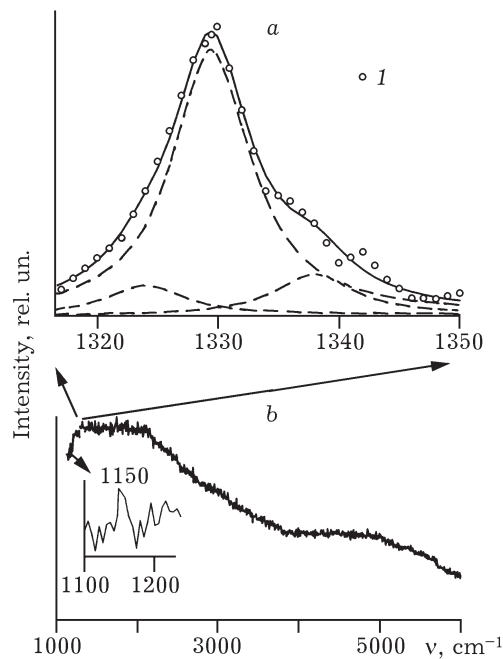


Fig. 3. Disintegration of the Raman spectrum of Karsk impact diamond (a) and Raman spectrum of the sample in the region of $1100\text{--}6000 \text{ cm}^{-1}$ (b): 1 – experimental spectrum composed of three overlapping bands with the frequencies of 1324 , 1329.5 and 1336 cm^{-1} (dashed curves); continuous curve – overall spectrum. Insertion shows the fragment of Raman spectrum in the region of $1100\text{--}1200 \text{ cm}^{-1}$.

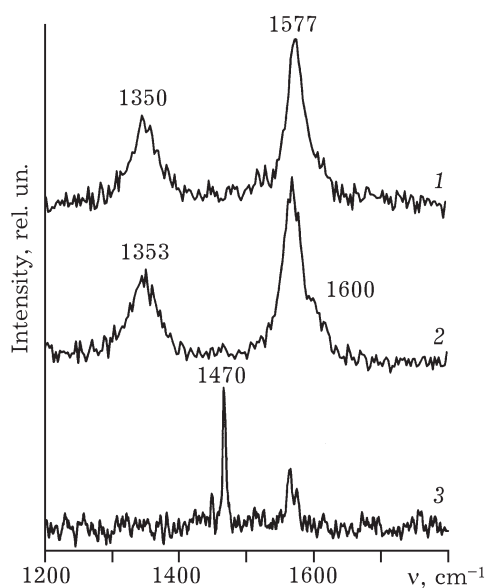


Fig. 4. Raman spectra of carbonaceous substances from ultrabasic rocks: 1 and 2 – samples I and II, respectively; 3 – fullerene.

additional bands at 1360 cm^{-1} (D -band) and 1600 cm^{-1} (D' -band). For sample II, a weak band at 1470 cm^{-1} is observed (see Fig. 4). Tuinstra and Koenig [17] attributed the band at 1360 cm^{-1} to the A_{1g} mode characteristic of microcrystal graphite.

The authors of [9] calculated the density of phonon states in graphite and tried to explain a series of additional bands in the region of fundamental vibrations on the basis of the violation of selection rules for small crystals. However, the positions of some bands observed experimentally do not coincide in all the cases with the calculated data on phonon density [9]. The reasons of experimentally stated sensitivi-

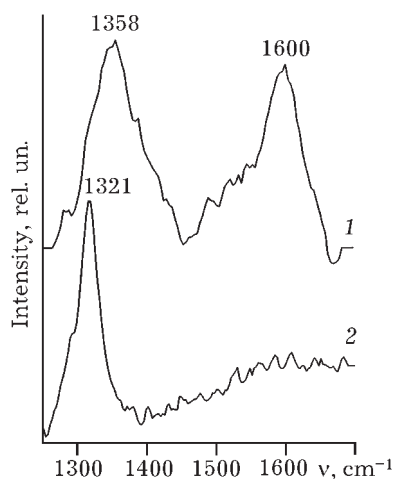


Fig. 5. Raman spectra of synthetic graphite III (1) and ultrafine diamond (2).

ty of additional bands at $1350\text{--}1360$ and $1600\text{--}1620\text{ cm}^{-1}$ to the defect content of graphite structure and dimensional effects are not quite clear yet. The bands at 1360 and 1620 cm^{-1} are observed not only for microcrystal graphite but also as surface modes when the violation of translation and local symmetry occurs [9].

The bands D , G and D' observed in the samples under investigation differ in position, intensity and half-width (see Figs. 4 and 5). Usually the degree of ordering in graphite is characterized by the ratio $R = J_{1360}/J_{1580}$. It has been demonstrated experimentally that this ratio decreases with increasing microcrystal order [18]. As Fig. 5 shows, the most disordered sample is turbostrate graphite obtained from anthracite ($R \geq 1$).

Substantial broadening and shift of the basic graphite band G to 1590 cm^{-1} can be caused by the presence of disordered structures between graphite layers, as well as by the presence of residual deformations of graphite layers themselves which accompanied the formation process [19]. A long-wave shoulder of the band at 1360 cm^{-1} is most likely connected with diamond nanostructures (see Fig. 5). Thus, ultrafine diamond obtained by detonation exhibits a clearly distinguished band of diamond nanostructures at 1321 cm^{-1} (sp^3 hybridization of carbon) and a broad halo with the maximum at 1600 cm^{-1} characteristic of the clusters with sp^2 hybridization [15]. It should be noted that substantial broadening of the main band at 1580 cm^{-1} ($\Delta\nu = 40\text{ cm}^{-1}$) occurs for samples I, II of CS (see Fig. 4). Since the procedure of pressing in KBr and the use of cylindrical lens at a minimum-powered excitation did not lead to strong heating of the samples, one can exclude such a large thermal broadening. One of the reasons of this broadening can be disordering in graphite layers due to the intrusion of the ions of different kinds between graphite layers [20].

A low-intensity band observed by us at 1470 cm^{-1} after excitation at 514.5 nm was not recorded earlier in graphite structures. The authors of [9] described the presence of a band at 1469 cm^{-1} during the excitation at 488 nm but it is still not clear yet how to attribute this band since it seems impossible to explain its appearance as an overtone or Raman band of the fun-

damental graphite frequencies. The presence of fullerene C_{60} ($\nu \cong 1470 \text{ cm}^{-1}$) in natural samples cannot be excluded (see Fig. 4) but this requires additional experiments aimed at the extraction and accumulation of CS from the ultrabasic rocks under investigation and their further fractioning [6, 21].

CONCLUSION

Thus, we have demonstrated that in natural CS from ultrabasic rocks there are, along with the crystal graphite phase (which is the major constituent) characterized by the frequency of 1580 cm^{-1} , also ultrafine phase and amorphous carbon ($1360, 1600 \text{ cm}^{-1}$). One of the reasons causing the broadening of the band at 1580 cm^{-1} can be the mechanism of disordering in graphite layers due to the intrusion of different kinds of ions between the layers. The possibility that fullerene can be discovered in one of the natural samples of CS is discussed.

A substantial broadening of the fundamental vibration in Raman spectrum of impact diamonds compared to the natural kimberlite diamond has been demonstrated. The observed triplet of the basic fundamental vibration in impact diamond is explained, first of all, by the removal of degeneration due to residual stresses (high-frequency splitting); second, by the presence of fine diamond grains with the size about 50 \AA which causes low-frequency shift explained in terms of the influence of dimensional effect on the phonon spectrum.

The data on structural ordering of different carbon modifications from macro- to nanoscale are important as an indicator of physicochemical conditions under which natural materials are formed.

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