Nature diamond luminescence induced by ultrashort UV-range laser pulses

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In this paper nature crystals of the pink and brown colored diamonds with the evident plastic deformations were comprehensively studied with IR-Fourier spectroscopy and photoluminescence methods. A- and B-centers presence were revealed by IR-Fourier specters. Femtosecond (250 fs) UV-range laser pulses with wavelength of 257, 320, 352 and 365 nm induced photoluminescence demonstrates N3 and H3 photoluminescence centers and broad structureless A-band luminescence. It was found that UV radiation with a wavelength of 257 and 320 nm does not cause A-band luminescence, which might be due to direct interband photoexcitation of diamond.

Keywords: femtosecond laser pulses, diamond luminescence, luminescence centers, ultraviolet laser radiation.

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Introduction

Diamonds are of special interest to industry and science because they have several unique optical and mechanical properties. In order to understand the correlation between optical properties and any defects, it is necessary to diagnose the diamond. IR Fourier spectroscopy method [1] is used for initial defect detection in order to get the information about the presence and concentration of A, B and C defects [2,3]. Defect C is a single donor nitrogen atom that has replaced carbon in the diamond crystal lattice. The most typical absorption bands of C defect are 1344, 1100, and $1130 \, cm^{-1}$ [2]. A defect is a dipole N-N molecule in the diamond carbon lattice whose presence is defined by the presence of absorption peaks with wavenumbers 1282, 1215, 1100 and $484 \, cm^{-1}$ [2]. B defect produced by four nitrogen atoms and one vacancy appears in IR absorption spectra in the form of bands with wave numbers 1332, 1175, 1100, 1010, $780 \, cm^{-1}$ [4,5].

Despite all efficiency of IR spectroscopy, there are defects which cannot be detected by this method. To detect them, it is necessary to use other methods, which one is diamond photoluminescence excitation, in particular, by UV radiation. It has high photon energy and is able to initiate luminescence of centers that do not appear in IR absorption spectra. Another argument for the use of UV radiation is generally higher absorption by a substance in this range because the photon energy is close to the lattice atom bond energy (for diamond $\sim 5.5 \, eV$[1]). Unfortunately, this problem is not sufficiently addressed in the modern literature. For example, in [6] it is also pointed out that there is limited understanding of the diamond defect response under UV radiation exposure where red region photoluminescence is focused, however, regions with photoluminescence of other optical centers are not addressed at all — N3, H4.

Diamond photoluminescence mechanisms under UV exposure are underexplored. Attempts to explain the nature of A band luminescence contradict each other or cover only individual cases. In [7], A band photoluminescence is explained by electron-hole recombination, and in [8], it is said that the recombination is performed through boron and nitrogen doping. For more details of this problem, see [9–11]. Generally for photoluminescence analysis, pumping wavelength $\sim 405 \, nm$ is used, and when wavelengths close to absorption edge ($\sim 5.5 \, eV$) are used, UV lamps or X-ray sources that do not have monochromaticity of laser emission are suitable.

Experiments for investigation of diamond luminescence spectra induced by 257, 320, 352 and 365 nm femtosecond laser radiation have been performed herein. The benefit of this study is that 257 nm and 320 nm wavelengths close to absorption edge were used compared with softer 352 nm and 365 nm UV light in unchanged pumping conditions.

Experimental setup description

Figure 1 shows the experiment setup. Diamond was excited by „TETA-20" laser with the following specifications: pulse length 250 fs, wavelength 1030 nm, pulse repetition

Table 1. Nitrogen defect concentrations in specimens № 1−3

Diamond	Infrared spectroscopy data							
	Total nitrogen, ppm	Nitrogen A, ppm	Nitrogen B1, ppm	%B	Nitrogen B2, cm^{-1}	Position B2, cm^{-1}	Nitrogen C, cm^{-1}	CH, cm^{-1}
Specimen № 1 (IaAB)	1563	653	910	58.2	−	−	0	8
Specimen № 2 (IaA)	44	44	0	0	−	−	0	1
Specimen № 3 (IaAB)	276	106	170	61.6	2.134	1365	0	0
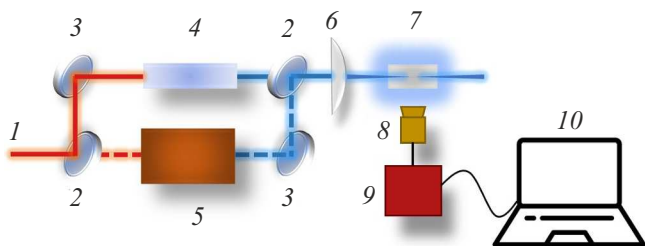
Figure 1. Experimental setup. *1* — „TETA-20" laser radiation, *2* — folding mirrors, *3* — metal mirrors, *4* — nonlinear KDP crystal, *5* — PARUS-NE-515-HP parametric amplifier and PARUS-SH frequency doubler, *6* — KU-1 collecting lens, *7* — diamond specimen, *8* — lens, *9* — Avesta ASP-150 spectrometer, *10* — PC.

rate 10 kHz, emission power max. 10 W. PARUS-NE-515-HP parametric amplifier with frequency doubler is used for pumping irradiation wavelength tuning within a wide range 320−2600 nm with vertical exit polarization. For fourth harmonic generation (257 nm), a nonlinear KDP crystal was used.

„TETA-20"laser radiation directed by folding mirrors into the parametric amplifier or nonlinear crystal was focused using a quartz lens (KU-1 $f = 95$ mm) into a specimen (spot size $\sim 50 \mu$m) to excite photoluminescence (PL) recorded by NA = 0.1, 10×, LOMO UV lens placed perpendicular to laser radiation and Avesta ASP-150 spectrometer. PC is used for further spectrum recording and processing. Preliminary analysis of the specimen impurity composition was carried out using Vertex V70 (Bruker) IR Fourier spectrometer. Three specimens were used in the experiment: two pink specimens (№ 1, № 2) and one brown specimen (№ 3) (Figure 2).

Specimen № 1 — 0.07 ct (14 mg), pink crystal, has one polished surface. Specimen № 2 — 0.08 ct (16 mg), pink-violet dodecahedral habit crystal with pronounced face relief due to sharp shifts over the plastic deformation plane, microrelief from deformation plane intersection in two directions on steps creates matting that scatters light. Surface separate lines bordering the whole crystal are noted. Specimen № 3 — 0.10 ct (20 mg), octahedral habit with flat faces, has single slip lines on the surface and strongly pronounced brown color. For preliminary characterization of specimens and analysis of their impurity composition,

IR Fourier spectroscopy method was used as shown in Figure 3. IR absorption spectra analysis allows to define the main types of diamond defects. Curves in Figure 3 show typical bands of A centers (1282 cm^{-1}) and B centers (1175 cm^{-1}) whose concentrations are calculated using equations given in [3], and are listed in Table 1.

Experimental results

Photoluminescence spectra (Figure 4) were recorded herein for specimens № 1−3 exposed to 257, 320, 352 and 365 nm 250 fs UV laser radiation. In all specimens, green luminescence of diamond in the form of a wide unstructured 475−570 nm band is observed. In specimens № 1 and № 2, bright luminescence of A band with maximum ~ 430 nm appears[12]. Specimen № 3 demonstrates highly bright N3 center with phonon repetitions [12]. The nature of A band has not been finally established by now. On the one hand, A band glow may be attributed to „vacancy-interstice" type defect generation under strong laser exposure [9,11]. On the other hand, A band luminescence correlates with the presence of plastic deformations in diamond crystals [12]. In our case, due to clearly pronounced shear deformations in specimens № 1−3 and moderate laser exposure, the second version is more probable. It should be also noted that near the absorption edge (pumping 257 nm and 320 nm), A band glow disappears (Figure 4). In this case photoluminescence of optical centers is preserved and may be used for more accurate detection of impurities in cases when A band luminescence hinders their detection.

In all specimens and at all used pumping wavelengths, other wide photoluminescence band with peak $\sim 520−540$ nm is observed. Acording to [3,12], B2 defect may be the source of this band. However, based on the obtained IR spectroscopy data (Table 1), B2 defect is onlypresent in specimen № 3, while bands 475−570 nm are observed in all diamonds. Therefore, photoluminescence in the yellow-green spectrum region cannot be attributed to B2 centers only. On the other hand, this wide luminescence band (475-570 nm) is probably defined by the presence of luminescence center H3 (zero-phonon line, ZPL, 503.2 nm), which is observed in photoluminescence spectra (Figure 5) with scale increase by spectrum.

**Table 2.** Observed spectral features of specimen luminescence № 1−3 [12]

Diamond	photoluminescence data			
	$\lambda = 257$ nm	$\lambda = 320$ nm	$\lambda = 352$ nm	$\lambda = 365$ nm
Sample № 1 (IaAB)	N3 (415 nm), H3 (503.2 nm)	N3 (415 nm), H3 (503.2 nm)	N3 (415 nm)	N3 (415 nm)
Sample № 2 (IaA)	—	—	A-band (~ 430 nm)	A-band (~ 430 nm)
Sample № 3 (IaAB)	N3 (415 nm), H3 (503.2 nm)	N3 (415 nm), H3 (503.2 nm)	N3 (415 nm), H3 (503.2 nm)	N3 (415 nm), H3 (503.2 nm)

Figure 2. Specimen photos. *a* — specimen № 1, pink, one polished surface, 14 mg; *b* — sample № 2, pink, dodecahedral habit, 16 mg; *c* — specimen № 3, brown, 20 mg, octahedral habit.
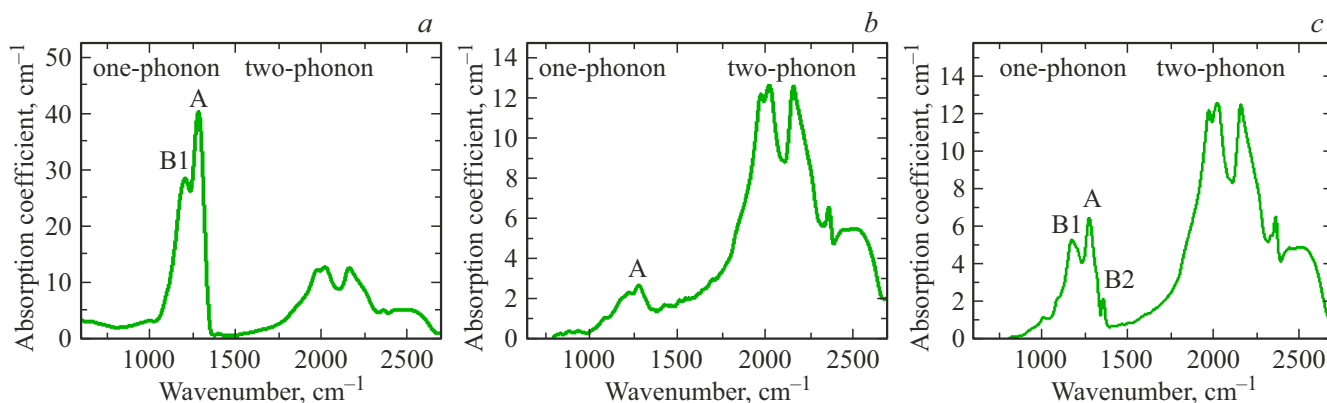
**Figure 3.** Infrared absorption spectra of diamonds (*a*) № 1, (*b*) № 2, (*c*) № 3.

Spectrum interpretation shown in Figure 4, *b* is complicated by irregular nonuniform shape of the specimen that scatters both pumping radiation and recorded spectral signal. A wide photoluminescence region with peak ~ 430 nm may correspond both to A band and to N3 center luminescence. However, in this case, ZPL (415 nm) with typical phonon repetitions shall be clearly present in the spectrum, which is not observed in Figure 4, *b*. Therefore, for unambiguous interpretation of blue photoluminescence band origin in specimen № 2, additional investigations after crystal polishing and grinding are required. All spectral features and luminescence centers observed in specimens № 1−3 are recorded in Table 2.

Thus, experimental results shown herein indicate some difference in photoluminescent response of pink (№ 1 and 2) and brown (№ 3) diamonds. Specimen № 3 (type IaAB, brown) in the photoluminescence spectrum has more pronounced center N3 compared with pink specimen № 1 of the same type, which may be due to its color. According to sources [13,14], high concentration of nitrogen defects such as N3 and H3 in specimens and the presence of plastic deformations influence the appearance of pink or brown color, which is supported by our experiments.

Remarkable is that N3 centers more often appear with photoluminescence in specimens containing B centers [15]. This statement agrees with the experiments where we observe N3 center in specimens № 1 and № 3 belonging
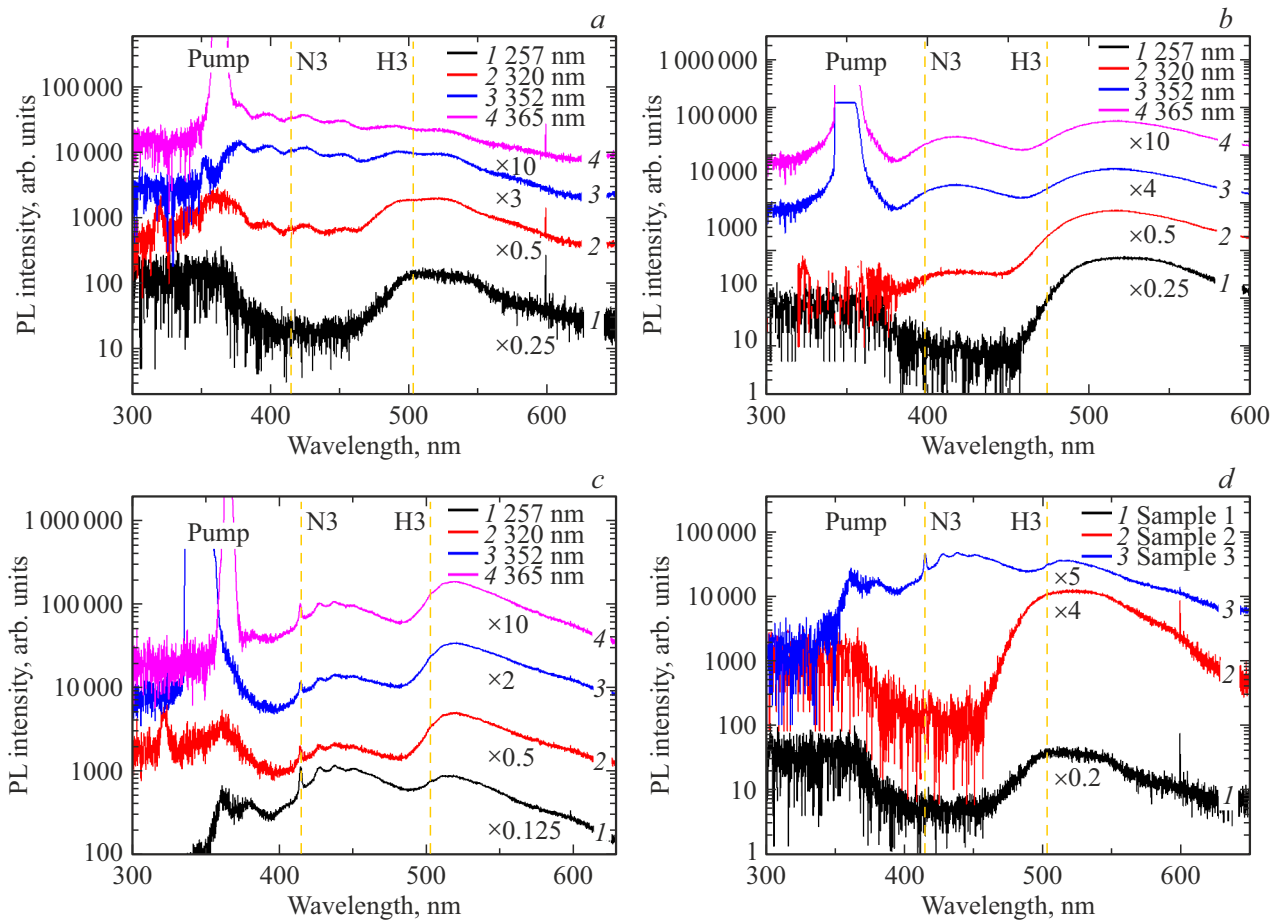
Figure 4. Luminescence spectra of specimens № 1 (*a*), № 2 (*b*) and № 3 (*c*) excited by laser pulses (Pump) with repetition rate 10 kHz, length 250 fs and wavelengths 257, 320, 352 and 365 nm. Dashed lines designate zero-phonon line (ZPL) N3 (415 nm) and H3 (503.2 nm). Comparison of diamond photoluminescence spectra № 1, № 2 and № 3 when pumped with 257 nm (*d*). For simplicity, the data is multiplied by the factors shown in the figures.
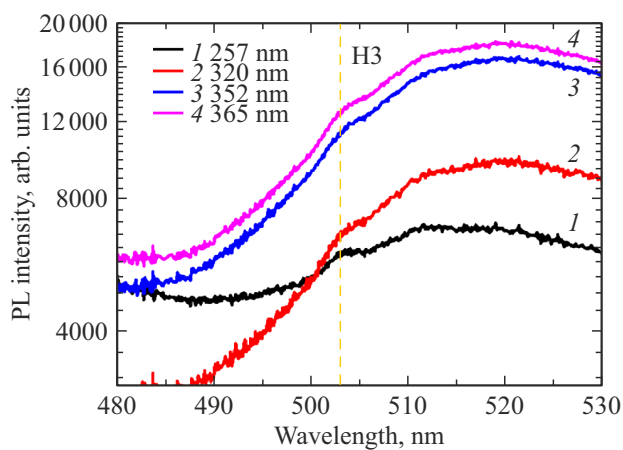
Figure 5. Photoluminescence region of center H3 with ZPL 503.2 nm in 480−530 nm with laset UV excitation of specimen № 3 with pumping wavelengths 257, 320, 352 and 365 nm.

to type IaAB, while in specimen № 2 (type IaA), N3 does not appear.

Conclusion

This study is focused on photoluminescence of IaA and IaAB type pink and brown natural diamonds pumped by UV ultrashort laser pulses. The photoluminescence spectra in all specimens demonstrate wide band $\sim 475-570$ nm associated with luminescence center H3 (ZPL 503.2 nm). Exposure of specimens № 1 and № 2 (pink) to femtosecond UV laser pulses also causes A band glow (~ 430 nm) associated with plastic deformations. Specimen № 3 in similar conditions shows high concentration of centers N3 in the form of photoluminescence with ZPL 415 nm. It is also demonstrated that 257 nm and 320 nm UV laser radiation may initiate luminescence of diamond luminescence centers without excitation of A band.

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Conflict of interest

The authors declare that they have no conflict of interest.

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