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The origin of color in natural C center bearing diamonds

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ABSTRACT

The properties of 152 natural diamonds with C centers – detectable by the absorptions at about 1344 and/or 2688 cm^{-1} in the infrared spectra – were analyzed in order to better understand their origin of color. While such diamonds are generally thought to be yellow, type Ib natural diamonds are usually not so, but mainly orange-yellow, orange, brown, 'olive' (a mixture of yellow with brown and/or gray with always a greenish component) and mixtures thereof. The only natural diamonds found to be of pure yellow coloration were – with very few exceptions – type IaA diamonds with a very minor Ib component, of cuboid–octahedral growth, often so-called re-entrant cubes. This was verified by the analysis of over 70,000 bright yellow and over 20,000 yellow-orange melee diamonds (i.e. diamonds weighing less than 0.20 cts) submitted for testing at the laboratory.

In natural type Ib diamonds of octahedral growth the color is strongly influenced by vacancy-related defects that originate mainly from plastic deformation; natural type Ib diamonds of regular octahedral growth generally show distinct deformation-related strain and often some associated color zoning or 'colored graining' along octahedral planes. None of the nickel-rich, C-center-containing natural diamonds included in this study showed any specific Ni-related absorption band in the visible range spectrum that had an influence on color.

The "olive" to brown color in type Ib diamonds was found to be caused by a combination of continuum absorption with increased absorbance from the NIR to about 480 nm plus distinct NV^{-} center absorption.

1. Introduction

Single substitutional nitrogen, also known as the C center, is the simplest nitrogen defect in diamond: a nitrogen atom replaces one carbon atom in the structure of diamond [1–3]. This defect is paramagnetic and hence detectable by EPR, the method by which it was first discovered in 1959 [4]. The C center is a form of nitrogen which is thought to be incorporated when diamond is formed, and aggregated into the A and B centers of nitrogen [5,6].

Diamonds are classified based on the presence/absence and form of nitrogen plus the presence of boron, as detected by infrared spectroscopy [7] and references therein. An extended version of the classification system with all its definitions has recently been presented in [8]. Diamonds characterized by dominant C center infrared absorption are known as "type Ib" [3].

C center containing diamonds are rare in nature but very common in HPHT synthetic growth [9]. HPHT synthetic diamonds grown without a nitrogen getter grow generally as type Ib with often a minor IaA component. When the nitrogen content is neither too low nor excessive and when there are no significant nickel-related defects present then such diamonds are essentially of a saturated yellow color. Saturated yellow natural samples are the so-called 'canary yellow' diamonds.

The C center defect causes absorption in the violet and blue portion of the visible spectrum due to its electron donor properties and the resulting energy level in the band gap at about 1.7 eV [10]. This generates a featureless, fairly steep absorption continuum from 560 nm towards lower wavelengths (higher energies). Because it is fairly steep, it generates a rather saturated color, mostly yellow. It may have further absorptions superimposed. The C center is responsible for a broad, complex absorption system in the infrared spectrum with its principal peak at 1130 cm^{-1} and a sharp absorption at 1344 cm^{-1} and at 2688 cm^{-1}. The peak at 1130 cm^{-1} has been attributed to a quasi-local vibration at substitutional nitrogen atoms [11]. The sharp 1344 cm^{-1} absorption is assigned to a vibration of the carbon atom at the C–N bond with the unpaired electron [12], and finally the small peak at 2688 cm^{-1} has been attributed to the first harmonic of the 1344 cm^{-1} line [8].

The color of natural dominantly type Ib diamonds contrasts often with that of synthetic diamonds of the same type. Natural type Ib stones are usually not pure bright yellow, but generally orange yellow, orange, brown, 'olive' and mixtures thereof [13]. 'Olive' is a term used by gemologists for brevity sake to name a desaturated color with always a green component, but often dominated by mixtures of yellow, brown and gray [14]. The various colors observed appear to be practically independent from the single nitrogen content, with few exceptions. This raises the

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question why such natural color type Ib diamonds exhibit these colors instead of yellow.

Then there are several varieties of gem colored diamond that have higher contents of aggregated nitrogen than C centers. Most of these are type IaA with a minor type Ib component, but there are very rare cases for which the A, B and C centers are present together naturally, the so-called "ABC diamonds" [15]. These diamonds, which are not dominantly type Ib, can vary from yellow to brown-yellow, almost the same color range as type Ib HPHT synthetics.

There are a number of natural diamonds which are strongly colored yellow to orange to brown, yet do not show any of the infrared absorptions related to type Ib at 1130, 1344 and/or 2688 cm^{-1}. Nevertheless, these show the same continuum in the visible range as described above. We name such specimens 'diamonds with Ib character'.

The indicators for a type Ib character are mainly hydrogen-related infrared absorptions that are found in C center containing diamonds only, such as the sharp bands at 3394, 3372, 3310, 3181, 3145 and 3137 cm^{-1} [16]. There are over 150 such hydrogen-related absorptions cataloged [13]. The question is then why diamonds are so strongly colored, yet there is no detectable C center signal in the infrared absorption; the C center concentration of these diamonds is far less than 1 ppm, hence it is undeterminable by infrared spectroscopy. Such low C center concentration is not sufficient to induce a strong color. To give an example a C center content of 1.5 to 2 ppm in synthetic diamonds was found to induce only a slight yellowish tinge in the O–P–Q range on the D to Z near-colorless diamond color grading scale of the GIA. We have determined that the detection limit for C centers by infrared spectroscopy is approximately 0.5 ppm as long as the aggregated nitrogen content was not high. In samples of high aggregated nitrogen content the detection limit was found to be approximately 4 to 5 ppm, based on the overtone of the 1344 cm^{-1} line at 2688 cm^{-1} [8].

The purpose of this study is to elucidate the origin of color in natural type Ib diamonds. A detailed understanding necessitates correlating color with the other optical and physical properties of these gems.

The analysis of the behavior of natural type Ib diamonds upon HPHT treatment and combined irradiation/HPHT treatment is fundamental for the understanding of defects and the color origin of these diamonds by experimental methods; therefore some important results of various treatment experiments are included in this paper.

2. Materials and methods

152 natural gem diamonds weighing 0.01 to 3.18 ct with C centers detectable with infrared absorption spectroscopy were analyzed for this study. They were selected from several reliable sources for gem diamonds in the past 15 years and 105 of them are in the collections of two of the authors (TH and FN). All of them have been tested thoroughly (by all analytical methods mentioned below) in order to assure their natural origin and natural coloration. They include type Ib diamonds of all known color groups, see Table 1 for details.

For the sake of clarity the term "type Ib" is used in this study for all diamonds exhibiting at least some 1344 cm^{-1} and/or 2688 cm^{-1} absorption. Nine of the stones were natural diamond crystals of mixed cuboid–octahedral growth (of the re-entrant cube variety [17]), five octahedral natural diamond crystals; all other diamonds were faceted into various shapes.

The color distribution and strain patterns of the diamonds were analyzed using a Leica M165C Trinocular Microscope, equipped with a Leica DFC420 CMOS camera; the color distribution was checked with the diamonds immersed in alcohol or diiodomethane, and the strain patterns were analyzed with the stones immersed between crossed polarizing filters.

The luminescence of the diamonds was observed under 254 nm shortwave and 365 nm longwave radiation from a model UVP UVSL-26P, 6 Watt UV lamp and by broad band UV using two different excitation bands (LW band: 300 to 410 nm; SW band: 200 to 300 nm) from a home-made luminescence microscope using a suitably filtered 300 Watt full spectrum Xenon lamp. Cathodoluminescence imaging was performed using a Jeol 5800 scanning electron microscope with a voltage of 12 to 20 kV and a current of a few nano-amperes.

Infrared spectra of all the samples were recorded with a resolution of 1 cm^{-1}, and for some also 4 cm^{-1}, on a PerkinElmer Spectrum 100S FTIR spectrometer equipped with a thermoelectrically cooled DTGS detector, using a diffuse reflectance accessory as a beam condenser [15]; the spectra of the crystals were recorded with a 5× beam condenser, over a range of 8500 to 400 cm^{-1}, with 100 to 1000 scans for each diamond.

The nitrogen concentration was determined by progressive spectral decomposition via spectral calculations ("progressive decomposition"). The nitrogen concentration is calculated based on the known average absorbance of the intrinsic diamond infrared feature at 1995 cm^{-1}, which has been defined by others as 12.3 absorbance units per cm of optical path [18]. All diamond spectra must be normalized before any concentration calculation can be reliably conducted. This normalization is performed by spectral calculation, for which the absorbance value of the intrinsic diamond absorption on the y axis at 1995 cm^{-1} is measured and then a multiplying factor is applied in order to obtain a value of 12.3 cm^{-1}. The spectrum is then multiplied by this factor. The method found to be the most satisfying and precise one was the progressive spectral decomposition in which the individual components (A, B, C and X centers) are subtracted from a given spectrum, using reference spectra of pure signals of the respective centers. The determination of type Ib diamonds and the C center concentration was based on the presence and intensity of the 1344 cm^{-1} and/or its first harmonic at 2688 cm^{-1} [8].

The values for the nitrogen concentration are indicated in ppm rounded to 1 ppm, with the exception of some samples with very low nitrogen content where values with a precision of 0.1 ppm are given. The obtained nitrogen concentration value has an approximate error of +/− 10 to 20%, based on the uncertainty of the published calibration factors and the measurement errors. Since the diamonds are often very inhomogeneous the indicated values are averaging nitrogen rich and nitrogen poor zones; the diamonds used for this study are generally small and the beam of the FTIR used relatively large, hence the obtained data represent good average spectra. In consequence the calculated nitrogen concentrations are average values.

Photoluminescence spectra were recorded on a home-made system using 405, 473, 532 and 635 nm laser excitations, and a high resolution Echelle spectrograph by Catalina Scientific equipped with an Andor EMCCD camera, thermoelectrically cooled down to −95 °C at most. The system was set up to record spectra in the range of 350 to 1150 nm with an average resolution of 0.06 nm. All photoluminescence spectra were recorded with the diamonds cooled to 77 K by direct immersion in liquid nitrogen.

UV–Vis–NIR spectra were recorded on a GGTL D-C 3 spectrometer system using a combined xenon, halogen and LED light source; a double channel spectrometer with a Czerny-Turner monochromator and a thermoelectrically cooled CCD detector was employed, with an average resolution of 0.7 nm. The spectra were measured with the samples cooled down to about 77 K, placed in an integrating sphere of 15 cm in diameter.

16 type Ib diamonds of different characteristics (different proportions of N species, varying amber center varieties [19] and concentration, different colors etc.) were treated by HPHT and by electron irradiation followed by HPHT. Of the 16 diamonds treated by HPHT, 7 were treated by electron irradiation prior to HPHT. These included yellow, brownish yellow, yellowish brown, orangey yellow and "olive" diamonds. 9 diamonds of "olive" to brown color were treated by HPHT only.

The irradiation was performed at the electron irradiation facilities of Leoni Studer AG in Däniken, Switzerland, using 2 MeV and 10 MeV electrons, with an irradiation time of 2 to 3 h. The exact irradiation

Table 1
The distribution and quantity of samples included in this study, by color and variety.

Color	Variety	Type	Nitrogen content	C center content	# samples, full documentation	# samples, only spectral documentation
Yellow	Octahedral	Ib, always with minor Y center component	3 to 100 ppm	3 to 47 ppm	9	7
	Mixed growth	IaA ≫ Ib[a]	43 to 1287 ppm	7.1 to 24 ppm	7	27
	Dominant Y center	Y center > X center ≫ Ib	2.1 to 28 ppm	<0.5 to 8.6 ppm	11	10
Brownish yellow	Octahedral	Ib ≫ IaA to IaA > Ib, always with minor to moderate Y center component	54 to 886 ppm	29 to 276 ppm	9	0
	Mixed growth	–	–	–	0	0
	Dominant Y center	Y center > X center ≫ Ib	7.5 to 35 ppm	3.8 to 21 ppm	6	0
Orange	Octahedral	Ib ≫ IaA to IaA > Ib, always with minor to moderate Y center component	22 to 129 ppm	18 to 72 ppm	18	7
	Mixed growth	IaA ≫ Ib[a]	825 to 940 ppm	45 to 64 ppm	6	
	Dominant Y center	Y center > X center ≫ Ib	17–38 ppm	10 to 11 ppm	2	1
Olive	Octahedral	Type Ib to Ib > IaA, often without Y center component	5 to 40 ppm, one sample 92 ppm	5 to 21 ppm, one sample 62 ppm	17	2
	Mixed growth	–	–	–	0	0
	Dominant Y center	Y center > X center ≫ Ib	1.5 ppm	1.5 ppm	1	1
Greenish yellow	Octahedral	Ib/IaA with or without minor Y center component	40–42 ppm	20 to 28 ppm	2	0
	Mixed growth	IaA ≫ Ib[a]	1260–1895 ppm	6.6 to 6.7 ppm	2	0
	Dominant Y center	Y center > X center ≫ Ib	4.2 ppm	2.4 ppm	1	0
Brown	Octahedral	Type Ib, without Y center component	3.6–10.5 ppm	3.6–10.5 ppm	6	0
	Mixed growth	–	–	–	0	0
	Dominant Y center	–	–	–	0	0
					Total 97	Total 55

[a] Y center often undeterminable because of strong A aggregate infrared absorption.

dose is unknown since (for reasons of treatment cost reduction) the samples were irradiated together with materials that passed through the accelerator for cross-linking treatment.

The samples were treated by HPHT at temperatures ranging from 1750 to 2250 °C and pressures ranging from 55 to 85 kbar, and kept at the maximum temperature for minimum 3 to maximum 30 min. The treatments were performed at the HPHT facilities of the Bakul Institute for Superhard Materials, Kiev, Ukraine, and of Sedkrist GmbH, Seddiner See, Germany.

3. Results

3.1. Standard gemological properties

The natural diamonds were all distinctly colored and represent common colors occurring for type Ib diamonds, including various hues of yellow, orange, "olive" and brown. The color of the natural samples showed very variable distribution, some were very homogenous while others were strongly zoned, with either narrow lamellar color zones following the (111) octahedral planes, called "colored graining" by gemologists [9,19], zoning following cuboid or mixed cuboid–octahedral growth [15] or colored patches of other shapes. In "colored graining", not only is there color zoning but also a slight difference in refractive index between the lighter color matrix and the colored lamellae, of thickness usually much less than 0.1 mm. It is well established that the lamellae are due to the concentration of defects related to plastic deformation in these zones [20].

The natural yellow diamonds exhibited either near homogenous coloration or, more frequently, irregular zoned color distribution with (near-) colorless and yellow zones; often the periphery of such zoned stones is colorless and the core distinctly colored.

Natural diamonds with a more orange hue generally showed a homogenous orange yellow to orange body color with variable degrees of overlaying narrow brown graining. The olive type Ib diamonds exhibited homogenous olive body color with generally very distinct overlaying narrow olive and/or brown graining along (111).

The rare natural brown type Ib diamonds all showed relatively homogenous coloration with only indistinct colored "graining".

Under crossed polarizing filters in immersion most natural type Ib diamonds of all colors showed distinct to very distinct strain along (111), typical for plastically deformed diamonds of octahedral growth (Fig. 1, right); the second most common type of appearance was strain caused between cuboid and octahedral growth sectors which results in a cross-like pattern (Fig. 1, left); this pattern is by far the most common one for bright purely yellow diamonds as these were found to be nearly exclusively of mixed growth. In some rare cases natural type Ib diamonds can appear nearly without strain when observed under crossed polarizers; those are usually found within the group of the purest yellow colored diamonds.

The appearance and distribution of the color and strain of the diamonds were found to be a good indicator for the growth mechanism involved in the formation of the diamonds: samples with graining along (111) are of octahedral growth, diamonds with unusual and often distinct patterned color distribution that exhibit cross-like extinction under crossed polarizing filters are of mixed cuboid–octahedral growth.

3.2. FTIR spectroscopy

All of the 160 diamonds showed infrared spectra with detectable 1344 and/or 2688 cm^{-1} absorption and were consequently type Ib, Ib > IaA, Ib ≫ IaA, Ib/IaA, IaA > Ib and IaA ≫ Ib; the C center related 1130 cm^{-1} absorption was detectable when the A center absorption was not too dominating. The majority of samples (87 of the 152 diamonds) had a Y center component in their spectrum with its principal peak at 1145 cm^{-1} [13], and the X center was often detectable with its main feature at 1332 cm^{-1} [21]. In consequence the "1130 cm^{-1} absorption" in most natural type Ib diamonds is broadened and shifted in position compared to the standard type Ib absorption found in the spectra of yellow HPHT synthetic diamonds; the position of such mixed C center/Y center absorption is found somewhere between 1135 and 1139 cm^{-1}.

3.2.1. Y center diamonds

The spectra of some rare diamonds exhibited dominant Y and X center absorptions with only very little C centers. These Y center diamonds represent a significant portion of the sampling of this work since they were specifically selected. They must be addressed separately from all others since even though of apparent octahedral growth they exhibit

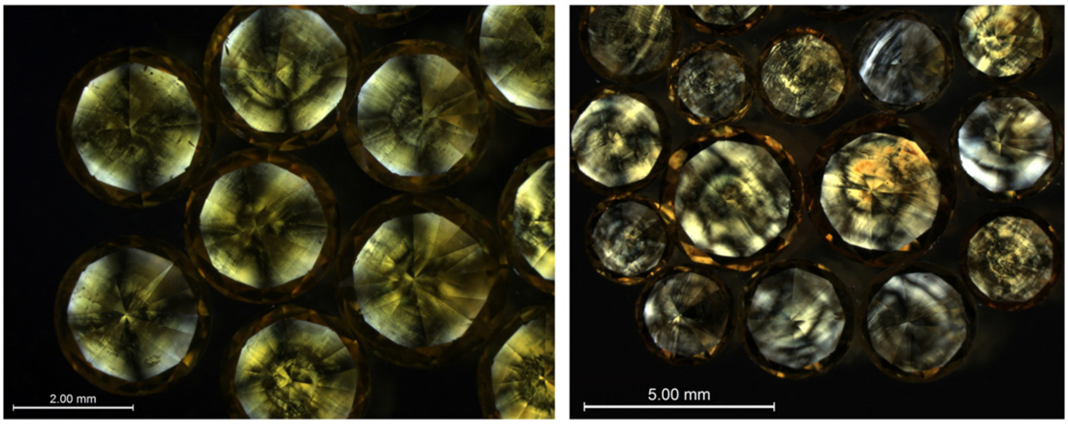

Fig. 1. Left: type IaA ≫ Ib diamonds of mixed cuboid–octahedral growth between crossed polarizing filters show gray to black cross-like extinction caused by strain between the cuboid and octahedral growth sectors. Right: type Ib ≫ IaA diamonds between crossed polarizers exhibit distinct extinction along (111) from slip planes caused by deformation.

unusual properties. Their one phonon absorption is strongly dominated by a complex absorption system with its principal peak at 1145 cm^{-1}. Such rare diamonds can be found in a range of colors, i.e. yellow, brownish yellow, orange and olive. The Y center diamonds studied had very low to low total nitrogen contents from 1.5 to 35.4 ppm, of which 1.5 to 21.0 ppm were C centers, and 1.0 to 14.4 ppm were X centers. Only six of the 22 Y center diamonds contained A centers, in concentrations ranging approximately from 5 to 25 ppm. Most Y center diamonds had a C center content of less than 8 ppm.

The Y center diamonds all showed hydrogen-related features that intensified with increasing 1145 cm^{-1} and X center absorption. The H-related features comprised a total of 155 sharp peaks, of which up to 80 absorptions were present in the infrared spectrum of one single stone [13,15].

Some sharp infrared absorptions between 1353 and 1387 cm^{-1} merit special mention, since they are only associated with the presence of a Y center one-phonon infrared absorption. These features have been seen only in natural diamonds that do show at least some Y center absorption in their infrared spectrum. The main peaks are found at 1353, 1358, 1374 and 1387 cm^{-1} and minor peaks are found at 1363 and 1369 cm^{-1}. They occur in differing intensity ratios from stone to stone. The first mention of these sharp peaks was made for diamonds with a type Ib character [16].

The large group of C center containing diamonds other than the ones with infrared spectra dominated by the Y center will be addressed in the following sections.

3.2.2. Yellow diamonds

The group of purely yellow natural type Ib diamonds can basically be subdivided into three sub-groups based on their infrared spectra:

1) Very high nitrogen and moderate to high hydrogen type IaA ≫ Ib (Fig. 2). Hydrogen is always present with precisely the same infrared absorptions in similar relative proportions, $3107 > 3310 > 3237 > 3144 > 3154 > 3139$ cm^{-1}; additionally a broader band at approx. 3474 cm^{-1} can always be detected. The total nitrogen content of the analyzed samples varied from 887 to 1901 ppm, of which 6.6 to 64 ppm were C centers.
2) Low to moderate nitrogen and low to very low hydrogen type IaA ≫ Ib, with or without Y center absorption. The main hydrogen-related absorptions are found at 3107, 3144 and 3310 cm^{-1} and the broader band at approx. 3474 cm^{-1} is also generally present. In contrast to the first group the relative proportions of the hydrogen-related peaks vary from stone to stone. The total nitrogen content of the analyzed samples varied from 80 to 160 ppm, of which 1.7 to 50 ppm were C centers.
3) Very low to moderate nitrogen and very low hydrogen (and rarely no detectable hydrogen) type Ib/IaA, Ib > IaA or Ib ≫ IaA, with Y center absorption (Fig. 3, trace b). Very weak hydrogen related absorptions are almost always present and found typically at 3394, 3342, 3310, 3144 and 3107 cm^{-1}. The total nitrogen content of the analyzed samples varied from 3.0 to 100 ppm, of which 3.0 to 47 ppm were C centers. Samples CP001 and CP002 were the only samples of this study that exhibited a Y center in their infrared spectrum but no detectable hydrogen peaks; likely this is related to the very low nitrogen content of these diamonds (3.0 and 7.6 ppm respectively).

Of these groups the first one is by far the most common—representing estimated 70 to 90% of all bright purely yellow diamonds colored by the C center (at least in small sizes, i.e. less than 0.20 cts)—, and the last one the rarest and seems to occur mainly in larger sizes. In the spectra of the three groups no noticeable amber center absorptions are present, which is consistent with the absence of “brown graining” in these gems. The Y center is presumably present even in the spectra of many of the diamonds of the first group, for which the very strong A center absorption forbids formal demonstration of its existence at trace level via spectral decomposition.

3.2.3. Orangey yellow to orange diamonds

The yellow orange to orange natural type Ib diamonds were almost exclusively of octahedral growth with low nitrogen type Ib > IaA or Ib ≫ IaA, in some exceptional cases the A aggregates dominated the C centers; in all the infrared spectra of such diamonds the Y center was detectable (Fig. 3, trace a). The total nitrogen content varied from 22 to 129 ppm, of which 17 to 72 ppm were C centers. Weak to very weak amber center absorptions could be found in the spectra of all the orange hued diamonds, with main absorptions at 4065, 4165 and 4275 cm^{-1}. This is logical as they do show some “brown graining”, which is an indicator for plastic deformation and which is always present in diamonds that exhibit an amber center in their infrared spectrum [18]. Hydrogen-related absorptions could be detected in the spectra of all samples, with weak features typically at 3394, 3342, 3310, 3144 and 3107 cm^{-1} plus additional extremely weak peaks. Part of the deep orangey yellow diamonds were of the high nitrogen A aggregate-dominant mixed growth type described above as being so typical for vivid yellow diamonds (Fig. 2).

3.2.4. “Olive” and brown diamonds

The “olive” and the brown natural type Ib diamonds were the only samples that exhibited 1130 cm^{-1} C center absorption without modification by the Y center; the 1130 cm^{-1} absorption was neither shifted in position nor did it exhibit any broadening. 13 out of the total 18 olive

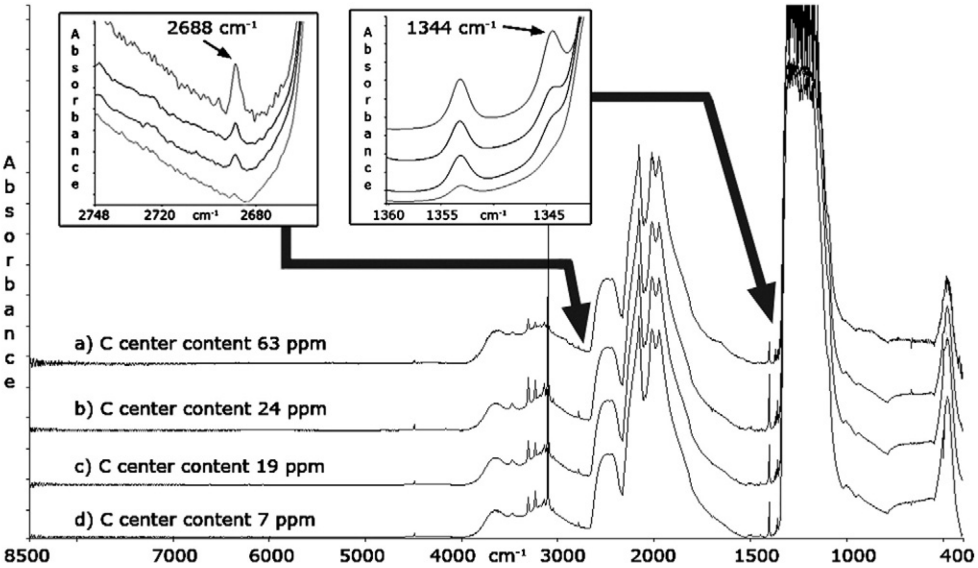

Fig. 2. The infrared spectra of four strongly yellow-colored, re-entrant cube diamonds. The spectra show that these diamonds are all similar being type IaA ≫ Ib with significant concentrations of hydrogen. Additionally the hydrogen signature of all stones is practically identical. The C center content of such stones varies and can sometimes only be determined via the overtone of the 1344 cm^{-1} line at 2688 cm^{-1} since in low C center samples the strong A center absorption hides the 1344 cm^{-1} line. The spectra are normalized to the diamond intrinsic band at 1995 cm^{-1} and shifted vertically for clarity.

diamonds and all of the brown diamonds did not exhibit any Y center infrared absorption. These "Y center free" diamonds were the only ones (beside two very low nitrogen yellow diamonds, samples CP001 and CP002) that showed no trace of hydrogen in their infrared spectra, but all showed prominent absorption due to the amber center with its main peaks at 4060, 4110, 4165 and 4245 cm^{-1} [19,22,23]. This correlates with the presence of "brown" or "olive" "graining" as expected in such plastically deformed diamonds. In the olive and brown groups of type Ib diamonds we found the only samples that were purely type Ib, without noticeable traces of aggregates and/or the Y center. The total nitrogen content of the olive stones was very low to medium and varied from 5 to 92 ppm, of which 5 to 23 ppm were C centers. For the rare brown type Ib diamonds the nitrogen content was always very low and varied from 4.8 to 10.5 ppm. Except for one stone that contained 3.6 ppm of A aggregates the nitrogen was present exclusively in the form of C centers and very minor X centers in the tested samples.

3.3. UV–Vis–NIR spectroscopy

The UV–Vis–NIR spectra of the natural type Ib diamonds are dominated by a continuum rising from the near-infrared towards the ultraviolet. This feature reaches total absorption at a point named the "cut off". There is no specific total absorption above 225 nm such as the total absorption at approximately 310 nm in type Ia diamonds. The cut-off position is driven by the intensity of the C center related continuum absorption plus the strength of the absorption band at 270 nm. The band at 270 nm has been attributed to electronic transitions from the valence band to a level at a substitutional nitrogen donor [3]. Thus, the "cut off" position depends on the optical path length in the sample, the C center content and finally it must be mentioned that the exact position of the cut-off may vary somewhat from instrument to instrument. However, the optical path length in the diamond is impossible to assess precisely in faceted gems. In consequence, theoretically type

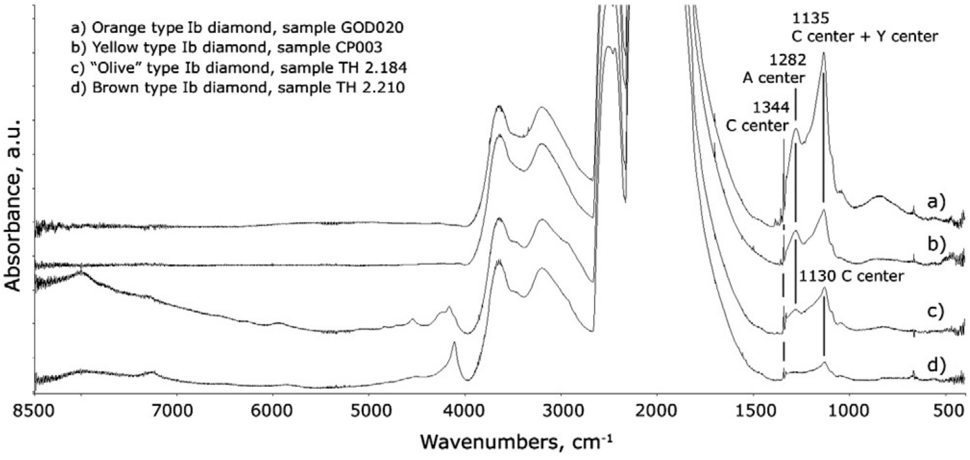

Fig. 3. Representative infrared spectra of the different color groups of type Ib diamonds (with C center strongly dominating). Typically the spectra of yellow and orange diamonds (traces a and b) are characterized by one phonon absorption due to mainly C centers with minor A and Y centers, while olive and brown type Ib diamonds (traces c and d) generally lack the Y center and often have lower nitrogen content. The amber center absorption (ranging from about 3400 to 8500 cm^{-1}) is most prominent in olive and brown type Ib diamonds while it is only weak to very weak in orange diamonds and practically absent in yellow samples. The spectra are normalized to thickness and shifted vertically for clarity.

Ib diamonds could present their point of total absorption at almost 225 nm (like type IIa diamonds), but in reality, in faceted gems, the cut-off is rarely observed at wavelengths shorter than 400 nm since the absorption in the UV is very strong, and in consequence the band at 270 nm is never observable. The lower the C center content the more the cut-off is shifted towards the UV domain. The following values were determined for purely yellow samples of variable nitrogen content, showing very minor deformation-related features: 307 nm (1.7 ppm C centers), 345 nm (3 ppm C centers), 390 nm (7.6 ppm C centers), 400 nm (14.1 ppm C centers).

In some samples, broadband absorptions from vibronic systems overlay this feature, such as H3, NV^- as well as H2. Many additional sharp weak to very weak bands were found in the spectra of certain diamonds, especially a sharp ZPL at 904.2 nm in Y center diamonds. When strong, this band shows a distinct vibronic structure [15].

The UV–Vis–NIR spectra of purely yellow type Ib diamonds were characterized by a continuum with rising absorbance from about 560 nm onwards. The less absorbance above 560 nm, the purer the yellow color of a diamond. If there is the slightest absorbance from about 560 nm towards the infrared, the gem has the tendency to show modifying colors such as orange and brown. The most intensely colored yellow diamonds showed a “cut off” somewhere between 385 to about 405 nm, some less saturated yellow natural diamonds showed total absorption at lower wavelengths, down to 340 nm. This lower slope of the continuum corresponds, as expected, to a more brownish color. These lower “cut off” generally occur in the spectra of Y center diamonds.

In three exceptional vivid yellow type Ib diamonds (samples CP001, CP002 and CP004), although they ranged in size from 3.01 to 3.18 ct, the cut off positions were below these values because of their exceptionally low nitrogen content.

The three main groups of natural yellow type Ib diamonds all show some spectral peculiarities; the spectra of the first group (nitrogen-rich with hydrogen, IaA $\gg$ Ib) never show classical defects such as N3, H3, NV^-, NV^0 or H2; instead they nearly always exhibit weak, relatively sharp absorptions, such as those at about 683.2, 709.2, 793.6 and 840 nm. The second group (lower nitrogen IaA $\gg$ Ib with less hydrogen) is also characterized by the lack of classical defects, but the absorptions that can be found on top of the continuum are more variable than for the first group. The spectra of the diamonds of the third group (very low to medium nitrogen content, C center dominates) nearly always exhibited at least some H2 absorption (Fig. 4, trace c).

The spectra of more orangey colored type Ib diamonds showed all the same type of UV–Vis–NIR absorption spectrum, with a continuum rising rapidly starting somewhere between 650 and 700 nm. In fact they show already some absorbance well before, from 980 nm onwards. Their cut-off is located between 410 and 455 nm. Furthermore weak to moderate H2 center absorption was present in the spectra of all orangey diamonds (Fig. 4, trace d).

The only exception to this was orange Y center diamonds: their spectra show a continuum that had a steady, slow increase from 1040 to 567 nm, and then a drastic increase in absorbance, leading to a cut-off around 400 nm. In addition to many very weak to weak sharp absorption bands that could be found in the domain from 550 to 1100 nm, the UV–Vis–NIR spectra exhibited a weak 480 nm band with its companion band at 426 nm [24].

The UV–Vis–NIR absorption spectra of natural “olive” diamonds were characterized by a continuum with steady increase from about 1000 to 510 nm, and then a steep increase. The cut off is located in the range 350 to 405 nm for all “olive” samples. Weak to moderate NV^- and H2 absorptions were always superimposed to this continuum and in most spectra some H3 absorption was also observed (Fig. 4, trace b). The slight greenish color component, easily visible with the naked eye, is actually due to a detail of the spectrum. A weak, shallow relative transmission window appears in the green, one side due to the continuum, the other due to the NV^- center. Let's not forget that the human eye is most sensitive to green, and therefore a spectral detail in this region will be more easily perceived than anywhere else in the visible range [25].

The spectra of the rare type Ib brown diamonds showed higher absorbance in the range 750 to 470 nm and a less steep continuum in the range 500 nm to the UV than all other diamonds. The total absorption was shifted to the UV in the range of 330 to 340 nm. Distinct NV^- absorption with its ZPL at 637 nm is always superimposed, with sometimes a weak H3 (Fig. 4, trace a). The H2 absorption is barely detectable for brown samples, but it is nevertheless always present. The brown color is due in any material to a continuum with a slow increase towards the UV, which can be assimilated to a straight line for a good portion of the visible, hence the less saturated color. The relative transmission window seen in the spectra of “olive” diamonds is here much less marked, nearly absent, hence the absence of greenish component in the color. This also explains why there is a continuum of color appearances between brown and “olive” type Ib diamonds.

3.4. Luminescence techniques

3.4.1. Fluorescence microscopy

The fluorescence excited by intense longwave broadband UV illumination from the UV microscope varied strongly among the C-center diamonds. In these specific conditions (very intense broadband UV excitation), approximately 90% of all type Ib diamond exhibits green to yellowish green PL, 7% yellow to orange-yellow PL, 2% orange PL, less than 1% orange red PL and far less than 1% are inert. In comparison, in the experience of the authors the vast majority of type Ia diamonds, no matter what their color is, exhibit blue PL under such UV excitation. The second most common luminescence is yellow, and then green; orange and pink are relatively rare. Inert type Ia diamonds are practically inexistent (again, in these specific conditions).

The vast majority (70 to 90%) of purely yellow diamonds (the type IaA $\gg$ Ib re-entrant cube variety of diamonds) were characterized by green to yellowish green luminescence with uneven distribution reminiscent of the mixed octahedral–cuboid growth seen in asteriated diamonds [26] such as “Mercedes stars” or triangles (three-fold symmetry) and “Christmas stars” (pseudo-six-fold symmetry). A far smaller portion – around 5 to 10% – of such mixed growth, cuboid–octahedral diamonds exhibited PL with a similar zonation but this time with a yellow, instead of green, color. Only very few of the yellow diamonds – less than 0.1% – were inert under such UV excitation. In fact the only inert type Ib diamonds were found in this group of re-entrant cube diamonds. Some rare bright yellow diamonds characterized by dominant Y center infrared absorption showed homogenously distributed yellow to orange PL; such stones represent far less than 1% of all bright yellow C center containing diamonds.

The orange-yellow to orange diamonds showed basically three types of fluorescent reactions:

- Green to yellowish green to yellow with the same distribution as described above for yellow re-entrant cube diamonds (orange yellow type IaA $\gg$ Ib re-entrant cube diamonds),
- Green with the PL distributed within lamellae following (111). It was found in diamonds with the C center dominating the A center and the Y center, thus low to medium nitrogen content type Ib > IaA and Ib $\gg$ IaA with some Y center absorption.
- Yellow to orange with various forms of distribution. As soon as the infrared spectrum of the previous category of stones was dominated by the Y center the PL was typically yellow to orange in very variable intensities from very weak to very strong.

The “olive” type Ib diamonds generally showed mixed green and orange luminescence, with the green PL following the octahedral growth sectors, while the orange PL was often found in irregular or roughly triangular sectors interrupting the green PL.

The PL of brown type Ib diamonds was always reddish orange, near homogenous or distributed along (111) “graining”; it was far stronger

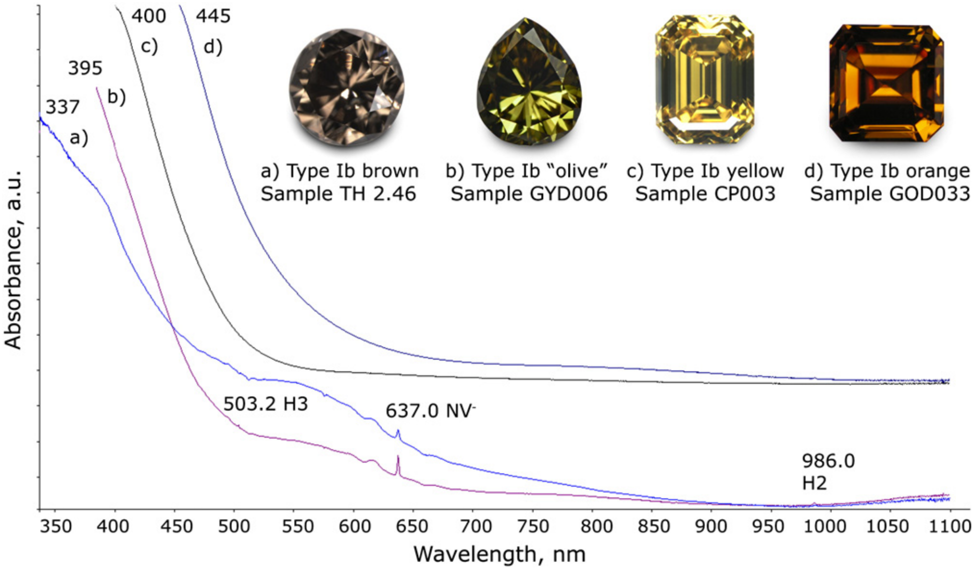

Fig. 4. Representative UV–Vis–NIR spectra of the different color groups of natural type Ib diamonds. It can be seen that the different colors are caused by variations in the slope of continuum, and overlaid broad band absorptions, in particular the NV$^-$ center for "olive" and brown gems.

than the orange PL of most "olive" diamonds, and in contrast to the luminescence of the "olive" samples, it was not intersected by any green PL.

As a general rule the highest PL intensity was observed for the brown diamonds followed by the "olive" gems, then the yellow samples, and the lowest PL intensity was found for most orange type Ib diamonds. This general rule is not applicable for the diamonds with dominant Y center infrared absorption, such stones had very variable PL intensity from very weak to very strong.

3.4.2. Cathodoluminescence

In cathodoluminescence two types of growth modes are observed, regular octahedral growth and mixed cuboid–octahedral simultaneous growth. All type IaA $\gg$ Ib, yellow to orangey yellow crystals showed growth patterns typical of re-entrant cubes. Cross-like CL with typically three-fold symmetry plus curious elongate rounded features that appeared like wormholes were typical for the re-entrant cube diamonds (Fig. 5, left).

Octahedral growth could be seen for all other type Ib diamonds and with prominent narrow CL bands along (111), identical to the observations made under UV excitation (Fig. 5, right).

An exceptional observation was made for Y-center diamonds: they showed completely homogenous CL, no zoning could be seen whatsoever. To the knowledge of the authors, such CL pattern is so far unknown for diamond, and described here for the very first time.

3.4.3. Photoluminescence spectroscopy

The yellow to orange-yellow re-entrant cube diamonds (thus high nitrogen type IaA $\gg$ Ib) all exhibited practically identical PL spectra when excited by the four lasers used for this work. Notably none of the stones of this study showed even the tiniest N3 emission, but under 405 nm excitation all of them were characterized by a broad band centered at 540 nm and associated ZPLs at 488.9 (S2), 496.6 (S3), 503.5 (S1 α line) and 510.7 (S1 β line), plus emissions at 691.9, 693.9, 709.0 to 709.2, 728.8, 793.4, 820.9 and 840 nm (Fig. 6, trace d). Under 473 nm excitation only the S2 and S3 ZPLs plus the associated broad band at 540 nm were detected and the S3 ZPL was found much sharper than under 405 nm excitation (Fig. 6, trace c). The reason for this phenomenon is not clear. One notable band detected under 473 nm but not under 405 nm laser is a doublet positioned at 925.2 and 926.1 nm. Under 532 nm laser excitation the line at higher energy disappeared and only the line at 926.1 nm was detected, instead of the doublet. Besides this the most notable features include lines at 581.3, 676.6, 684.4, 687.6, 689.1, 692.0, 693.9, 700.3, 705.3, 708.9, 728.9 and 793.4 nm (Fig. 6, trace a). The center clearly dominating under 635 nm excitation was the vibronic system with ZPL at 793.4 nm. The features at 676.6 and 708.9 nm were also observed (Fig. 6, trace b).

The very rare purely yellow type Ib diamonds exhibited a mix of classical diamond centers including distinct N3 and H3, weak NV^0 and distinct NV$^-$. The only other emission of interest appears at 565.7 nm with 532 nm laser excitation.

The more "typical" orange type Ib diamonds – with low to moderate nitrogen and C centers dominating A and Y centers – were also characterized by weak to very weak N3, distinct H3, weak to distinct NV^0 and generally distinct NV$^-$ center emissions. In contrast to the few purely yellow type Ib diamonds, the 532 nm-excited PL of all of the orange diamonds exhibited a more distinct 565.7 nm center, sometimes even dominant (Fig. 7, trace b). There are also lines at 553.1 and 554.6 nm which do not correlate in intensity with the 565.7 nm center; however, they were strongest when the 565.7 nm feature was most intense. In the 532 nm-excited PL the NV$^-$ center was generally accompanied by a much weaker line at 635.2 nm and often by weak bands at 634.2, 640.4, 646.0 and 648.2.

The "olive" type Ib diamonds typically showed PL spectra dominated by classical diamond centers of which the H3, NV^0 and NV$^-$ center emissions were the most intense ones; the N3 center emission varied from weak to distinct (Fig. 8, traces a). Compared to the yellow to orange type Ib diamonds the PL intensity of "olive" diamonds was far stronger and especially the NV^0 center was more apparent in the spectra of many of the samples. The 565.7 nm center was excited by 532 nm laser in all of the samples. Its intensity stretched from extremely weak to very strong, becoming the dominant feature for one diamond (Sample BOY002).

There was a major difference between the PL spectra of the three "olive" diamonds containing the Y center and those of olive diamonds without the Y center in their infrared spectra. The difference is mainly a large number of sharp emissions of which some are known to be nickel-related, such as the doublet emission at 882.9 and 884.6 nm, and which are excited by the different lasers (Fig. 8, traces b). Additionally the spectra with 405 nm excitation were characterized by broad bands centered at 570 nm for one sample, at 555 nm and at 645 to 650 nm for the other two samples. The broad band PL at 570 nm

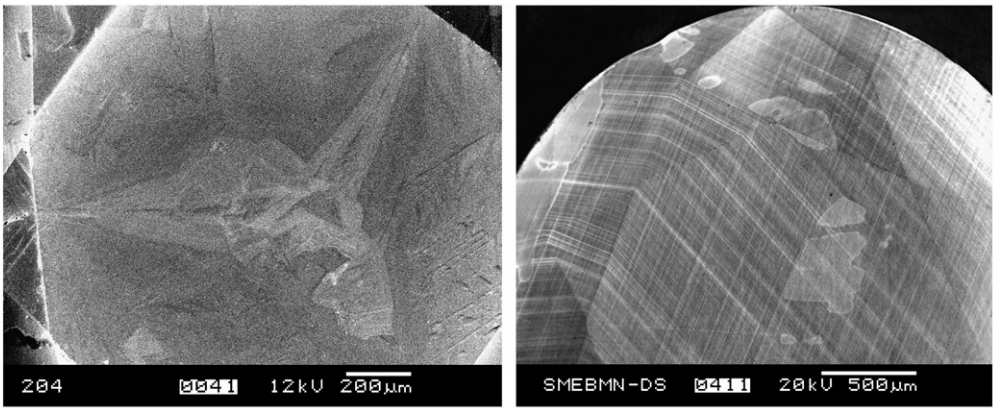

Fig. 5. Monochrome cathodoluminescence images of a re-entrant cube, type IaA $\gg$ Ib yellow diamond (left) and a type Ib "olive" diamond of octahedral growth (right). No signs of plastic deformation are visible in the re-entrant cube, while the octahedrally-grown sample shows distinct CL along (111) slip planes introduced by post-growth plastic deformation.

corresponds to a yellow emission while the double band at 555 and 645 to 650 nm corresponds to an emission of orange color. The 555 nm band is caused by the S1 and S3 centers; the S1 ZPLs can be seen at 503.1 nm (S1 α line) and at 511.2 nm (S1 β line), and the S3 ZPL at 496.6 nm.

The reddish orange UV excited PL of the very rare brown type Ib diamonds is caused by a dominating NV^0 emission; these were the only diamonds in which the 405 nm laser strongly excited this defect; in all others the H3 defect emission was much more distinct than the NV^0 center emission. The spectra of three of the only four brown type Ib diamonds found during this study did not exhibit any other emissions than N3, H3, NV^0 and NV$^-$; only sample TH 2.210 showed a very weak 565.7 nm line. The three brown stones represent the only type Ib diamonds tested so far that did not show the faintest trace of this center under 532 nm laser excitation. Intensity-wise the PL of the brown type Ib diamond was by far the strongest, followed by the emission of the olive diamonds, and then the yellow to orange type Ib samples, which had comparatively weak to very weak PL.

4. HPHT treatment, with and without electron irradiation

HPHT treatments were split into two groups: HPHT treatment only of "olive" to brown type Ib diamonds and HPHT treatment after electron irradiation of mainly yellow, brown yellow and orangey yellow type Ib diamonds. It was found that HPHT treatment for short times ($<$1 h) only was ineffective at temperatures below 1900 °C. The color of only one "olive" type Ib sample was affected at 1850 °C/85 kbar. The diamond's color was modified from "olive" to brown. Spectroscopically the only change besides a slight change of slope in the UV–Vis–NIR absorption continuum could be seen in the infrared: the amber center absorption was modified and reduced – but not suppressed – by the treatment, while the nitrogen speciation remained unaffected (13.6 ppm C centers and 1 ppm A centers). This apparent color change is basically a change of saturation which is seen from the less steep slope of the continuum.

HPHT treatment of a brown, pure type Ib diamond with very low nitrogen content of 10.5 ppm at above 2000 °C for 30 min suppressed the

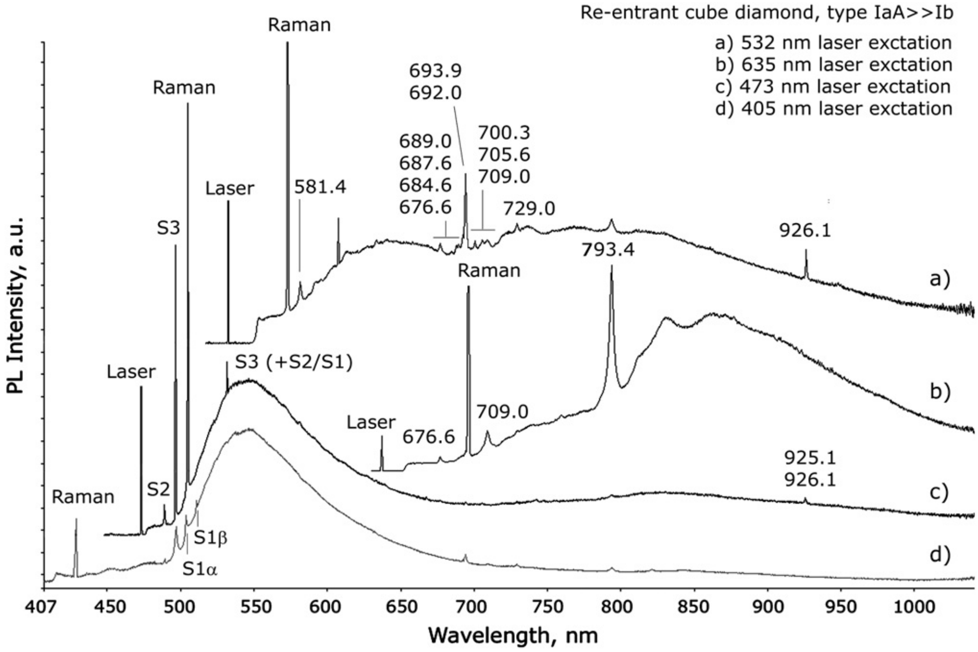

Fig. 6. The photoluminescence spectra (405, 473, 532 and 635 nm excitations) of a bright yellow re-entrant cube, type IaA $\gg$ Ib diamond. From the data obtained by the use of four different lasers it is clearly visible that nickel-related defects are dominating in such stones (e.g. S1, S2, S3 and 794 nm), No classical defects such as H3 (503 nm), NV^0 (575 nm) and NV$^-$ (637 nm) can be detected. The spectra are shifted vertically for clarity.

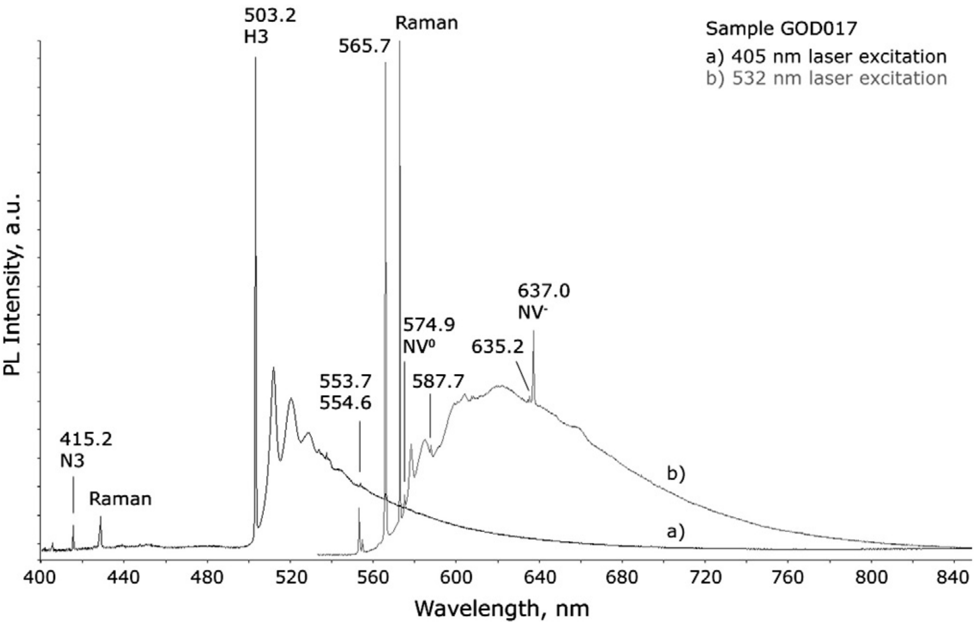

Fig. 7. The photoluminescence spectra (405 and 532 nm excitations) of a yellowish orange type Ib ≫ IaA diamond with substantial Y centers. For such diamonds, classical defects accompanying octahedral growth such as H3, NV^0 and NV^- are characteristic. The 565.7 nm center is a little-known feature which is actually present in virtually all PL spectra of type Ib diamonds of octahedral growth. It appears as the dominant peak in the PL spectrum of this diamond (trace b).

amber center and aggregated 43% of the single nitrogen into A centers (4.5 ppm) and 24% into B centers (2.5 ppm). Consequently the UV–Vis–NIR absorption spectrum was changed from a spectrum characterized by continuum absorption with overlaying NV^- center absorption into a spectrum characterized mainly by N3 and H3 absorption, without much continuum absorption. The color was thus changed from dull brown to light greenish yellow.

Several "olive" diamonds were HPHT treated at 2250 °C for 3 min; the color of these diamonds changed from "olive" to yellow and became distinctly lighter. This treatment annealed out the amber center absorption and caused the aggregation of between 10 and 30% of the C centers into aggregates. Interestingly, even in the samples with the lowest percentage of the C center aggregation, the isolated nitrogen aggregated not only to A aggregates during the treatment: B aggregates and N3 centers were formed readily. This last center could be detected easily thanks to its strong blue PL (mainly in the graining), contrasting with the green luminescing graining of the formerly "olive"-colored gem. The UV–Vis–NIR spectrum before treatment exhibited some steadily increasing absorbance from 900 to 500 nm, where the absorbance increased strongly. After treatment the steadily increasing absorbance was gone and absorbance in the domain 1100 to 500 nm was almost inexistent. Also the cut-off was found to shift from 390 nm before, to 340 nm after treatment. The NV^- absorption was reduced and the H3 and H2 absorptions were strengthened. Further, the N3 absorption – undetectable before the treatment – was formed by this process.

An orange yellow type Ib diamond with a concentration of 46.4 ppm C centers was irradiated by 2 MeV electrons prior to HPHT treatment at 2250 °C for 3 min. About 40% of the C centers (18.1 ppm) was

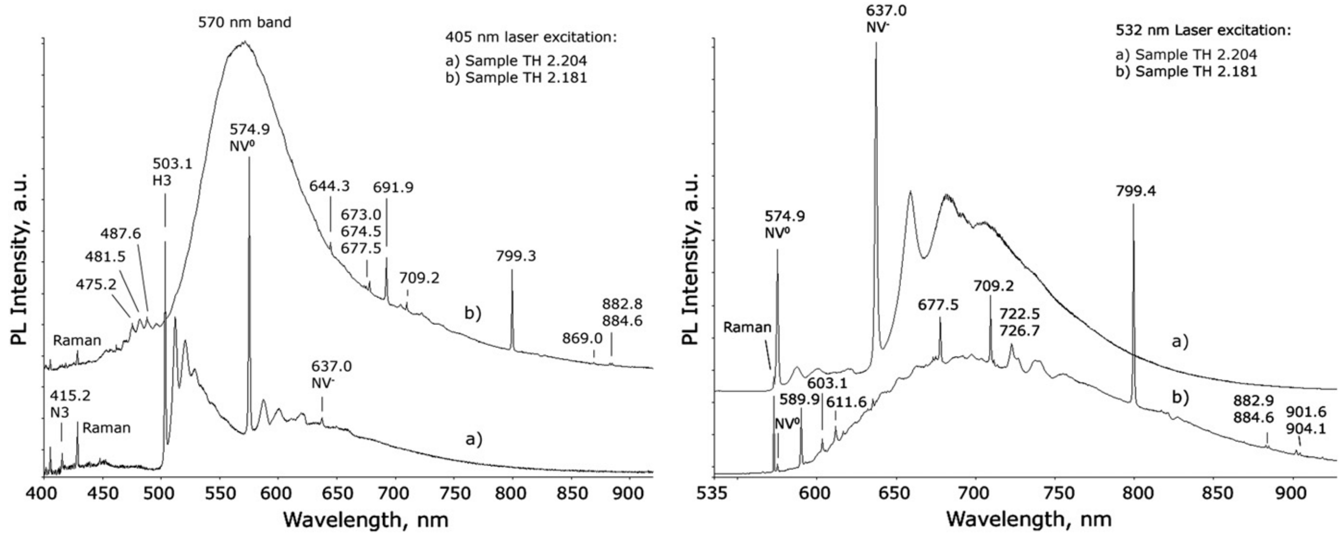

Fig. 8. The photoluminescence spectra (405 and 532 nm excitations) of two varieties of "olive" type Ib diamonds with octahedral growth: -a) A typical pure type Ib diamond without Y center (trace a). -b) A Y center diamond with only 1.5 ppm of C centers (traces b). While the PL spectra of the typical type Ib diamond (trace a, bottom) are characterized by H3, NV^0 and NV^- centers, the spectra of the Y center diamond (trace b, top) are mainly dominated by nickel-related emissions. The spectra are shifted vertically for clarity.

aggregated into A and B centers, and only 28.3 ppm nitrogen as C center remained after the treatment (Fig. 9). As a consequence of this aggregation N3 centers were formed and were easily detectable by PL spectroscopy (Fig. 11) and even by UV–Vis–NIR absorption spectroscopy (Fig. 10). The color of the stone changed from orange yellow to yellow (Fig. 10, inset) and the stone developed blue PL along the deformation-related graining that exhibited very weak green PL prior to the treatment (Fig. 11, inset). In the UV–Vis–NIR spectrum this change in body color is visible as a change of slope; while there is some absorbance from as far as 950 nm and an increasingly steep raise in absorbance from 620 nm towards shorter wavelengths before treatment, after treatment the absorbance from 1100 nm all the way to 560 nm is almost entirely gone and absorbance increases steeply from 560 nm towards shorter wavelengths. Additionally, the cut-off logically shifted from 420 nm before treatment to 395 nm after (Fig. 10).

The main difference between samples HPHT treated post irradiation and those being only HPHT treated was the percentage of nitrogen aggregation, as expected by earlier published results [27]. No significant difference was found on the effect of 10 MeV versus 2 MeV electron irradiation on the nitrogen aggregation enhancement.

A very interesting result was obtained through the HPHT treatment of diamonds that show Y center infrared absorption: the Y center absorption was reduced while the C center absorption increased. In the UV–Vis–NIR spectrum of such samples the 480 nm band absorption was formed and the correlating red PL band centered at 680 nm appeared (473 nm excitation). Since several diamonds with a variable Y center component were treated a direct correlation between the Y center component prior to the treatment and the intensity of the 480 nm band absorption/680 nm emission could be established: a low Y center content resulted in low intensity bands, a high Y center content resulted in high intensity bands.

Together with the reduction of the Y center the sharp absorptions at 1353, 1358, 1374, 1387, 1363 and 1369 cm^{-1} were annealed out. The band at 480 nm was strong enough in some samples that it had an apparent influence on the final color of the diamonds.

The HPHT treatment of type Ib diamonds has shown that all modifying colors can be eliminated by a short treatment at temperatures of ≥2000 °C, and that at lower temperatures around 1850 °C the color of some "olive" type Ib diamonds can be changed to brown.

5. Discussion and conclusions

The cause of color of natural type Ib diamonds is complex. The comparison of extensive amount of data of the differently colored type Ib diamonds clearly separates them into distinct groups. A classification of type Ib diamonds based on photoluminescence and infrared spectroscopy has been proposed recently [28]; while the classification is based on various criteria, one of the main criteria is the presence and concentration of deformation-related defects.

The vast majority of type Ib diamonds of octahedral growth show distinct signs of plastic deformation; they all show amber center absorption in their infrared spectra and the intensity of the amber centers has proven to be a good indicator of the deformation-related defects present in type Ib diamond, as is the case for all type I diamonds [19]. The deformation related defects that result in a continuum that induces brown coloration are likely extended vacancy defects such as those described for type IIa diamonds [29]. The behavior of the continuum upon HPHT treatment is identical to what is observed for other diamond types, in that it anneals out at temperatures above 2000 °C. Besides the amber center such diamonds exhibit variable concentration of vacancy-related defects of which the group of nitrogen-vacancy defects (H3, H2, NV^0, NV^-) can be directly detected by PL spectroscopy in all cases, and by UV–Vis–NIR spectroscopy in samples with higher concentrations of such defects.

Based on the colored graining and strain along (111), the intensity of the amber center infrared absorption, the NV^-/H3 center absorption/emissions and based on the behavior upon HPHT treatment the density of deformation-related defects was estimated qualitatively for each of the color categories. The deformation-related defects are only of importance for the octahedrally grown type Ib diamonds and practically absent in the samples of mixed growth. The olive type Ib diamonds of octahedral growth exhibit the highest density of deformation-related defects, closely followed by brown diamonds, and finally orange to yellow diamonds which markedly lower concentrations. The lowest defect concentration could be found in three unusually large (3.0 to 3.2 ct) brightly colored purely yellow natural diamonds, which also had among the lowest C center contents (3.0, 7.6 and 14.1 ppm). In contrast to the deformation defect concentration the brown diamonds exhibited the lowest C center nitrogen content (4.8–10.5 ppm), followed by olive samples (5 to 21 ppm, one exceptional stone with 62 ppm) and finally orange diamonds, which had the highest C center nitrogen content of 30 to above 70 ppm.

In synthetic diamonds free from defects other than nitrogen the intensity of color (correctly said, the importance of the absorption in the visible range) correlates directly with the C center concentration. On the contrary, in natural diamonds there are cases for which this is no longer true. There are even bright yellow diamonds which show a "type Ib-like" UV–Vis–NIR absorption spectrum but which are actually

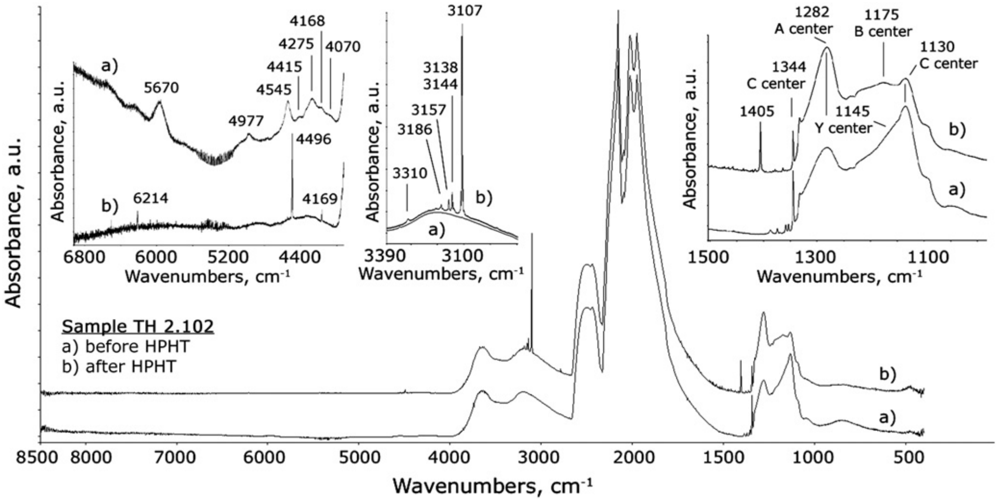

Fig. 9. The infrared spectra of sample TH 2.102, a yellow orange type Ib ≫ IaA diamond with minor Y center content, before (trace a) and after irradiation followed by HPHT treatment at 2250 °C/6.5 GPa (trace b). The treatment resulted in the aggregation of 40% of the C centers to A and B centers, as well as the suppression of the amber center absorptions, and the apparition of distinct hydrogen-related peaks. The spectra are shifted vertically for clarity.

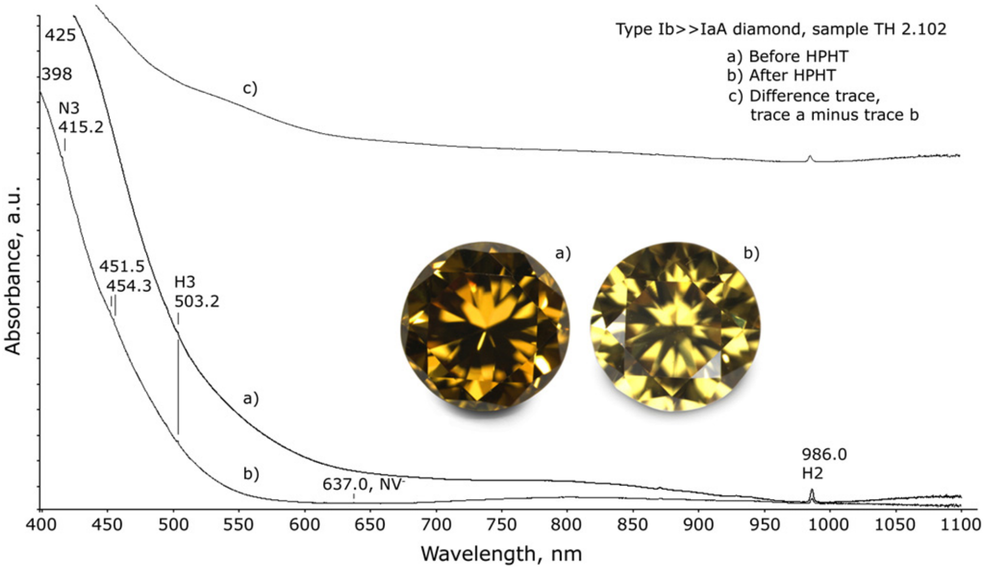

Fig. 10. The UV–Vis–NIR absorption spectra of sample TH 2.102, before (trace a) and after irradiation followed by HPHT treatment (trace b). The brownish orange appearance of the gem (picture a) disappears after treatment, as it becomes purely yellow (picture b), and is distinctly lighter. The "residual" trace is shifted vertically for clarity.

type IIa (based on the lack of infrared absorption in the one-phonon region), hence are practically nitrogen-free. Similar situations of type IIa diamonds, vividly colored by nitrogen related defects have been reported before [9,30] without proposing any explanation. In Fig. 12 a vivid yellow mixed-growth, cuboid–octahedral type IaA $\gg$ Ib natural diamond is shown with a very low C center content of 1.7 ppm. In addition it was found to be practically free of strain and showed no deformation-related features whatsoever. In comparison a light yellow synthetic diamond crystal with a similar C center content of 2.2 ppm is shown. They both have UV–Vis absorption spectra of comparable shape (Fig. 12). Here the question arises why a diamond with 30% less C center content than a light yellow diamond is of such stronger coloration. It appears logical that some other defect, yet with similar absorption, must be responsible for part of this yellow color. There is a possibility that the Y center is optically active and that it causes also a continuum absorption, and thus yellow coloration. This possibility is based on the observation that nearly pure Y center diamonds are always strongly colored, even though they have rather low C center content, in some cases even undetectable by infrared spectroscopy. There is of course the possibility that an unknown defect, undetected by methods used in this work, is responsible for the additional absorption continuum. This second possibility applies to strongly colored type IIa diamonds.

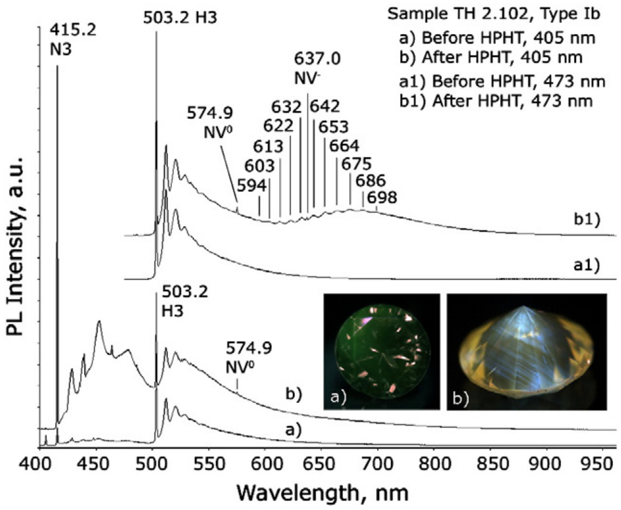

Fig. 11. The photoluminescence spectra (405 and 473 nm excitations) of sample TH 2.102, before (traces a and a1) and after irradiation followed by HPHT treatment (traces b and b1). The images show the diamond's luminescence under broadband long wave UV excitation before (a) with a dominant green H3 emission, and after (b) the treatment, with a dominant blue N3 emission. The spectra are shifted vertically for clarity.

While photoluminescence proved the best method for the characterization of the majority of defects in type Ib diamonds, it could only be used as an indicator for defect concentration in samples of similar C center nitrogen concentration: the PL intensity from the NV^-, NV^0 (and from the H3 defects when A aggregates are present) was highest in deformed diamonds of very low C center nitrogen content (i.e. less than about 15 ppm) and there was a clear tendency that the intensity decreased with increasing C center content. The order of materials in which strong NV center related PL appears, also reflects the order of materials in which strong NV center absorptions are measured. The NV^- center absorption is most intense in "olive" diamonds, closely followed by brown diamonds, and it is generally very weak or undetectable in orange and yellow type Ib diamonds.

The PL measurements and observations by luminescence microscopy appear to suggest that C center nitrogen quenches luminescence. This would be consistent with published results [31,32], suggesting that the quenching happens via a non-radiative energy transfer of the NV centers to the C center by a dipole–dipole mechanism.

A closer look at the PL spectral data and the PL imaging caused a doubt on the quenching mechanism involved: the apparent quenching was evident under broadband UV, 405 nm and 473 nm laser excitations, but practically no intensity difference was observed under 532, 635 and 785 nm laser excitations. Comparing the UV–Vis–NIR absorption spectra of diamonds with apparent quenching under the shorter wavelength excitations and stones with stronger PL under such excitations showed that the UV–Vis–NIR spectra of the stones with "quenching" had their absorption cut-off shifted clearly into the visible – up to >460 nm – while the stones without quenching had their cut-off located somewhere between the UV and 400 nm. These observations suggest that the apparent quenching is mainly caused by the very strong UV–Visible absorption of the C center, which absorbs UV light before it gets to the emitting centers. As a consequence of this strongly reduced UV excitation, there is less PL emission. Hence it could just be that the C center, absorbing UV to green light, acts as a suntan lotion. The lotion (C center equivalent

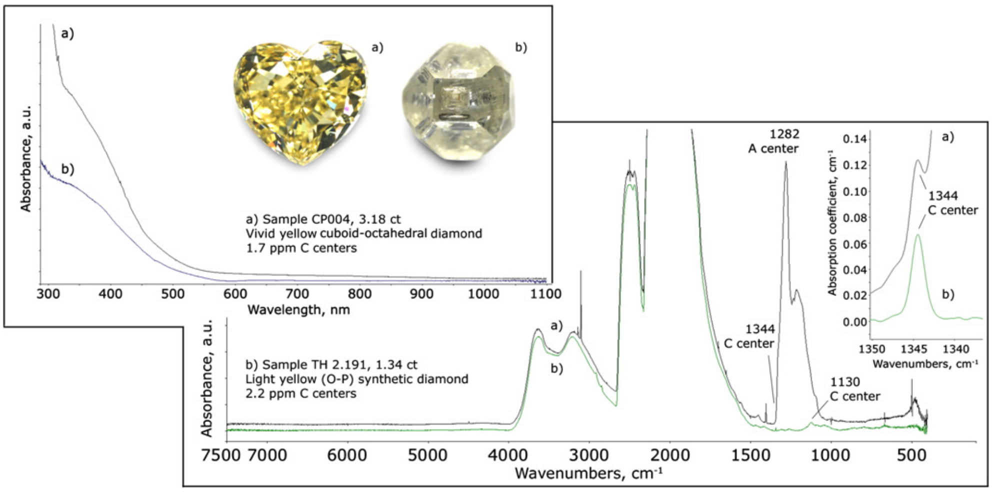

Fig. 12. The infrared spectra of a vivid yellow mixed growth cuboid octahedral type IaA ≫ Ib natural diamond (image a and trace a) and a light yellow (O–P color) synthetic diamond (image b and trace b). While the pale synthetic diamond contains 2.2 ppm of C centers the natural strongly colored diamond contains only 1.7 ppm of C centers. The two stones have similar UV–Vis absorption spectra and a similar thickness of ~5 mm. Even though the comparison is of a facetted gem and a rough diamond it is clear from the spectra and also visually that no matter how one would cut the rough diamond, its final color would be much lighter than the vivid yellow heart shaped diamond. The origin of the much stronger yellow coloration of the natural stone is unknown but it must be assumed that there is another type of defect besides the C center that results in yellow coloration, through the same shape of continuum absorption. The spectra are shifted vertically for clarity.

here) absorbs UV before it gets to sensitive cells (the emitting center's equivalent), hence avoiding sunburns (PL emission equivalent).

FWHM measurements of the major ZPLs (H3, NV^- and NV^0 centers) have shown that basically two factors influence the FWHM in type Ib diamonds: the C center content and the plastic deformation.

In consequence diamonds with low C center content show ZPLs with lower FWHM while the ZPLs in the spectra of stones with high C center content have larger FWHM. Hence there is a clear tendency that the lowest FWHM is found in diamonds of low C center content and as little deformation as possible, and the largest FWHM in samples is found in diamonds of high C center content and as much deformation as possible (Fig. 13).

This is in total agreement with published data for type Ia and IIa diamonds on certain defects such as GR1 and the NV centers [33] and follows the general rule that lattice disorder causes an increase of the bandwidths of bands observed e.g. in absorption and emission spectroscopy [34].

In stark contrast with octahedral type Ib diamonds, mixed cuboid/octahedral growth (in many cases "reentrant cube" growth) type Ib diamonds (actually type IaA ≫ Ib) are virtually free from deformation related defects: neither amber center absorption nor NV center group absorption could be detected in such diamonds; instead they are characterized by S1, S2 and S3 centers. Such mixed growth type Ib diamonds have not yet been found in brown or "olive" colors, but exclusively in pure yellows and more rarely yellowish orange in the deeper color gems. From the examination of large parcels of "vivid yellow" diamonds it has been determined that the vast majority of these purest and brightest yellow natural diamonds are of this specific group.

The Y center seems to play a particular role in the type Ib diamonds; while present in the infrared spectra of most type Ib yellow to orange diamonds it has not yet been detected in brown type Ib diamond and only exceptionally in "olive" diamonds. When this defect dominates the one-phonon infrared absorption then the properties of such "Y center diamonds" are unique. There seems to be a continuous series, spanning from octahedral growth type Ib diamonds with very low Y center content, to practically pure Y center/X center diamonds with very low C center content. There appears to be a threshold of Y center/X center dominance above which no more deformation-related defects can be detected.

The HPHT treatments of natural type Ib diamonds of various colors demonstrate that colors other than yellow are caused by a combination of C centers plus defect(s) very similar to the defects responsible for the brown color of type Ia diamonds. Short HPHT treatments of such deformed type Ib diamonds show that the color of orange, olive and brown type Ib diamond is modified to purely yellow, as the continuum and cut-off of the UV–Vis–NIR spectrum are modified. At the same time, in the IR, the amber center intensity diminishes and there are slight changes due to minor nitrogen aggregation. Hence extended vacancy defects such as vacancy clusters are the proposed candidates for the additional continuum absorption that occurs in the orange, "olive" and brown type Ib natural diamonds. The extended vacancy defect causes the additional continuum absorption visible at wavelengths above 560 nm, which disappears upon HPHT.

In orange type Ib diamonds the color is caused by comparatively high concentrations of C centers plus deformation-related continuum absorption. In brown and olive diamonds the color is caused by low to very low concentrations of C centers plus dominant deformation-related continuum absorption, plus NV^- absorption. Hence a combination of very low C center content plus strong deformation related defects results in either a dull brown or a dull "olive" color. More intense NV^- center absorption results in a greener "olive" color via a small transmission window in the green, due to the slight trough formed on one side by the continuum (related to isolated nitrogen and possibly deformation-related defects) and the other side, by the broad vibronic structure of the NV^- center. In type Ib brown diamonds the nitrogen content is typically even lower than in olive diamonds, and the NV^- absorption weaker; in consequence the absorption cut-off is shifted towards the UV, and the continuum is relatively straight and featureless.

While this paper gives an in-depth view of defects in natural type Ib diamonds and supplies suggestions for a variety of colors observed, some points require further research, as the exact atomic nature and optical activity of the Y center remain unknown for example. There is no explanation for the unusually strong yellow coloration of some diamonds that should be pale yellow, if reasoning is based only on their very low C center content. This leads to the question: why some diamonds with undetectable C centers (only with a type Ib character) can be strongly colored, and finally why there are IIa diamonds with strong yellow and strong orange colors? These challenges bring us to believe that there are some yet unknown color-causing defects that are found associated with isolated nitrogen. Hence, although we seem to have a large body of knowledge on diamond color, some discoveries remain to be made.

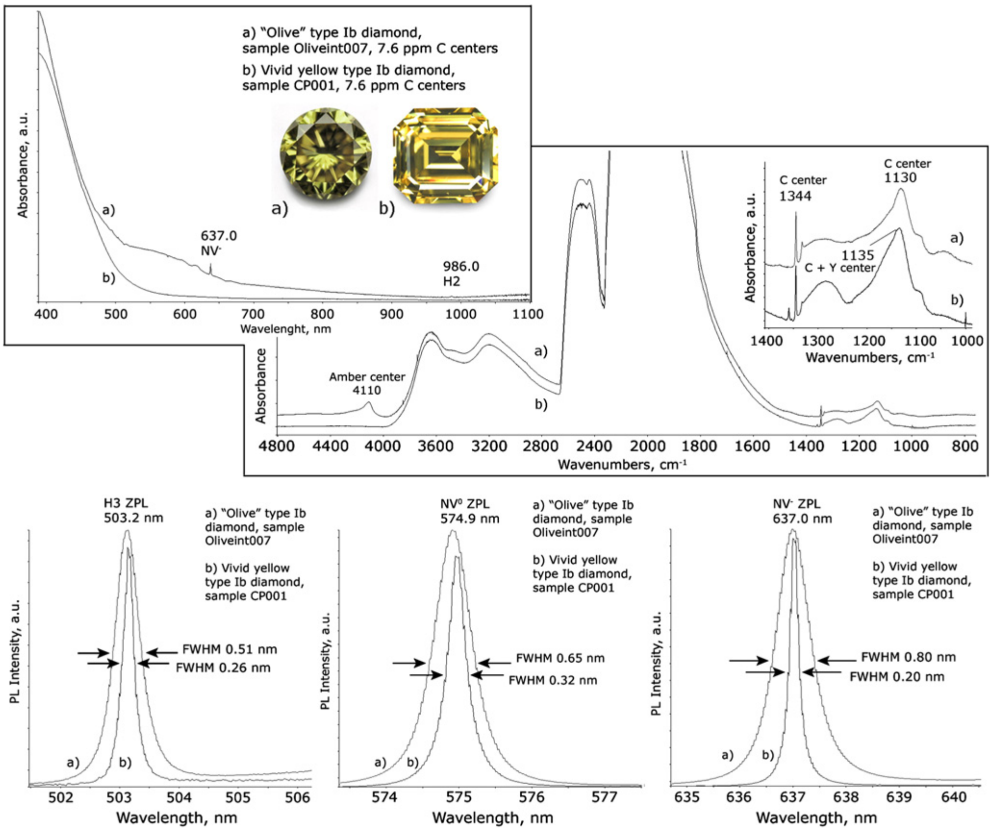

Fig. 13. The infrared and UV–Vis–NIR spectra (top graph) of an olive (a) and a yellow (b) natural diamond with identical C center concentrations (7.6 ppm). While the infrared spectrum of the yellow diamond shows only some Y center one-phonon absorption besides the C center absorption, the spectrum of the olive diamond is characterized by distinct amber center absorption, related to plastic deformation. On the bottom graphs the photoluminescence ZPLs of the two diamonds for the major defects (H3, NV^0 and NV^-) are shown and their FWHM is compared. The ZPLs of the olive diamond are distinctly larger, and since C center content of the samples is identical the phenomenon can be attributed to the deformation-related defects of the olive diamond only. The infrared spectra are shifted vertically for clarity.

Prime novelty statement

This paper represents the first full characterization of the group of natural diamonds with C centers detectable in their infrared spectra, in order to determine the cause of the various colors observed for these rare diamonds.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.diamond.2013.07.007.

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