Raman scattering in diamond microcrystals and their composites

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Abstract. In this paper, the features of the Raman spectra in diamond microcrystals were investigated. The Raman spectra in microdiamonds were characterized by high intensity due to the effects of trapped radiation and total internal reflection. A characteristic line with a frequency of 1332 cm⁻¹ and additional bands located in the overtone region of fundamental modes was registered in the observed spectra. Raman spectra in diamond-substances composites (diamond: K₂Cr₂O₇, NaBrO₃, NaNO₂, HgI₂, K₂CrO₄, PbO, KIO₃, sulfur, iodine, stilbene, triglyceride sulfate, and POPOP) were detected.

1. Introduction
Previous studies of Raman scattering spectra in diamond crystals have been conducted in many studies [1–8]. Investigations were carried out on natural [1–4] and synthetic [5–8] diamond samples. An important feature of the Raman spectrum in diamonds is that there is always only one basic mode with a frequency of 1332 cm⁻¹. This opens up the possibility of identifying diamonds from the Raman spectrum. As the intensity of the excitation radiation increases, additional satellites are detected in the Raman spectrum due to the manifestation of the two-phonon states [9,10]. Earlier, the Raman spectroscopy in diamonds of rather large sizes were mainly studied. Recently, high pressure and high temperature (HPHT) [11–13] technologies have been developed that allow synthesizing diamonds of various sizes ranging from a few nanometers to centimeters. Microdiamonds were synthesized as polyhedrons of various colors depending on the presence of impurities and defects in them. In particular, quite large colorless (“white” diamonds [14]), promising for the jewelry industry, were synthesized. Various methods for diamond plate growing have also been developed [15–17], such as chemical vapor deposition (CVD). In this work, we have studied the Raman spectra in microdiamonds of various sizes (0.1 μm–1.2 mm) and compared them with the Raman spectrum in CVD diamond plate. The objects of study were samples obtained by the HPHT method in which impurities were present and CVD diamond plate. In addition, studies were made of the Raman spectra in composites of chemical substances with diamond microparticles.

2. Experimental technique
Samples for research were monodisperse microdiamonds with particle sizes in the range from 0.1 μm to 1 mm. The investigated samples of small size (0.1–10 μm) had the appearance of an opaque brown-yellow powder. With the increase in size, microdiamonds became transparent and had the appearance of regular polyhedrons (see figure 1) of yellow color. Some samples were covered with graphite film (see figure 1). A colorless (“white”) diamond with a size of 1.2 mm was investigated. The Raman
spectrum in a diamond plate with a size of 3*3*1 mm was registered. The plate was obtained by CVD method. Composites were created as a result of introducing microdiamonds (250–300 µm) into a solution of inorganic (K₂Cr₂O₇, NaBrO₃, NaNO₂, HgI₂, K₂CrO₄, PbO, KI, O₃, sulfur, and iodine) and organic (stilbene, triglyceride sulfate and POPOP) compounds with further evaporation of the solvent.

Raman spectra were recorded by using of the experimental setup, which is described in detail in [18]. The excitation source was a laser with wavelength \( \lambda_0 = 785 \text{ nm} \) and power of 100 mW. Laser radiation was introduced into the fiber optic light guide terminated by a two-channel tip. Then this radiation was focused on the sample. A 180-degree scattering geometry was used, in which the Raman signal from the sample under investigation fell on the second channel of the tip. The scattered radiation passed through a refocusator containing a photonic crystal (or notch filter) selectively reflecting exciting and transmitting Raman signals.

Raman radiation was fed to the input of the compact Raman spectrometer BWS465-785H. The analysis of the Raman spectra in digital form was carried out with a computer. The spectral range for the Raman spectra recording was 50–2750 cm\(^{-1}\). The spectrometer resolution of the study area was 1 cm\(^{-1}\). The exposure time required to record the full Raman spectrum was 1–100 seconds.

3. Experimental results and discussion

Figure 2 shows the recorded Raman spectra in microdiamonds with different sizes (figure2 (a–c)), “yellow” diamond with a size of 1 mm (figure2(d)), “white” diamond with a size of 1,2 mm (figure2(e)) and CVD diamond plate (figure2(f)). The fundamental line of diamond crystal with frequency \( v=1332 \text{ cm}^{-1} \) was detected in Raman spectra of all the diamond samples. For diamonds with small sizes (d ~ 0.1 µm) an intense background was observed (see figure 2 (a)). In Raman spectra in diamonds with sizes 15–17µm, 250–300µm and 1mm (see figure 2 (b–d)), in addition to the intense diamond \( v=1332 \text{ cm}^{-1} \) line, there was also a band at \( v=2620 \text{ cm}^{-1} \). In the spectrum in “white” diamond, besides the main \( v=1332 \text{ cm}^{-1} \) line, there was an intensive band at 1407 cm\(^{-1}\). An intense background presented in the Raman spectrum in CVD diamond plate (see figure 2 (b)), the intensity of which was higher than fundamental 1332 cm\(^{-1}\) line.
Figure 2. Raman spectra in diamond crystals with various sizes: a—“yellow” diamond with a size of \( d = 0.1 \) µm, b—“yellow” diamond with a size of \( d = 15–17 \) µm, c—“yellow” diamond with a size of \( d = 250–300 \) µm, d—“yellow” diamond with a size of \( d = 1 \) mm, e—“white” diamond with a size of \( d = 1.2 \) mm, f—CVD diamond plate with a size of \( 3*3*1 \) mm.

In figures 3(a–l) the Raman spectra in several composites of organic or inorganic substances with microdiamonds 250–300 µm were present. At these spectra the fundamental diamond line 1332 cm\(^{-1}\) was always revealed. Besides, there were different lines, corresponding to Raman spectra in the substances, on the basis of which composites were created: \( \text{K}_2\text{Cr}_2\text{O}_7 \), \( \text{NaBrO}_3 \), \( \text{NaNO}_2 \), \( \text{HgI}_2 \), \( \text{K}_2\text{CrO}_4 \), \( \text{PbO} \), \( \text{KIO}_3 \), sulfur, iodine, stilbene, triglyceride sulfate, and POPOP.
Figure 3. Raman spectra in composites of chemical substances with 250–300 μm microdiamonds: a—K₂Cr₂O₇, b—NaBrO₃, c—NaNO₂, d—HgI₂; e—K₂CrO₄, f—PbO, g—KIO₃, h—sulfur, i—iodine, j—stilbene, k—triglyceride sulfate, l—POPOP.

Refractive index of diamond is high enough: 2.4–2.5 [19]. Accordingly, there was a high reflection of Raman scattering emission from the diamond surface inside the sample. Therefore, the intensity of Raman scattering signal enhanced, i.e. Raman opalescence was observed. As a result, we have recorded Raman spectra in diamond samples and CVD diamond plate at small exposure time (1–10 s). The presence of additional Raman bands at 1407 cm⁻¹ (see figure 2(e)) and at 2620 cm⁻¹ (figure 2 (b–d)) may be related to the second-order Raman scattering, induced by lattice defects. The molecules substances in the composite near the surface of diamond microcrystals were in an intensive field of exciting radiation. The capture of excitation radiation in microdiamond in the composites provides an increase of the Raman scattering spectrum intensity of the materials, based on which the composites were created (see figure 3(a–l)). Accordingly, microdiamond can play the role of amplifiers of Raman scattering spectra.

4. Conclusions
Therefore, the Raman spectra in diamonds with various structures and sizes and composite materials were recorded. Besides the fundamental line of diamond ν=1332 cm⁻¹, the Raman scattering spectra in some samples revealed additional bands at 1407 cm⁻¹ and at 2620 cm⁻¹. Due to the high refractive index of diamond and total internal reflection, the exciting and Raman scattering radiation in diamond microparticles in the composite was captured. This opens up the possibility to create amplifiers of the Raman scattering spectra in organic and inorganic substances by creating on their basis composites with microdiamonds.
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