

Use of spectroscopic methods for determination of diamond origin and treatment

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AGEOS Použitie spektroskopických metód na určenie pôvodu a úprav diamantov

Abstract: Eleven brilliant cut yellow and brown diamonds were studied by non-invasive spectroscopic methods and devices. At first, identification was proven by Raman spectroscopy according to presence of Diamond Raman band at ca. 1330 cm⁻¹ in each sample. UV/Vis/NIR spectroscopy was used as a potential tool to determine the diamond type. All studied stones were classified based on the presence of N3 – zero phonon line at 415 nm attributed to diamond Ia type which is the most abundant type in natural diamonds. This type consists of N atoms surrounding a vacancy. It suggests that diamond structure contains domains of type IaB diamond. Consequently, on the basis of type was excluded synthetic origin of the samples because this type was already not prepared artificially. Using Raman and UV/Vis/NIR spectroscopy, defects in diamond structure were detected and HPHT treatment was also determined. The main observable defects include N-V⁰ at 575 nm, N-V⁻ at 638 nm, N3 at 415 nm, and H3 at 503 nm. The presence of these defects can be main indicator in HPHT treated stones. Only two studied samples significantly displayed all of these defects attributed to HPHT treatment, but other samples also showed tracks of treatment. This gemmological investigation results in estimating the original most likely brown diamond colour and probably intermediate temperature during HPHT processing.

Keywords: diamonds, identification, „Type“ classification, origin, HPHT treatment, UV/Vis/NIR spectroscopy, Raman spectroscopy

1. INTRODUCTION

Diamonds are unique gemstones which consist of one major element – carbon. It is the only gemstone on which discolouration is appreciated although diamonds can have wide variety of colours. It can be red, pink, blue, green, yellow, brown or black due to impurities or colour centres but pure, only carbon-bearing diamond without any of them is colourless. Pink and red colour is due to plastic deformation of the diamond structure which can result in displacement of the carbon atoms along glide planes (Fritsch et al., 2007b; Shigley & Fritsch, 1993). Purple also results from plastic deformation (Titkov et al., 2008). Blue colour is caused by boron impurities (Pagel-Theisen, 2010). Brown diamonds typically contain nitrogen impurities and graining associated with deformation of the diamond structure (Massi et al., 2005). Black to grey diamonds contain micro-inclusions of dark minerals such as graphite, magnetite, hematite, and native iron (Titkov et al., 2003). Green coloured diamonds are produced by irradiation. Surface “staining” of natural diamonds is commonly caused by the interaction of radioactive alpha and beta particles with the diamond surface, producing a green-coloured diamond (Kane et al., 1990). Chameleon diamonds change colour, from grey-green to yellow, with a change in temperature (thermochromic behaviour) or with a change in light exposure (photochromic). These diamonds contain high concentrations of hydrogen along with some nitrogen and nickel (Fritsch et al., 2007a).

Most of natural diamonds are nitrogen bearing with yellow, yellow-green or brown-yellow colour. In commercial assessment, these yellow coloured diamonds are assigned to a group of colourless diamonds and are referred as group “Cape” (colour grade from D to Z according to GIA – Gemological Institute of America – grading system). Coloured diamonds are well-known under the “fancy colours” trade name (Pagel-Theisen, 2010).

Compared to coloured diamonds, slightly or deep yellow stones are much more common. Fancy coloured, especially with very vibrant colours, and absolutely colourless diamonds are very rare in the nature and consequently extremely expensive (Pagel-Theisen, 2010). Less valuable diamonds (pale yellow, brown) are artificially treated with several colour-changing methods and procedures such as irradiation, HPHT (high pressure, high temperature) treatment with intent to get colourless or fancy coloured stones. These are better marketable, saleable and valuable because diamond colour is the one of the four important parameters which determines its market value (Collins, 2003).

Nowadays, the production of synthetic and treated diamonds by several methods increases. For example rare fancy coloured canary yellow diamonds are far more valuable than pale yellow stones. Permanent changes in the colour of diamond may be produced by radiation damage and annealing, or by HPHT processing. Permanent colour changes should not be altered by temperatures used in fashion jewellery, or by illumination with daylight or bright artificial light (Collins, 2003).

The aim of this study is to identify faceted stones, then if they are positively identified, to determine the type of individual eleven diamonds, recognize the origin of the samples and subsequently detect possible treatments by spectroscopic methods and devices. The analytical determination of enhancement is important because various treatments are almost routinely performed on diamonds. These treated diamonds are usually sold by retailers as non-treated. Detection of this fraud leads to discovery of retailer's moral credit and helps to reduce the price of diamonds.

2. CAUSES OF COLOUR IN DIAMOND AND THE "TYPE" CLASSIFICATION

Diamonds are divided into two types depending on two dominant chromophores. The "Type" classification of diamonds is based on the presence or absence of nitrogen and boron; nitrogen is the most common impurity in diamond (Breeding & Shigley, 2009).

Type I diamonds are defined as containing sufficient N to be measurable by IR (infrared) absorption spectroscopy, whereas type II diamonds do not contain enough N to be detected by this method (Breeding & Shigley, 2009). Diamonds of the type I contain much more nitrogen than type II (40 ppm) (Pagel-Theisen, 2010). Type I diamonds are subdivided into type Ia and type Ib based on the way how nitrogen is dispersed throughout the crystal structure (Fig. 1). In type Ib diamonds, single nitrogen atoms that have replaced carbon atoms in the structure are isolated from one another, they do not occur in adjacent structural positions (Fig. 1). These N impurities are called C centres (Breeding & Shigley, 2009). Type Ib diamonds account for less than 0.1 % of all jewel diamonds, these diamonds are yellow, canary yellow and brown (Pagel-Theisen, 2010). In contrast, type Ia (Fig. 1) diamonds contain N atoms that are in close proximity to one another in one of two spectroscopically detectable configurations. The most common

configuration for type Ia diamonds involves two N atoms adjacent to each other in the structure. Although these two atoms occupy neighbouring sites, each pair is isolated from other N atoms in the structure. These N impurities are commonly referred as A centres, and the diamonds that contain them are termed type IaA (Fig. 1). The other configuration involves four N atoms that symmetrically surround a vacancy. This complex grouping is formed when two A centres combine. These N impurity groupings are called B centres, and the associated diamonds belong to type IaB (Fig. 1) (Breeding & Shigley, 2009). Ninety-eight % of all natural diamonds suitable for jewellery are type Ia and are known as "Cape series", they can appear colourless, near-colourless, yellow or brown (Pagel-Theisen, 2010). Other arrangements of N atoms can also occur but they are not included in the diamond type classification system (Collins, 1982, 2001).

Type II diamonds are divided into subtypes IIa and IIb (Fig. 1). Diamonds of type II make up approximately 2 % of all diamonds (Pagel-Theisen, 2010). Type IIa (Fig. 1) diamonds contain no easily measurable N or boron impurities (Breeding & Shigley, 2009). They are usually colourless, near-colourless, brown, and pink (Pagel-Theisen, 2010). Natural type IIb (Fig. 1) diamonds likewise contain no IR-measurable N impurities. Instead, type IIb diamonds contains boron impurities that are thought to be isolated single atoms that replace carbon in the diamond structure. Characteristic properties of type IIb diamonds, such as electrical conductivity, are a direct result of the boron impurities (Breeding & Shigley, 2009). The IIb diamonds make up 0.1 % of all jewel diamonds and are usually blue and grey (Pagel-Theisen, 2010).

3. HPHT TREATMENT

The HPHT treatment of diamonds is a method that is used to remove or induce colour. It can be applied to brown coloured

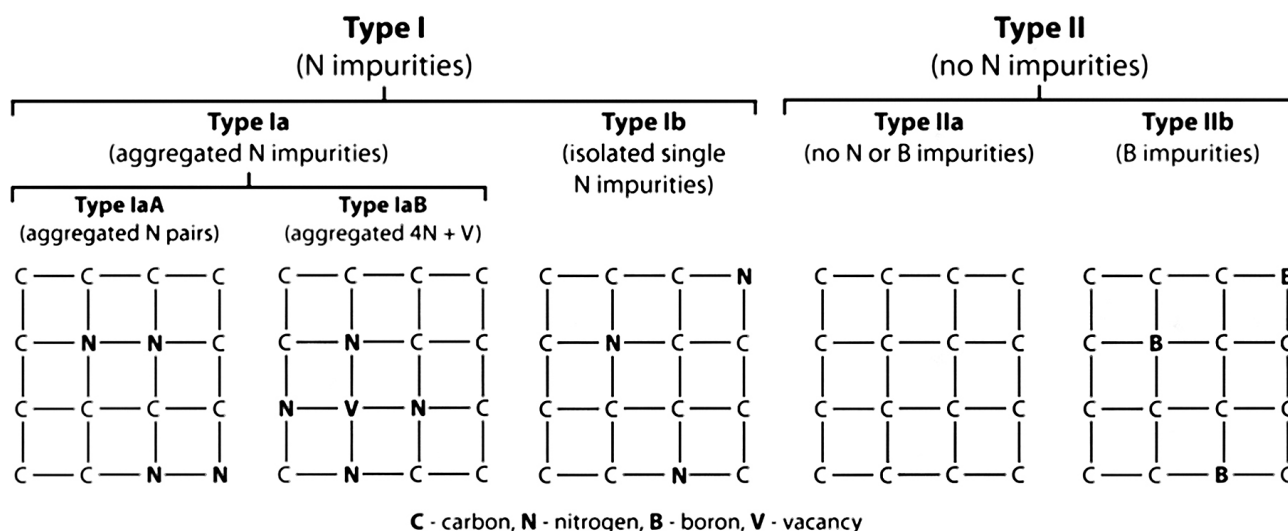


Fig. 1. The "Type" classification of diamonds (modified after Breeding & Shigley, 2009).

Obr. 1. Typová klasifikácia diamantov (upravené podľa Breeding & Shigley, 2009).

Tab. 1. Main colour changes induced by HPHT treatment (modified after Fisher, 2009).

	Temperature	Diamond type			
		Type IIa	Type IIb	Type IaAB	Type IaB
Starting colour		Brown	Brown/gray	Brown	Brown
Colour after HPHT treatment	Intermediate	Pale brown or pink		Yellow/green	Near-colourless
	High	Colourless	Blue	Yellow/orange	Yellow

Tab. 1. Zmeny farieb vplyvom použitia HPHT procesu (upravené podľa Fisher, 2009).

type I and II diamonds (Fisher, 2009). In 1999, General Electric Co. and Lazare Kaplan International announced the commercial application of an HPHT process for faceted diamonds (Pegasus Overseas Limited, 1999) that removed colour from brown type IIa stones; IIa diamonds of any size could be transformed to a colourless stone (Fisher, 2009; Smith et al., 2000). After HPHT treatment, the majority of these diamonds received D through G colour grades – exceptional white + to rare white according to CIBJO (World Jewellery Confederation) rules (Tab. 1), and the results were permanent (Moses et al., 1999).

Refinements to HPHT processing have yielded commercial production of variable colours in both type I (orange yellow, yellow, to yellow green) and type II (pink or blue) diamonds

(Shigley, 2008; Fisher, 2009) (Tab. 1). In type IIa brown diamond before HPHT, plastic deformations results in abundant distorted and broken carbon bonds and associated vacant structural sites concentrated along bands of brown colour (Fig. 2a). HPHT treatment heals structural distortions and broken bonds, releases vacancies, and thus removes brown colour in graining, leaving only remnant colourless internal graining that is common in HPHT treated diamonds (Fig. 2a). IIa brown diamonds contain no impurities; vacancies migrate through the diamond structure, until they are eliminated by recombination with an interstitial C atom during HPHT annealing. No new colour centres are formed. Type Ia diamond contains nitrogen impurities and structural distortion due to strain causing brown

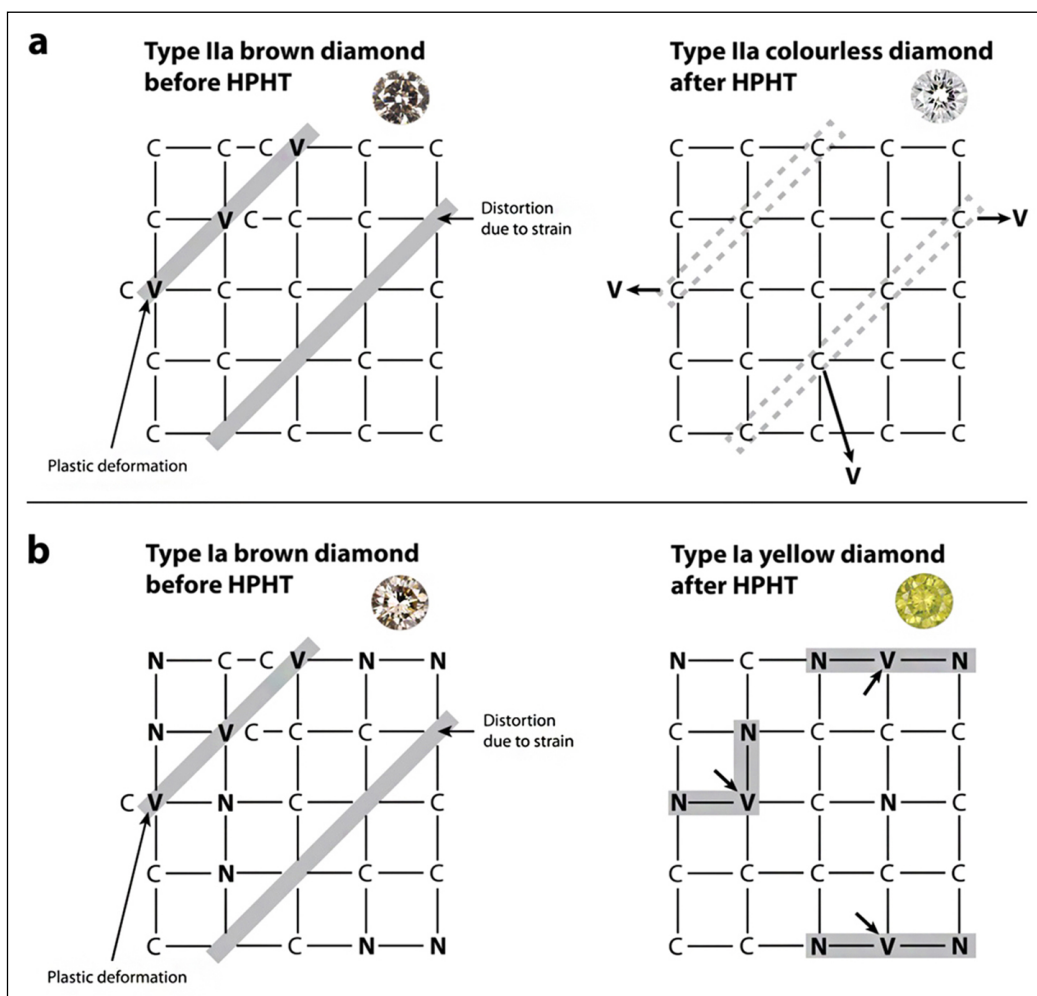


Fig. 2. The effect of HPHT treatment according to diamond type (modified after Breeding & Shigley, 2009). Grey fields highlight colour centres. **Obr. 2.** Vplyv HPHT úpravy na jednotlivé typy diamantov (upravené podľa Breeding & Shigley, 2009). Sivé plochy reprezentujú farebné centrá.

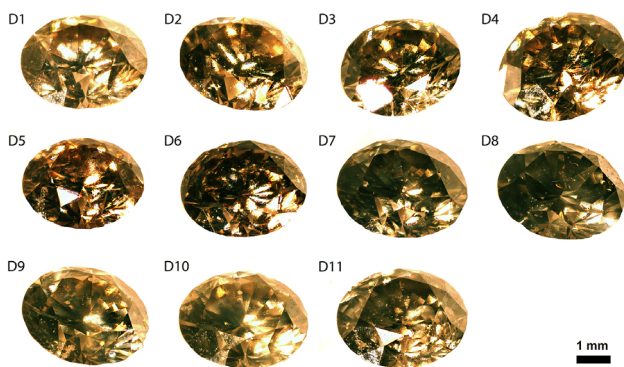


Fig. 3. Macrophoto of studied diamond samples in visible light.

Obr. 3. Makrofotografia študovaných vzoriek diamantov vo viditeľnom svetle.

graining (Fig. 2b). As vacancies migrate through the diamond structure during HPHT annealing, they are trapped by aggregated N impurities (A centres) to form H3 defects (N-V-N)⁰. Some aggregated N breaks down to release isolated N atoms at high temperatures. The combination of H3 defects and isolated nitrogen imparts a yellow colour to the diamond. If abundant N occurs adjacent to the original brown graining, H3 defects will become concentrated along the formerly brown grain lines and will appear as treated yellow graining (Fig. 2b) (Breeding & Shigley, 2009).

4. EXPERIMENTAL AND ANALYTICAL METHODS

All 11 studied samples were brilliants (round faceted diamonds) and could have been analysed only by non-destructive and non-invasive methods because they are expensive and valuable. Faceted gemstones are usually analysed by spectroscopic devices which satisfy the requirements of non-destructivity. The analysed spectra are random because it was not possible to orientate faceted sample specifically to the crystallographic axis.

UV/Vis/NIR (ultraviolet/visible/near-infrared) spectra of cut stones in region (300–1000 nm) were measured on Jasco V-530 apparatus at room temperature on the Department of Inorganic Chemistry, Comenius University in Bratislava.

Raman analyses were performed on LabRAM-HR Evolution (Horiba Jobin-Yvon) spectrometer system with Peltier cooled CCD detector and Olympus BX-41 microscope (Masaryk University, Department of Geological Sciences). Raman spectra were excited by diode (532 nm) laser. Silicon wafer (520.6 cm⁻¹) was used for spectral calibration. Spectra in the range of 500–6000 cm⁻¹ were collected from each brilliant cut with table oriented perpendicular to the polarisation of the laser using 100× objective. The acquisition time of 3 s per frame and 5 accumulations were used to improve signal-to-noise ratio.

Both Raman and UV/Vis/NIR spectra were processed in Seasolve PeakFit 4.1.12 software. Raman and absorption bands

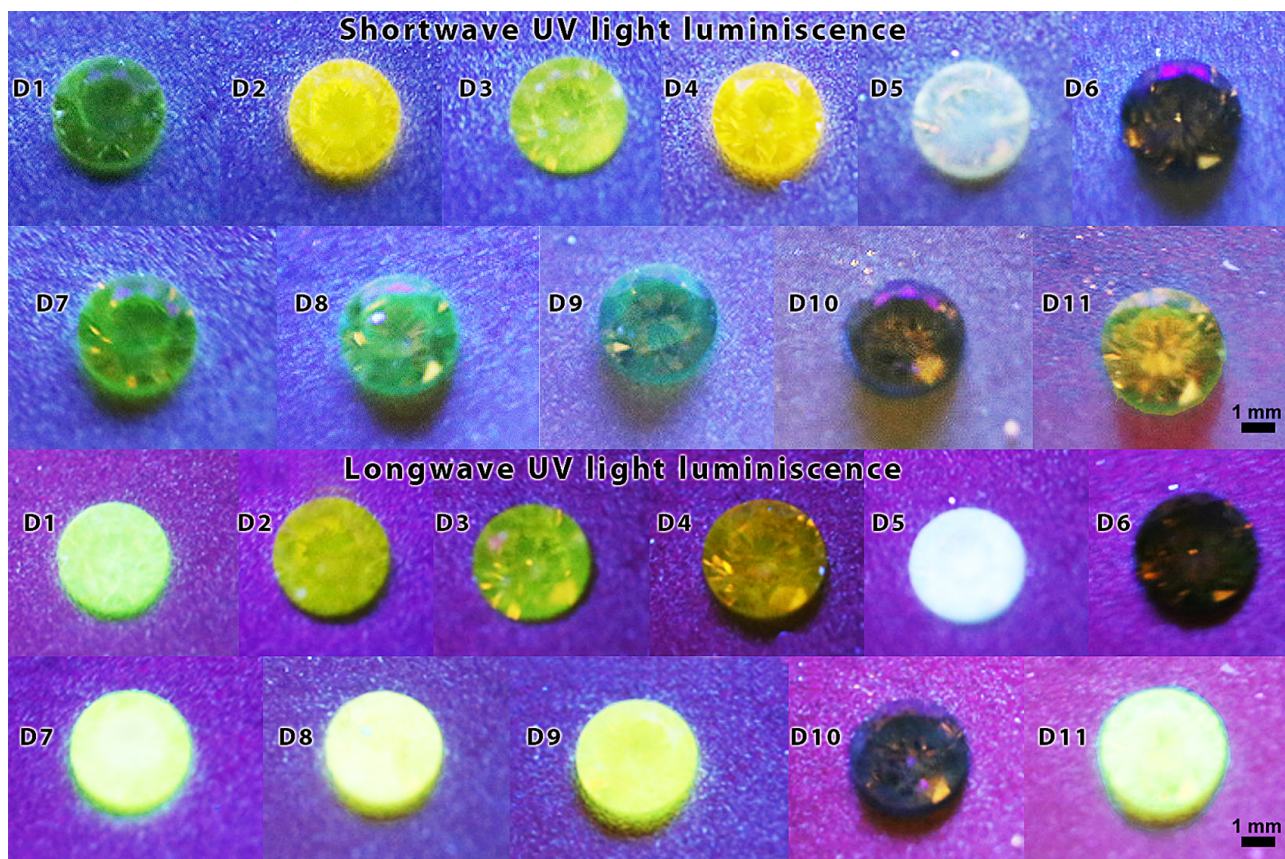


Fig. 4. Luminescence of studied diamond samples in UV light: a) shortwave; b) longwave.

Obr. 4. Luminescencia študovaných vzoriek diamantov v UV svetle: a) krátkovlnnom, b) dlhovlnnom.

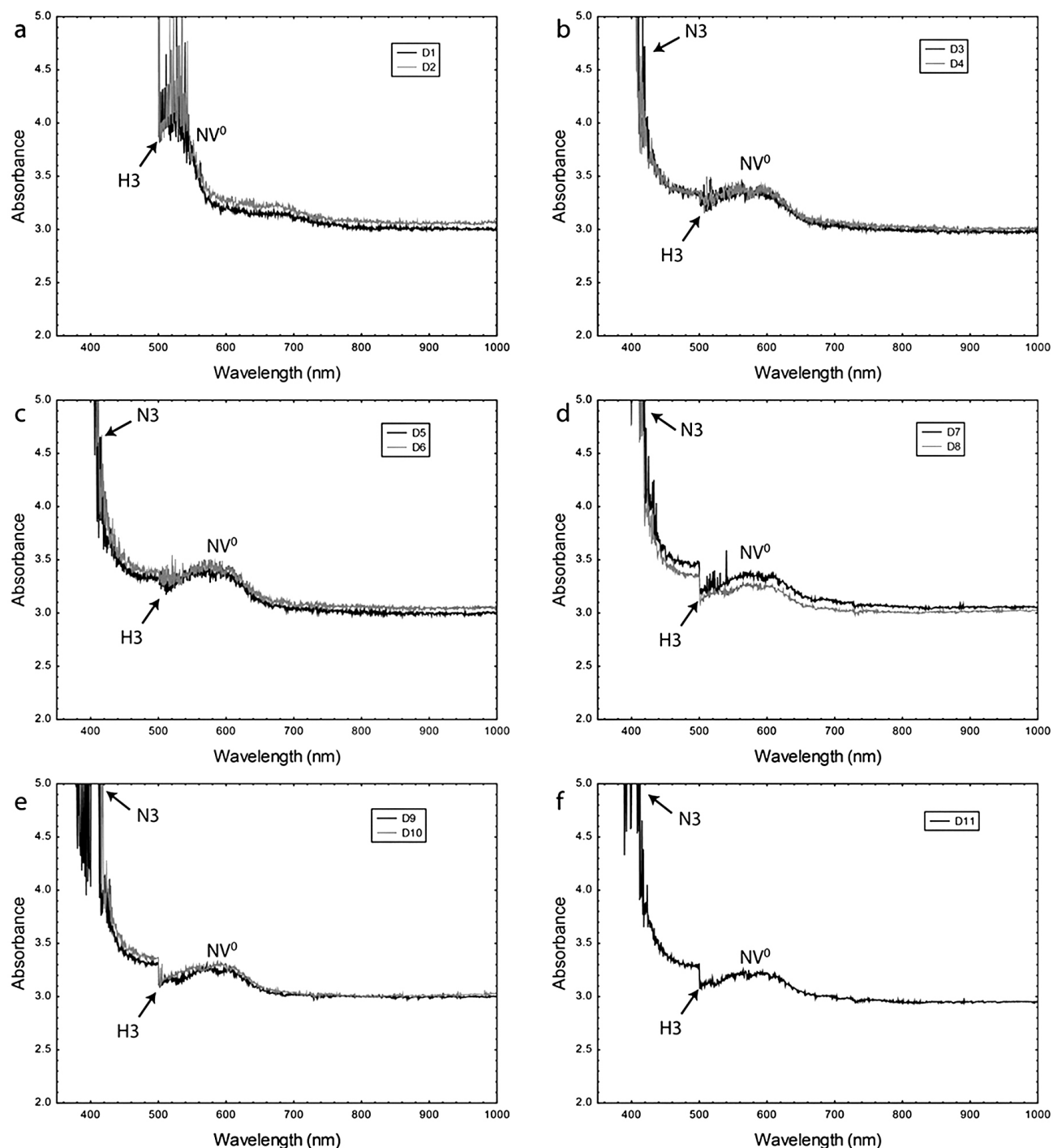


Fig. 5. UV/Vis/NIR spectra of studied diamonds.

Obr. 5. UV/Vis/NIR spektrá študovaných diamantov.

were fitted by Gauss function with the automatic background correction.

5. RESULTS

All studied brilliants had a diameter about 3.5 mm to 4 mm. Their colour was pale to medium yellow-green except two samples D6 and D10 which were light brown (Fig. 3). The best

observable clarity was observed in D8 and D9 brilliants – VVS, samples D1, D2, D7 and D11 had VS clarity. SI clarity was assigned to D3 and D4 samples and the poorest clarity – P1 was exhibited in D5, D6 and D10. Clarity was graded under 10 × magnification.

Luminescence was observed in both shortwave (SW – 254 nm) and longwave (LW – 365 nm) UV light (Tab. 2) (Fig. 4). Six samples exhibit weak yellow to yellow-green luminescence in SW, five of them had strong yellow and one

Tab. 2. Colour of UV light luminescence in studied samples.**Tab. 2.** Farba luminiscencie študovaných vzoriek v UV svetle.

	Shortwave (254 nm) UV light luminescence	Longwave (365 nm) UV light luminescence
D1	weak yellow-green	strong yellow
D2	strong yellow-orange	yellow-orange
D3	yellow-green	yellow-orange
D4	strong yellow-orange	yellow-orange
D5	weak yellow-green	chalky blue
D6	none	none
D7	weak yellow	strong yellow
D8	weak yellow	strong yellow
D9	weak yellow	strong yellow
D10	none	none
D11	weak yellow	strong yellow

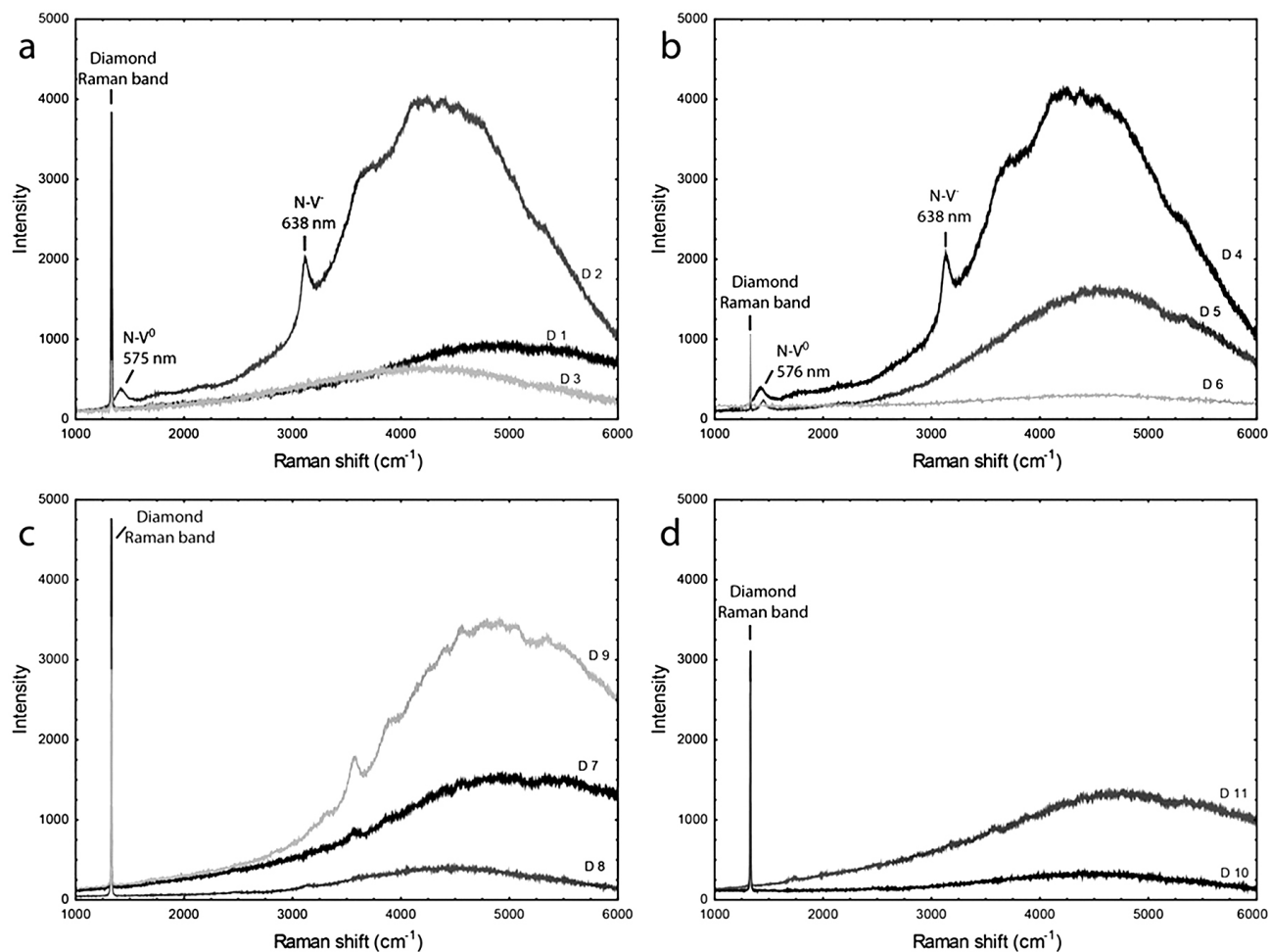
had chalky blue luminescence in LW. Strong yellow luminescence was observed in two samples in SW and one had slightly weaker yellow-green luminescence. These displayed

significantly weaker luminescence in LW. Only two diamonds were inert in UV.

5.1. UV/Vis/NIR spectroscopy

All of the diamonds optical spectra are almost similar. Three main absorption bands N3 (415 nm), H3 (503 nm) and NV⁰ (575 nm) were observed (Fig. 5).

Zero phonon line N3 indicated that all of the studied diamonds are type Ia although it was not observed in D1 and D2 samples (Fig. 5a). This resulted from strong absorption effect of H3 feature. However, the progress of both spectra with similar features to other samples suggests that N3 band is also present in the part of spectra which is not observable due to strong absorption. This line – 415 nm is also not clearly visible in D7–D11 samples (Fig. 5d–f) in which light scattering on the surface of facets results in weakening of light delivered from sample to the detector. It was manifested by an excessive absorption increase in the UV region. However, the absorption increase between 400 and 420 nm surrounded by the absorption decrease between 390 and 400 nm and in area from 420 nm to higher wavelength could be likely referred to the zero phonon line (415 nm), although we do not have the entire

**Fig. 6.** The Raman spectra of studied diamonds.**Obr. 6.** Ramanové spektrá študovaných diamantov.

absorption band. In D3–D6 samples the N3 band is relatively well observable (Fig. 5b,c).

The luminescence and absorption effect of H3 defect was observed in all samples but with different intensity. It was the most pronounced in D1 and D2 samples (Fig. 5a), medium in D7–D10 samples (Fig. 5d,e) and the weakest in D3–D6 samples (Fig. 5b,c). Broad band of NV⁰ defect was present in all studied spectra (Fig. 5). However, all differences in spectra could be attributed to measurement procedures more than to variability in samples which in fact can be structurally very similar.

5.2. Raman spectroscopy

We have chosen Raman spectroscopy because it is relatively common method used to identify faceted gemstones. Diamond Raman band is visible in each sample at 1330 and 1331 cm⁻¹ (573 nm) depending on individual sample (Fig. 6). D1, D3 (Fig. 6a), D6 (Fig. 6b), D7, D8, D9 (Fig. 6c), D10, D11 (Fig. 6d) samples are characterized only by Diamond Raman band without any specific photoluminescence features. However, there was wide photoluminescence band between 3000–6000 cm⁻¹ with interference effects displayed in D1, D3, D7, D8, D9, and D11 spectra, only D6 and D10 had relatively narrow progress. Two samples D2 and D4 were very similar (Fig. 6a,b). D2 (Fig. 6a) exhibited two other additional bands – N-V⁰ at 1417 cm⁻¹ (575 nm) and N-V⁻ at 3125 cm⁻¹ (638 nm). D4 (Fig. 6b) had similar photoluminescence artefacts at 1422 cm⁻¹ (576 nm) N-V⁰ and 3130 cm⁻¹ (638 nm) N-V⁻. In contrast, D5 (Fig. 6b) exhibited, along with main Diamond Raman band, only one photoluminescence band at 1450 cm⁻¹ which can be attributed to 576 nm (NV⁰).

6. DISCUSSION & CONCLUSIONS

In the gemmological research, non-destructive gemstone identification is the primary procedure. In our case, stones were identified by Raman spectroscopy and subsequently the diamond type was determined to specify the origin of samples and to better understand crystal-chemical properties of studied diamond structure. Determination of the type was provided by UV/Vis/NIR spectrometer which gives the most comprehensive data but there are several other devices and methods which are applicable to gain required result including DiamondSure (Welbourn et al., 1996), SSEF Type II Diamond Spotter (Boehm, 2002; Hänni, 2002), short-wave UV transparency, strain patterns, electrical conductivity (Breeding & Shigley, 2009). In consequence, the further step was the detection of possible treatments. Raman spectroscopy was also used for this purpose.

6.1. Identification and origin

Identification was established on the presence of Diamond Raman band (Knight & White, 1989) at about 1330 cm⁻¹ which is attributed to 573 nm (Fig. 6) in all samples. Slight shifts in the frequency of the Diamond Raman band occur depending on several factors including origin of the diamond and perfection

of the diamond structure (Huong, 1992). Frequency and width of this band is also temperature-dependent (Liu et al., 2000).

We may exclude synthetic origin of studied samples. There are two main processes to synthesize diamond: (1) HPHT process, which uses high pressure and high temperature, and (2) CVD (chemical vapour deposition) process which is based on chemical vapour deposition. Almost all of HPHT-grown synthetic diamonds are type Ib and CVD diamonds are most commonly type IIa. Occasionally, both HPHT and CVD growth techniques can produce IIB synthetic diamonds (Breeding & Shigley, 2009). On the basis of UV/Vis/NIR spectroscopy we determined the type of all studied samples as Ia which is the most common type in natural samples. As the main indicator the N3 absorption band at 415 nm – zero phonon line (Fig. 5) occurring only in Ia diamond type was used. N3 absorption band is caused by the presence of aggregated nitrogen in the diamond structure. This defect consists of three nitrogen atoms surrounding a vacancy (Breeding & Shigley, 2009). Moreover, the presence of N3 absorption band in studied samples suggests that their structure contains domains of Type IaB diamond.

6.2. Treatment detection

The final colour of almost all studied diamonds is yellow-green. Only two samples D6 (Fig. 6b) and D10 (Fig. 6d) are brown. When a type I brown stone is subjected to HPHT treatment conditions, the presence of N impurities results in the change to various shades of yellow (Breeding & Shigley, 2009). Fisher & Spits (2000) report that diamonds exposed to HPHT treatment commonly display band at 638 nm (NV⁻) and its neutrally charged counterpart at 575 nm (N-V⁰). The NV⁰ defect consists of a nitrogen atom adjacent to a vacancy and it has a neutral charge, NV⁻ also consists of a nitrogen atom adjacent to a vacancy but it is in a negative charge state (Breeding & Shigley, 2009).

In the D2 (Fig. 6a) and D4 (Fig. 6b) samples, N-V⁰ at 575 nm and N-V⁻ at 638 nm were significantly exhibited; other samples did not show these significant bands. However, while commercial treatment temperatures generally destroys N-V defects, new ones may be formed depending on original concentration of single nitrogen defects and vacancy clusters in the stone (Dobrinets et al., 2013). Most of natural diamonds are mixed type e.g. type Ia may contain a low single nitrogen content in the structure (Collins et al., 2005). Therefore, both treated and untreated diamonds may contain N-V defects. Sometimes 638 nm band can be very strong in HPHT treated stones. Typical spectra of HPHT-treated diamond show only Diamond Raman band and possibly N-V defects at 575 nm and/or 638 nm. Strong 638 nm band is a typical product of originally highly dislocated (darker brown) diamond. It is important to note, that some of the treated stones do not reveal any photoluminescence bands. Some of the stones can exhibit only a solitary band in the 560–580 nm range which is also an indicator of treatment (Dobrinets et al., 2013). This could be the case of D5 sample (Fig. 6b) which showed only one photoluminescence artefact at 1450 cm⁻¹ (576 nm). All of the studied samples showed absorption bands N3 at

415 nm, H3 at 503 nm and broad band at about 550 nm in UV/Vis/NIR spectra (Fig. 5); this is consistent with observation of Reinitz et al. (2000) according to which spectra of HPHT treated stones show weak absorption at the N3 band (415 nm), strong absorption at H3 band (503 nm) and a weak to moderate broad band centred at 550 nm. H3 band at 503 nm is an uncharged defect consisting of two nitrogen atoms separated by a vacancy [i.e., (N-V-N)⁰]. H3 absorption alone creates yellow colour and the defect can also produce green luminescence in response to illumination (Breeding & Shigley, 2009). Most of our studied stones exhibited yellow luminescence except two D6 and D10 samples. Broad band at 550 nm is poorly understood and thought to be associated with plastic deformation of the diamond structure. This is the most common defect that produces pink-to-red colour in natural diamonds but it is also common in brown stones (Breeding & Shigley, 2009).

On the basis of study by Raman spectroscopy we can conclude that samples D2 and D4 significantly displayed tracks of HPHT treatment, other samples did not show convincing evidence but absorption spectra, colour and luminescence may prove that most of the samples were heavily treated. We can estimate on the basis of final colour (Tab. 1) that the operating temperature during HPHT processing was intermediate and original colour of samples was brown (Fisher, 2009). In D6 and D10 samples no photoluminescence bands in Raman spectra were observed and they were also inert to UV light. Moreover, their colour is not yellow-green but brown hence these two samples appear to be non-treated or alternatively, it was not possible demonstrate the treatment using applied methods.

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