

Photoluminescence and optical transmission of diamond and its imitators

Victor F. Tarasenko^{*a}, Evgenii I. Lipatov^a, Sergei M. Avdeev^a

^a High Current Electronics Institute SB RAS, Akademicheskii ave., 2/3, Tomsk, Russia, 634055

ABSTRACT

Photoluminescence and optical transmission spectra of several samples of natural and synthetic diamond and its imitators – fianite and corundum – are investigated. The band-A of luminescence at 440 nm, the vibronic N3 system of luminescence and absorption at 415.2 nm, the fundamental absorption edge at 225 nm, and the secondary absorption below 308 nm are the main identifying markers of natural diamonds. For synthetic diamonds, however, such identifying markers are the exciton luminescence at 235 nm, the band-A, and the fundamental absorption edge. Fianites can be identified by the structureless wide band at 500 nm and the wide transmission band in the entire visible range. Colored corundum samples with chrome impurities emit the narrow line at 693 nm and show the absorption band in the 500-600 nm spectral range. A new method for diamond express identification is developed on the basis of measurement of photoluminescence and optical transmission spectra of the samples. It is shown that a diamond tester can be designed combining a spectrometer and a KrCl-excimer lamp radiating at 222 nm.

Keywords: diamond, CVD, jewelry, gem, fianite, zirconium, corundum, excimer lamp, luminescence, optical transmission

1. INTRODUCTION

The advancement of technologies for synthesis of materials which can imitate diamonds brings about the necessity of improving the methods for diamond identification. A well-trained specialist can distinguish between a diamond and its imitation very easily using only a tenfold lens. In laboratory conditions any gem stone is identified with 100 % certainty using advanced gemological methods, because the material has a unique set of physical parameters [1].

However, it is often required to identify diamond without relevant person skill, outside the gemological laboratory. In this case, the so-called diamond-testers are very convenient [2]. These devices for express identification are based on the measurement of one or several physical parameters of tested sample – thermal conductivity, electrical conductivity, refractive index, and optical transmission in the short ultraviolet (UV) range.

In our days, the main materials-imitators of diamond are fianite (stabilized cubic zirconia – $\text{ZrO}_2\text{:Y}_2\text{O}_3/\text{CaO/MgO}$) and synthetic moissanite (silicon carbide – 6H-SiC) [1,2]. At room temperature (RT), thermal conductivity of fianite is about 0.2-0.4 W/(cm·K), which is much less than that of diamond – 5-25 W/(cm·K). In the case of fianite, it is sufficient to determine thermal conductivity using a diamond-tester. Thermal conductivity of moissanite at room temperature is about 2-5 W/(cm·K) and the diamond-tester takes its for diamond. Fortunately, all synthetic moissanites have numerous defects in the structure and demonstrate a pronounced electrical conductivity at voltage of several volts [2,3]. In this connection, advanced diamond-testers have an option for measuring electrical conductivity and identify moissanites.

Another identification method is to measure the refractive index (~2.17 – fianite, ~2.42 – diamond, ~2.65/2.69 – moissanite). However, among the “older generation” of diamond imitators there are materials whose refractive indices are very close to that of diamond (spinel, strontium titanate, etc.). Therefore, in order to make reliable express-identification of diamond, it is not sufficient to measure the refractive index alone. The second parameter to be measured is the thermal conductivity of the sample under study.

In addition to stones made of materials-imitators, there are synthetic (= man-made) diamonds and natural diamonds with improved properties are available on the market. The authors are unaware of diamond-testers capable of identifying synthetic diamonds. For express-identification of natural diamonds subject to high-pressure, high-temperature (HPHT)

* vft@loi.hcei.tsc.ru; phone (3822) 491-685; fax (3822) 492-410; www.hcei.tsc.ru

treatment use is made of a method for measuring optical transmission (OT) of samples at 254 nm (shortwavelength UV line of a mercury lamp). Most of natural gem diamonds (up to 98 %) exhibit the secondary absorption below ~308 nm and belong to the Ia type diamonds [4,5]. Only about 2 % of gem diamonds are classified as those of IIa and IaB types and exhibit the fundamental absorption edge below ~225 nm. In this connection, it is assumed that a diamond transparent at 254 nm is an HPHT treated sample (HPHT treatment improves optical properties, especially in the shortwavelength UV region, and increases the cost of stones).

The main method for diamond synthesis is HPHT growth at ~60 kbar and ~1500 K on seeds from a mixture containing metals of the iron group [6-8]. Such HPHT diamonds belong to the Ib type diamonds because of nitrogen impurities in the form of disperse-distributed substitutional nitrogen atoms, have yellow color, and demonstrate identifying luminescent lines due to structure defects caused by nickel [6,7] or cobalt [8]. The following HPHT treatment of such diamonds at higher temperatures (1950-2200 K) leads to agglomeration of nitrogen atoms and solvent-catalyst metal atoms into the defects of complicated structure. It results in enhancing optical properties of the stones. However in the photoluminescence (PL) and optical transmission (OT) spectra, one can observe characteristic vibronic systems of structure defects containing iron-group metal atoms. Such vibronic systems are very rare observed in the PL spectra of natural diamonds [9].

Gem-quality diamond single crystals of big size are now synthesized by the chemical vapor deposition (CVD) method [10]. Such CVD diamonds are characterizing by high quality of diamond lattice and low quantity of amorphous carbon and impurities. These gem-quality CVD diamonds exhibit exciton luminescence in the 230-250 nm range close to the fundamental absorption edge [11]. Synthetic diamonds with low nitrogen concentration show exciton luminescence even at room temperature [12]. In these conditions, the band-A intensity is very low. The value of the exciton luminescence intensity to the band-A intensity (I_{ex}/I_A) ratio characterizes the quality of CVD diamonds [13]. Note, that pure natural diamonds can demonstrate exciton luminescence, with the I_{ex}/I_A ratio being much lower than unity (0.001-0.1) [14]. At the same time, optically transparent CVD diamonds have the I_{ex}/I_A higher than unity.

Thus, studying luminescence of diamond in the 225-800 nm range allows us to recognize a method for growth – natural, HPHT, or CVD. In addition, measuring an OT spectrum of a sample makes it possible to characterize diamonds in terms of the standard physical classification and identify its characteristic structural defects [4]. The combination of OT and luminescence spectra provides information on the material of the sample under study. In other words, measuring OT and luminescence spectra and using a wide data base, one can readily identify diamond and its imitators. Moreover, it is possible to determine the nature of any luminescing sample with an optical transmission band.

In the work, we develop a method for express identification of diamond and its imitators based on the measurement of sample photoluminescence (PL) and OT spectra. The possibility of development of a diamond-tester using our method is discussed. Barrier-discharge excilamps with emission in the 160-350 nm range are used as light sources in the spectral measurements. The optical characteristics of natural and synthetic diamonds, fianites, and synthetic corundum samples are investigated. Identifying features of the PL and OT spectra of the samples are determined. An electron accelerator RADAN-220 and a KrCl-laser at 222 nm are used to observe exciton luminescence of CVD diamonds.

2. PL EXCITATION WAVELENGTH IN DIAMONDS

The main methods for excitation of luminescence in crystal materials are excitation by the UV light, electron beam (e-beam), and X-rays [15]. X-rays are used in setups for separation of diamonds from rock. However, up to 40 % of samples do not luminesce due to weak absorption of X-rays in diamond [16]. Due to high excitation intensity and band-to-band transitions, a pulsed e-beam causes cathodoluminescence (CL) of practically all diamonds [15,16]. When using cathodo- and X-ray luminescence, one needs certain biological protection, this, in turn, leads to increasing the mass and size of the device making it less attractive for customers. Thus, PL is more preferable for express identification of diamonds. Moreover, UV radiation sources are tens - hundred times cheaper than e-beam accelerators and X-ray sources.

PL excitation in gem diamonds is conventionally performed by the UV lines of a mercury lamp at 365 nm (3.38 eV, long-wavelength UV) and at 254 nm (4.86 eV, short-wavelength UV). Up to 65 % of the samples exhibit no luminescence at all or luminesce very weakly [17]. This is accounted for by the fact that excitation results from quanta whose energy is lower than an indirect band gap of diamond 5.49 eV. In this case, lamp radiation is absorbed on the lattice defects forming allowed states in the band gap. One absorbed photon with the energy lower than that of the band gap gives rise to one free charge carrier and a center with an altered charge state.

During hundreds of million years of geological history, natural diamonds underwent a natural HPHT treatment. In so doing, defects and impurities were agglomerated in the process. That is, in local regions of crystal lattice, the defects accumulated and their structure became more complex. Along with luminescence centers (N_3V , N_2V , N_2V_2 etc.) in natural diamonds, the widespread defects are N_2 -defects (or A-defects) causing the secondary absorption below ~ 308 nm and becoming a radiationless recombination center effectively quenching luminescence.

Under illumination of a sample by photons whose energy is lower than the band gap of diamond, the absorption coefficient is in no excess of several cm^{-1} . Under such conditions, the concentration of generated carriers is not high $< 10^{15} \text{ cm}^{-3}$, i.e., linear recombination of charge carriers dominates. Due to close neighborhood, the probability of excitation transfer from luminescence centers to radiationless recombination centers is very high. Thus, quenching of luminescence results [18].

Under illumination of the sample in the spectral region of fundamental absorption, the absorption coefficient increases rapidly up to hundreds of cm^{-1} , an absorbed photon creates an electron-hole pair (EHP), the EHPs are generated with the uniform concentration in a layer independent of the presence of structure defects and, hence, quadratic recombination becomes dominant [15]. This leads to decreasing effect of luminescence quenching, therefore up to 100 % of the samples exhibit luminescence.

Thus, it is necessary to use radiation at the wavelength in the spectral region of the fundamental absorption of diamond (i.e. $\lambda \leq 225$ nm) to reliably obtain PL in all diamonds with the intensity to be measured.

3. EXCILAMPS – POWERFUL UV SOURCES

During the last two decades, excilamps have extensively been developed [19-22]. The excilamps are alternative UV radiation sources based on dimers and halogenides of inert gases. Excilamp radiation (> 80 % of energy) is concentrated in relatively narrow spectral bands ~ 2 nm in the background of wide low-intensity bands of tens-hundreds nm. A change in the working mixture allows one to obtain main emission bands with the maxima at 172, 206, 222, 253, 283, and 308 nm.

Earlier, different types of discharges were used for pumping excilamps, including glow discharge, microwave discharge, nonself-sustained pulsed high-pressure discharge, etc. However, in [20,21], it was found that using capacitive discharges with dielectric barriers between electrodes and active medium makes it possible to significantly improve excilamp performance. A quartz tube is usually used as a dielectric barrier. Without interaction between the active medium and metallic electrodes, halogen is lost at a slower rate and the electrode degradation is prevented. Nowadays the lifetime of barrier-discharge excilamps is more than 2000 hours. The initial intensity of UV radiation is usually tens of mW/cm^2 , does not virtually decrease during warranted lifetime, and even increases in some cases due to achieving a halogen concentration optimum [22].

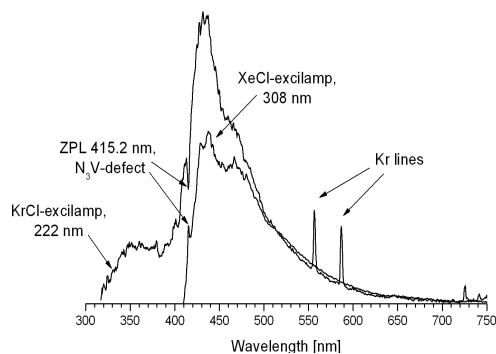


Fig. 1. PL spectra of natural faceted Ia-type diamond under excitation by a KrCl-excilamp at 222 nm and a XeCl-excilamp at 308 nm.

toxic mercury occurs, and there is no need to clean the room.

Excilamps with the spectral maxima at 172 (Xe_2^*), 206 (KrBr^*) and 222 (KrCl^*) emit in the fundamental absorption spectral range of diamond, so they potentially suit for PL excitation in all gem diamonds. Excilamps with maxima at

Conventional mercury lamps have two main modes of operation. At low pressure and low pumping power, mercury lamps emit, in general, at a 254 nm resonance line, and under certain conditions – at 185 nm. In high-pressure and high pumping-power lamps, the emission spectrum consists of numerous lines in the UV spectral region with the dominant being at 365 nm.

The main advantage of excilamps as compared with mercury lamps is its ecological compatibility, because, in spite of halogens present in the excilamp gas mixture (fluorides, chlorine, bromine, iodine), their concentration is very low (less than 2 %). Thus at incidental breaking an excilamp tube no contamination by high-

253 (XeI^{*}), 283 (XeBr^{*}) and 308 (XeCl^{*}) nm emit in the so-called secondary absorption spectral range of diamond due to N₂-defects, therefore, the intensity of excited PL is lower than in the case of excitation in the fundamental absorption range of diamond. However, for comprehensive examination of luminescence centers in diamond it is reasonable to excite PL by photons from different spectral areas, which allows us to avoid competition between luminescence centers [23].

In optically transparent CVD diamonds and most pure natural diamonds of type IIa, PL is very weak under excitation by photons at $\lambda \geq 225$ nm. At excitation by photons with the energy lower than the energy of the diamond band gap, the

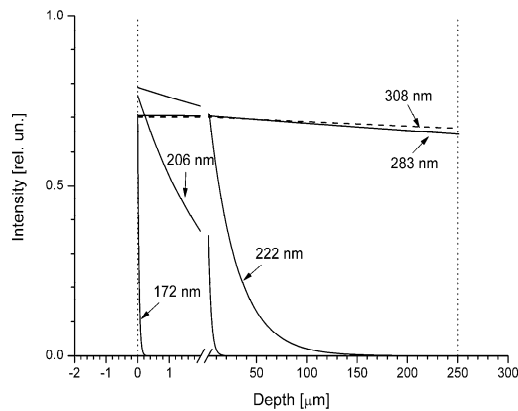


Fig. 2. Calculated distributions of light intensity at different wavelengths in natural IIa-type diamond.

side-bands in 420-460 nm range were observed in the PL spectra of the samples. However, under excitation at 222 nm, there was an absorption N3-system with a ZPL at 415.2 nm and a phonon side-band in the 350-410 nm range overlapping the band-A. An interpretation of this phenomenon will be given below.

In Fig.2, the calculated distributions of radiation intensity $I(x)$ are shown for spectral maxima of various excilamps versus increase in penetration depth x in the IIa-type diamond sample characterized by the OT spectrum shown in Fig.4b, curve 2. The values of absorption coefficient in the fundamental absorption region of diamond were taken from [25]. The refractive indices were taken from [4]. The calculations were made using the following formula:

$$I(x) = I_{INC} \cdot \frac{(1-r) \cdot (e^{-\alpha \cdot x} - r \cdot e^{-\alpha \cdot (2d-x)})}{1 - r^2 \cdot e^{-2\alpha \cdot d}}, \quad (1)$$

where x [cm] – depth, I_{INC} [arb. un.] – incident radiation intensity, r – reflection coefficient, α [cm⁻¹] – absorption coefficient, and d – thickness [cm] of the sample under study. It is evident that for different wavelength at $x = 0$ the penetrating radiation intensity in crystal is also different. Increasing the wavelength from 172 to 222 nm results in an increase in penetrating radiation intensity in crystal due to a decrease in the reflection coefficient. However, a further increase in the wavelength to the range of extrinsic absorption of diamond leads to a drastic decrease in the absorption coefficient and a significant increase in the contribution from a back crystal face to the reflectance. It again decreases the intensity of radiation penetrating into the crystal.

Thus it follows from Fig.2 that the highest pumping density of PL is achieved at the wavelength 172 nm. But in this case, the PL is excited in a very thin layer. For radiation at 172 and 206 nm (emission of Xe₂^{*} and KrBr^{*} molecules) the intensity decreases by an order of magnitude in the layers 0.1 and 6.3 μm, respectively. In order to exclude the influence of absorbed impurities and contaminations on the measured spectrum, it is necessary to prepare the surface of the sample

natural diamonds of type Ia exhibit PL whose intensity can be from invisible to very strong one [17,24]. In Fig.1, the PL spectra of Ia-type crystal under excitation by a KrCl-excilamp at 222 nm and by an XeCl-excilamp at 308 nm are shown for the same average radiation power. The PL intensity under excitation by the foregoing KrCl-excilamp was twice that resulting from excitation by the XeCl-excilamp. It should be noted that under excitation at 308 nm, a band-A and a luminescent N3-system (N₃V-defects) with a zero-phonon line (ZPL) at 415.2 nm, and phonon

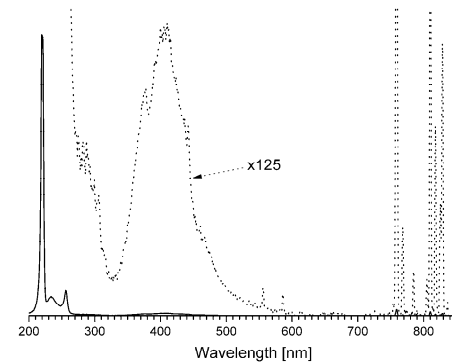


Fig. 3. Emission spectrum of a barrier-discharge KrCl-excilamp with average power density of 29 mW/cm².

under study. However, in the case of a KrCl-excilamp with the spectral maximum at 222 nm, PL is excited in the layer $\sim 65 \mu\text{m}$. Hence, on the one hand, high PL excitation density is obtained, and on the other hand – a sufficient layer thickness for excluding the influence of defect surface on the measured spectrum.

Sometimes, for improving optical properties of the stone (or for producing a diamond imitation) a CVD diamond film of $\sim 1 \mu\text{m}$ thickness is deposited on its surface [26]. For identification of such a stone it is possible to measure the PL spectra under excitation at 222 and 172 nm. This procedure enables one to produce initial stone and deposited CVD layer spectra, respectively.

Another advantage of the above KrCl-excilamp is its emission spectrum shown in Fig.3. In addition to the dominant $B \rightarrow X$ transition band of a KrCl^* molecule with the maximum at 222 nm, there are wide emission bands of discharge plasma in the 225-800 nm range and narrow atomic lines of Kr I at 556.4, 587.3, 758.9, 768.7, and 785.7 nm. The presence of these bands and lines makes it possible to use a KrCl-excilamp not only for PL excitation, but also for measuring the OT spectrum of the sample in the entire UV-visible range.

4. EXPERIMENTAL SETUP AND SAMPLES

Thus, for PL excitation and OT measurement of the samples we used a barrier-discharge KrCl-excilamp with the spectral maximum at 222 nm working in a pulse-periodic regime with the pulse repetition rate $\sim 100 \text{ kHz}$. The average intensity of excilamp radiation was measured by a HAMAMATSU H8025-222 sensor and was 29 mW/cm^2 . In addition, excilamps with the wavelengths 172, 206, 282, and 308 nm were also used in preliminary experiments.

The experimental arrangement is shown in Fig.4. Excilamp 1 excited PL in the samples. PL emission passed through sample 2 and through optical fiber 3 to EPP-2000C (Stellar-Net Inc.) spectrometer 4, equipped with a diffraction grating and a CCD detector. After accumulation for 1-5 seconds the measured signal was transferred to PC 5. The spectral responses of the spectrometer and the contribution from wideband plasma radiation of the KrCl-excilamp discharge in the 225-800 nm range were taken into account by software processing.

During the measurement of the OT of the samples a reference spectrum of excilamp radiation without sample 2 was measured in the first place. Then we measured the OT spectrum of the sample. Since the KrCl-excilamp radiation intensity was higher in the 200-260 nm spectral region as compared to the 260-800 nm region, the foregoing procedure was performed for each of the ranges individually. The two OT spectrum parts were matched by multiplication of a short-wavelength part by a corresponding coefficient.

The KrCl-excilamp size was $30 \times 9 \times 9 \text{ cm}^3$, the power unit – $25 \times 10 \times 10 \text{ cm}^3$ and the spectrometer – $15 \times 11 \times 7 \text{ cm}^3$. All required devices for measuring the PL and OT of the samples had the total mass 5 kg and could be put on a small table.

We have studied the PL and OT for 10 diamond samples, 3 fianite samples, and 3 synthetic corundum samples. Among the 10 studied diamonds, 8 were of natural origin and 2 were polycrystalline CVD diamonds of the “electron grade”. Two of natural diamonds had a round cutting and were of the Ia type. Six of natural diamonds were of the IIa type and cut like plane-parallel plates and disks. The diamond samples of the same type or same nature demonstrated similar optical properties. All natural diamonds were characterized by visually blue luminescence. The CVD samples luminesced much weaker than the natural samples, the luminescence color being close to white rather than blue.

The fianite samples visually looked like faceted diamonds demonstrated practically the same spectra and visually yellow-green PL. The corundum samples had different degree of coloration from pale pink to deep red, which affected the PL and OT band intensities.

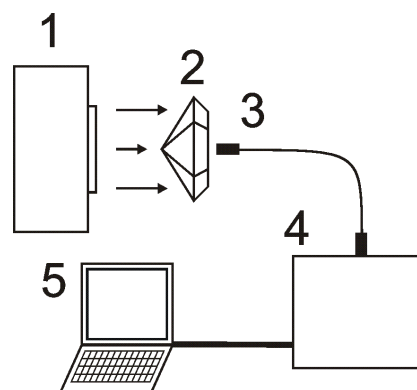


Fig. 4. Experimental setup. 1 – excilamp, 2 – sample, 3 – optical fiber, 4 – spectrometer, 5 – PC.

5. RESULTS AND DISCUSSION

The examined natural Ia type diamonds had a round cutting ($\varnothing 5$ mm, 0.43 carat) and were set in gold holders (earrings). During PL and OT measurements it was not necessary to remove the brilliants from the holders. These two diamonds demonstrated practically the same PL and OT spectra. The spectra of one of these samples are shown in Figs.5 a and b, curves 1. A luminescent band-A with the maximum at 440 nm was dominant in the PL spectrum. To the best of our knowledge, the band-A is a recombination emission on extensive intrinsic defects of a diamond crystal structure, therefore it is observed in the samples produced by different methods of synthesis [27-30]. Earlier it was suggested that the band-A of luminescence in natural diamonds is due to dislocations [28]. However, not all dislocations luminesce, and there is no clear correlation between the dislocation type and its emission ability [28, 29]. Later it was reported for CVD diamonds that the band-A and amorphous carbon are related [30], amorphous carbon being concentrated on the crystallite grain boundaries [31]. Amorphous carbon is present both in natural and HPHT diamonds.

It is clear from Fig.5a, curve 1 that in the case of PL excitation at 222 nm, a vibronic absorption N3 system with a zero-phonon line (ZPL) at 415.2 nm and phonon replicas in the 350-410 nm range is superimposed on the luminescent band-A. However, for PL excitation at 308 nm (Fig.1) the vibronic luminescence N3 system with ZPL at 415.2 nm and phonon replicas in the 420-460 nm range was superimposed on the luminescent band-A.

It is well known that the vibronic N3 system is due to nitrogen N_3V -defects, which are three nitrogen atoms in the (111) plane "bonded" with a common vacancy [4]. The N_3V -defects show no Yahn-Teller effect [32], therefore are observed both in the luminescence and OT spectra, being a mirror-like reflection around the ZPL. In the OT spectrum of the sample, the N3 system is manifested as an absorption band with the ZPL at 415.2 nm and phonon replicas in the 350-410 nm as is shown in Fig.

5b, curve 1. In accordance with [5], the concentration of the N_3V defects in the sample can be estimated to be $\sim 3.5 \cdot 10^{18} \text{ cm}^{-3}$. The OT spectrum demonstrated a secondary absorption below ~ 308 nm due to the presence of nitrogen N_2 -centers (two substitutional nitrogen atoms in the neighboring lattice sites). In conformity with [33], the N_2 -center concentration is $\sim 2.4 \cdot 10^{20} \text{ cm}^{-3}$ in the sample.

The N3 system luminescence intensity is in inverse dependence on the N_2 -center concentration [18], i.e. the latter caused quenching of the N_3V -center luminescence. Indeed, as is obvious from Fig.1, the ZPL intensity at 415.2 nm was not high under excitation at 308 nm. That is, the N3 system intensity is weak in the stone. Under excitation at 308 nm, PL occurs from the entire crystal volume, and the N3 system is detected. But under excitation at 222 nm, PL occurs from a $\sim 65\text{-}\mu\text{m}$ layer (see Fig.2). Propagating through a 5-mm sample layer, the N3 system and band-A emission are weakened by the N_3V -centers in the 350-420 nm range. As a result, we observed the luminescent A-band band with a superimposed absorption N3 system in the PL spectrum of the Ia-type sample shown in Fig.5a, curve 1.

Figure 5a, curve 2 shows the PL spectrum of a natural IIa-type diamond sample cut like a plane-parallel disk of $\varnothing 5 \times 0.25 \text{ mm}^3$. The band-A is dominant in the spectrum and the N3 system of luminescence is observed clearly. The PL spectrum shape of the sample is similar to that observed in [34] for the sample. The PL intensity for the sample was 10 times lower than that of a faceted Ia-type sample, therefore the PL spectrum of the diamond disk was multiplied by a factor of 5 for the sake of comparison. The estimated concentrations of N_s - and N_2 -centers are not high ($< 10^{18} \text{ cm}^{-3}$) and the fundamental absorption edge is observed at 225 nm (Fig.5b, curve 2). In addition, no N3 system is observed in the OT spectrum of the IIa-type sample, which points to a low concentration of the N_3V -defects ($< 10^{17} \text{ cm}^{-3}$). The other IIa-type samples demonstrated similar OT spectra, and band-A, and ZPL at 415.2 nm of different intensity.

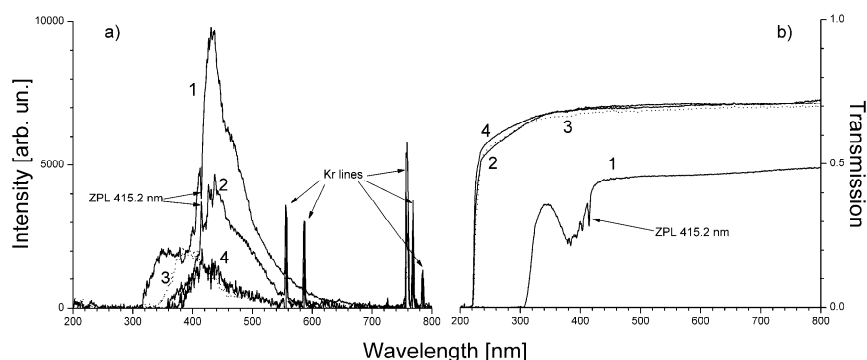


Fig.5. a) PL and b) OT spectra of natural and synthetic diamonds. Lamp – KrCl-excilamp at 222 nm. 1 – natural faceted Ia-type diamond, 2 – natural IIa-type diamond, 3 – CVD diamond of 0.5 mm thickness, 4 – CVD diamond of 0.1 mm thickness.

Note that under PL excitation by a KrCl-excilamp at 222 nm, all natural samples show the intensive luminescent band-A. The Ia-type samples show no N3 system in the PL spectra, but show it in the OT spectra. However, the IIa-type samples demonstrated a contrary situation, i.e. showed the N3 system in the PL, but no such system in the OT spectrum. In addition, under PL excitation by a KrCl-excilamp at 222 nm, a short-wavelength band was observed in the PL spectra of the Ia-type samples in the 320-380 nm range with the maximum at 350-360 nm (~ 3.5 eV), whereas this short-wavelength band was not observed in the PL spectra of the samples of the Ia-type under excitation by a XeCl-excilamp at 308 nm. Nor was it observed in the IIa-type diamond samples examined.

The band at ~ 3.5 eV is attributed to boron impurity in diamonds [4,5,27,35]. It was observed in natural [4,27] and HPHT [4,35] diamonds. According to [5], boron is present in all natural diamonds, but at high nitrogen concentrations, boron is overcompensated, and no band at ~ 3.5 eV is observed. For this band to appear in the luminescence spectrum of an HPHT diamond, it was necessary to perform the HPHT treatment at 1600 K [4,27] or use nitrogen getters during HPHT synthesis [35]. Therefore, clear identification of the nature of the band at ~ 3.5 eV in the PL spectrum of the Ia-type samples requires further studies.

CVD diamonds were cut like plane-parallel plates with the size $10 \times 10 \times 0.5$ mm³ and $10 \times 10 \times 0.1$ mm³. The supplier has characterized them as “electron grade” samples. The OT spectra of such CVD samples are shown in Fig. 5b, curves 3 and 4, for the samples with a thickness of 0.5 and 0.1 mm, respectively. Judging by the OT spectra, these samples correspond to the IIa-type diamonds, because they demonstrate the fundamental absorption edge at 225 nm and the total absence of evidence of highly aggregated nitrogen in the form of N₃V-defects and absorption lines of B-centers (four nitrogen atoms surrounding a vacancy, N₄V-defects) [36].

The PL spectra of the samples show a weak band-A. The spectra 3 and 4 had a 100-fold magnification for the sake of easy comparison. In contrast to natural IIa-type samples, the N3 system was not present in the PL of CVD diamonds. It is obvious that CVD diamonds contained a few nitrogen impurities. Besides, CVD diamonds were not subjected to HPHT treatment like natural or specially treated HPHT samples [8,36].

It should be noted that for a 0.5 mm thick CVD diamond a short-wavelength shift of the band-A maximum takes place by 20-40 nm with respect to its position in the natural samples spectra. For a 0.1 mm thick CVD diamond the band-A maximum position corresponded to that of the natural samples.

The cathodoluminescence (CL) spectra of the above CVD samples at normal conditions are shown in Fig. 6, curves 3 and 4, respectively. CL was excited using a RADAN-220 electron accelerator, which generated e-beams of ~ 2 ns pulse duration and with the electron-energy distribution maximum at ~ 100 keV behind the foil [37]. The measurements were performed using the same method as for measuring PL of the samples.

The CVD diamonds have demonstrated free-exciton luminescence under e-beam excitation. In so doing, the ratio of exciton line intensity to band-A intensity was $I_{ex}/I_A \approx 50$ for the 0.5 mm-thick sample and $I_{ex}/I_A \approx 12$ for the 0.1 mm-thick sample. It testifies to a higher quality of the 0.5 mm thick CVD sample. It should be noted that none of the natural samples demonstrated measurable exciton luminescence in the CL and PL spectra.

At the same time, in the PL spectra of the CVD samples shown in Fig. 5a, curves 3 and 4, the exciton lines are not practically observed. The exciton luminescence of diamonds is usually observed in the CL spectra under liquid nitrogen cooling [11,13,14] (see Fig. 6, dashed curve), because high excitation density provides a radiative path for recombination of free excitons, and low temperature decreases the influence of temperature quenching of luminescence. However, in [12], the exciton luminescence of the CVD sample was observed in the PL spectrum even at room temperature and at relatively low excitation level of a dye laser at 215 nm and 223 nm with the pulse duration ~ 2 ns and intensity on the sample 100 kW/cm² (see Fig. 7, dashed curve).

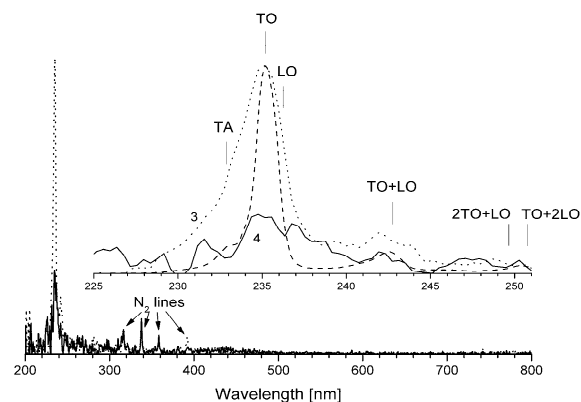


Fig. 6. CL spectra of CVD diamonds of 3) 0.5 mm and 4) 0.1 mm thickness at room temperature. Electron beam accelerator – RADAN-220 (2 ns, 180 keV). Dashed curve – CL spectrum of CVD diamond at 90 K scanned from [11].

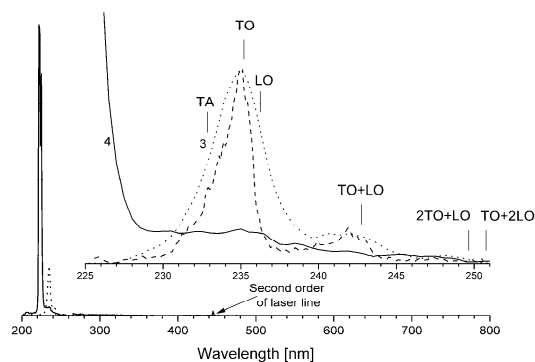


Fig.7. PL spectra of CVD diamonds of 3) 0.5 mm and 4) 0.1 mm thickness at room temperature. KrCl-laser – FOTON-2 (10 ns, 222 nm, 200 kW/cm²). Dashed curve – PL spectrum of CVD diamond at room temperature scanned from [12].

average KrCl-excilamp radiation power 50-100 mW/cm² will be sufficient for measuring free-exciton luminescence at 235 nm at room temperature.

The PL spectrum of a fianite sample under KrCl-excilamp excitation at 222 nm is shown in Fig.8a, curve 5. All examined fianites demonstrated a similar characteristic structureless PL band in the 420-700 nm range with the maximum near 500 nm [1,38,39]. The emission color was visually yellow-green. The same structureless luminescent band is usually observed only for natural IaB-type diamonds [4,5,27]. Natural diamonds of the IaB type demonstrate the fundamental absorption edge at 225 nm in the OT spectrum and characteristic bands of N₄V-defects (or B-defect) at 234.8, 235.5, 235.9, and 248 nm (N₉- and N₁₀-centers) in the OT and PL spectra [4,5,32].

However, the OT fianite spectrum shown in Fig.8b, curve 5, demonstrate only structureless band in the 300-800 nm range, which is more characteristic of the IaA-type diamonds with high concentration of N₂-defects which give rise to the secondary absorption edge at ~308 nm than of the IaB-type diamonds. Thus, the combination of the PL and OT spectra allows us to recognize diamonds from fianites with high probability.

The PL spectra of corundum samples (Fig.8a, curves 6 and 7) demonstrate emission of chrome impurity at 693 nm. Due to low intensity, the PL spectrum of pale-pink corundum was increased by a factor of 5 for the sake of convenience. The pale-pink sample demonstrated only chrome R-lines with the total contour maximum at 693 nm. The second weakly colored corundum exhibited much similar PL and OT spectra. The PL spectrum of a deep-red corundum sample was shown in Fig.8a, curve 6. In addition to R-lines, the sample demonstrated chrome S- and N-lines in the 650-690 and 700-750 nm ranges, respectively [40,41].

The absorption edge at 410 nm and the broad absorption band in the 500-600 nm range were observed in the corundum OT spectra (Fig.8b, curves 6 and 7) due to optical transitions in Cr³⁺ ions [42]. It should be noted that chrome PL lines were observed in the OT spectra of corundum samples due to high emission yield of chrome luminescence. In the OT spectra of pale-pink samples there was an absorption line of vanadium impurities at 474 nm (Fig.8b, curve 7), which points to the synthetic nature of the samples. Red luminescence of chrome impurities was observed in synthetic HPHT diamonds, which contain corundum inclusions [43]. Thus, the coloration features of corundum samples allow recognizing them easily from very rare pink-colored natural diamonds [4, 5] by means of measuring their PL and OT spectra. Perfect corundum samples are characterized by optical band gap 7 eV (~180 nm) [44] permitting their identification from the OT spectra.

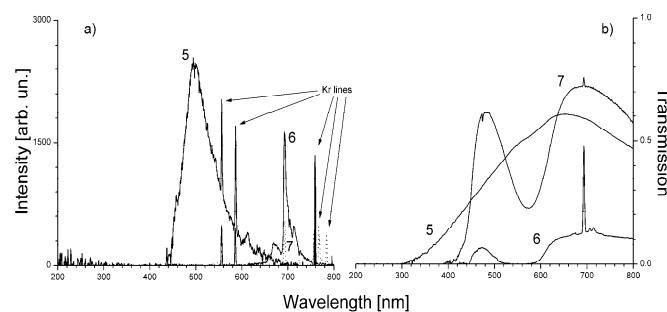


Fig.8. a) PL and b) OT spectra of fianite and synthetic corundum samples. Lamp – KrCl-excilamp at 222 nm. 5 – faceted fianite, 6 – faceted corundum of red color, 7 – faceted corundum of pale-pink color

6. CONCLUSION

Thus, the PL and OT spectra of 2 natural diamonds of the Ia type, 6 natural diamonds of the IIa type, 2 CVD diamonds, 3 fianite and 3 synthetic corundum samples were studied. Luminescence in the samples was excited by radiation of KrCl- and XeCl-excimer lamps, KrCl-laser radiation, and e-beam of a RADAN-220 accelerator.

The method for express identification of diamond and its imitators was developed on the basis of measurement and digital processing of the PL and OT spectra of the samples under consideration. It was shown that an express diamond-tester can be designed on the basis of a spectrometer and a KrCl-excimer lamp with the spectral maximum at 222 nm.

It was experimentally demonstrated that the main markers for natural diamond spectra were a luminescent band-A with the maximum at ~430 nm, a vibronic N3 system (OT and luminescence) with a ZPL at 415.2 nm, a secondary absorption edge at ~308 nm, and a fundamental absorption edge at ~225 nm. The optically transparent CVD diamonds were characterized by the fundamental absorption edge at ~225 nm, free-exciton luminescence in the 230-240 nm range, and a weak luminescent band-A with the I_{ex}/I_A ratio higher than unity.

Fianite samples are recognized by studying the PL and OT spectra due to a wide structureless OT band in the whole visible range and a yellow-green PL band with the maximum at ~500 nm. Pink-colored corundum samples are identified due to chrome PL lines in the 680-710 nm range and an OT band in the 500-600 nm range.

This work was supported by the Federal Target Program "The scientific and scientific-pedagogical personnel of Innovative Russia", State contract No. 02.740.11.0562.

REFERENCES

- [1] T. Lu, J.E. Shigley, Materials evaluation. 58 (2000) 1204
- [2] O.L. Nelson, Diamond detecting apparatus and method. U.S. Patent 6439766; S. Menashi, D. Barrett, W. Duderwick, et al. Electrical conductivity gem tester. U.S. Patent 6265884
- [3] K. Nassau, Current science. 79 (2000) 1572
- [4] A.M. Zaitsev, Optical properties of diamond, Springer, Berlin, 2001
- [5] P.P. Vecherin, V.V. Zhuravlev, V.B. Kvaskov, et al, Natural diamonds of Russia, Polyaron, Moscow, 1997 (in Russian)
- [6] A. Yelisseyev, S. Lawson, I. Sildos, et al, Diamond Relat. Mater. 12 (2003) 2147
- [7] K. Johnston, A. Mainwood, Diamond and related materials. 12 (2003) 516
- [8] S.C. Lawson, H. Kanda, K. Watanabe, et al, J. Appl. Phys. 79 (1996) 4348
- [9] C.J. Noble, Th. Pawlik, J.-M. Spaeth, Journal of physics: Condensed matter. 10 (1998) 11781
- [10] W. Wang, T. Moses, R.C. Linares, et al, Gems and Gemology. 39 (268) 2003; R. Linares, P. Doering, Diamond Relat. Mater. 8 (1999) 909
- [11] H. Kawarada, Y. Yokota, A. Hiraki, Appl. Phys. Lett. 57 (1990) 1889
- [12] K. Takiyama, M.I. Abd-Elrahman, T. Fujita, et al, Solid state communications. 99 (1996) 797
- [13] H. Kawarada, T. Tsutsumi, H. Hirayama, et al, Appl. Phys. Lett. 64 (1994) 451
- [14] P.J. Dean, E.C. Lightowers, D.R. Wight, Phys. Rev. 140 (1965) A352
- [15] V.I. Solomonov, S.G. Mikhailov, Pulsed cathodoluminescence and its application in condensed matter analysis, Publishing house of Ural Branch of Russian Academy of Science, Ekaterinburg, 2003 (in Russian)
- [16] S.G. Mikhailov, V.I. Solomonov, Opt. Spectrosc. 80 (1996) 702
- [17] T.M. Moses, I.M. Reinitz, M.L. Johnson, et al, Gems and gemology. 33 (1997) 244
- [18] E.A. Vasil'ev, V.I. Ivanov-Omskii, B.S. Pomazanskii, I.N. Bogush, Tech. Phys. Lett. 30 (2004) 802
- [19] U. Kogelschatz, H. Esrom, J.-Y. Zhang, et al, Appl. Surf. Sci. 168 (2000) 29
- [20] U. Kogelschatz, Plasma Chemistry and Plasma Processing. 23 (2003) 1
- [21] M.I. Lomaev, V.S. Skakun, E.A. Sosnin, et al, Phys. Usp. 46 (2003) 193
- [22] M.I. Lomaev, E.A. Sosnin, V.F. Tarasenko, et al, Instruments and Experimental Techniques. 49 (2006) 595
- [23] K. Iakoubovskii, G.J. Adriaenssens, Physical review B. 61 (10174) 2000
- [24] E. Gaillou, J.E. Post, Gems and gemology. 43 (2007) 352
- [25] M.S. Afanas'ev, V.B. Kvaskov, Naukoemkie tekhnologii. 1 (2003) 67 (in Russian)
- [26] J.E. Shigley, Gemmologie: Zeitschrift der Deutschen Gemmologischen Gesellschaft. 56 (53) 2007; T. Hainschwang, Gemlab. (2001)
- [27] J.F. Prins, Materials research innovations. 1 (1998) 243

- [28] S.J. Pennycook, L.M. Brown, A.J. Craven, Philosophical magazine A. 41 (1980) 589
- [29] N. Yamamoto, J.C.H. Spence, D. Fathy, Philosophical magazine B. 49 (1984) 609
- [30] D. Takeuchi, H. Watanabe, S. Yamanaka, et al, Physical review B. 63 (2001) 245328
- [31] C. Manfredotti, F. Fizzotti, A. Lo Giudice, et al, Diamond and related materials. 8 (1999) 1592
- [32] J. Walker, Reports on progress in physics. 42 (1979) 1607
- [33] W. Kaiser, W.L. Bond, Physical review. 115 (1959) 857
- [34] E.I. Lipatov, V.M. Lisitsyn, V.I Oleshko., et al, Russian physics journal. 50 (2007) 53
- [35] S.C. Lawson, H. Kanda, H. Kiyota, et al, J. Appl. Phys. 77 (1995) 1729
- [36] K. Iakoubovskii, I. Kiflawi, K. Johnston, et al, Physica B. 340-342. (2003) 67-75
- [37] E.Kh. Baksht, I.D. Kostyrya, E.I. Lipatov, et al, Technical Physics. 52 (2007) 489
- [38] N.G. Petrik, D.P. Taylor, T.M. Orlandoc, J. Appl. Phys. 85 (1999) 6770
- [39] M.E. Kompan, Yu.M. Bakov, B.A.-T. Melekh, et al, Physics of Solid State, 12 (2002) 1263
- [40] V.I. Solomonov, S.G. Mikhailov, A.M. Deikun, Opt. Spectrosc. 80 (1996) 447
- [41] E.I. Lipatov, V.F. Tarasenko, V.M. Orlovski, et al, Technical physics letters. 31 (2005) 231
- [42] Y. Aoki, N.T. My, S. Yamamoto, et al, Nuclear instruments and methods in physics research B. 114 (1996) 276
- [43] J. Lindblom, J. Hölsä, H. Papunen, et al, American Mineralogist. 90 (2005) 428-440
- [44] V.V. Sobolev, A.I. Kalugin, V.Val. Sobolev, et al, Physics of Solid State, 12 (2002) 870