

Diamond & Related Materials

Spectroscopic Characterization of Yellow Gem-Quality CVD Diamond

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Abstract:	<p>CVD (chemical vapor deposition) diamond in the gem market today is dominated by colorless and pink material. However yellow CVD material is also found and it is concluded that all the yellow CVD diamonds found in the gem market have been post growth HPHT (high pressure high temperature) processed. This study shows that HPHT and LPHT (low pressure high temperature) treatments are essential for removal of the brown and gray color associated with as grown CVD material. The distinguishing temperatures and conditions of these treatments can be determined from the spectroscopic study of vacancy-related optical centers.</p> <p>CVD (chemical vapor deposition) diamond in the gem market today is dominated by colorless and pink material. However yellow CVD material is also found and it is concluded that all the yellow CVD diamonds found in the gem market have been post growth HPHT (high pressure high temperature) processed. This study shows that HPHT and LPHT (low pressure high temperature) treatments are essential for removal of the brown and gray color associated with as grown CVD material. The distinguishing temperatures and conditions of these treatments can be determined from the spectroscopic study of vacancy-related optical centers.</p>

Spectroscopic Characterization of Yellow Gem Quality CVD Diamond

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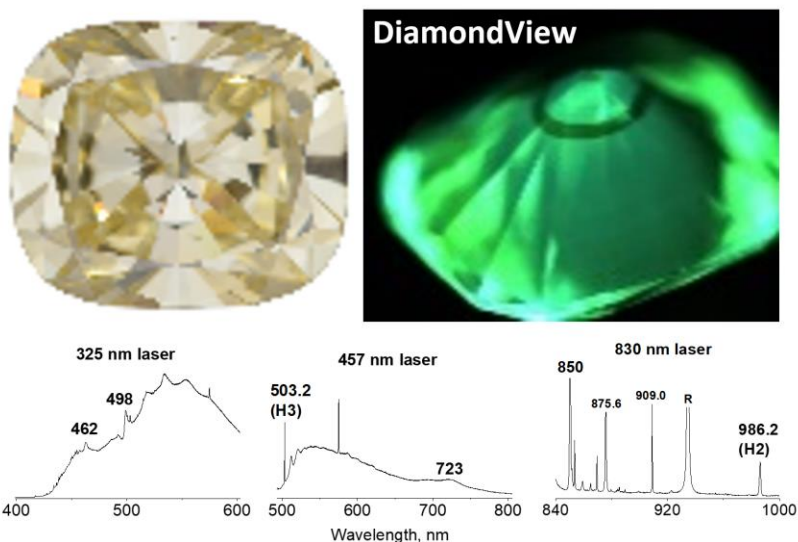
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Intense yellow CVD diamond and its photoluminescence



Highlights

1. Gem quality CVD diamonds of intense yellow color are nitrogen doped and in most cases HPHT-treated.
2. HPHT-treated nitrogen-doped CVD diamonds show higher efficiency of formation of NVN defects detected as H3 and H2 centers as compared with LPHT-treated ones.
3. The dominating optical centers in photoluminescence of yellow CVD diamonds are the 462 nm and 498 nm centers excited with 325 nm laser, the 503.2 nm (H3) center excited with 457 nm laser and the 850 nm and 986.2 nm (H2) centers excited with 830 nm laser.

1. Introduction

Vast majority of CVD-grown diamonds on the diamond jewelry market are colorless or near colorless. Colored CVD-grown diamonds comprise only a small portion, of these CVD diamonds with dominating pink color are the most common. Yellow gem quality CVD diamonds are rare and can rival the color of natural cape yellow diamonds. The production of colorless and near colorless CVD diamonds requires maintaining perfect growth conditions in a relatively impurity-free environment minimizing the concentration of impurities and structural defects which may affect the diamond color. The production of colored CVD diamonds involves intentional impurity doping during growth and post-growth treatments (irradiation, high temperature annealing or combinations thereof). For yellow color doping with nitrogen is used. The problem with the growth of nitrogen-doped CVD diamonds is the formation of an intense brown color which, if not removed, can substantially deteriorate the anticipated yellow color. The defects responsible for the brown color are vacancy nanoclusters [1 - 5]. Vacancy nanoclusters vary in size and shape and may comprise tens of vacancies in one cluster [6]. Vacancy nanoclusters have no definite atomic structure. Hence, the electrons located in vacancy nanoclusters may have many energy levels in a broad range. The optical transitions between these levels are detected as complex multiline, broad-band and continuum-like features in absorption and luminescence spectra. Vacancy nanoclusters are common defects in natural brown diamonds too.

In CVD diamonds, optically active vacancy nanoclusters are not very temperature stable. High temperature annealing at temperatures over 1600°C destroys them. It was assumed that at high temperatures small-size vacancy nanoclusters aggregate into larger ones [7]. This transformation results in the loss of brown color. Similar experiments have been performed in [8]. Vacancy nanoclusters can also dissolve into point defects with definite atomic and electronic structure. As a result, the broad-band spectroscopic features disappear and numerous optical centers with well-structured electron-phonon spectra appear. High temperature treatment, which can be performed in vacuum or inert gas (low pressure high temperature treatment, LPHT), or at high pressure (high pressure high temperature treatment, HPHT), is an essential step in production of colorless and fancy color CVD diamonds.

High temperature treatment, especially HPHT treatment, is of particular importance in the production of yellow CVD diamonds. The defects responsible for the yellow color are single nitrogen atoms in neutral charge state occupying substitutional positions (C-defects) [9]. C-defects absorb blue and green light with a threshold at wavelengths 500-560 nm. It is the same absorption which also makes natural type Ib diamonds yellow or even yellow-orange if the C-defect concentration is high. If C-defect loses one electron, it becomes positively ionized and form N^+ -defect.

During growth of CVD diamond most of nitrogen is captured presumably in association with vacancy nanoclusters and carbon nano-inclusions [5]. A fraction of nitrogen enters the growing crystal in form of dispersed atoms. These nitrogen atoms interact with vacancy nanoclusters and part of them become positively ionized N^+ -defects. The concentration of neutral C-defects remains low, and their weak "yellow" absorption is practically invisible on the strong background of the brown absorption continuum of vacancy clusters. HPHT treatment destroys vacancy nanoclusters, eliminates the brown absorption, and releases nitrogen from vacancy and carbon nanoclusters. As a result, the concentration of C-defects increases, and the diamonds acquire distinctive yellow color.

Commercially gem quality CVD diamonds are produced by the growth on (100)-oriented diamond seeds. This crystallographic orientation favors the growth of large perfect diamond crystal, but it does not favor the capture of impurity atoms. Thus, the nitrogen concentration in most commercial nitrogen-doped CVD diamonds is low (a few ppm) and their yellow color is relatively light. However, CVD diamond with unusually high concentration of C-defects can be encountered with. A small diamond of this sort was

reported in [10]. It was found that the diamond had intense yellow color and the concentration of C-defects in it was about 175 ppm. It is remarkable that the diamond was identified as non-treated [10].


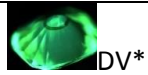



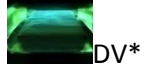





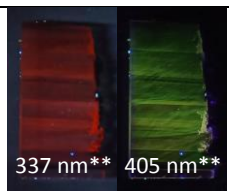
The reports on yellow CVD diamonds and their characterization are few [10 - 13]. To give more insight into the nature of these diamonds we have performed comparative studies of commercial yellow CVD diamonds and nitrogen-doped diamonds grown in GIA CVD Diamond Lab. We discuss spectroscopic features which are characteristic and unique for yellow nitrogen-doped CVD diamonds. We have found that these features undergo changes during high temperature annealing and as such can be used for identification of as-grown, LPHT-treated, and HPHT-treated CVD diamonds.


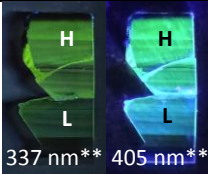

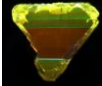

2. Materials and Methods

2.1. Samples

Four commercial faceted yellow diamonds, one commercial yellow rough, and five samples grown in GIA CVD lab have been studied in detail (Table 1). Many more nitrogen-doped CVD diamonds grown in GIA CVD lab and acquired from commercial producers were used for comparative studies.

Table 1.

Sample	Image	Fluorescence	Color	Treatment	Source
#356580			Fancy Yellow	HPHT	Commercial
#857801			Yellow**	HPHT	Commercial
#857802			Yellow**	HPHT	Commercial
#857804			Yellow**	HPHT	Commercial
#5254			Yellow**	HPHT	Commercial
#4035b			As-grown brown; near-colorless after LPHT.	LPHT in vacuum	GIA
#5293-4			Layers: light brown, grayish brown	As grown	GIA

#5293-5			Layers: gray, colorless, very light yellow	HPHT	GIA
#3975-2			Layers: near colorless to gray	LPHT in vacuum	GIA
#3975-2			As-grown brown. Near colorless after LPHT	As grown; LPHT in vacuum	Commercial

* DiamondView™ image; ** Illumination wavelength.

** Color grade not assigned

2.2. Measurements

Fluorescence images were taken with the Diamond Trading Company (DTC) DiamondView™ microscope with deep ultraviolet (wavelength <math><230\text{ nm}</math>) excitation. Photos of samples #5293-4 and #5293-5 were taken under illumination with nitrogen laser (wavelength 337 nm) and 405 nm LED.

Infrared absorption spectra were collected at room-temperature over the 400 - 6000 cm^{-1} spectral range at a resolution of 1 cm^{-1} using Thermo Fisher Scientific Nicolet™ iS50 FTIR spectrometer equipped with KBr and quartz beam splitters and a DRIFT (diffuse-reflectance infrared Fourier transform) unit.

UV-Vis absorption spectra were collected at room temperature with samples cooled to liquid nitrogen temperature using a liquid nitrogen bath. GIA built spectrometer with Avantes AvaLight-HAL-S-mini2 light source, AvaSphere-50 integrating sphere and Ocean Optics HR4000 high resolution spectrometer (spectral range from 200 to 1000 nm with a spectral resolution of 2 nm) was used.

Photoluminescence (PL) was measured at liquid nitrogen temperature using Renishaw InVia Microspectrometer™ equipped with 830nm, 633 nm, 514 nm, and 457 nm solid state lasers and 325 nm He-Cd metal vapor laser. Measurements were performed with a standard non-confocal 5x objective for 830nm, 633 nm, 514 nm, and 457 nm lasers while for 325 nm laser a 15x non-confocal objective was used. Spectral ranges were out to 850 nm (1800 mm^{-1} grating) for 457, 514, 633 and 850 nm lasers and out to 1000 nm (2400 mm^{-1} grating) for 830 nm laser.

2.3. High temperature treatment

Several samples grown in GIA CVD lab were annealed in LPHT regime at different temperatures in vacuum of $1\text{e-}4$ mbar. A modified version of commercial furnace LPHT-20 (<https://high-technologies.com/index.html>) was used for the treatment. One of the samples (#4035b) was annealed isochronously at temperatures from 1200°C to 1900°C with 100°C increments for 10 minutes at each temperature. The final annealing at temperature 2000°C was performed for 5 minutes. Fig. 1 shows the change in color of sample #4035b with annealing.

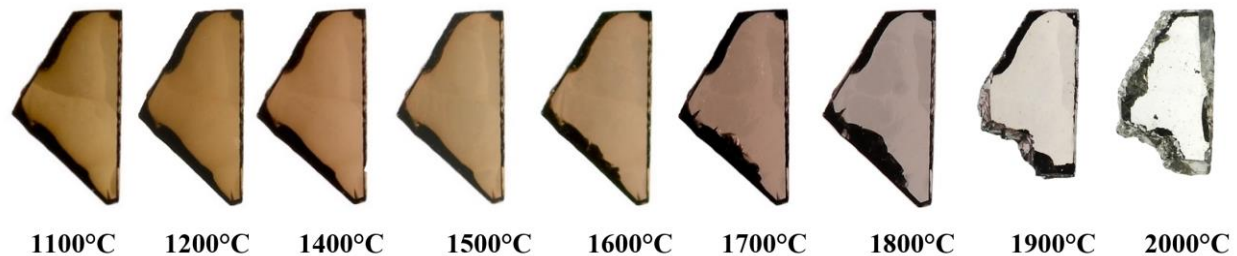


Fig. 1. Change in visual appearance of sample #4035b with isochronous LPHT annealing. Substantial color change occurs after annealing at 1700°C. The loss of brown color occurs after annealing at temperatures over 1800°C.

Sample #5293-5 was subjected to HPHT annealing at a temperature of 1870°C under pressure 55 kbar for 4 hours using high pressure apparatus BARS-20.

3. Results and discussion

The analysis of visual and spectroscopic features of commercial cut yellow CVD diamonds was performed in comparison with nitrogen-doped CVD diamonds subjected to LPHT and HPHT treatments. They all showed qualitatively similar results. Through the analysis, we have established that all commercial faceted yellow diamonds in this study were HPHT-treated. They all revealed similar color appearance and spectroscopic characteristics. Henceforth the samples will be referred to as "as-grown", "LPHT-treated", and "HPHT-treated" without indication of their identifying number.

3.1. Fluorescence color

All commercial yellow CVD diamonds produce intense green fluorescence when excited by UV light (Table 1). This fluorescence is the result of intense emission of H3 center and a broad complex band with maximum at a wavelength of 445 nm (Fig. 2, trace 3). Both features dominate in HPHT-treated CVD diamonds with elevated nitrogen concentration. If the nitrogen concentration is low, the fluorescence of H3 center is weaker and the blue color fluorescence of the 445 nm band dominates (Fig. 2, trace 2; fluorescence images of sample #5293-5 in Table 1, L and H mark the areas with low and elevated nitrogen doping). The nature of the 445 nm band is not known. We preliminary ascribe it to some defects remaining after annealing of the vacancy nanoclusters responsible for brown color (details will be published elsewhere).

As-grown brownish nitrogen-doped samples show red fluorescence in DiamondView™ microscope under short wavelength UV illumination. This luminescence color is the result of emission of NV⁰ center. If illuminated with long-wave UV light, e.g. 405 nm LED, the luminescence is green (sample #5293-4 in Table 1) due to dominating emission of 468 nm center (Fig. 2, trace 1). This difference in the fluorescence color excited by short- and long-wave UV excitations remains after LPHT treatment (sample #3975-2). After HPHT treatment, intensity of the NV⁰ center is strongly reduced and the luminescence is dominated by H3 center and/or 445 nm band. The shades of green colors produced by 468 nm center and H3 center are different and can be distinguished visually.

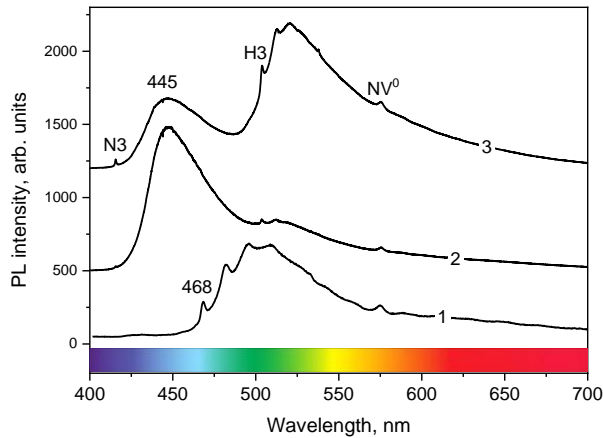


Fig. 2. Luminescence spectra taken at room temperature from nitrogen-doped CVD diamonds under long wavelength UV excitation: (1) as-grown, C-defect concentration is about 8 ppm; (2) after HPHT annealing, low nitrogen concentration (2 ppm of C-defects); (3) after HPHT annealing, high nitrogen concentration (8 ppm of C-defects).

3.2. Absorption

3.2.1. IR absorption

FTIR spectra in the spectral range $1260 - 1460 \text{ cm}^{-1}$ reveal the presence of nitrogen-related lines in all studied samples (Fig. 3a). These lines were reported previously in spectra of colorless and pink CVD diamonds [13 - 15]. Among them the C-center and N^+ -center are clearly seen as the lines at 1344 cm^{-1} and 1332 cm^{-1} respectively [16, 17]. The concentration of C-defects in all studied samples ranges from 1 to 3 ppm. The concentration of N^+ -defects vary from 0.2 to 0.5 ppm.

No obvious presence of the features of A- and B-defects has been found. A broad band with maximum at a wavenumber of 1295 cm^{-1} and a narrow line at 1341 cm^{-1} are present in spectra of all commercial yellow and high-temperature treated samples [18]. Intensities of the 1295 cm^{-1} band and 1341 cm^{-1} line correlate. These features are not detected in as-grown samples [19]. Heating at a temperature as low as 1200°C may generate both centers. After annealing at higher temperatures, the intensity of the 1295 cm^{-1} band and the 1341 cm^{-1} line noticeably increases (Fig. 3b). Both features are more pronounced in HPHT-treated diamonds compared with LPHT-treated ones. Tentatively, the 1295 cm^{-1} band and 1341 cm^{-1} line are ascribed to nitrogen A-aggregates decorated by hydrogen [12].

It is noteworthy that the intensity ratios of the lines 1332 , 1344 and 1341 cm^{-1} are different for HPHT- and LPHT-treated samples. In HPHT-treated samples $I_{1344}/I_{1341} \sim 1$ and $I_{1344}/I_{1332} \sim 1$, whereas $I_{1344}/I_{1341} < 1$ and $I_{1344}/I_{1332} < 1$ in LPHT-treated ones.

LPHT annealing does not change noticeably the concentration of neutral C-defects. In contrast, the concentration of the positively charged N^+ -defects reduces with LPHT annealing as temperature increases (Fig. 3a). An opposite behavior is observed in commercial yellow CVD diamonds, which were identified as HPHT-treated. A relatively high intensity of the 1344 cm^{-1} line in these diamonds suggests that HPHT treatment does favor the formation of C-defects in nitrogen-doped CVD diamonds. This conclusion may seem to contradict the well-known fact that HPHT annealing leads to aggregation of C-defects into A-, B- and N3 complexes. A possible resolution of this contradiction and an explanation of the increase of C-

defect concentration in HPHT-treated CVD diamonds could be as follows. The vacancy clusters formed in CVD diamonds are acceptor-like defects and, when in high concentration, convert most of C-defects into N^+ -defects. Thus, the nitrogen-doped brown CVD diamonds reveal in IR absorption spectra strong 1332 cm^{-1} line but weak 1344 cm^{-1} line. HPHT annealing is more efficient in destruction of vacancy nanoclusters than LPHT annealing and hence in conversion of N^+ -defects back to C-defects. HPHT annealing is also expected to be more efficient than LPHT annealing in dissolution of optically non-active nitrogen complexes into dispersed nitrogen atoms. These two processes may occur faster than the nitrogen aggregation. As a result, an unproportionally high increase in the C-defect concentration occurs. This difference between LPHT and HPHT treatments could explain the observation that nitrogen-doped CVD diamonds acquire yellow color after HPHT treatment, but they become colorless or near colorless after LPHT treatment (Fig. 1).

The 1332 cm^{-1} line has relatively strong intensity in spectra of as-grown, LPHT-annealed and yellow HPHT-annealed samples. Thus, CVD diamonds retain a high percentage of single nitrogen defects in ionized form irrespective of the conditions of post-growth treatment. This suggests that CVD diamonds contain very stable acceptor-like defects compensating nitrogen donors. Dislocations could be these defects. Dislocations are abundant in regular CVD diamonds, and they behave as acceptors [20].

Other characteristic features of treated CVD diamonds are 1454 , 1405 , 1396 , 1371 , 1362 and 1353 cm^{-1} lines (Fig. 3a). Some of these lines are also observed in spectra of natural diamonds [19]. The 1353 , 1362 , 1371 and 1454 cm^{-1} lines reduce their intensity and may eventually disappear after LPHT annealing (Fig. 3b). The line at 1396 cm^{-1} is stimulated by annealing. Interestingly the line at 1454 cm^{-1} is present and the line 1396 cm^{-1} is absent from spectra of HPHT-treated yellow samples.

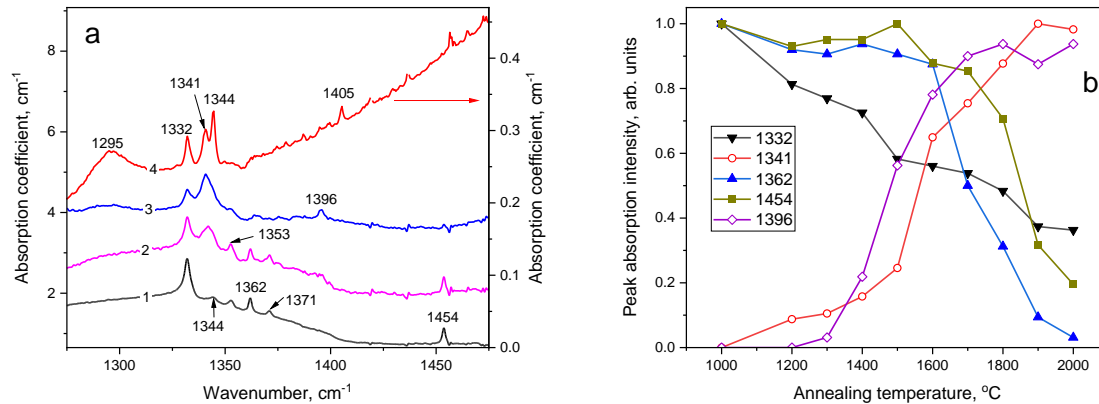


Fig. 3. (a) Representative FTIR absorption spectra in one-phonon spectral range obtained on nitrogen-doped CVD diamond subjected to high temperature annealing: 1 - as-grown, 2- LPHT-treated at temperature 1500°C ; 3 - LPHT-treated at temperature 2000°C ; 4 - after commercial HPHT treatment (plotted against right vertical axis). (b) LPHT annealing curves for the most characteristic lines. (The spectra are shifted vertically for clarity).

Absorption lines observed in the spectral range from 2700 to 3200 cm^{-1} are commonly ascribed to hydrogen-related defects [21, 22] (Fig. 4a). These features also reveal differences when measured in as-grown, LPHT-treated, and yellow HPHT-treated CVD diamonds. It was shown that all these lines may relate

to nitrogen-hydrogen defects [12]. The major features in the spectra of as-grown nitrogen-doped CVD diamonds are a broad band of irregular shape with maximum at 2925 cm^{-1} and a narrow line at 3123 cm^{-1} [13 - 16]. After annealing the broad band splits into several lines, the most intense of which are at 2815, 2870, 2901 and 2948 cm^{-1} in LPHT-treated diamonds. In HPHT-treated diamonds, the lines shift to 2828, 2874, 2907 cm^{-1} , whereas 2948 cm^{-1} remain at the same position. This change in the spectral position suggest that these lines are not singlets but groups of overlapping narrow lines. Relative intensities of these lines may change with the annealing conditions, thus changing the maxima of the groups. The integral intensity of the broad band at 2925 cm^{-1} and the integral intensity of the lines in the range $2800 - 3000\text{ cm}^{-1}$ are approximately equal. This suggests that the line-constituents of the 2925 cm^{-1} band have high temperature stability. With treatment, they do not anneal out, but become narrower and well distinguishable. A complex system of well resolved lines in the spectral range $2800\text{-}3000\text{ cm}^{-1}$ is a reliable indicator of high-temperature system of treatment of nitrogen-containing CVD diamonds.

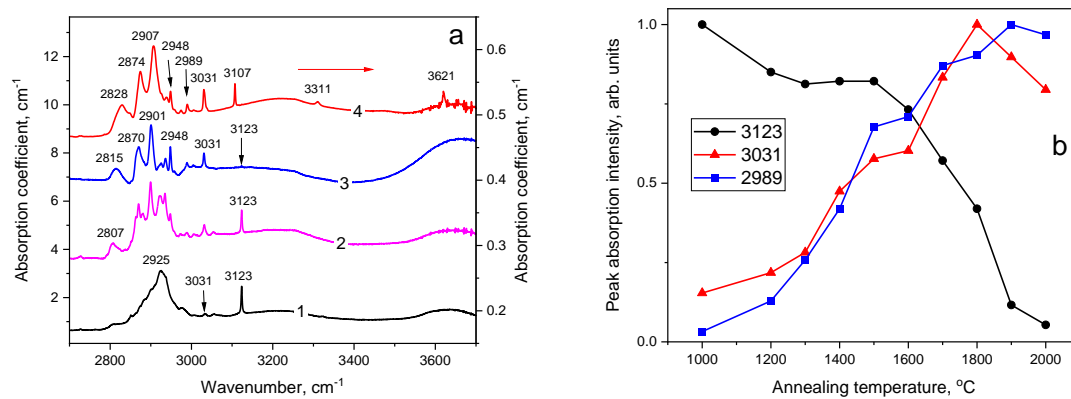


Fig. 4. (a) Representative FTIR absorption spectra in the range of absorption of hydrogen-related defects measured on nitrogen-doped CVD diamond subjected to high temperature annealing: 1 - as-grown, 2- LPHT-treated at temperature 1500°C ; 3 - LPHT-treated at temperature 2000°C ; 4 - after commercial HPHT treatment (plotted against right vertical axis). (b) LPHT annealing curves for the most characteristic narrow lines. (The spectra are shifted vertically for clarity).

Other narrow lines of interest are at 3031, 3107, 3123 cm^{-1} , 3311 and 3621 cm^{-1} . A weak line at 3031 cm^{-1} is present in spectra of as-grown samples. With annealing, the line intensity increases by an order of magnitude (Fig. 4b). Its spectral position and relative intensity are the same in LPHT- and HPHT-treated samples.

The line at 3123 cm^{-1} is believed to be associated with the NV-H defect [22, 23]. The line is usually strong in as-grown samples. It starts to anneal out at temperatures over 1600°C and practically disappears after LPHT annealing at temperature 2000°C (Fig. 4b). Yet, traces of the 3123 cm^{-1} line can be seen in spectra of LPHT-treated samples. In HPHT-treated samples this line becomes undetectably weak.

The line at 3107 cm^{-1} is a well-known hydrogen-related feature observed in spectra of diamonds of any origin. It is ascribed to a local vibration of $\text{N}_3\text{V-H}$ defect [24]. The 3107 cm^{-1} line is strong in HPHT-treated nitrogen-doped CVD samples, but very weak in LPHT-treated ones. This may suggest that pressure during annealing is a factor stimulating the transformations of nitrogen defects. It should be noted that the ineffectiveness in formation of the 3107 cm^{-1} center is not a general trait of LPHT heating. Electron irradiation performed prior to LPHT annealing may substantially facilitate formation of 3107 cm^{-1} center

(to be reported in detail elsewhere). The other lines observed in IR absorption spectra of HPHT-treated, but not in spectra of LPHT-treated diamonds, are at 3311 and 3621 cm^{-1} . Thus the presence of the 3107, 3311 and 3621 cm^{-1} lines and the absence of the 3123 cm^{-1} line is an indicator of HPHT treatment.

3.2.2. UV-Visible absorption

UV-Vis absorption spectra of yellow CVD diamonds are those of classical type Ib diamonds - strong C-defect (N^0) absorption with a threshold at wavelength 500-550 nm (Fig. 5). High pressure during heating promotes the conversion of optically non-active nitrogen into C- and N^+ -defects with their partial aggregation in A-defects. The vacancies released from the collapsed vacancy clusters are captured by A-defects and form H3 defects. The H3 defects are very active both in absorption and luminescence and when in a substantial concentration they impart visible green luminescence which adds a greenish color component to the dominant yellow bodycolor [25, 26].

Although the above discussion explains why LPHT-treated nitrogen-doped CVD diamonds become yellow, it is strange to see that the yellow color in the studied commercial samples is unexpectedly intense considering low concentration of C-defects in them (on average about 2 ppm). Formally, these diamonds fall into the category of type IIa, not type Ib. Similar discrepancy between the yellow color intensity and the C-defect concentration was reported in [27] for some natural diamonds. The authors of [27] assumed that the Y-defects, which are common in natural type Ib diamonds, may also create a "canary yellow" absorption continuum similar to that produced by C-defects. We are wondering whether this explanation could be applicable for the nitrogen-doped yellow CVD diamonds too. Although the formation of Y-defects in CVD diamonds has not been established yet, we draw attention of the reader to the sharp absorption lines at wavenumbers 1454, 1396, 1371, 1362 and 1353 cm^{-1} . They are very common for nitrogen-doped CVD diamonds and some of them seem to be the same always observed in Y-defect containing natural diamonds. Thus, we assume that Y-defects possibly form in the nitrogen-doped CVD diamonds too and contribute to their yellow color.

The spectra taken from as-grown and LPHT-treated nitrogen-doped CVD diamonds are qualitatively similar (Fig. 5). They both show the brown absorption continuum which is strong in as-grown brown samples and weak in LPHT-treated ones. The absence of the threshold-like absorption ascribed to the nitrogen C-defects explains why LPHT treatment does not induce yellow color in nitrogen-doped CVD diamonds. After LPHT treatment, the originally brown CVD diamonds become colorless, near colorless, light brown, light gray, or light pink.

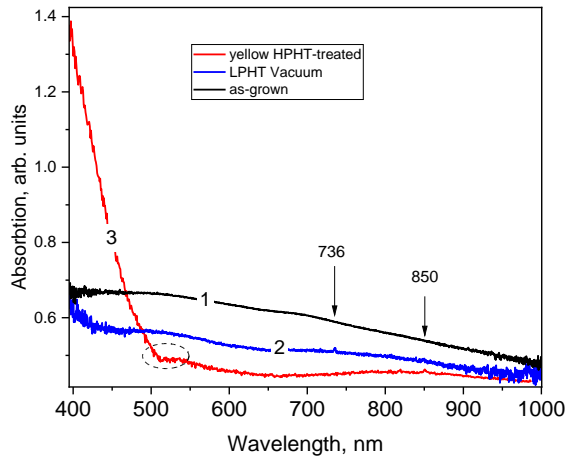


Fig. 5. Representative UV-Visible absorption spectra of nitrogen-doped CVD diamonds: 1 - as-grown; 2 - near colorless LPHT-treated; 3 - yellow HPHT-treated. Dashed oval shows the spectral area of luminescence of H3 center ("negative absorption" effect).

3.3. Photoluminescence

3.3.1. 325 nm laser excitation

PL excited with 325 nm laser reveals characteristic features of nitrogen-doped CVD diamond subjected to high temperature treatment (Fig. 6a). The most prominent one is a broad complex band in the spectral range from 420 to 650 nm [28 - 30]. The distinguishing features of this band are two lines at wavelengths about 462 and 498 nm. These lines are relatively broad (about 15 meV) compared with regular ZPLs of other optical centers in the same sample (1 to 3 meV). Other characteristic features of this broad band are several narrower bands at wavelengths 519, 534, 553 and 575 nm (note that the band at 575 nm overlaps with narrow ZPL of NV^0 at 575 nm). These narrow bands are equidistant in energy scale and therefore can be vibrational replicas of the 498 nm line.

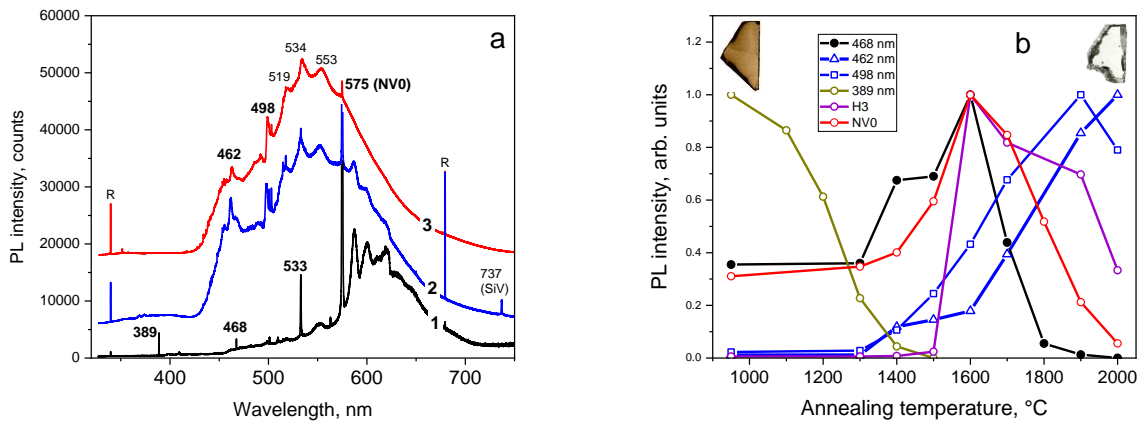


Fig. 6. (a) Representative PL spectra taken with 325 nm laser from nitrogen-doped CVD diamond: 1 - as grown; 2 - after LPHT treatment; 3 - after HPHT treatment. (b) Change in intensity of some characteristic PL centers of nitrogen-doped CVD diamonds subjected to isochronal LPHT annealing in vacuum.

Another peculiarity of the 462 and 498 nm centers is that their spectral positions vary from sample to sample and change with the heating conditions. For instance, they are located at 461.8 nm and 498.0 nm in some LPHT-treated samples whereas they shift to 463.0 nm and 499.0 nm correspondingly in some HPHT-treated samples (Fig. 7a). These spectral variations together with the large spectral width suggest that the lines 462 and 498 nm are not singlets but superpositions of multiple narrow lines arising from some point defects the atomic structure of which is randomly distorted by other large defects in their vicinity. These defects could be the remnants of the collapsed vacancy nanoclusters. The 462 and 498 nm centers are always present in spectra of CVD diamonds grown in nitrogen-containing environment and subjected to high temperature treatment. These centers are very reliable distinguishing features of LPHT- and HPHT-treated CVD diamonds.

Isochronal annealing curves of the 463.0 nm and 499.0 nm centers along with several other optical centers commonly seen in PL spectra of nitrogen-doped CVD diamonds are shown in Fig. 6b. After heating at 1400°C the intensity of 463.0 nm and 499.0 nm centers starts to increase and steadily grows with temperature up to 2000°C. Intensity of other centers, but 389 nm center, strongly decline after heating at temperatures over 1600°C. The 389 nm center anneals out completely after heating at temperatures above 1400°C.

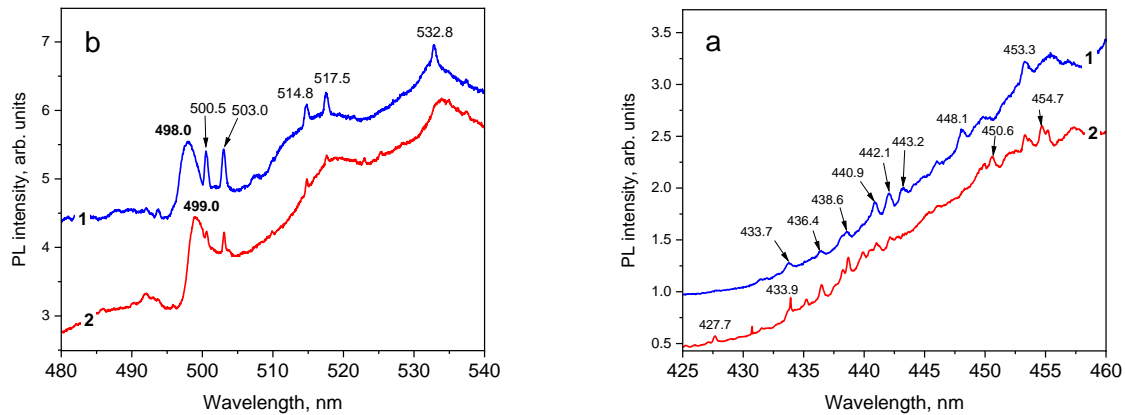


Fig. 7. Detailed spectra taken with 325 nm laser from nitrogen-doped CVD diamonds after LPHT (1) and HPHT (2) treatment: (a) in spectral range 480-540 nm; (b) in spectral range 425-460 nm.

Many more small lines are seen in the spectral ranges 425-470 nm and 490-530 nm of the treated samples (Fig. 7). The spectral structure of this complex luminescence can be different for HPHT-treated and LPHT-treated diamonds. In general, these lines are narrower after HPHT treatment suggesting that annealing under pressure reduces stress of crystal lattice of CVD diamond.

Another optical centers useful for characterization of yellow CVD diamonds is the nitrogen-related center with ZPL at 389 nm [16]. This center is always detected in PL spectra of as-grown nitrogen-doped CVD diamonds. The 389 nm center has low thermal stability, and its presence is a strong proof that high temperature heating was not applied. However, if the 389 nm center is observed in spectra with obvious

features of high temperature treatment (e. g. the 462 and 498 nm centers), then definitely the high temperature treatment was followed by irradiation. In this case the final irradiation treatment can be confirmed by the presence of characteristic radiation centers: GR1 (neutral vacancy, ZPL at wavelength 741 nm), ND1 center (negatively charged vacancy [31], ZPL at wavelength 393 nm) and TR12 center (ZPL at 471 nm, a defect related to self-interstitials).

3.3.2. 457 nm laser excitation

The most characteristic PL feature excited with 457 nm laser in as-grown nitrogen-doped CVD diamonds is the 468 nm center (ZPL at 467.7 nm) [28, 30, 32] (Fig. 8a). This center is active in photo- and cathodoluminescence. The optimal excitation wavelengths for the 468 nm center are in the spectral range of its intrinsic absorption (380-460 nm) [33]. When excited within this spectral range, as-grown nitrogen-doped CVD diamonds produce characteristic green fluorescence (Fig. 8b). The 468 nm center has a relatively high thermal stability (Fig. 6b). It survives short-time LPHT annealing at temperatures of 2000°C. However, in spectra of HPHT-treated CVD diamonds the 468 nm center is usually absent.

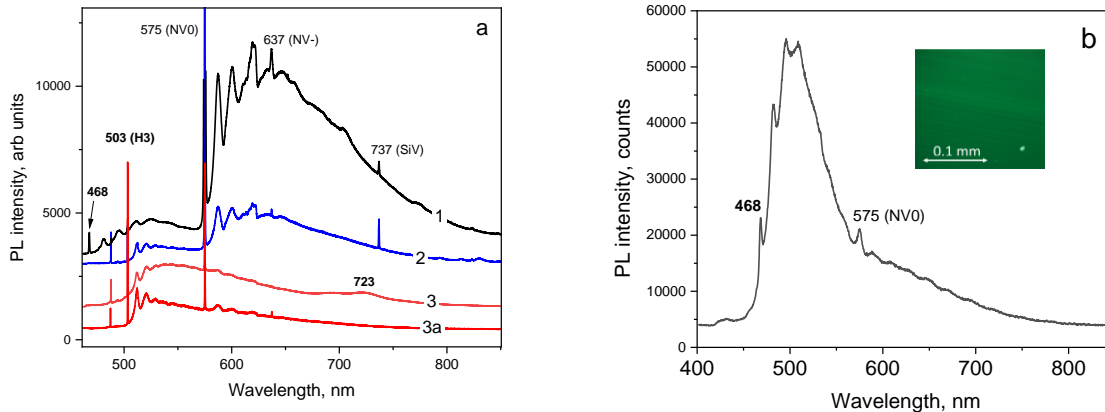


Fig. 8. PL spectra of nitrogen-doped CVD diamonds: (a) excitation with 457 nm laser, as-grown (1), LPHT-treated (2), HPHT-treated (3. 3a); (b) measured at room temperature with mercury lamp excitation (365 nm line). Green color insert is an image of the excited area as seen in fluorescence microscope.

Centers important for characterization of nitrogen-doped CVD diamonds are 575 nm (NV^0 center) and 503.2 nm (H3 center). The 575 nm center is very strong and H3 center is vanishingly weak in spectra of as-grown samples. With annealing at temperature up to 1600°C the intensity of both center increases (Fig. 6b). Especially dramatic intensity increase occurs for the H3 center. This increase manifests the beginning of aggregation of C-defects into A-defects and H3-defects. At higher temperatures the intensity of 575 nm and H3 centers center decreases.

In HPHT-treated diamonds, the H3 center is stronger than the 575 nm center (Fig. 8a). In LPHT-treated diamonds, even after heating at temperature 2000°C, the 575 nm center remains strong and may dominate the spectrum. This difference between LPHT and HPHT treatments is explained by a higher rate of aggregation of single-nitrogen defects (including NV defects) into double-nitrogen defects like H3 defects if the heating is performed under pressure.

Multiple weak narrow ZPLs are frequently seen in the spectral range 475-575 nm of treated nitrogen-doped CVD diamonds when excited with 457 nm laser [12, 29] (Fig. 9a). The sets of these lines and their

relative intensities may substantially vary from sample to sample. However, they all are detected only after high temperature annealing after substantial reduction of the 468 nm center. The presence of multiple narrow lines in the spectral range 475-575 nm is characteristic feature of CVD diamonds heated at high temperature.

Several weak broad lines and bands are detected in PL spectra of treated samples in the range 650-850 nm (Fig. 9b). These features are different for as-grown, LPHT-treated and HPHT-treated samples. In as-grown samples, they can be found at wavelengths 658, 705, 773 and 823.3 nm. They all, but the 823.3 nm line, disappear after high temperature annealing. If the treatment was performed in LPHT regime, new features at wavelengths 893, 813 and 830 nm appear. These features are very characteristic of LPHT treatment. We observed them in spectra of all nitrogen-doped CVD diamond subjected to LPHT treatment. HPHT treatment may completely suppress all the above-mentioned bands. However, some HPHT-treated samples may show luminescence of two bands with maxima 694 and 723 nm [29].

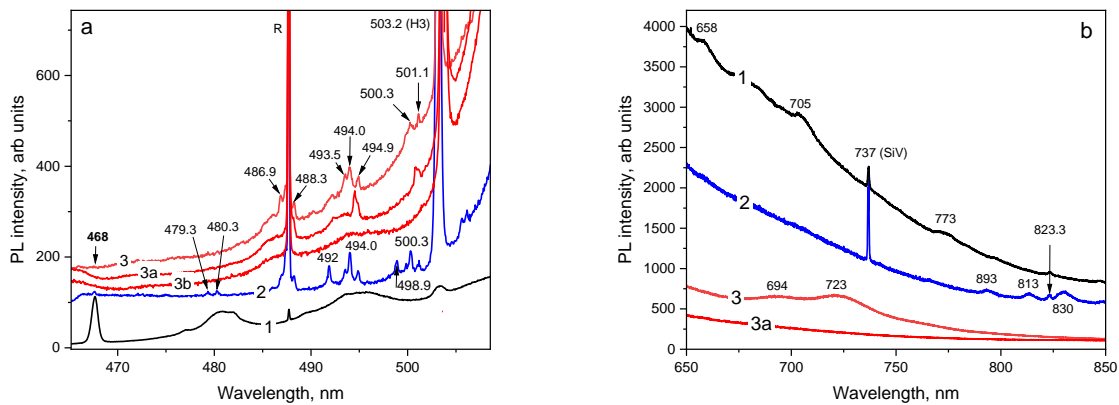


Fig. 9. PL spectra of as-grown (1), LPHT (2) and HPHT (3, 3a, 3b) treated nitrogen-doped CVD diamonds taken with 457 nm laser: (a) spectral range 460-510 nm; (b) spectral range 650-850 nm.

3.3.3. 514 nm laser excitation.

The dominating features of the spectra taken with 514 nm laser are NV^0 and NV^- (ZPL at 637 nm) centers (Fig. 10a). These centers dominate in as-grown samples and in treated ones. With treatment, the intensity of NV^- center grows faster than the intensity of NV^0 center suggesting an increase in the concentration of nitrogen donors (C-defects) and the change of the charge state of NV defects from neutral to negative.

Particular attention should be paid to the spectral range from 510 to 570 nm where as-grown samples may reveal only three weak lines at 534.4, 543.2 and 563.3 nm. High temperature annealing generates many narrow lines ("forest of peaks", [34]) in this spectral range. Relative intensity and spectral positions of these lines may differ for HPHT- and LPHT-treated samples (Fig. 10b). The "forest of peaks" is observed only in the spectra of treated CVD diamonds suggesting that all these lines probably relate to point defects resulting from the destroyed vacancy nanoclusters. The "forest of peaks" appears always after LPHT treatment but can be absent from the spectra of some HPHT-treated yellow CVD diamonds (Fig. 10b, spectrum 3a). We tentatively assume that the yellow CVD diamonds without the "forest of peaks" in their spectra were HPHT-treated at very high temperature (well above 2000°C).

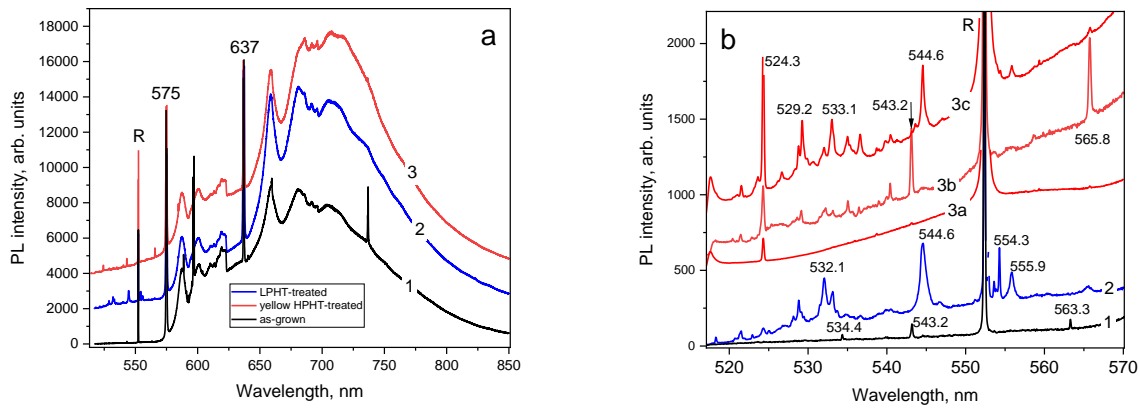


Fig. 10. PL spectra of as-grown (1), LPHT (2) and HPHT (3, 3a, 3b, 3c) treated nitrogen-doped CVD diamonds taken with 514 nm laser: (a) full spectra; (b) spectra in the spectral range 515-570 nm.

3.3.4. 633 nm laser excitation.

In the spectra obtained with 633 nm laser, the NV⁻ center is by far the dominating feature before and after treatment (Fig. 11). The spectral range from 770 to 900 nm is the most informative. As-grown diamonds have no noticeable features in this spectral range. After high temperature treatment several broad and narrow lines appear [11]. These lines are different for LPHT- and HPHT-treated diamonds. Relatively strong broad lines appear after LPHT treatment. These features are very characteristic of LPHT annealing. We have observed them practically in all LPHT-treated nitrogen-doped CVD diamonds. In contrast, no broad lines but several weak narrow lines are detected in spectra of yellow HPHT-treated diamonds. Analysis of these features may give a reliable proof of high temperature treatment and even reveal the type of treatment.

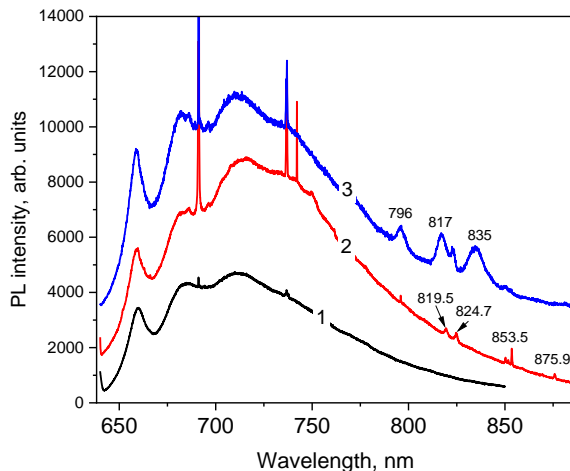


Fig. 11. Representative PL spectra of nitrogen-doped CVD diamonds measured with 633 nm laser: 1 - as-grown; 2 - yellow HPHT-treated; 3 - LPHT-treated.

3.3.5. 830 nm laser excitation.

PL spectra taken with 830 nm laser excitation are very different for as-grown, LPHT-treated, and HPHT-treated samples. The major feature observed in the spectra of as-grown diamonds is an intense broad band with maximum at a wavelength of 863 nm [15, 34] (Fig. 12). Smaller bands are seen over the whole spectrum. The most prominent of these features is a complex band in the spectral range 895-960 nm with the major components at 933, 939, and 950 nm. After LPHT treatment, these bands disappear giving way to several narrower bands at wavelengths 859, 877, 901, 928 and 954 nm. After HPHT treatment, all broad-band features disappear, and many narrow lines appear in the range 840-920 nm. The most intense of these lines locate at wavelengths 850, 853.5, 870, 875.6 and 909.0 nm [34]. The line at 850 nm is usually the strongest one. This line is also active in absorption [12]. All these lines are detected in spectra of most HPHT-treated nitrogen-doped CVD diamonds. Yet, some of these diamonds may show practically no luminescence when excited with 830 nm laser (Fig. 12, trace 3a). However, in both cases, the spectra of HPHT-treated diamonds strongly differ from the spectra of LPHT-treated ones. Thus, the narrow line PL excited with 830 nm laser, or the absence of any PL features, are the indications of HPHT treatment.

Another center valuable for the recognition of high temperature treatment of nitrogen-doped CVD diamonds is the H2 center with ZPL at 986.2 nm (the manifestation of the negatively charged NVN⁻ defects). PL of the H2 center is always observed in PL spectra of treated CVD diamonds excited with 830 nm laser irrespective of the type and temperature of treatment [34].

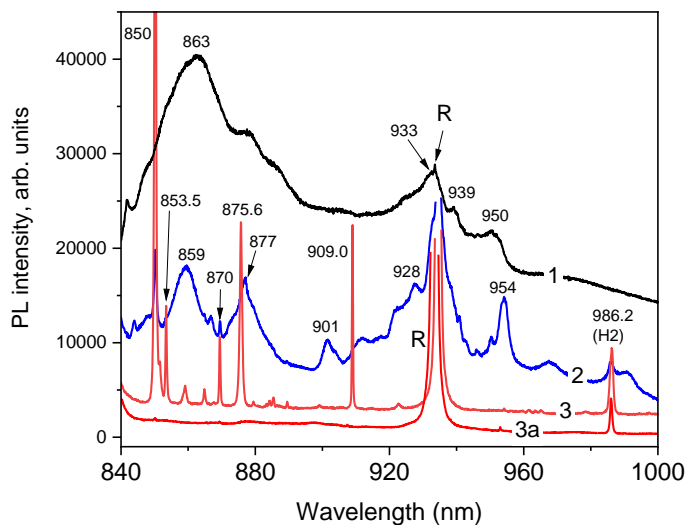


Fig. 12. PL spectra of nitrogen-doped CVD diamonds measured with 830 nm laser: 1 - as-grown; 2 - LPHT-treated; 3, 3a - yellow HPHT-treated.

4. Concluding remarks: Spectroscopic criteria of identification of high temperature treatment of nitrogen-doped CVD diamonds

The above data and their analysis show that most of yellow CVD diamonds currently on the gem market have distinctive spectroscopic characteristics of nitrogen-doped diamonds subjected to HPHT treatment. Comparative studies of these diamonds with the CVD diamonds treated by LPHT annealing suggest that it is the HPHT treatment that promotes creation of C-defects and makes the nitrogen-doped CVD diamonds yellow.

Analysis of the sets of optical centers in nitrogen-doped CVD diamonds and their changes with annealing temperature allows us to establish the temperature criteria for high-temperature treatment. Substantial changes in the intensities of the major optical centers occur at temperatures above 1400°C. Since these changes may cause visual change in color of CVD diamond, the temperature 1400°C can be taken as a threshold for high temperature treatment. In practice, more important temperature threshold is 1700°C. At this temperature CVD diamonds start to lose their brown color. Comparing relative intensities of various optical centers, it is possible to estimate the temperature at which treatment was performed (Table 2).

Table 2. Change in the relative intensities of optical centers in nitrogen-doped CVD diamonds with temperature of LPHT treatment.

Temperature	389 nm*	468 nm**	NV ⁰ *	H3 *	462/498 nm*	1341 cm ⁻¹	1396 cm ⁻¹	1362 cm ⁻¹	1454 cm ⁻¹	3123 cm ⁻¹	3031 cm ⁻¹
Below 1400°C	strong	strong	strong	very weak	very weak	very weak	very weak	very weak	string	strong	very weak
1500°C	none	strong	strong	very weak	weak	Weak	substantial	weak	strong	strong	substantial
1600-1700°C	none	strong	strong	Strong	substantial	substantial	strong	weak	strong	strong	strong
1800°C	none	weak	strong	Strong	strong	strong	strong	substantial	substantial	substantial	strong
1900-2000°C	none	very weak	weak	Strong	strong	strong	strong	strong	weak	very weak	strong

* As measured with 325 nm laser.

** As measured with 457 nm laser.

In PL spectra of as-grown untreated diamonds, the centers 389 nm, 503.5 nm (3H) are well detectable, the centers 468 nm and 575 nm (NV0) are dominant whereas the centers 503.2 nm (H3), 462 nm and 498 nm are hardly detectable. A unique PL feature of as-grown diamonds is a broad band with maximum at 863 nm excited with 830 nm laser. This band is destroyed by high temperature treatment and as such can be used as a reliable indicator of untreated CVD diamond.

In FTIR absorption spectra of untreated diamonds the line 1332 cm⁻¹ dominates while the band 1293 cm⁻¹ is absent. In the spectral range 2800-3200 cm⁻¹ a complex band with maximum at 2925 cm⁻¹ and the line 3123 cm⁻¹ are the most prominent features. The 3107 cm⁻¹ center is not detected in as-grown untreated diamonds. The intensity ratio of the 3107 cm⁻¹ and 3123 cm⁻¹ centers can help to distinguish between LPHT and HPHT treatments. If a nitrogen-doped CVD diamond shows many signs of high temperature treatment but reveals hardly detectable 3107 cm⁻¹ center and very weak 3123 cm⁻¹ center this diamond is very likely LPHT-treated. If the intensity of the 3107 cm⁻¹ center is substantial and the 3123 cm⁻¹ center is absent the diamond is most likely HPHT-treated.

The most reliable indicator of high temperature treated nitrogen-doped CVD diamonds are the 462 nm and 498 nm PL centers excited with 325 nm laser. These centers are equally strong in spectra of HPHT- and LPHT-treated diamonds. The bands at wavelengths 796, 817, and 835 nm excited with 633 nm laser are distinctive features of LPHT-treated CVD diamonds. These bands are not observed after HPHT treatment. Distinctive features of HPHT-treated diamonds are multiple narrow lines excited with 830 nm laser.

It is important to note that all the observations and the criteria presented in this research pertain only to the nitrogen-doped CVD diamonds in either as-grown state or subjected to high temperature treatment. These criteria cannot be directly applied to CVD diamonds treated with involvement of irradiation. Irradiation changes the defect composition very differently compared with high temperature annealing.

Consequently, the criteria of recognition of CVD diamonds treated by combination of high temperature annealing and irradiated are different from the described above.

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