

Article

A Defect Study and Classification of Brown Diamonds with Non-Deformation-Related Color

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Abstract: While the first part of this study took a detailed look at the properties, defects and classification of brown diamonds with deformation-related (DR) brown color and compared them to pink to purple to red diamonds, this second part covers diamonds with non-deformation-related (referred to as NDR in this study) brown color, including diamonds with treatment-induced brown color and synthetic brown diamonds. It was found that the natural NDR brown diamonds include CO₂ and Pseudo CO₂ diamonds as well as certain hydrogen-rich diamonds. Based on these, the new classification of NDR brown diamonds has been elaborated, resulting in 5 different classes. The detailed defect study performed has shown and confirmed the complexity of the CO₂ and Pseudo CO₂ diamonds; the probable link between structurally bound oxygen and some of the spectroscopic features such as the 480 nm absorption band is apparent in these diamonds. One of the most interesting findings was made through the low temperature NIR spectroscopy of some usually hydrogen-rich diamonds, which has defined a defect of great interest, the 1330 nm center; we suggest that this defect, together with the many lines in the 970 to 1000 nm range—referred to as the 990 nm series in this study—are responsible for the complex UV-Vis-NIR spectra seen of these diamonds. The results indicate that both features are nickel-nitrogen-related defects, the 1330 nm defect without involvement of hydrogen and the 990 nm series likely with hydrogen involved. Another surprising result was that during various treatment experiments performed we created dark orangish brown color in originally pale yellow “cape” diamonds by HPHT treatment at 2500 °C. It is suggested that the creation of this brown hue is related to the destruction or transformation of the N3 center at such extreme conditions.

Keywords: natural diamonds; defect characterization; optical properties; hydrogen; CO₂ absorption

1. Introduction

Brown diamonds that owe their color to defects that are not related to post-growth plastic deformation (DR = deformation-related [1], NDR = non-deformation related) are quite rare, particularly in larger sizes (Figure 1); earlier studies of brown diamonds have shown that parcels of melee-sized brown diamonds contained approximately 1.3% of brown diamonds with no signs of significant plastic deformation, designated as CO₂ diamonds and Pseudo-CO₂ diamonds [2]. CO₂ diamonds were first described by Schrauder and Navon based on a single diamond [3]. The IR spectra of such diamonds exhibit absorptions at the approximate positions of where the CO₂ ν_3 (asymmetric stretch) and the CO₂ ν_2 (bend) absorption are expected, and—in the experience of the authors—whenever these absorptions are very strong, then overtone and combination bands can be detected. Pseudo-CO₂ diamonds are stones that exhibit optical and spectroscopic properties very similar to CO₂ diamonds, but that do not show CO₂ absorptions in their IR spectra [2]. The presence and position of the CO₂ absorptions were used to suggest that they are caused by pressurized solid CO₂ inclusions [3]. Unpublished

work on large numbers of CO₂ diamonds by the authors has shown that the CO₂ absorptions show significant fluctuations in both, position and shape; the spectral positions were found to show illogical shifting behavior, indicating the impossible scenario of different pressures calculated for ν_3 and ν_2 in one and the same diamond. Alternative suggestions like CO₂ bound within the diamond structure were postulated [4]. A study of CO₂ and Pseudo CO₂ diamonds by X ray small angle scattering (SAXS) and by chemical analysis using SIMS (secondary ion mass spectroscopy) has concluded that the oxygen in such diamonds might be present both structurally bound within the diamond as well as in inclusions [5]. That study was in line with another study by the authors [4], in which CO₂ and Pseudo CO₂ diamonds were HPHT treated, and in which it was found that HPHT (High Pressure High Temperature) treatment created CO₂ absorption in Pseudo-CO₂ diamonds; this also suggests that structurally bound oxygen is present in such diamonds. During that study it was found that these NDR brown diamonds barely changed color upon HPHT treatment, they stayed basically brown after HPHT.

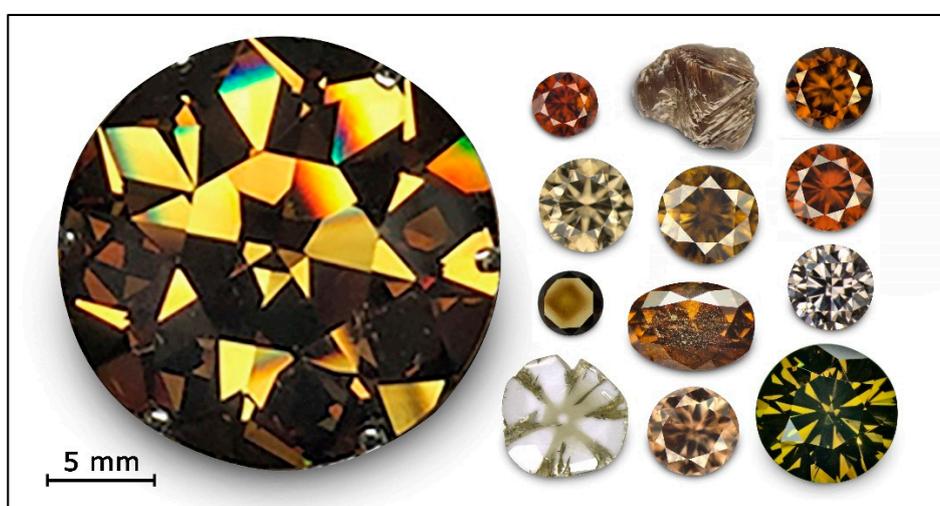


Figure 1. Part of the non-deformation-related (NDR) brown diamonds tested for this study, from left to right: First stone plus second column—hydrogen rich diamonds; second column—CO₂ and Pseudo—CO₂ diamonds; third column top two stones—treated brown diamonds; third column bottom two stones—synthetic brown diamonds.

When the first classification of brown diamonds was suggested in 2003 [2], the classification was split into two groups based on the presence or absence of amber center (AC) IR absorption, not based on the relation of the color to plastic deformation. The research performed here has shown that a splitting into two groups, one with deformation-related (DR) brown color—represented in the first part of this study—and one with non-deformation-related (NDR) brown color—represented by this second part of the study—is more appropriate. One reason is that with enhanced IR and NIR absorption spectroscopy techniques we were able to detect ACs in many diamonds where before the ACs appeared to be undetectable, such as type IIa diamonds. The sampling of the 2003 study was also lacking hydrogen-rich brown diamonds, a category that clearly belongs into the group of NDR brown diamonds, even though such brown diamonds are rare; the vast majority of NDR hydrogen-rich diamonds are—in the authors experience—not brown but rather brownish yellow to “olive”.

In NDR non-brown diamonds a dominantly brown color can be induced by heavy irradiation followed by annealing. The most efficient method to do this is neutron irradiation since it penetrates the entire volume of a diamond and since it very efficiently induces vacancies compared to other radiations such as electrons; when diamonds are irradiated by large doses of neutrons to turn them black and then annealed at 800 °C, then the resulting color is generally a dark orangey brown to deep brownish orange [6].

Brown diamonds can also be found in synthetically grown stones; as-grown synthetic brown diamonds are very commonly grown by CVD (chemical vapor deposition) synthesis, since the vast majority of such stones are grown rapidly and are thus very rich in dislocations and vacancies [7]. These defects are responsible for the brown color and can be eliminated by HPHT treatment, hence the majority of (near-) colorless CVD synthetic diamonds are HPHT treated brown CVD synthetic diamonds [7]. Generally, such synthetic brown diamonds are not of dark color, mostly they occur—in the experience of the authors—in brown color within the N to Z color range, which corresponds to very light brown to light brown [8].

The purpose of this paper is a detailed characterization of brown diamonds, with non-deformation-related color, particularly of the defects that can be detected by various spectroscopic methods, plus a newly proposed classification of such colored diamonds. Further, the creation of brown color by treatment and in synthetic diamonds are explored. Some of the most interesting results of this study is the definition of the 1330 nm defect and the 990 nm series in H-rich diamonds as well as the creation of brown color by HPHT treatment of yellowish cape diamonds through the annealing of the N3 center.

2. Materials and Methods

Besides brown diamond samples collected in the past 20 years by TH and FN, approximately 30,000 brown diamonds in various sizes and from various sources were screened for this study and different groups of stones were selected based on their luminescence spectra. A total of 22 gem-quality brown diamonds weighing 0.02 to 61.56 ct were analyzed in detail for this study. Samples include all different categories of brown diamonds owing their color to non-deformation-related defects (referred to as “NDR”—non-deformation-related—in this study). Only diamonds with dominantly brown color were included, all of them faceted into various shapes with the exception of one rough CO₂ diamond. See Table 1 for details on the diamonds. Besides these diamonds tested specifically for this study, the data of the likely largest hydrogen-rich gem-quality yellow brown diamond in existence analyzed in the past was included (the Tigers Eye diamond). To better understand the complex UV-Vis-NIR spectra of NDR hydrogen-rich brown diamonds, 15 hydrogen-rich diamonds and one low hydrogen diamond of yellow, olive, gray and violet color, all exhibiting the 1330 nm center were included in this study (not listed in sample table); these were only tested by UV-Vis-NIR, NIR, and FTIR spectroscopy.

The color distribution and strain patterns of the diamonds were analyzed using a Leica M165C Trinocular Microscope, equipped with a Leica DFC450 CCD camera; the color distribution was checked with the diamonds immersed in alcohol or diiodomethane, 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. Detailed luminescence imaging was performed with a GGTL Mega-DFI luminescence imaging and spectroscopy system that produces 5 different intense UV excitation bands (centered at 340, 320, 280, 265, and 210 nm) as well as 405 nm laser excitation.

Infrared spectra of all the samples were recorded with a resolution of 4 cm⁻¹, and for some also 1 cm⁻¹, on a Perkin Elmer Spectrum 100S and on a Perkin Elmer Frontier FTIR spectrometer, both equipped with a thermoelectrically cooled DTGS (deuterated triglycine sulphate) detector, using a diffuse reflectance accessory as a beam condenser and a 5x beam condenser. The spectra were recorded over a range of 8500 to 400 cm⁻¹, with 50 to 1000 scans for each diamond.

Table 1. An overview of the samples studied with some of their basic optical and infrared spectroscopic properties.

Key:	Sample	Description Weight	Color	Type	Nitrogen/Boron Content, ppm (+/−5%)	IR Characteristics	Treatments Performed
NDR CO ₂ diamond	TH 2.54	RBC, 0.776 ct	F. pinkish brown	IaA	240 tot.; 240 A	CO ₂ (low)	
	TH 2.67	RBC, 0.110 ct	F. brownish olive	Undefined	–	CO ₂ (medium)	
	TH 2.69	RBC, 0.075 ct	F. brown	IaA >> B	186 tot.; 161 A, 25 B	CO ₂ (low)	
	TH 2.71	Plate, 0.040 ct	F. light brown	IaA > B + undef.	53 tot.; 38 A, 15 B	CO ₂ (very high)	
	TH 2.72	RBC, 0.053 ct	F.dk. olivish brown	IaAB + undef.	8 tot.; 6 A, 2 B	CO ₂ (high)	
	TH 2.78	RBC, 0.224 ct	F.dk. olivish brown	IaA >> B + undef.	15 tot.; 12 A, 3 B	CO ₂ (very high)	
	TH 2.93	RBC, 0.032 ct	F. yellowish brown	IaB > A	565 tot.; 180 A, 385 B	CO ₂ (low), H-rich	
	SGDF-5864	Slice, 0.056 ct	Brown, “zebra striped”	Undefined	–	Very low CO ₂ , limit Pseudo CO ₂ and CO ₂	
NDR Pseudo CO ₂ diamond	TH 2.70	Slice, 0.050 ct	F. brown	Undefined	–	Pseudo CO ₂	
	TH 2.79	Slice, 0.045 ct	F. brown	IaA >> B + undef.	22 tot.; 17 A, 5 B	Pseudo CO ₂	
	TH 2.99	RBC, 0.049 ct	F.lt. brownish yellow	IaAB + undef.	15 tot.; 8 A, 7 B	Pseudo CO ₂	
NDR H-rich diamond	TH 2.49	Slice, 0.022 ct	F.dk. yellowish brown	Ib > IbXY >> IaA	197 tot.; 36 A, 144 C, 17 X	H rich	
	TH 2.327	RBC, 0.055 ct	F.dp. orange brown	IbXY	65 tot.; 51 C, 14 X	H rich	
	TH 2.618	RBC, 0.161 ct	Light yellow brown (X-Y)	IaA >> B	1622 tot.; 1324 A, 298 B	H rich, NIR structure	
	TH 2.626	Slice, 0.279 ct	Brown/near colorless, sectored	IaA >> B	B: 2415 tot.; 2115 A, 300 B C: 2853 tot.; 2623 A, 230 B	H rich	
	Tigers Eye	RBC, 61.56 ct	F.dp. brown yellow	IaA > B	885 tot.; 530 A, 355 B	H rich, NIR structure	
NDR diamond with treated brown color	TH 2.32	Pear, 0.322 ct	F.dk. yellowish brown. originally f.dk. brown	Undefined	–	Pseudo CO ₂ , H1b	Irrad. 2 MeV e [−] , HT 800 °C
	TH 2.163	RBC, 0.109 ct	F.dp. brown orange, originally colorless (F)	IaA >> B	140 tot.; 132 A, 8 B	H1b, H1c	Irrad. 1.8x10 ¹⁷ neutrons/cm ² , HT 1100 °C
	TH 2.416	RBC, 0.068 ct	F. dark orangey brown, originally light yellow	IaB > A	1730 tot.; 500 A, 1200 B, 30 C	1660 cm ^{−1} peak	Irrad. 2 MeV e [−] , HPHT 2500 °C
	TH 2.417	RBC, 0.065 ct	F. dark orangey brown, originally light yellow	IaB >> A	1780 tot.; 350 A, 1400 B, 30 C	1660 cm ^{−1} peak	Irrad. 2 MeV e [−] , HPHT 2500 °C
Synthetic diamond	TH 2.22	RBC, 1.053 ct	F. dp. red brown, originally deep yellow	Ib > IaA, synth. HPHT	121 tot.; 40 A, 81 C	H1b	Irrad. 2 MeV e [−] , HT 800 °C
	TH 2.589	RBC, 0.164 ct	Light brown (S-T)	Ila, synth. CVD	–	7354, 6857, 6425, 5565 cm ^{−1} peaks	–

Irrad. = irradiated. HT = annealed. HPHT = High Pressure High Temperature treated. A = A center/A aggregate; B = B center/B aggregate; C = C center/Single substitutional nitrogen. F.lt. = fancy light; F. = fancy; F.dp. = fancy deep; F.dk. = fancy dark.

The nitrogen concentration was determined by progressive spectral decomposition via spectral calculations (“progressive decomposition”). The nitrogen concentration was 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 [9]. All diamond spectra were normalized before the concentration calculation could be reliably conducted. This normalization was performed by spectral calculation, for which the absorbance value of the intrinsic diamond absorption on the y axis at 1995 cm^{-1} was measured and then a multiplying factor was applied in order to obtain a value of 12.3 cm^{-1} . The spectrum was 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 center) were 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} [10], and not on the intensity of the 1130 cm^{-1} band because of possible false results from underlying Y center absorption [11].

Near infrared spectra on the range $11,200$ to 4000 cm^{-1} (900 to 2500 nm) were recorded using a custom-built GGTL NIR spectrometer system using a thermoelectrically cooled InGaAs (indium gallium arsenide) detector, in a 15 cm diameter integrating sphere using a special high power NIR light source. Spectra were recorded with 50 to 150 scans for each diamond, at a resolution of 4 cm^{-1} , at room temperature and with the samples cooled to 77 K using special low temperature accessories.

Photoluminescence spectra were recorded on a GGTL Photoluminator RS6 system using 360, 402, 473, 532 and 635 nm laser excitations, and a high-resolution Echelle spectrograph by Catalina Scientific equipped with an Andor Neo CMOS (complementary metal–oxide–semiconductor) camera, thermoelectrically cooled down to $-30\text{ }^{\circ}\text{C}$. 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 quadruple channel spectrometer with a Czerny–Turner monochromator and a thermoelectrically cooled CCD (charge coupled device) detector was employed, with an average resolution of 0.3 nm . The spectra were measured with the samples cooled down to about 77 K , placed in an integrating sphere of 15 cm diameter.

A series of NDR brown and diamonds were treated by the different treatments applied to diamonds, including irradiation by electrons or neutrons, irradiation followed by annealing as well as HPHT with and without prior irradiation treatment. Some of these treated diamonds have been published in earlier articles and some are unpublished, a selection of the most typical and most interesting results will be included in this paper.

Irradiation was performed at the electron irradiation facilities of Leoni Studer AG in Däniken, Switzerland, using electrons of variable energies from 1.5 to 10 MeV (megaelectronvolt), with an irradiation time of 2 to 4 h. The exact irradiation doses are generally unknown since (for reasons of treatment cost reduction) the samples were irradiated together with materials that were passed through the accelerator for cross-linking treatment. Neutron irradiation was performed in a nuclear reactor in Poland with a dose of 1.8×10^{17} neutrons/cm² using mostly fast neutrons of energies of several MeV. Simple annealing and post-irradiation annealing have been realized at our laboratory using a Nabertherm LHT 02/17/P 470 oven with maximum temperature of $1750\text{ }^{\circ}\text{C}$. For the annealing experiments the diamonds were kept in a reducing atmosphere, to keep the diamonds from burning at conditions above $500\text{ }^{\circ}\text{C}$. Annealing was performed for the diamonds up to a temperature of $1100\text{ }^{\circ}\text{C}$.

Some samples were treated by HPHT at temperatures ranging from 2000 to $2500\text{ }^{\circ}\text{C}$ and pressures ranging from 55 to 85 kbar and kept at the maximum temperature for minimum 2 to maximum 30 min. The treatments were performed at the HPHT facilities of the Bakul Institute of Superhard Materials, Kiev, Ukraine, of SedKrist GmbH, Seddiner See, Germany, and of Suncrest in Orem, UT, USA.

3. Results and Discussion

3.1. Natural Brown Diamonds Colored by Mechanisms not Related to Plastic Deformation

3.1.1. CO₂ and “Pseudo CO₂” Brown Diamonds

Four Pseudo CO₂ and seven CO₂ diamonds were included in the sampling for this study. The diamonds were chosen as representative samples from a large amount of such diamonds in the collections of TH and FN. This said, it must be mentioned that this group of diamonds has a very wide range of properties, and that characterizing them in more details would not be of specific interest in this study. Such a specific large study on CO₂ and Pseudo CO₂ diamonds will be published at a later point.

Microscopic Examination

Under the microscope, these diamonds showed rather unusual properties in terms of inclusions, color distribution and strain. The most characteristic inclusions in both CO₂ and Pseudo CO₂ diamonds are very small reflective particles, which are either rounded or perfectly hexagonal and which are very likely graphite crystals. They appear black to brown or highly reflective white, depending on the orientation in which they are viewed; with these particles, needle-like inclusions of unknown nature sometimes occur (Figure 2).

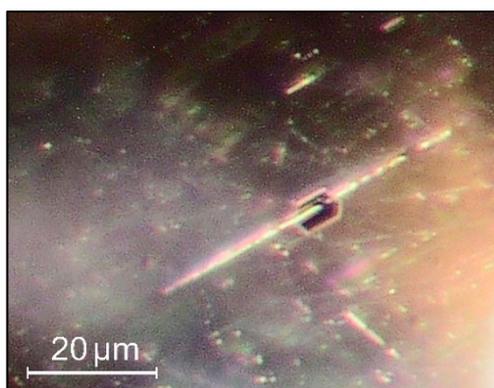


Figure 2. The characteristic inclusions in a CO₂ diamond—hexagonal platelets and needle-like inclusions. Photo: Dr. Thomas Hainschwang.

In immersion, the CO₂ diamonds studied typically showed an irregular color distribution with a brown colored patch in the core of the diamond, surrounded by a colorless sector along the periphery (Figure 3, left). This distribution is identical to what has been described in earlier publications. Under crossed polarizing filters some extinction was visible in most diamonds, but not clearly related to slip planes along octahedral directions; much of the extinction was observed within the brown color patch and most of it appeared to be caused by small inclusions such as microfractures and the tiny particles so abundant in the brown zones (Figure 3, right). Rarely, random deformation-related extinction and strain can be seen in CO₂ diamonds, but there is no brown color associated with it.

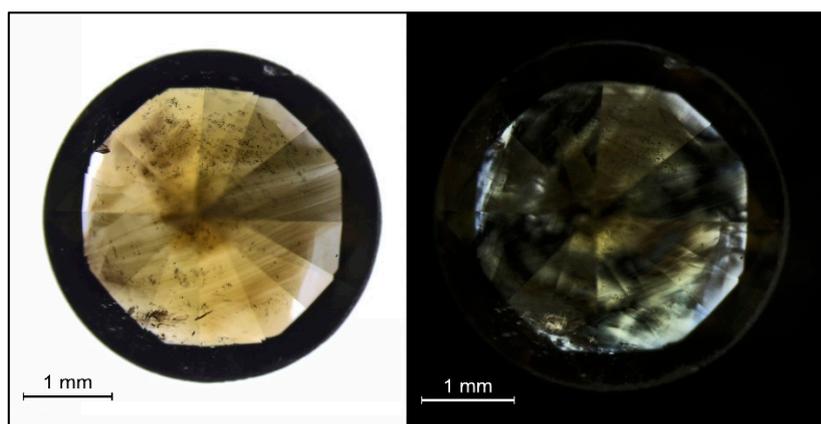


Figure 3. A very typical CO₂ diamond (TH 2.78) in immersion (**left**) and crossed polarizing filters (**right**). The brown color patch was shown to contain the CO₂ while the colorless sectors are free of CO₂. The strain in CO₂ diamonds is not related to deformation, but most likely to micro-inclusions. Photos: Dr. Thomas Hainschwang.

In contrast to CO₂ diamonds, the color distribution of Pseudo CO₂ diamonds showed parallel gray to brown color bands. A very small CO₂ absorption was only detectable in one of the diamonds with such strong color banding, and this stone appeared to represent the limit between CO₂ and Pseudo CO₂ diamonds (Figure 4, left). When these color banded diamonds were observed between crossed polarizing filters, it became apparent that these color bands did not relate to post-growth plastic deformation, but that their origin was related to NDR defects or inclusions. The lighter yellow brown and the darker brown color bands appeared isotropic since they remained dark when rotated under crossed polarizing filters, while the colorless bands and the olive gray bands were clearly anisotropic; they lightened up and extinguished alternatingly every 45°, with this effect most strongly visible in the olive gray bands (Figure 4, right).

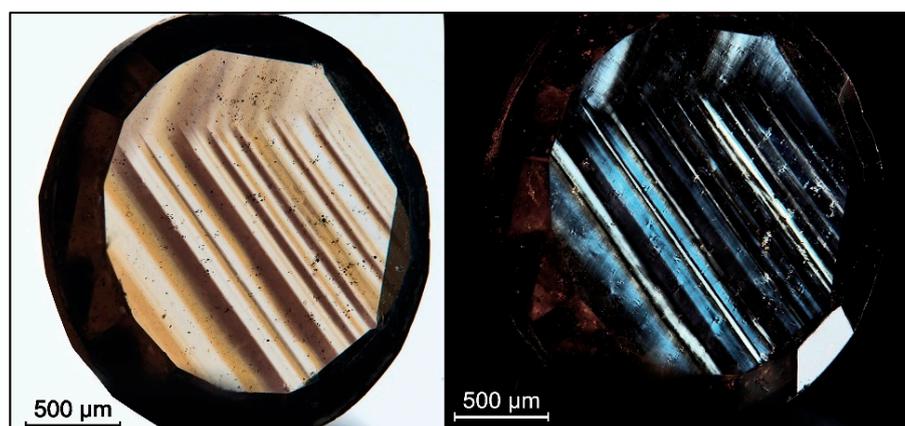


Figure 4. A very low CO₂ content diamond (sample SGDF 5846), representing the limit between CO₂ and “Pseudo CO₂”, in immersion (**left**) and under crossed polarizing filters (**right**). The amazing “zebra” layering of the diamond did not relate to plastic deformation. The lighter yellow brown and the darker brown zones were apparently isotropic—they stayed dark during rotation of the sample—while the colorless and olive-gray zones were clearly anisotropic—they lightened up and turn dark alternating every 45°; the olive-gray zones showed this effect most strongly and appear white in the image above on the right.

Infrared and Near-Infrared Spectroscopy

The infrared spectra of the CO₂ diamonds were characterized by the CO₂ ν_3 (asymmetric stretch) and the CO₂ ν_2 (bend) absorptions and by one-phonon absorption varying from regular A and B aggregate absorption to highly unusual absorption not related to any known form of nitrogen. The measured positions for the CO₂ absorptions ranged from 2369 to 2405 cm⁻¹ for ν_3 and from 660 to 644 cm⁻¹ for ν_2 . The one phonon absorption of these diamonds varied strongly and while some showed regular A and B aggregate absorption (Figure 5, trace a and b), in others the absorptions were unknown and no nitrogen-related absorptions were detected (Figure 5, trace c). Hydrogen was detected in all samples, but only one exceptional CO₂ diamond rich in aggregated nitrogen was found with high hydrogen content (Figure 5, trace b); generally, the amount of IR active hydrogen was very low. Pseudo-CO₂ diamonds exhibited spectra very similar to CO₂ diamonds, with the difference that the spectra of the Pseudo-CO₂ diamonds were lacking the CO₂ peaks (Figure 5, trace d); this characteristic combined with the fact that all other optical and spectroscopic properties of such diamonds are clearly in line with CO₂ diamonds has led to the designation “Pseudo-CO₂ diamond”. HPHT treatment of CO₂ and Pseudo-CO₂ diamonds performed for an earlier study [4] has shown that the CO₂ absorption can be created in Pseudo-CO₂ diamonds by HPHT treatment; if and how this newly formed CO₂ is structurally bonded or if it somehow forms micro inclusions through this process is not clear at this point.

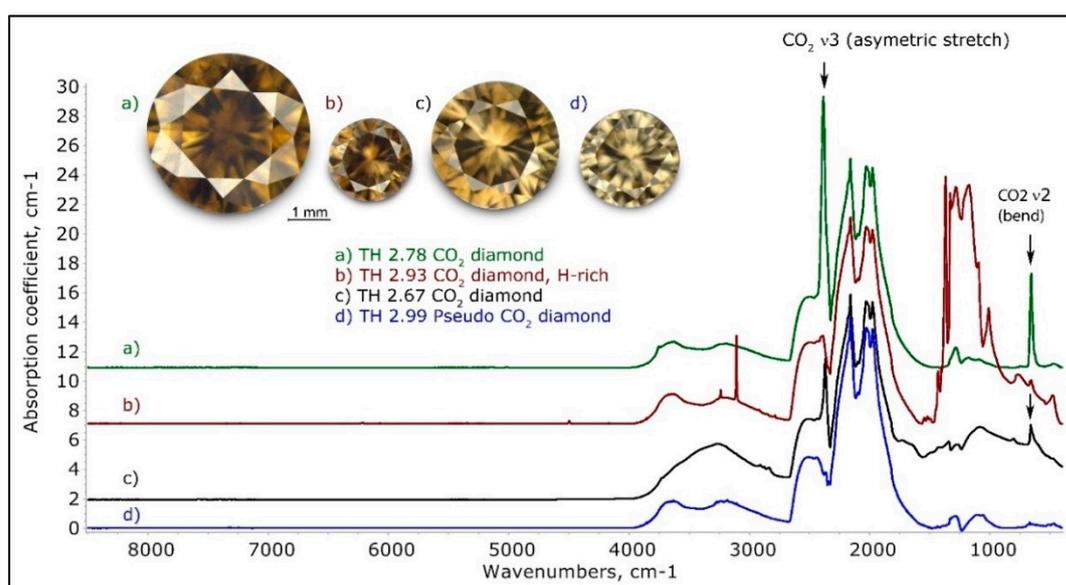


Figure 5. A few representative normalized IR spectra of brown CO₂ and Pseudo CO₂ diamonds. Trace (a) is a typical CO₂ diamond spectrum, spectrum (b) a very unusual hydrogen and nitrogen-rich CO₂ diamond, and trace (c) an example of a CO₂ diamond not exhibiting any trace of known nitrogen-related absorptions. Trace (d) is a typical Pseudo-CO₂ diamond, but it must be mentioned that these spectra vary widely; they may exhibit some known nitrogen-related absorptions but generally a significant portion of the one-phonon absorption is of unknown cause. The spectra have been shifted vertically for clarity.

For a diamond that was cut into a slice with two large parallel faces (sample TH 2.71) spectra were recorded in both the brown and the colorless zones and it was obvious that the CO₂ was only present in the brown sector (Figure 6, trace a), while known nitrogen absorptions and hydrogen absorptions were only detected in the colorless sector (Figure 6, trace b).

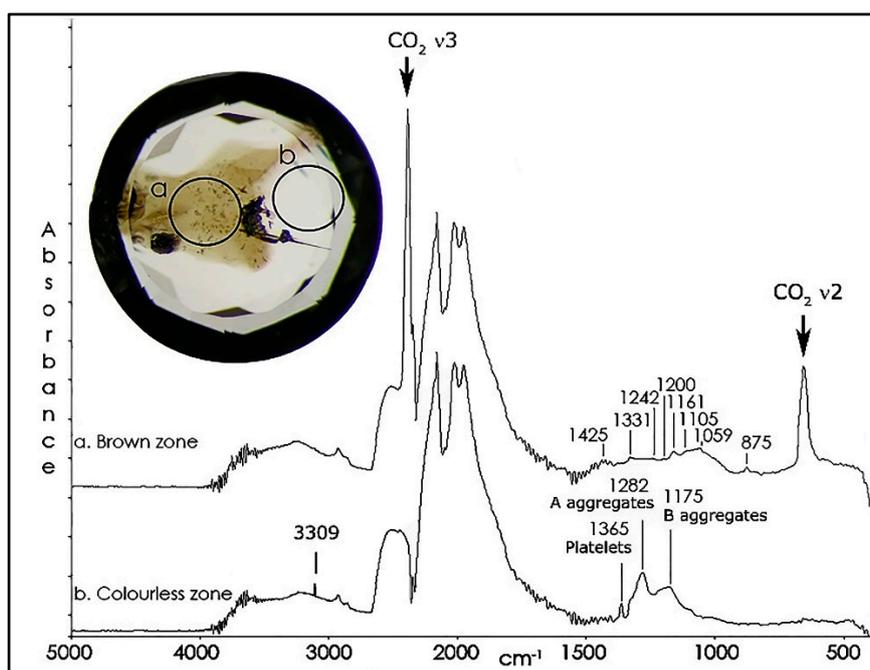


Figure 6. The IR spectra of the brown (trace **a**) and the colorless (trace **b**) sector of a brown CO₂ diamond (Sample TH 2.71) clearly show that the CO₂ is confined to the brown sector, while the A and B aggregate nitrogen plus the hydrogen is only detected in the colorless sector. The one-phonon absorption in the brown color zone is of unknown cause. The spectra have been shifted vertically for clarity.

This observation could be interpreted as a negative correlation between CO₂ and nitrogen or by optical inactivity of the nitrogen when it occurs in the CO₂ rich sectors, as it was suggested by [4]. The SIMS analysis performed for a later publication [5] have indeed shown that oxygen and nitrogen do have a positive correlation, hence the brown sector was found to be richer in nitrogen than the colorless sector. This fact seems to indicate that nitrogen is involved in the defects exclusive to the CO₂ rich sectors, thus likely with oxygen; this involvement transformed the nitrogen into a defect other than the known forms of nitrogen in diamond. Whether the resulting defect(s) are responsible for the some of the unknown one phonon absorptions is not known, but it is clearly a possibility. It can be suggested that nitrogen and oxygen form one or multiple new defects, which would indicate that oxygen is present structurally bound to diamond. The question remains whether the CO₂ is present in form of inclusions, bound to the diamond structure or both.

UV-Vis-NIR Spectroscopy

The NDR CO₂ and Pseudo CO₂ diamonds tested for this study exhibited UV-Vis-NIR spectra characterized by a pretty featureless continuum, overlaid by weak broad bands centered at 480 nm and at 370 nm and often a narrower weak peak at 427 nm (Figure 7); these features indicate the presence of oxygen in these diamonds and have been described for other diamonds that are supposedly oxygen-rich, such as the so-called 480 nm band yellow to orange diamonds [12,13] as well as chameleon diamonds [14]. An increase in the 480 nm band was observed when CO₂ and Pseudo-CO₂ diamonds were HPHT treated [4] and the same phenomenon was seen when chameleon diamonds were processed by HPHT [15]. It has also been demonstrated that the HPHT treatment of any diamond with Y center infrared absorption induced the 480 nm and the 427 nm absorptions [11,15]. With oxygen playing a significant role in all these diamonds, the confirmation that the 480 nm band very likely relates to an oxygen containing defect should not be surprising. Additional weak sharp absorptions were occasionally observed, particularly in the NIR (Figure 7, trace b).

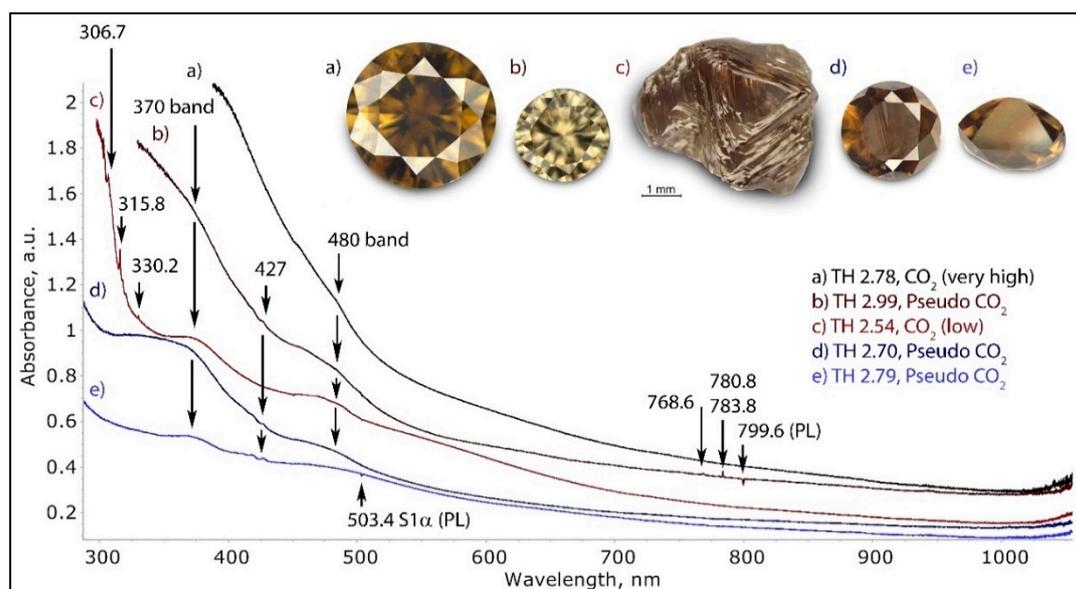


Figure 7. The low temperature UV-Vis-NIR spectra of a series of different CO₂ and Pseudo CO₂ diamonds. As with other brown diamonds, the NDR CO₂ and Pseudo CO₂ diamonds exhibit spectra characterized by a rather featureless continuum. Each one of them exhibits weak broad bands at 480 nm and at 370 nm and often a narrower weak peak at 427 nm; these features indicate the presence of oxygen in these diamonds. The spectra have been shifted vertically for clarity.

Photoluminescence Spectroscopy

The PL spectra of all CO₂ (Figure 8) and Pseudo-CO₂ (Figure 9) diamonds were very similar to each other, consisting of several broad bands overlaid by large quantities of sharp peaks and—particularly characteristic—also overlaid by somewhat broader oscillating bands spaced by approximately 10 nm (Figures 8 and 9). The broad bands centered between 520 and 565 nm are mostly related to the S1 and S2 defects with ZPLs at 503.4/510.6 nm and 489.1 nm respectively (Figure 8, trace a) and the S3 defect with ZPL at 496.6 nm (Figure 9, trace b). The S centers are characterized by intense and relatively featureless broad vibronic bands and surprisingly weak ZPLs, with the exception of the S3 defect in synthetic diamond that will show strong ZPLs. The vibronic band of the S1 defect is centered at 565 nm, of the S2 defect at about 550 nm and S3 defects at about 540 nm; the S2 and S3 defects often occur together. With these S centers linked to nickel impurities, it is not surprising that the spectra of all samples showed numerous other nickel-related PL peaks, of which particularly the double peak at 882.9/884.6 nm attributed to positively charged interstitial nickel (Ni_i⁺) is well known [16], and can be very intense in the spectra of such diamonds (Figure 9, trace e).

The broad band centered between 660 and 690 nm depending on sample and/or the laser excitation is identical to the band found in the PL spectra of yellow to orange “480 nm band” diamonds and in chameleon diamonds, and is the counterpart in PL linked to the 480 nm absorption; the overlaying oscillating absorptions on this broad band are always found at the following approximate positions: 605, 615, 625, 634, 644, 654, 665, 676, 688, 700, 712, and 724 nm (Figure 8 trace b and Figure 9 trace c). The many sharp PL emissions detected could be found repetitively in most samples, with some variations from diamond to diamond, particularly in the intensity of the peaks. The most characteristic sharp PL features besides the S centers and the 882.9/884.6 nm nickel center were found to be the peaks at 440.3, 510.7, 518.0, 578.0, 578.5, 581.3, 590.0, 590.4, 635.1, 636.0, 638.0, 639.0, 687.4, 758.6, 763.3, 771.4, 784.8, 793.6, 799.5, 818.9, 838.3, and 869.2 nm.

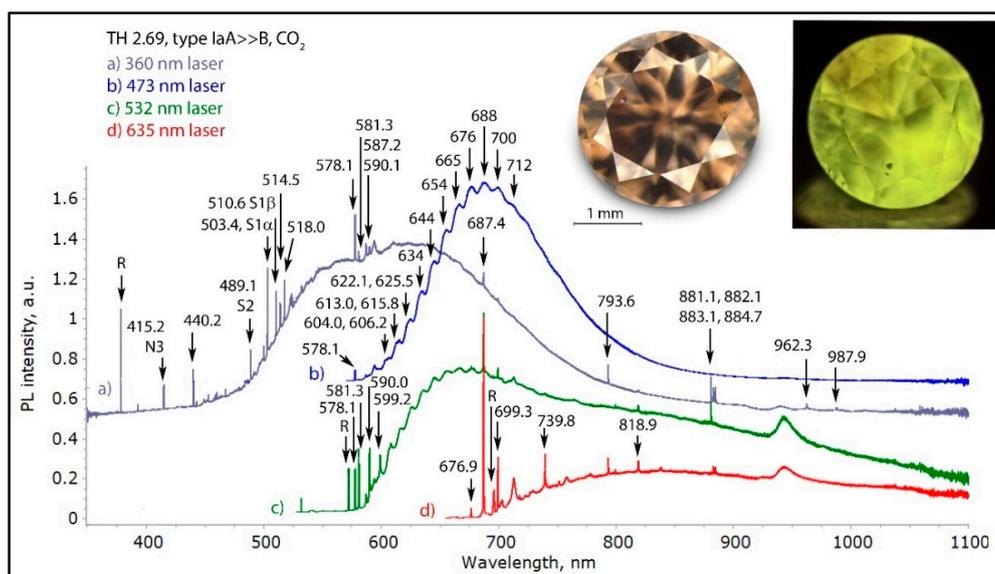


Figure 8. The highly complex PL spectra of a CO₂ diamond (TH 2.69) under four different laser excitations. The yellow PL seen in the photo is caused by the S1 and S2 defect. The complex band centered at about 690 nm with all its oscillating peaks separated by 10 to 12 nm each seen in trace (b) is very typical for diamonds rich in oxygen, and it relates directly to the 480 nm absorption band. Such diamonds always contain nickel as well, as can be seen by the presence of S1 and S2 as well as many of the sharp features seen in the spectra. The spectra have been shifted vertically for clarity.

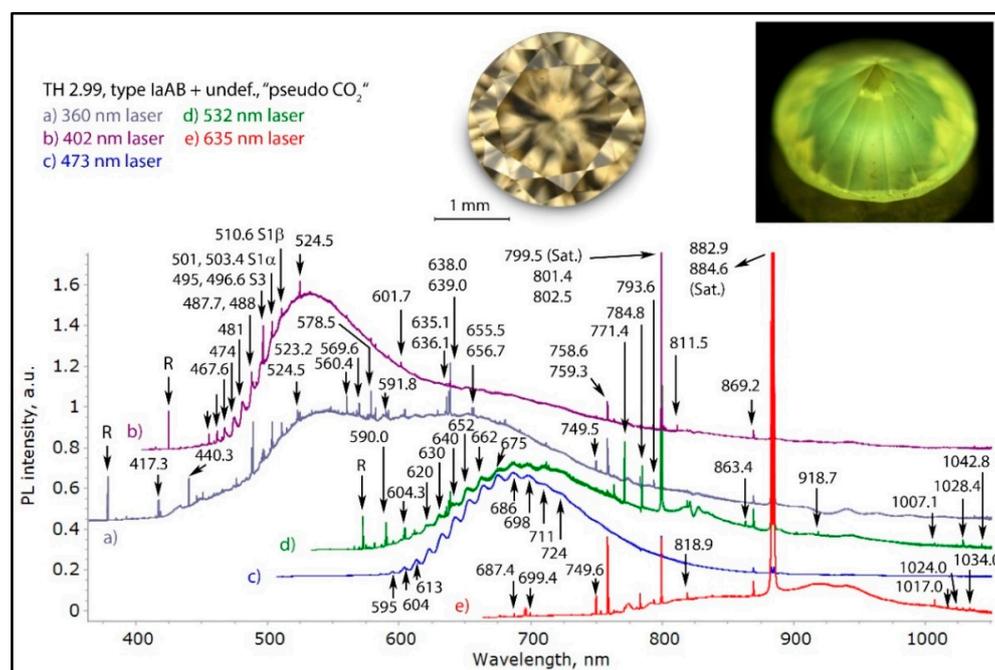


Figure 9. The highly complex PL spectra of a Pseudo CO₂ diamond (TH 2.99) under five different laser excitations. The yellow PL seen in the photo is caused mainly by the S1 and S3 defect. The complex band centered at about 690 nm with all its oscillating peaks separated by 10 to 12 nm each seen in trace (c) and (d) is very typical for diamonds rich in oxygen, and it relates directly to the 480 nm absorption band. Such diamonds always contain nickel as well, as can be seen by the presence of S1 and S3, the very strong 882.9/884.6 nm Ni_i⁺ doublet as well as many of the sharp features seen in the spectra. The PL spectra of CO₂ and Pseudo CO₂ diamonds are very similar and typical features present are identical. The spectra have been shifted vertically for clarity.

DFI Fluorescence Imaging and Spectroscopy

The CO₂ and Pseudo-CO₂ diamonds fluoresced yellow to green under the various excitations of the Mega-DFI (Figures 10 and 11). The fluorescence was determined to mostly relate to the S1, S2 and or S3 centers. The S1 center caused the dominantly yellow PL as seen in Figure 10 because of its broad emission centered at 565 nm, while S2 and S3 caused the dominantly green PL as seen in Figure 11, because of their broad emission bands centered at 540 to 550 nm. The presence of all three defects at the same time explains the observation of mixed green-yellow fluorescence color in certain diamonds.

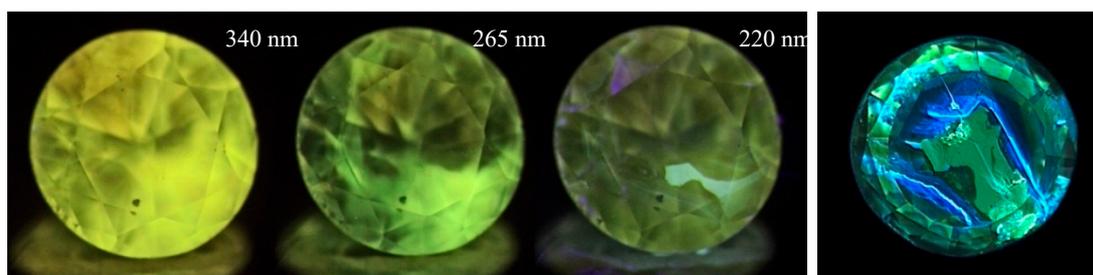


Figure 10. A brown CO₂ diamond (sample TH 2.69) under three different UV excitations of the DFI system. The yellow to yellow green PL is caused mainly by the S1 defect. The fluorescence is concentrated to the brown CO₂-rich zones. The image on the far right shows sample TH 2.71 that was cut into platelet, under the DiamondView™ system.

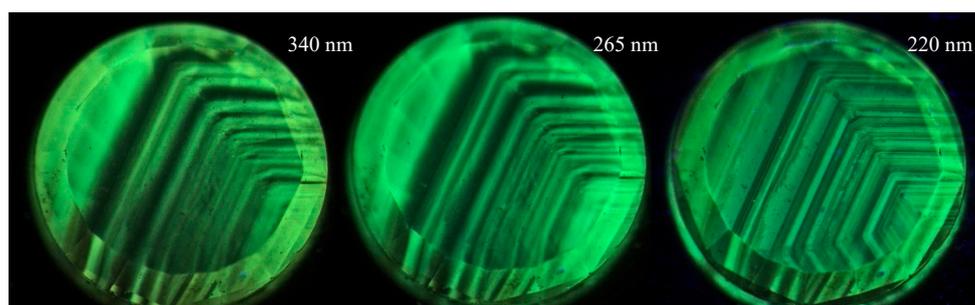


Figure 11. A brown “Pseudo CO₂” diamond (sample SGDF-5864) under three different UV excitations of the DFI system. The yellowish green to green PL is caused mainly by the S2 defect; the PL is much stronger in the colorless sectors than in the colored ones, the darkest brown sectors are practically inert.

The fluorescence was found concentrated within the brown color in the vast majority of the CO₂ diamonds, at least in all samples with the characteristic patchy brown color distribution (Figure 10), and contrasting this, the fluorescence was much stronger in the lighter and the colorless sectors of the Pseudo CO₂ diamonds, including the borderline CO₂/Pseudo-CO₂ diamond, sample SGDF-5864 (Figure 11).

3.1.2. Hydrogen-Rich Type Ia and Ib Brown Diamonds

Hydrogen is a very common impurity in diamond in significant concentrations and it has been shown that all natural diamonds contain hydrogen in concentrations ranging from 500 to 3600 ppm [17]. The problem with hydrogen is that by far not all of it is infrared-active in diamonds, such as hydrogen termination dangling bonds on diamond surfaces. So what we call hydrogen-rich are diamonds that exhibit significant concentrations of infrared-active hydrogen detectable through IR absorptions like the most common one at 3107 cm⁻¹; for type Ia diamonds, the term hydrogen-rich has been assigned to stones exhibiting hydrogen-related absorptions in their IR spectra that are higher than the intrinsic diamond absorption at 2450 cm⁻¹ [18]. Hydrogen-rich diamonds occur in virtually any color except blue, but only in some of them defects linked to the hydrogen may actually be responsible for the

color. The diamonds which very likely have at least part of their color origin linked to the richness in hydrogen are certain gray to violet [19,20], “olive” and brownish yellow to brown diamonds [20]. In all others the hydrogen-related defects seem to have no major influence on the way the diamonds absorb visible light, hence are not linked to their color [20]. Truly brown NDR type Ia H-rich brown diamonds are—with the exception of “asteriated diamonds” [21], very uncommon, and most of them show at least some influence of yellow color. Even more unusual are H-rich type Ib diamonds with dominantly brown color; such stones are generally very small and of deep to dark yellow brown to orange brown color [22]. Five diamonds representing the NDR brown diamonds are included in this study, even if technically speaking the largest diamond—the Tigers Eye diamond of 61.65 cts—did not satisfy the intensity threshold for the hydrogen absorptions, which were somewhat below the 2450 cm^{-1} intrinsic diamond absorption. Nevertheless, the properties of that diamond are typical for certain H-rich diamonds, hence it has been included in this study.

Microscopic Examination

The H-rich type Ia NDR brown diamonds showed practically no apparent color zoning (Figure 12, left), and no deformation-related strain, or no visual strain whatsoever when observed under crossed polarizing filters (Figure 12, right). The strongly sectored cuboid-octahedral H-rich NDR brown diamond (Sample TH 2.626) showed obvious color zoning with brown cuboid sectors and colorless octahedral sectors (Figure 13, left). Under crossed polarizers strain between the growth sectors was obvious (Figure 13, center), a phenomenon known from mixed growth natural diamonds [22] and mixed growth synthetic diamonds. The cuboid brown sectors were characterized by dense cloud-like inclusions (Figure 13, right). In immersion, the H-rich type Ib NDR diamonds showed strong color zoning separating the cuboid from the octahedral sectors; under crossed polarizing filters these diamonds showed a cross-like extinction pattern, related to their mixed growth just like the mixed growth sample described above (Figure 14).

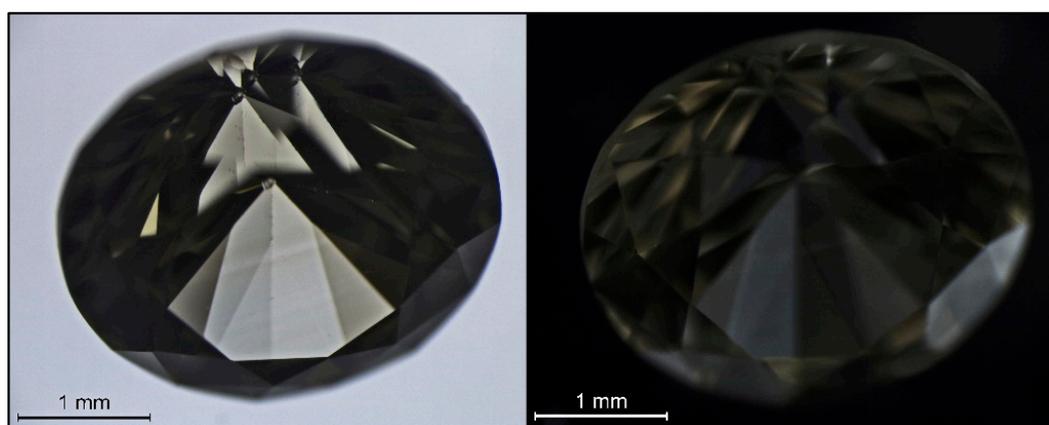


Figure 12. A hydrogen-rich light yellow-brown diamond (TH 2.618), not colored by deformation-related defects, but by nickel-nitrogen-(hydrogen?)-related defects in immersion (**left**) and under crossed polarizing filters (**right**). Very faint parallel color zoning can be seen, the strain in the diamond is virtually undetectable using crossed polarizers.

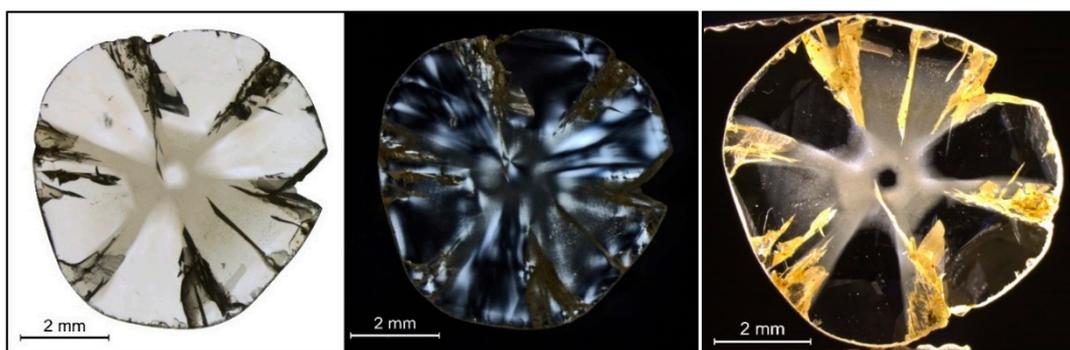


Figure 13. A mixed cuboid-octahedral growth hydrogen-rich diamond (TH 2.626), not colored by plastic-deformation-related defects. The obvious color zoning of the sample (**left**) is linked to the growth sectors, with the octahedral sectors being colorless and the cuboid sectors being light brown. The strain of this diamond (**center**) is clearly caused by the sector growth, hence strain between the brown cuboid and the colorless octahedral sectors. The light brown cuboid sectors are filled with tiny dust-like inclusions (**right**).

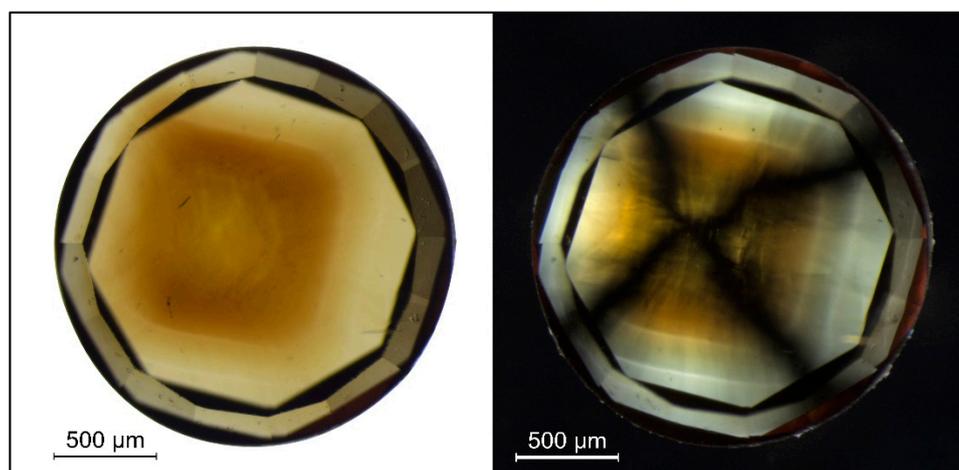


Figure 14. A mixed cuboid-octahedral growth hydrogen-rich type Ib > IbXY >> IaA diamond (TH 2.49), not colored by plastic-deformation-related defects. The obvious cuboid color zoning in the core of the sample (**left**) is apparent, and under crossed polarizing filters (**right**) cross-shaped extinction can be seen which is linked to strain induced caused by the mix of cuboid and octahedral growth.

Infrared and Near-Infrared Spectroscopy

The infrared and near-infrared spectra of the type Ia hydrogen-rich NDR brown diamonds—represented by samples TH 2.618 (Figure 15) and the Tiger’s Eye diamond plus sample TH 2.626 (Figure 16)—identified them as type IaA >> B with very high nitrogen content, hence the A aggregates strongly dominated the B aggregates. By definition of hydrogen-rich, they all exhibited the characteristic sharp hydrogen-related absorptions with main absorptions in the range between 3000 and 3400 cm^{-1} . The three samples represented two different groups, one being of octahedral growth with only the 3107–3237 cm^{-1} systems (represented by sample TH 2.618, Figure 15—and the Tigers Eye diamond), and one of cuboid-octahedral growth with 3107–3237 cm^{-1} systems, and a series of additional weaker absorptions at 3310, 3190, 3171, 3154, 3144, 3139, 3124, 3093, 3050 cm^{-1} plus a somewhat broader peak at 3474 cm^{-1} (represented by sample TH 2.626, Figure 16). All these additional absorptions are unique to cuboid growth sectors [20,21,23,24], which is nicely demonstrated by sample TH 2.626. The IR spectra of this diamond were recorded in the brown colored cuboid sectors and the colorless octahedral sectors. It was obvious that the hydrogen was strongly concentrated in the brown sectors, and that many of the H-related IR absorptions were only present in these cuboid

sectors (Figure 16, trace a), while only the 3107–3237 cm^{-1} systems were found in the colorless sectors (Figure 16, trace b). Other weak likely H-related lines could be found in the spectra of the cuboid sectors of this sample, including peaks at 6102, 6184, 6196, 6215, 6248, 6290, 6309, 6382, 6474, and 6621 cm^{-1} .

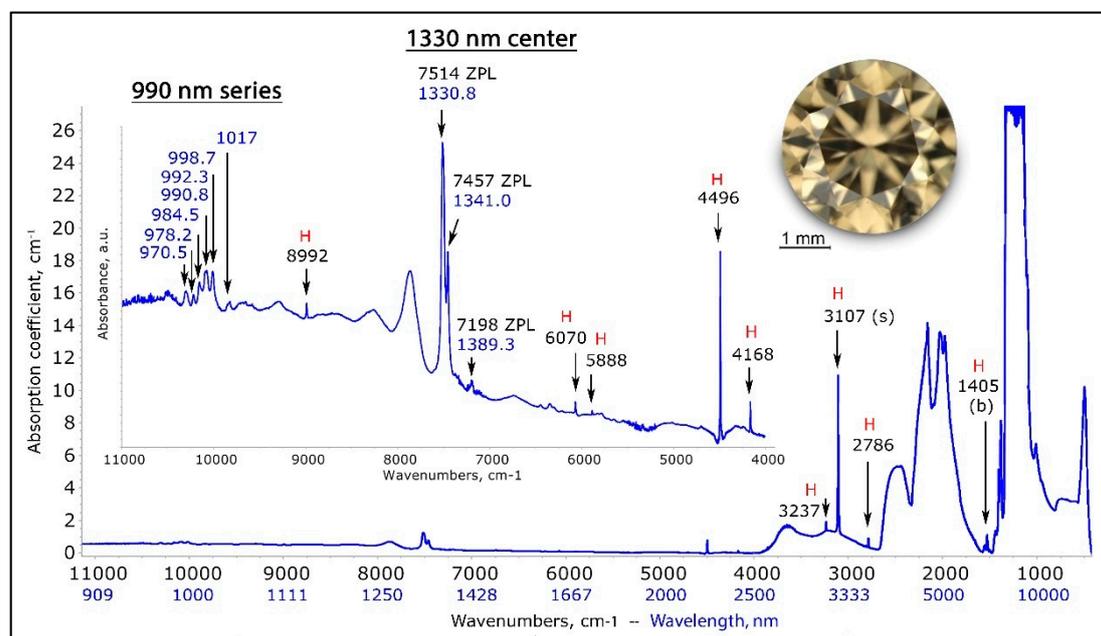


Figure 15. The normalized near to mid-infrared spectrum (range 900 to 25,000 nm) of a NDR hydrogen- and nitrogen-rich type IaA \gg B diamond (TH 2.618) exhibits the typical hydrogen-related sharp absorption (indicated with a red “H”), plus a very distinct 1330 nm center and the domain from 4000 to 11,200 cm^{-1} was recorded with the diamond at 77 K.

The 3107 cm^{-1} absorption was five times stronger in the brown sectors than in the colorless sectors, and the 3238 cm^{-1} absorption was 21 times stronger. Also, the nitrogen content was somewhat variable in the sectors, with \approx 2415 ppm in the cuboid (brown) sectors and \approx 2853 ppm in the octahedral (colorless) sectors.

The 3107 cm^{-1} system has been assigned to the VN_3H defect by [25]; this means that the defect consists of a hydrogen atom bound to an N_3 center. All of its components were detected in the tested samples; they consist of the 3107 cm^{-1} (stretch [s]) absorption, the 1405 cm^{-1} (bend [b]) absorption, and their combinations and overtones at 2786 (2b), 4168 (3b), 4496 (s + b), 5555 (4b?), 5888 (s + 2b), 6070 (2s), and at 8992 cm^{-1} (2s + 2b); the line at 8992 cm^{-1} has—to the authors knowledge—not been described before. A frequently observed absorption at 6214 cm^{-1} —even though precisely at the double frequency of the 3107 cm^{-1} absorption, was found not to be linked to that system. The 3237 cm^{-1} system has only one obvious line that relates to it, at 4704 cm^{-1} [20,26]. Another described correlating system includes the 3154 + 3050 cm^{-1} absorptions [21], with possible the peaks at 3092 and 3082 cm^{-1} . Comparing data from other hydrogen-rich diamonds with the data of sample TH 2.626, we have determined that the 3310 cm^{-1} absorption correlates with the 1363 cm^{-1} line; that line is distinctly narrower than the platelet peak and hence should not be confused with it (Figure 16, trace a) inset).

Further into the NIR domain and towards the visible portion of the spectrum, the spectra of the type Ia octahedral NDR brown diamond sample TH 2.618 (Figure 15)—and also of the Tigers Eye diamond—showed a band at 7495 cm^{-1} that was first described in hydrogen rich diamonds by Fritsch et al.—together with bands at 7850, 8255, and 8615; they have all been assigned to hydrogen-related defects. These bands have also been observed in hydrogen-rich gray to violet diamonds from the Argyle mine [19]. The authors have noticed the presence of the 7495 cm^{-1} and associated absorptions in many H-rich NDR brownish yellow, green yellow, olive, brown, gray and violet diamonds. For this

study, such spectra have been recorded at 77 K for the first time, and these experiments have revealed the actual spectral appearance of these bands and shown that they represent distinct ZPLs with their vibronic sidebands. In the low temperature spectra of the brown diamond sample TH 2.618 a significant sharpening and splitting of the strongest band into three components was observed, which identified the absorption as a typical ZPL with characteristic vibronic structure. At 77 K, a triplet absorption was found at 7514, 7507, and 7457 cm^{-1} which corresponds to 1330.8, 1332.0, and 1341.0 nm, and its vibronic sidebands were found at 7865 cm^{-1} (1271 nm), 8270 cm^{-1} (1209 nm) and 8690 cm^{-1} (1150 nm) (Figure 15). Since the positions of these ZPLs vary somewhat from sample to sample we will refer to this defect as the “1330 nm center”.

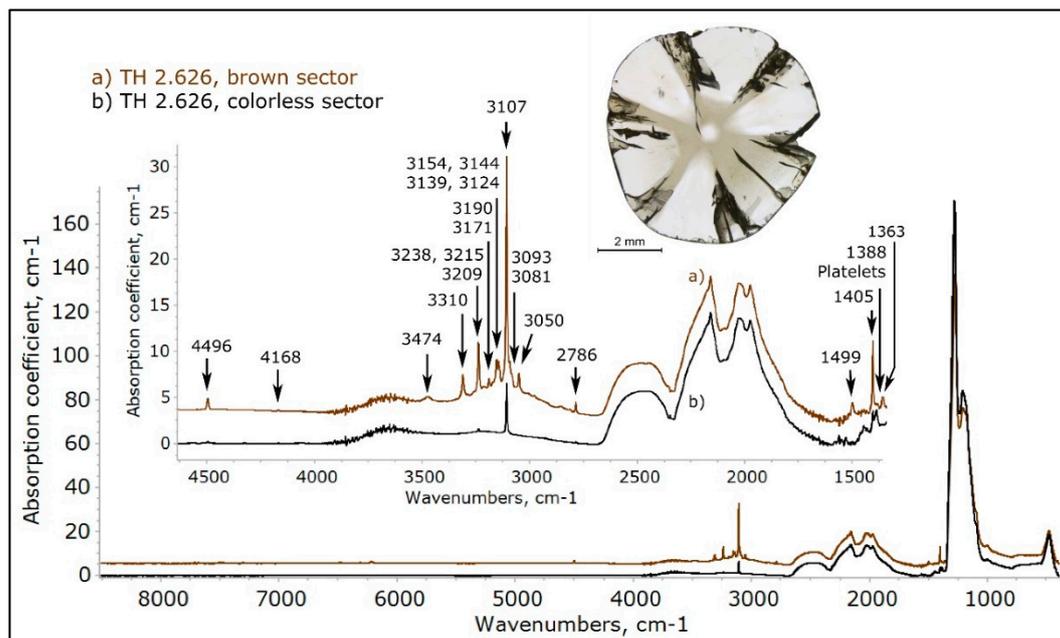


Figure 16. The normalized IR spectra of the brown (trace a) and the colorless (trace b) sectors of a NDR mixed growth hydrogen- and nitrogen-rich type IaA>>B diamond (TH 2.626). While the spectrum of the colorless sector shows only comparatively weak H related peaks at the classical positions 3107/1405 cm^{-1} and 3238 cm^{-1} , the H- related features in the brown sectors are significantly more complex and the 3107/1405 and 3238 cm^{-1} lines are distinctly stronger; the 3107 cm^{-1} line is 5 times stronger in the brown than in the colorless sector. The NIR peaks recorded for the other hydrogen-rich diamond were very weak in the spectrum of this sample and undetectable at RT. The spectra have been shifted vertically for clarity.

Even closer to the visible spectral range, a series of peaks was present, that has equally been described for violet diamonds before [19,20] and also for other H-rich diamonds [20], at 1017, 998.7, 992.3, 990.8, 984.5, 978.2, and 970.5 nm (Figure 15); this series of absorptions that may or may not show all of the mentioned peaks will be referred to as the “990 nm series” in this study.

Looking at spectra of a series of violet, olive and yellow H-rich diamonds that all exhibited the 1330 nm center it was apparent that this center did not directly correlate with the intensity of the hydrogen-related absorptions at 3107 and/or 3237 cm^{-1} , and there was no direct link with A and B center nitrogen. Also, no correlation between the 990 nm series of absorptions and this triplet was found. More info leading to the understanding of these structures was found in the UV-Vis-NIR spectroscopy in the next paragraph.

When the NIR spectra from the colorless and the brown colored sectors of sample TH 2.626 were recorded at 77 K, a distinct H1b and weak H1c absorption plus a series of weak absorptions not related to hydrogen were detected in the brown sectors, and among these a hardly detectable 1330 nm center

was found. The H1b and H1c absorption plus probably most of the other absorptions detected can be linked to the presence of irradiation stains within the brown sectors.

Two type Ib NDR brown diamonds were included in this study; these are very rare and generally small diamonds of rather saturated orange brown to dark yellow brown color of cuboid or cuboid octahedral growth. The diamonds were both identified as mainly type IbXY, and hydrogen-rich (Figure 17). Diamonds of type IbXY are defined as diamonds that exhibit an infrared spectrum with the Y center and the X center absorptions dominating the C center absorptions [15]; the Y center is a complex one-phonon absorption with its main band at 1145 cm^{-1} [27] that possibly relates to oxygen defects, since the HPHT treatment of Y center diamonds was found to lead to the formation of the 480 nm band and related PL at 690 nm [11,15,28], features that have been assigned to oxygen-related defects before [29]. The X center has been identified as positively charged single substitutional nitrogen (N^+); its main line can be found at 1332 cm^{-1} in the spectra of type Ib diamonds, where it occurs very commonly [30].

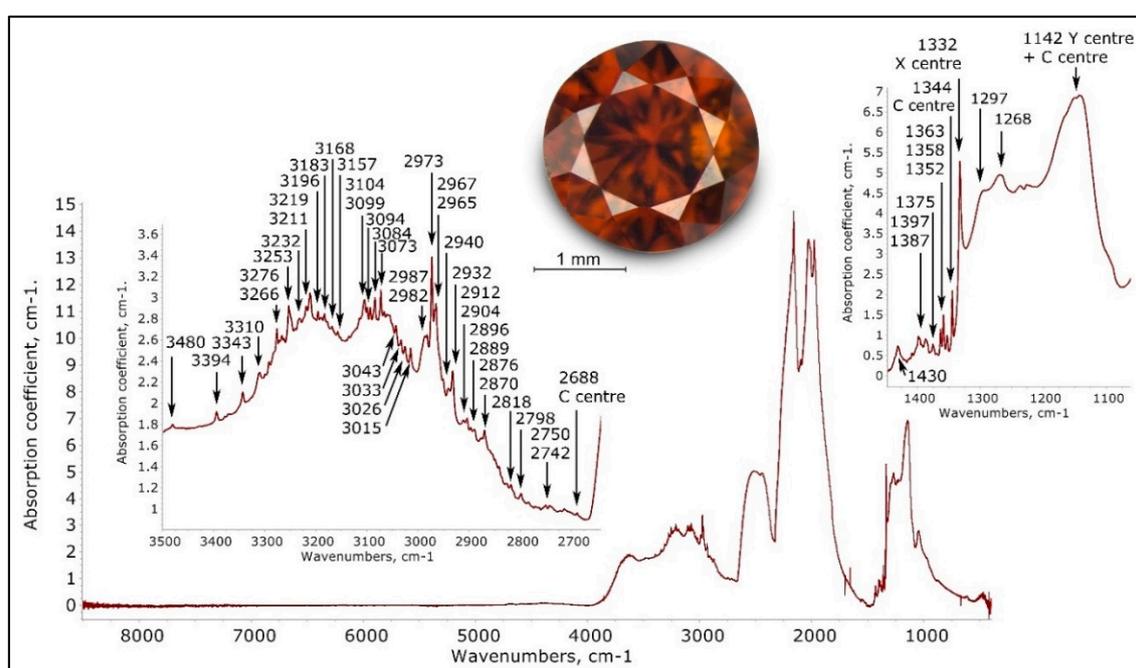


Figure 17. The normalized infrared spectrum of a NDR hydrogen-rich orange brown type IbXY diamond (TH 2.327)—recorded at 1 cm^{-1} —exhibited a complex band with numerous hydrogen-related sharp absorption only known in type Ib diamonds with dominant X and Y center absorption. The 1142 cm^{-1} absorption is the result of the overlaid 1130 cm^{-1} C center absorption and the 1145 cm^{-1} Y center absorption.

The definition of hydrogen-rich is different for type Ib diamonds compared to type Ia diamonds since in such diamonds the 3107 cm^{-1} line is generally absent and since hydrogen-related absorptions in type Ib diamonds are never very intense. Hydrogen can only be detected in the IR spectra of type Ib diamonds that exhibit Y center absorption or that are high nitrogen IaA>>Ib of mixed cuboid octahedral growth. Hydrogen cannot be detected in pure type Ib diamonds by IR spectroscopy [15]. We suggest here that any type Ib sample with H-related IR absorptions higher than the intrinsic diamond absorption at 2340 cm^{-1} should be called hydrogen-rich.

In the diamonds tested here, the domain between 3400 and 2800 cm^{-1} consisted of a broad band overlaying the regular intrinsic diamond absorption band centered at 3200 cm^{-1} , with numerous sharp peaks overlaying this band (Figure 17). Of these, the 2973 cm^{-1} absorption was the most distinctive feature. A total of over 50 tentatively H-related absorptions could be seen in the spectra, which have been published before [20,22,27].

UV-Vis-NIR Spectroscopy

The type Ia H-rich NDR brown diamonds that exhibit the 1330 nm defect (sample TH 2.618 and the Tigers Eye diamond) were characterized by very complex UV-Vis-NIR spectra that were found to be the continuation of the complex NIR spectra shown in Figure 18. The most prominent absorptions in the spectra were the N3 center, 474.7, a broad band at about 545 nm, 554.2, 562.7, a broad band at approximately 729 nm, 793.6, 807.6, 823.8, a relatively broad band with three maxima at about 828/836/843 nm, 892.9, 966.0, 968.1, 968.7, 970.7, 974.1, 977.0, 978.3 to 978.8, 983.2, 984.9 to 985.3, 989.3/991 doublet or 990.0, 997.4/998.3 doublet or 997.7 and 1001.4 nm (Figure 18). These spectral features have been observed in H-rich NDR diamonds in a range of colors from brownish yellow to brown, greenish yellow to olive and gray to violet by the authors and in earlier publications [19,20]. In the spectra of the brown diamonds these features were distributed in intensity so that they represented basically a somewhat irregular continuum absorption; the spectrum shown of the Tigers Eye diamond (Figure 18) shows stronger absorption than the other H-rich brown diamond tested, because the Tigers Eye diamond was of rather saturated brown yellow color.

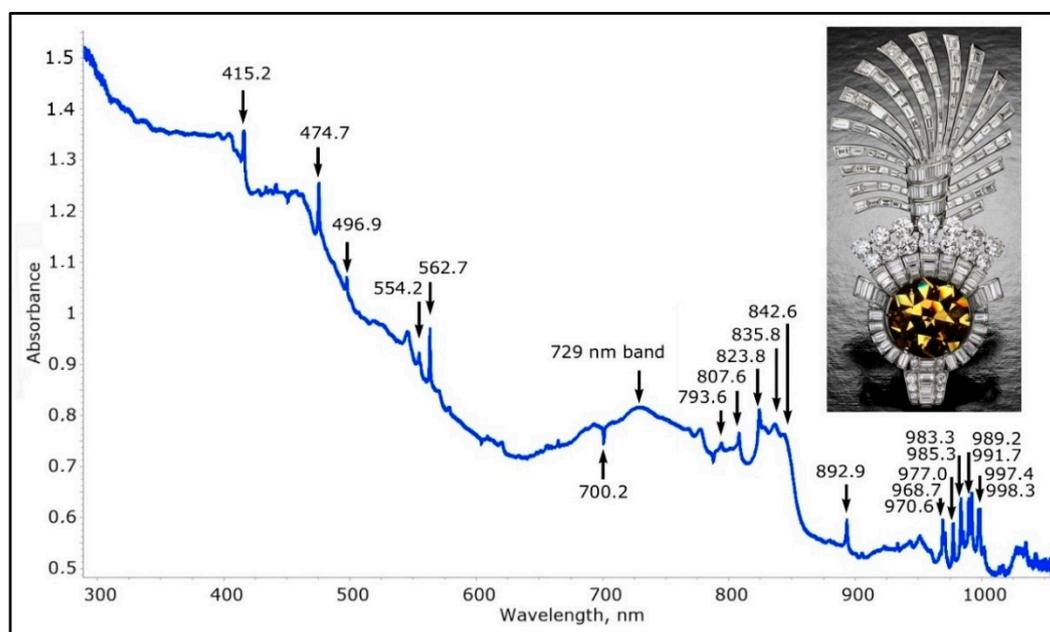


Figure 18. The low temperature UV-Vis-NIR spectrum of the most famous and biggest hydrogen-rich brown yellow diamond that is colored by NDR defects—the Tiger’s Eye diamond, 61.56 cts. The highly complex spectrum is characteristic for these diamonds, and is always the continuation of the very distinct triplet ZPL at 1330.8/1332.0/1341.0 nm ($7514/7507/7457\text{ cm}^{-1}$); this intense ZPL—which is the strongest vibronic absorption feature in the entire NIR, Vis and UV range, is also present in the NIR spectrum of the Tiger’s Eye diamond. The majority of the features of these spectra are likely related to nickel-nitrogen defects, possibly with the incorporation of hydrogen.

While the UV-Vis-NIR spectra with their limited range to 1040 nm did not give much insight into the color cause, other than the observation of the absorption features, a look at the entire domain up to 2500 nm and comparison with 18 hydrogen-rich diamonds and one low-hydrogen diamond, all exhibiting the 1330 nm defect in their IR spectra, brought much more light into the mystery of these complex spectra. These detailed results have been published recently [31] and here only a summary will be given. Among the carefully selected diamonds tested for comparison with the type Ia H-rich diamonds we found a green yellow diamond in the collection of TH that was a high nitrogen pure type IaB diamond with very low hydrogen content; nevertheless the UV-Vis-NIR spectrum of the sample resembled the spectra of the H-rich brown diamonds included in this study, with a significant

difference: The spectrum did not exhibit the 990 nm series, and neither the broad bands at 545 nm and 729 nm were present. The main absorption feature of the diamond was the broad band with three maxima at about 828/836/843 nm and an associated broad band with maxima at approximately 803 nm, 755 nm, 725 nm, and 690 nm. Nevertheless, a strong 1330 nm absorption was detected in the low temperature NIR spectrum of this diamond (Figure 19). PL spectroscopy with the stone held at 77 K was conducted to understand some of the underlying defects, and the result was as revealing as we expected: Besides distinct N3 center PL, the PL spectra revealed exclusively nickel-related defects such as the S2 and S3 centers, the 700 nm center and the 793.6 nm center. Now when looking at the full-range spectrum of this specific diamonds—from 300 to 25,000 nm—and comparing it with the PL spectra and then comparing the data of this diamond with the data of the other diamonds, the complex UV-Vis-NIR spectrum made much more sense.

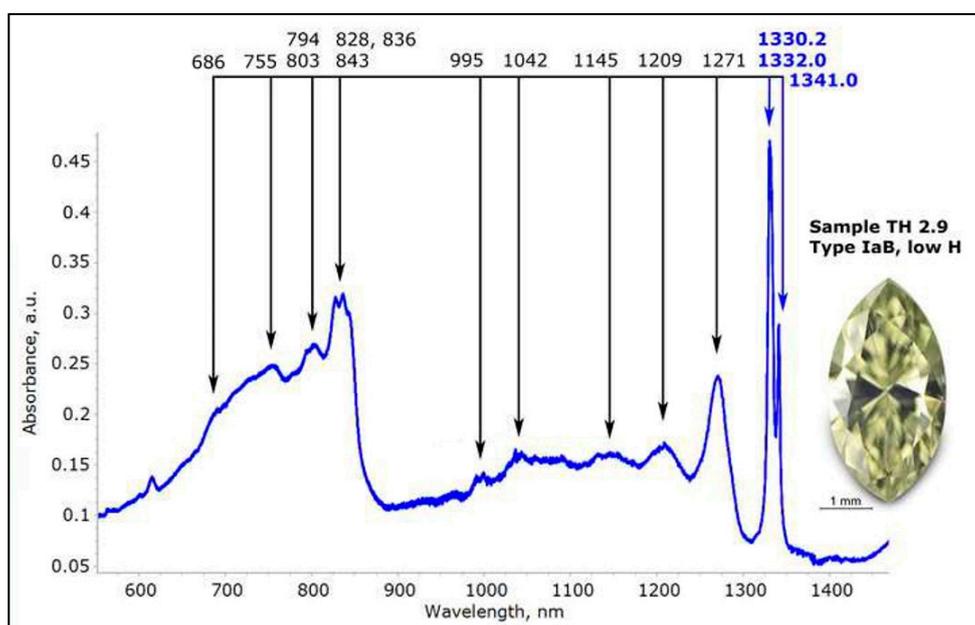


Figure 19. The extended low temperature UV-Vis-NIR spectrum of sample TH 2.9, an almost hydrogen deficient 1330 nm center diamond; the practical absence of hydrogen in the spectra of this diamond demonstrate that the 1330 nm center has no link to hydrogen. The structure seen from 820 to 550 nm is proposed to be an electronic transition to a higher excited state of the defect.

This comparative analytical work has finally permitted to propose a series of conclusions. First of all, the 1330 nm peaks are clearly the ZPLs of an electronic defect with a vibronic structure and components reaching far into the visible range of the spectrum; besides the obvious vibronic bands at 1271, 1209, and 1151 nm, it is suggested that the 836 nm band and the associated broad bands extending all the way to 550 nm are also part of the 1330 nm defect. The 836 nm band which consists of three absorptions at 828, 836, and 843 nm is proposed to be an electronic transition to a higher excited state of the 1330 nm defect, and the bands ranging to 550 nm are the vibronic structure of the 836 nm band. The other broad bands seen in the spectra, particularly the 545 nm and 729 nm bands, are proposed to be components of the 990 nm series since there is a linear correlation between the intensity of the ZPLs of the 990 nm series and these broad band features (Figure 20). It is unclear whether some are vibronic sidebands or not since they are found too far from the ZPLs for a typical vibronic feature and since they are not part of a continuous broad band such as e.g., the vibronic band of a strong H2 center that extends to 650 nm. From the defect causing these types of spectra, the PL spectroscopy combined with the IR spectra did allow us to suggest that—with exception of the N3 defect—the entire spectra are the result of nickel-containing defects. The 1330 nm center clearly seems to be the result of a defect containing nickel and nitrogen—possibly the B aggregate—but no hydrogen, while the 990 nm series

appears to involve nickel, nitrogen and likely hydrogen. The in-depth results on these defects and their influence on the color of diamonds have been published recently [31]. In these results the detailed analyses of the ZPLs, their spectral components and their influence on the color can be found.

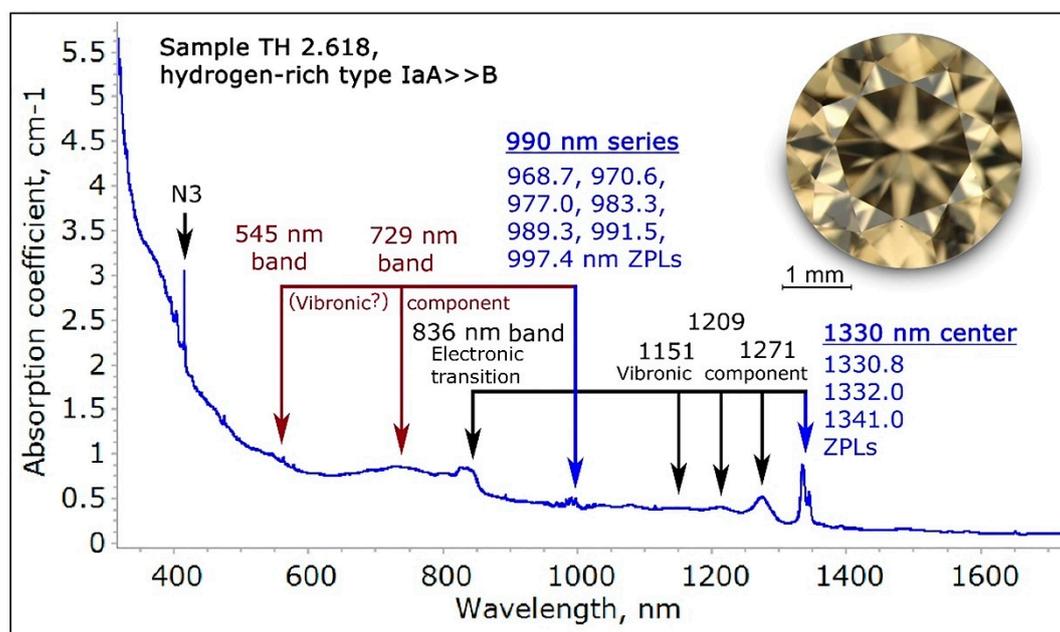


Figure 20. The extended low temperature UV-Vis-NIR spectrum covering the range to 1700 nm of a type Ia hydrogen-rich yellowish brown diamond. The figure shows the correlation between the complex absorptions in the 500 to 850 nm range with the 1330 nm center and the 990 nm series. The complex broad bands are proposed to relate to these two spectral features, and some represent vibronic components of these centers.

The low temperature UV-Vis-NIR spectra of the strongly sectored cuboid-octahedral H-rich diamond were recorded in both, the colorless and the brown sectors (Figure 21). The colorless sectors exhibited rather featureless spectra with a cut-off at 310 nm plus small N4 (344.0 nm) and N5 (330.2 nm) absorptions (Figure 21, trace b). The spectra of the brown sectors were characterized by an absorption continuum overlaid by a weak broad band at 435 nm and a series of weak to very weak rather sharp absorptions between 546 and 978 nm (Figure 21, trace a). The NIR spectra of the diamond, also recorded for both the brown and the colorless sectors, confirmed very weak 1330 nm center absorption in the brown sectors. The absorption was too weak to cause detectable vibronic absorption bands, hence had no influence on the color of the diamond. In the lack of any obvious cause for the brown color of the cuboid sectors and seeing the correlation of cloud-like inclusions in the cuboid sectors, it must be wondered whether the color is not simply inclusion-related. Brown micro-inclusions might be the cause of the observed color, just like graphite inclusions have been identified as the cause of gray color in cuboid growth sectors in “asteriated” diamonds [21].

The hydrogen-rich type IbXY diamonds’ UV-Vis-NIR spectra showed an absorption continuum reminiscent of the continuum shown by “normal” type Ib diamonds, but the continuum did not only increase distinctly at 560 nm as it is the case for type Ib diamonds that lack signs of plastic deformation [11], but started its increase as far back as 980 nm, and most strongly from 630 nm until its cut-off at about 400 nm. In deeply colored type Ib diamonds with a plastic-deformation-related color component, such as deep brownish orange type Ib diamonds, the spectra show a similar continuum, but the cut-off is shifted into the visible by up to more than 50 nm, hence is typically found between 430 and 455 nm. These diamonds showed no sign of plastic deformation and the C center content was ≈ 51 and ≈ 144 ppm respectively; if only taking the C center content into account, the samples should be of very intense yellow color.

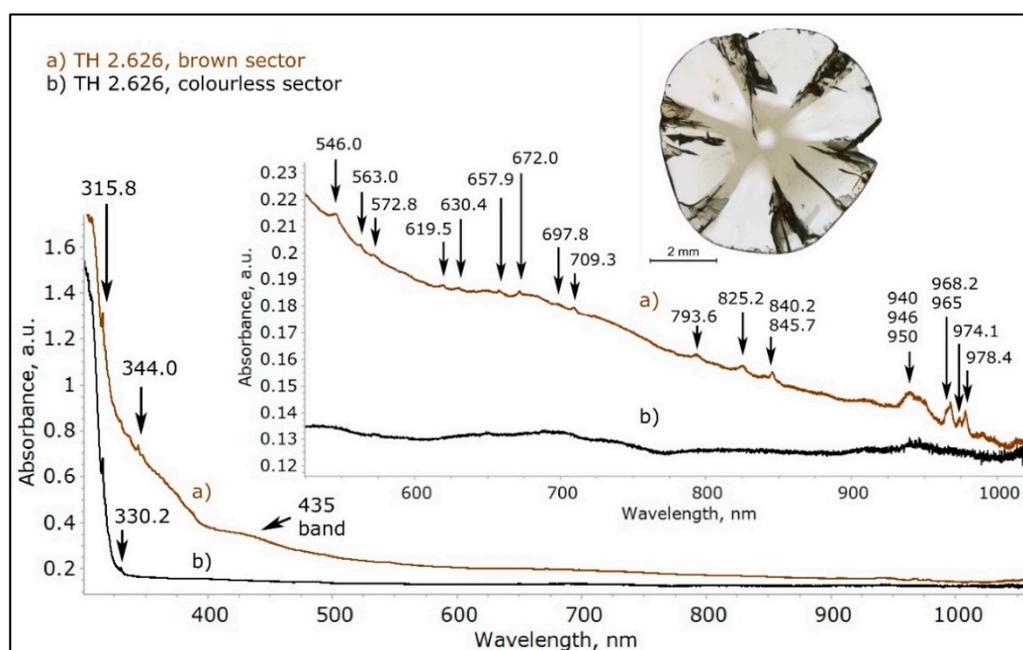


Figure 21. The low temperature UV-Vis-NIR spectra of the colorless and brown sectors of a hydrogen-rich mixed growth cuboid-octahedral “asteriated” diamond (sample TH 2.626). Compared to the spectra of hydrogen-rich diamonds with the distinct 1330 nm center absorptions, the spectra of these diamonds are pretty featureless and for the brown sectors consist mainly of a continuum with an overlaying broad band at 435 nm, a large quantity of weak peaks in the UV domain—including the N4 center at 344.0 nm—and a series of very weak peaks between 546.0 and 978.4. The colorless sector is featureless with only an absorption peak at 315.8 (N6 center) and 330.2 nm (N5 center) detectable.

While some erroneously believe that a high C center content results in orange or brownish yellow color, we have shown in earlier work that this is not the case. To give an example, synthetic diamonds included in the PhD of TH [15] with a C center content of 38 to 201 ppm have been graded “vivid yellow” and two diamonds with a C center content of 235 and 241 ppm were graded deep yellow. Increasing the C center content only increases the depth of the yellow color and it takes a lot of C centers to make a stone appear brownish yellow. Not having any indications of plastic deformation, the origin of the brown color of these unusual diamonds must relate to other—currently unknown—defects. Overlaying the absorption continuum, a series of sharp absorptions were detected, the most intense being at 904.2 nm, published for the first time in “ABC” diamonds, hence diamonds containing nitrogen in form of the A, B, and C centers [22]. A local vibrational mode at 805 nm always occurs together with this center. It has been described as very common in diamonds showing significantly more X and Y center absorption than C center absorption, and it was suggested that the center does not relate to the C center because of its annealing behavior [15]. While in one diamond—sample TH 2.327—only the 904.2 nm center and two very weak peaks at 622.4, 635.2 nm were seen, in the spectra of the other sample—sample TH 2.49—a more complex series of absorptions were present and the 904.2 nm absorption was associated by a distinct H2 absorption with its ZPL at 986.0 nm and vibrational mode at 870.3 nm, like the ones shown by Hainschwang et al., 2006 [22]. In the high-resolution and high-quality spectrum recorded for this study, the precise positions found for the other weaker absorptions were 606.4, 614.1, 622.2, 635.2, 765.6, 827.6, and 818.0 nm (Figure 22).

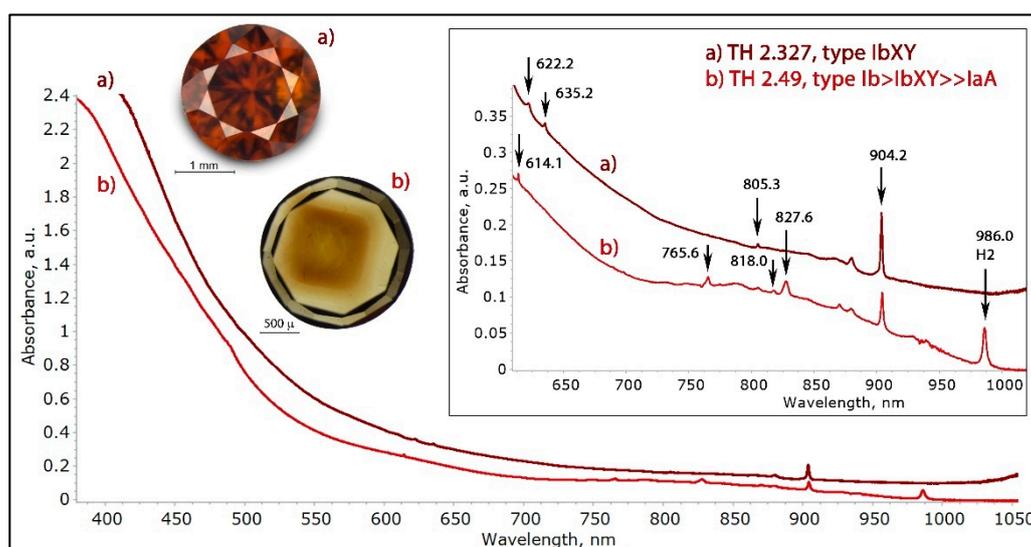


Figure 22. The low temperature UV-Vis-NIR spectra of the two hydrogen-rich mixed growth cuboid-octahedral type IbXY diamonds (samples TH 2.327 and TH 2.49). Such spectra are very different to the ones of type Ia hydrogen-rich diamonds, and consist mainly of the C center-related absorption continuum with an overlaying unrelated absorption continuum from 560 nm towards the NIR domain, and a series of sharper absorptions from 600 nm to 1000 nm. Of these, the most characteristic absorption is the 904.2 nm center.

Photoluminescence Spectroscopy

The PL spectra of the hydrogen-rich type Ia diamonds were characterized by mostly nickel-related features. While the diamonds with “asteriated” brown diamond’s PL was dominated by the S3 center with its ZPL at 496.6 nm (Figure 23), the 787.0 and 793.6 nm defects were dominant features in both the hydrogen-rich diamonds with distinct 1330/1332/1341 nm absorption (Figure 24) as well as the “asteriated” diamonds. While the S3 and the 793.6 nm centers are nickel-related defects, the origin of the 787.0 nm defect is unclear; it has been described as nitrogen-related [32,33] even though it is—in the experience of the authors—particularly strong in nickel-rich diamonds. The peaks at 926.3 and 925.4 nm were detected in all type Ia H-rich diamonds studied, and these same peaks were very intense in another asteriated diamond published earlier [34]; in that instance, the two intense peaks at 925.4 and 926.3 nm were associated by a series of weaker PL features at 919.8, 921.6 and 924.0 nm; it was suggested that these peaks as well are likely related to a nickel containing defect. In the asteriated cuboid octahedral diamond, all PL peaks shown in the spectra in Figure 23 were only detected in the cuboid brown zones, while the colorless sectors showed practically no PL beyond artefacts from neighboring cuboid sectors.

The 523.8 nm NE3 center with its small associated bands at 521.2, 522.4, 526.4, and 527.4 nm, the 603.8 nm center and the 700.6 nm center are very commonly present and strong in the PL spectra of the H-rich diamonds with distinct 1330 nm center absorption (Figure 24), while they are less prominent and sometimes even absent in the “asteriated” diamonds (Figure 23).

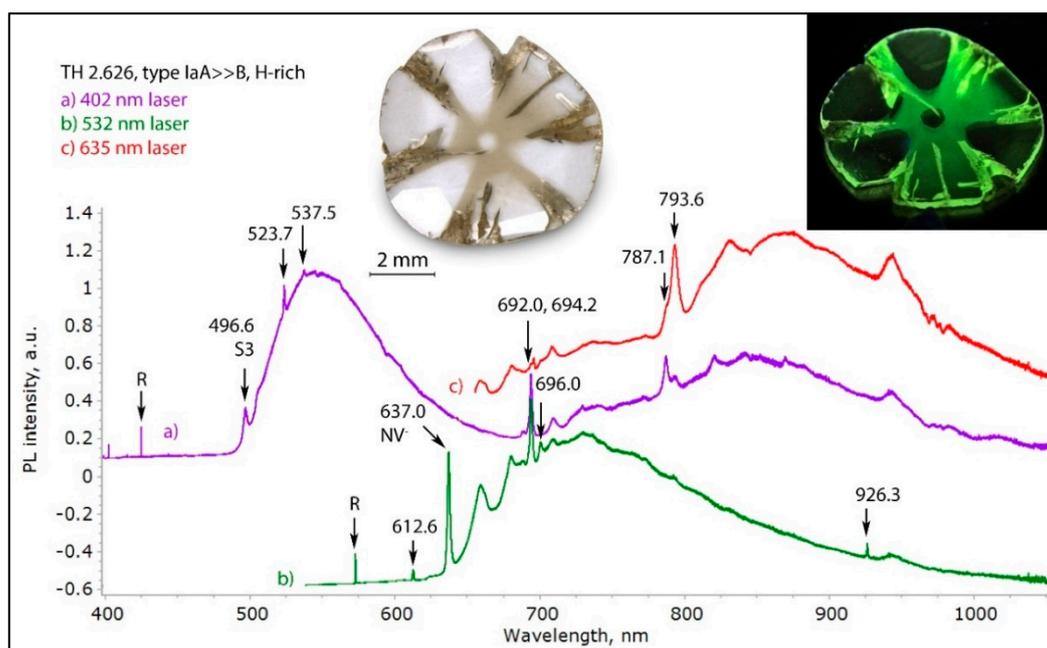


Figure 23. The photoluminescence spectra of the brown sectors of an NDR hydrogen-rich “asteriated” colorless/brown type IaA >> B diamond (TH 2.626) recorded with three different lasers. The intense broad vibronic S3 band centered at about 545 nm is related to nickel defects and responsible for the green fluorescence of the brown sectors of the diamond. The 692.0/694.2 doublet, the 787.0 and the 793.6 nm centers are characteristic for such diamonds, and all of these are likely related to nickel containing defects. The spectra have been shifted vertically for clarity. Photos: Gianna Pamies and Dr. Thomas Hainschwang.

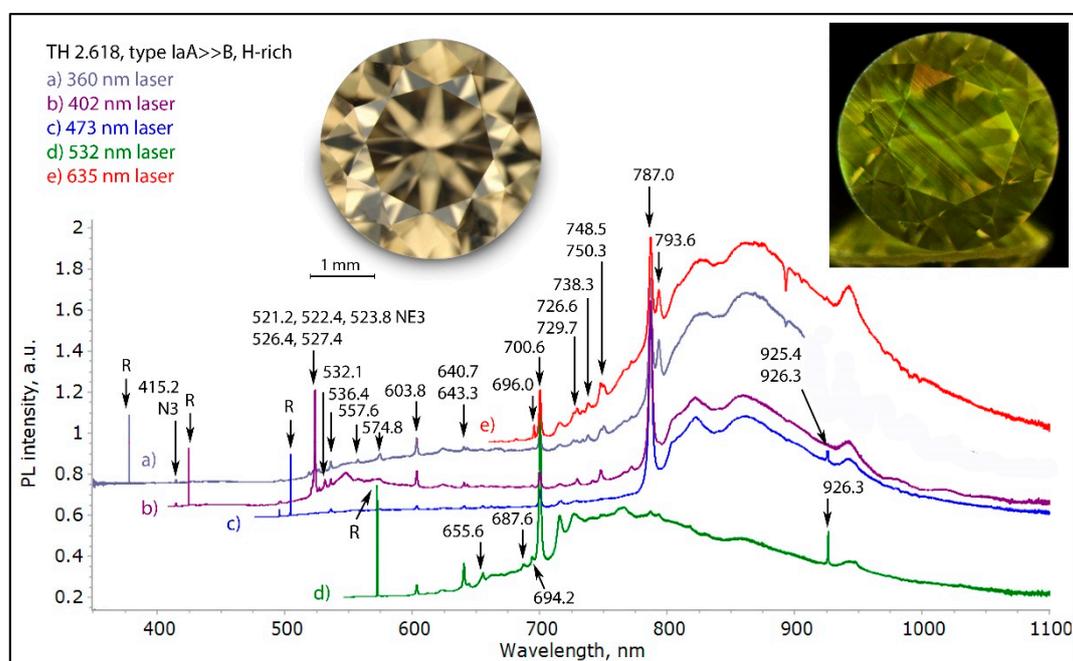


Figure 24. The photoluminescence spectra of a NDR hydrogen-rich yellow brown type IaA >> B diamond (TH 2.618) recorded with five different lasers. The 521.2 to 527.4 nm features, the 700.6, the 787.0 and the 793.6 nm centers are characteristic for such diamonds; at least the 700.6 and 793.6 nm centers are linked to nickel-related defects. The spectra have been shifted vertically for clarity. Photos: Gianna Pamies and Dr. Thomas Hainschwang.

The overall look at the PL spectra of hydrogen-rich type Ia NDR brown diamonds shows that such stones, no matter of which type, may exhibit a large number of PL peaks, most of which are or seem to be related to nickel-containing defects; while some are more typical in one kind of H-rich diamond than the other, it appears that they occur in both types of H-rich type Ia NDR brown diamonds. This indicates that both types of type Ia H-rich NDR brown diamonds contain very similar nickel-related defects, but that their ratios are generally very different. The S center defects (S1, S2 and S3) are known to cause yellow (S1) to green (S2, S3) PL but they cause no absorption in the visible range. To give an example that confirms this statement, strong S3 center/523.7 nm (NE3)/692.0–694.2 nm/787.0–793.6 nm PL is not uncommon in colorless type Ia diamonds; actually, the IR spectra of such colorless diamonds define them as near pure type IaA with the same hydrogen absorptions as described for sample TH 2.626 (Figure 23). While the PL spectra are clearly indicative that these diamonds are rich in nickel-containing defects, we were unable to find a direct link between any of the PL active defects and the nickel-related absorptions detected from the UV to the NIR that are responsible for much of the color of the 1330 nm center diamonds.

The type IbXY diamonds PL data stood in stark contrast to the data presented for the type Ia diamonds, just like it was the case for the IR and UV-Vis-NIR data. These diamonds are in no way linked to the type Ia samples. The spectra of both diamonds featured the 904.2 nm center that was also detected in their UV-Vis-NIR spectra and a sharp distinct peak at 525.4 nm. Otherwise the spectra of the two diamonds were rather different: Sample TH 2.327 was characterized by broad band PL centered between 670 and 700 nm, the 635.3 center, NV⁻ center, a band at 648.3 nm (Figure 25, traces a and b) and a very strong 692.0 nm center (Figure 25, trace c); the spectra of sample TH 2.49 did not show any of those PL features but instead showed distinct H3 PL (503.2 nm ZPL), and strong 689.3 and 698.0 nm centers. The 525.4, 689.3, 692.0, and 904.2 nm centers seem all to be exclusively present in the PL spectra of diamonds with dominant X and Y center one-phonon IR absorption [15]. For none of the Y center specific PL features there are currently any suggested defects, at the time of this publications all of them are still assigned to unknown defects.

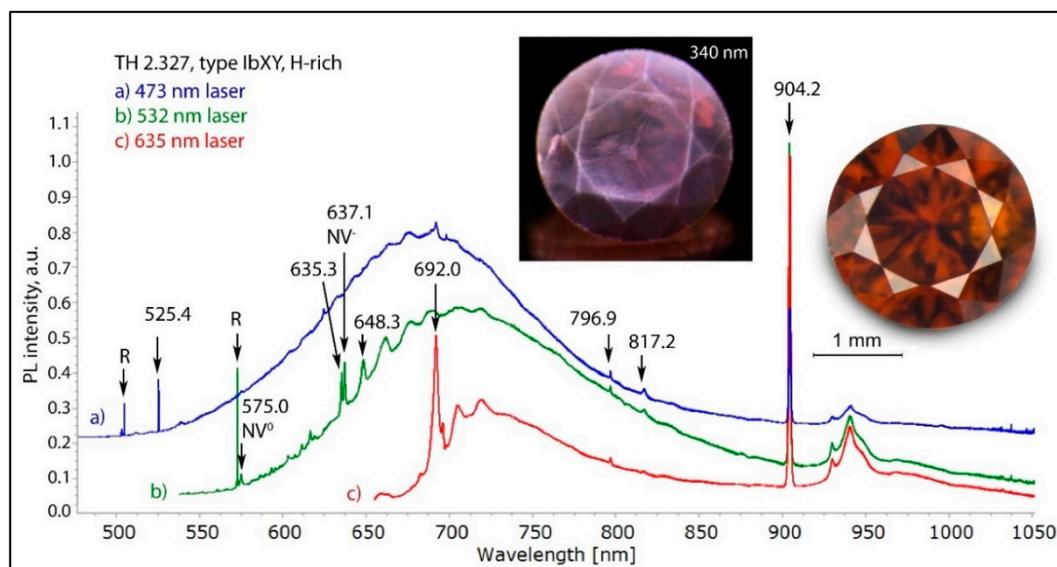


Figure 25. The photoluminescence spectra of a NDR hydrogen-rich deep brown orange type IbXY diamond of mixed cuboid octahedral growth (TH 2.327) recorded with three different lasers. The 693 nm and particularly the 904.2 nm features are very characteristic for such diamonds. The spectra have been shifted vertically for clarity. Photos: Gianna Pamies and Dr. Thomas Hainschwang.

DFI Fluorescence Imaging and Spectroscopy

The fluorescence reaction of the H-rich type Ia NDR brown diamonds was found somewhat variable and depended on a lot on the presence or absence of the N3 center. In the 1330 nm center H-rich diamonds the N3 center was typically detectable and did, particularly for the Tigers Eye diamond, influence the fluorescence response. For that stone, the fluorescence was a mix of yellow with blue sectors. In the other sample of this type, sample TH 2.618, the N3 center was extremely weak and had no influence on the apparent luminescence. As seen in Figure 26, the diamond fluoresced greenish yellow to yellowish green under the DFI excitations, with distinct zoning of the fluorescence. This fluorescence was found to be caused by the 523.7 nm NE3 defect, hence yet another center that can be responsible for visible fluorescence in diamond.

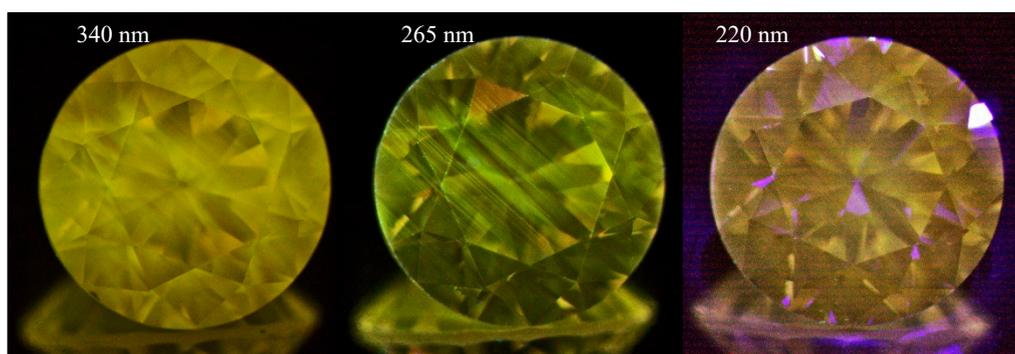


Figure 26. A light yellow-brown hydrogen-rich type IaA >> B diamond (sample TH 2.618) under three different UV excitations of the DFI system. The yellow to yellow green PL is caused mainly by the 523.7 nm defect. Photos: Dr. Thomas Hainschwang.

In the other type of type H-rich type Ia brown diamond, the strongly sectorized cuboid-octahedral “asteriated” diamonds—represented by sample TH 2.626—the fluorescence was limited to the cuboid sector which fluoresced distinctly yellowish green, while the colorless octahedral sectors were completely inert (Figure 24, photo inset). The green fluorescence was caused by the S3 center, with its ZPL at 496.6 nm and its broad and intense vibronic sideband centered at 545 nm. This kind of fluorescence reaction is characteristic for such diamonds; all asteriated diamond samples analyzed by the authors in the past 15 years have shown very similar results, but the colorless sectors showed a somewhat variable PL response as shown by other samples tested by the authors (Figure 27, left) and particularly by one of the most spectacular asteriated diamond ever unearthed, the Rhodesian Star diamond.

This 11.38 ct polished octahedron showed green S3 fluorescence in the cuboid sectors while the octahedral sectors fluoresced orange-red to pink (Figure 27, right) from a combination of the N3 center and a strong featureless band centered at 655 nm [34]; the 655 nm band is a very common feature in “cape” diamonds; it always occurs together with the N3 center and results in the shift from the blue N3 PL to violet when the band is weak, purple when it is stronger to nearly red PL when it is unusually strong. The cause of this band, that is always found in the spectra of the colorless octahedral sectors of such asteriated diamonds is not known.

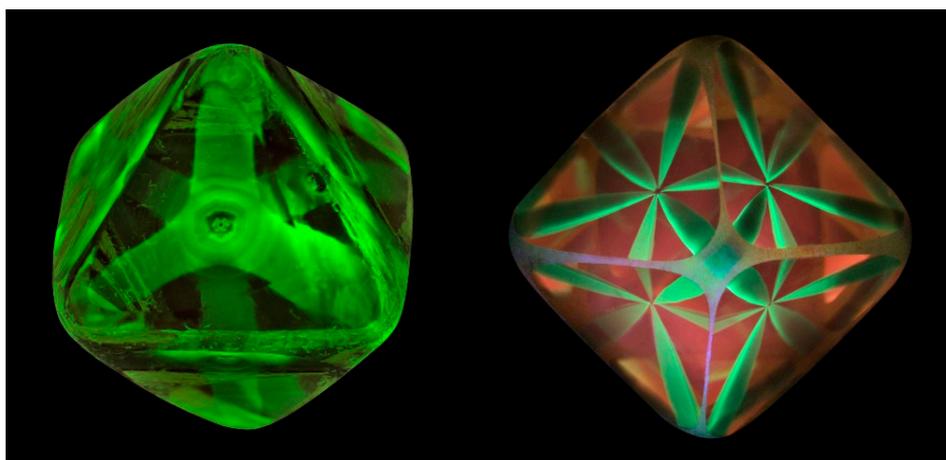


Figure 27. The fluorescence under 340 nm of two asteriated diamonds, a 2.50 ct polished octahedron on the left and the 11.38 ct Rhodesian Star on the right. While the sample included in this study (TH 2.626) shows only the S3 center green PL of the cuboid sectors while the octahedral sectors were totally inert, these two samples show the same S3 center green PL while the octahedral sectors fluoresces faint pink in the smaller sample and distinctly orange red in the larger stone. The fluorescence seen in the near colorless octahedral sectors is caused by a combination of the N3 center with the 655 nm broad band PL. Photos: Dr. Thomas Hainschwang.

The type IbXY NDR brown diamonds showed very weak whitish appearing pink fluorescence (Figure 28) that was caused by a very large PL band ranging from 400 to 800 nm, centered at about 640 nm. The fluorescence distribution with its apparent Y or “Mercedes star” shaped core is indicative of a mixed cuboid octahedral growth, with the Y representing the octahedral sectors. The fluorescence of these stones is typically very weak because of their lack of plastic-deformation related defects such as H3 or nickel-related fluorescent centers such as the S1, S2, and S3, combined with their high C center content. The C center appears to be a very efficient fluorescence quencher via non-radiative by a dipole-dipole mechanism [35]. In natural type Ib diamonds, only stones with very low nitrogen content (<10 ppm) and significant deformation-related defects tend to fluoresce more strongly [15].

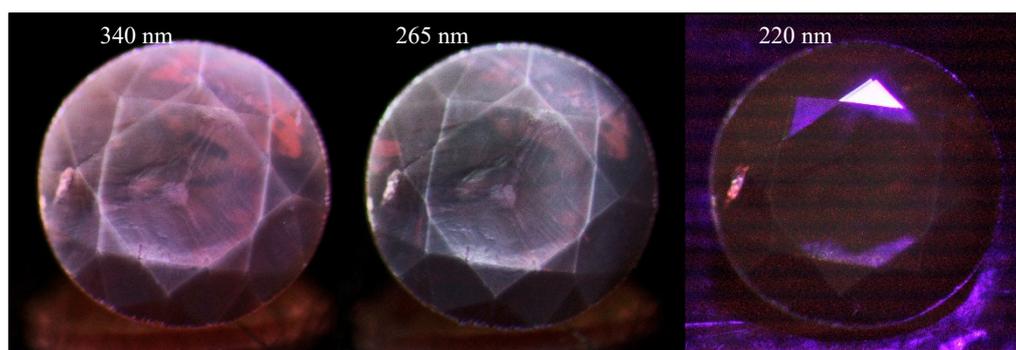


Figure 28. A deep orange-brown hydrogen-rich type IbXY diamond (sample TH 2.327) under three different UV excitations of the DFI system. The fluorescence distribution with the “Mercedes star” in the core (three-fold symmetry) is indicative of the mixed cuboid octahedral growth of the diamond. The “Mercedes star” is representative of the octahedral growth sector. The PL at 340 nm is caused by a very broad PL band centered at about 640 nm and that ranges from 400 to 800 nm.

3.2. The Classification of Natural Brown Diamonds with Non-Deformation-Related Color

A total of 17 diamonds of this category were analyzed for this study, but many more samples analyzed in the past have been taken into consideration for this classification. The samples studied in

detail represent all variations of such brown diamonds and they were carefully selected to give an accurate view of the properties of the typical and the less common brown diamonds with NDR color.

The group of NDR brown diamonds was subdivided into 5 different classes, which gives combined with 6 different classes of DR brown diamonds [1] a total of 11 classes of brown diamonds. The different classes and their properties are given in Table 2.

Table 2. The newly elaborated classification of natural untreated NDR brown diamonds.

Natural Non-Deformation-Related (NDR) Brown Diamonds					
Main Type	Type I and/or Undefined Type			Type I	
Sub type	CO ₂	Pseudo-CO ₂	Type IaAB, hydrogen-rich	Type IaAB hydrogen-rich	Type IbXY, hydrogen-rich
AC (RT)	None	None	None	None	None
Other characteristic IR features	CO ₂ peaks, often very uncommon one-phonon absorption	Often very uncommon one-phonon absorption, no CO ₂ absorption	“Standard” H absorptions—3107, 3237 cm ⁻¹ 1330 nm center (LNT)	Cuboid-growth related H absorptions in brown sectors: 3050, 3124, 3139, 3144, 3154, 3310, 3474 cm ⁻¹ , 1330 nm center (LNT) very weak or undetectable	Very complex band with multiple H-related absorptions, 3309–2741 cm ⁻¹ , linked to Y center.
Characteristic PL feature	Complex 690 nm band, 882.9/884.6 (Ni _i ⁺)		521.2 to 527.4, 700.6, 787.0, 793.6 nm	496.6 (S3), 787.0, 793.6 nm	904.2, 692.0, 689.3, 698.0 nm
Characteristic UV-Vis-NIR features	Absorption continuum from NIR to the UV, 480 nm band		Complex spectrum caused by 1330 nm center and 990 nm series	Absorption continuum from NIR to the UV	Absorption continuum from NIR to the UV, 904.2 nm defect
Class name	CO ₂ NDR brown diamond	Pseudo-CO ₂ NDR brown diamond	“1330 nm center” hydrogen-rich NDR brown diamond	“3310 cm ⁻¹ defect” hydrogen-rich NDR brown diamond	Hydrogen-rich type IbXY NDR brown diamond

3.3. Treated NDR Brown Diamonds

While only four representative samples are included in the sampling of this study, we have comparative data from a significant number of irradiated and annealed NDR diamonds that turned essentially brown after annealing and even certain diamonds that were HPHT treated and were brown after the treatment; some of these were brown prior to the treatment, others were either colorless or had other colors.

From a commercial standpoint it is obviously not desirable to end up with a brown diamond via any treatment, unless the color is, e.g., strongly orange, which represent a color that is quite rare in untreated natural diamonds.

To explain what leads to brown color after any color treatment, the following paragraphs give a short summary of results obtained by our own treatment experiments.

3.3.1. Irradiation and Annealing

There are basically two scenarios to produce a very brownish color by irradiation and annealing. In the first one a type Ia or IIa or IIb diamond of any color is irradiated with a very high dose of electrons or even better neutrons and therefore turned into an (opaque) black color, and then heated at any temperature between 800 to 1100 °C. Such diamonds will be typically anywhere from brown to brown orange after the annealing. The sample included here represents a typical result when a colorless type Ia “cape” diamond is irradiated by a very high dose of neutrons and then annealed.

The resulting spectrum was dominated by a continuum absorption with an absorption cut-off shifted into the visible part of the spectrum. Total absorption was observed around 490 nm, and the spectrum exhibited a large amount of absorptions related to irradiation and annealing, such as the peaks at 503.2 (H3), 533.9, 592.3, 644.2, 649.3, 695.5, 917 and 986.0 (H2) (Figure 29, trace a). This continuum responsible for the very brownish color is related to the large accumulation of vacancies induced by such heavy irradiation and has been called the UV band [36–38]. The continuum absorption and all shown absorptions were annealed out when we heated the sample to 1500 °C, while the H2 and H3 absorptions got distinctly stronger and NV⁻ absorption was formed. The increase in H3 centers is likely linked to the release of vacancies at the high temperatures, the very strong increase in H2 absorption occurred because some of the aggregated nitrogen was dissociated into C centers through the annealing of the diamond. With the C center being an electron donor, the neutrally charged H3 defect gets negatively charged to form the H2 center [39]. The sample changed its color from orange brown to olive green after 1500 °C because of the suppression of the continuum and the creation of extremely strong H2 absorption.

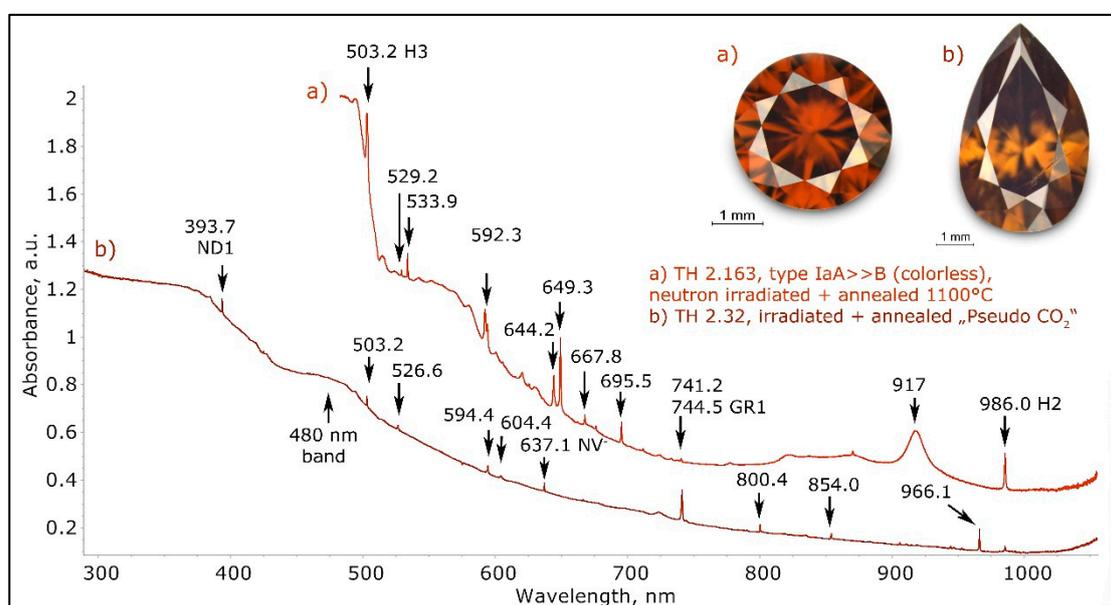


Figure 29. The low temperature UV-Vis-NIR spectra of two type I brown diamonds with artificial irradiation-related color are shown in this graph. Trace (a) shows the spectrum of a colorless diamond that has been exposed to a large dose of mostly fast neutron irradiation, which turned the stone opaque black; the stone was then heated to 1100 °C for 3 h, which resulted in this deep orange brown color. The strong absorption continuum is the result of the large accumulation of vacancies-cluster-like defects induced by irradiation which—unlike the single vacancies that induce GR1 and ND1—are stable to rather high temperatures. Trace (b) shows what happens when a brown Pseudo-CO₂ diamond is irradiated by electrons and heated to 700 °C—it will be mostly brown again after the treatment. Such diamonds are not suitable for any treatment, the results are never satisfactory, as basically such stones are unaffected color-wise. The spectra have been shifted vertically for clarity.

The second scenario involves CO₂ and Pseudo CO₂ diamonds; such diamonds do often contain very little to no nitrogen in the known forms in their colored sectors, and in consequence irradiation followed by annealing does create very little optically active defects such as H3, H4, NV⁰ and NV⁻; therefore, such stones return basically to the same color that they exhibited prior to the treatment when GR1 anneals out at about 800 °C. Such a diamond is shown in Figure 29, trace b/image b. The spectrum shows how little irradiation/annealing-induced absorption was created by heating the electron irradiated Pseudo-CO₂ sample at 800 °C, and that the color of the sample was essentially caused by the same continuum absorption that was present prior to the treatment.

3.3.2. HPHT Treatment

Brown color by HPHT treatment seems like a contradiction to anybody who knows typical facts about HPHT treatments: One of the main purposes of that treatment is to eliminate brown color, not to create it. Here we also have two scenarios, one about brown diamonds that stay brown even after HPHT treatment, and the second one about a process to create brown diamond out of cape yellow diamond.

Just like by the irradiation/annealing treatment, CO₂ and Pseudo CO₂ diamonds were shown to be practically unaffected by HPHT treatment, at least at temperatures below 2200 °C. The diamonds analyzed back in 2007/2008 were not included in this work, and here only a review of the results published in 2008 by TH and FN and co-authors [4] is elaborated. In that earlier study 13 diamonds were HPHT treated at 2000 to 2100 °C and their properties before and after the treatment were compared. While the main purpose of this study was the observation of the behavior of the CO₂ absorptions at such conditions, other characteristics such as the color modification and the entire spectroscopy were of course also included. It was noted that the color of the diamonds barely changed, they all stayed essentially brown. A slight shift towards a somewhat more yellow color was noted in many of them, but the change was very slight. A look at the UV-Vis-NIR spectra pre- and post-treatment revealed that neither the continuum absorption responsible for the brown color was suppressed, nor were any of the classical defects formed that we know from HPHT treated type I diamonds (i.e., H3, H2, NV⁰ and NV⁻). The only thing that was noted is a distinct increase in the intensity of the 480 nm absorption band. The increase/formation of the 480 nm band in certain diamonds has since been published by the authors on several occasions [11,40]. This band has been linked to an oxygen defect in diamond [29] and the properties of all diamonds with this band and for which this band is formed via HPHT treatment clearly points towards such an oxygen-containing defect as well.

In the second scenario, brown color has been created by HPHT treatment at rather extreme conditions of HPHT at 2500 °C. For this experiment, the authors have selected four cape-type diamonds, two being colorless and two being light yellow in color. The defects of the diamonds were verified prior to the treatment and all four stones were essentially found to be the same, with classical defects one would expect in cape-type diamonds. The only significant difference between them was their nitrogen content and the N3 center concentration. Prior to HPHT treatment, the four diamonds were irradiated by 2 MeV (samples TH 2.368, TH 2.377, and TH 2.416) and 10 MeV (sample TH 2.417) electrons to enhance nitrogen aggregation and dissociation, an effect well-known in diamond [41]. Then the diamonds were HPHT treated for a few minutes at the maximum temperature of 2500 °C and the result was rather surprising: The two originally colorless diamonds turned vivid yellow—which corresponds to the expected result—while the two originally light yellow diamonds turned dark orangy brown (Figure 30, inset photos). The nitrogen concentration and speciation of the samples were compared before and after the treatment, and it was noted that significant concentrations of C centers were formed; interestingly, the C center concentration was distinctly higher in the samples which turned vivid yellow with 50 ppm and 55 ppm of C centers compared to the orangy brown samples which contained only 30 ppm of C centers each. Based on the C centers produced, all four diamonds should be of vivid yellow color, and obviously the question arose why two samples turned out dark orangy brown. To investigate this, the data of the stones before and after the treatment were evaluated and compared in detail.

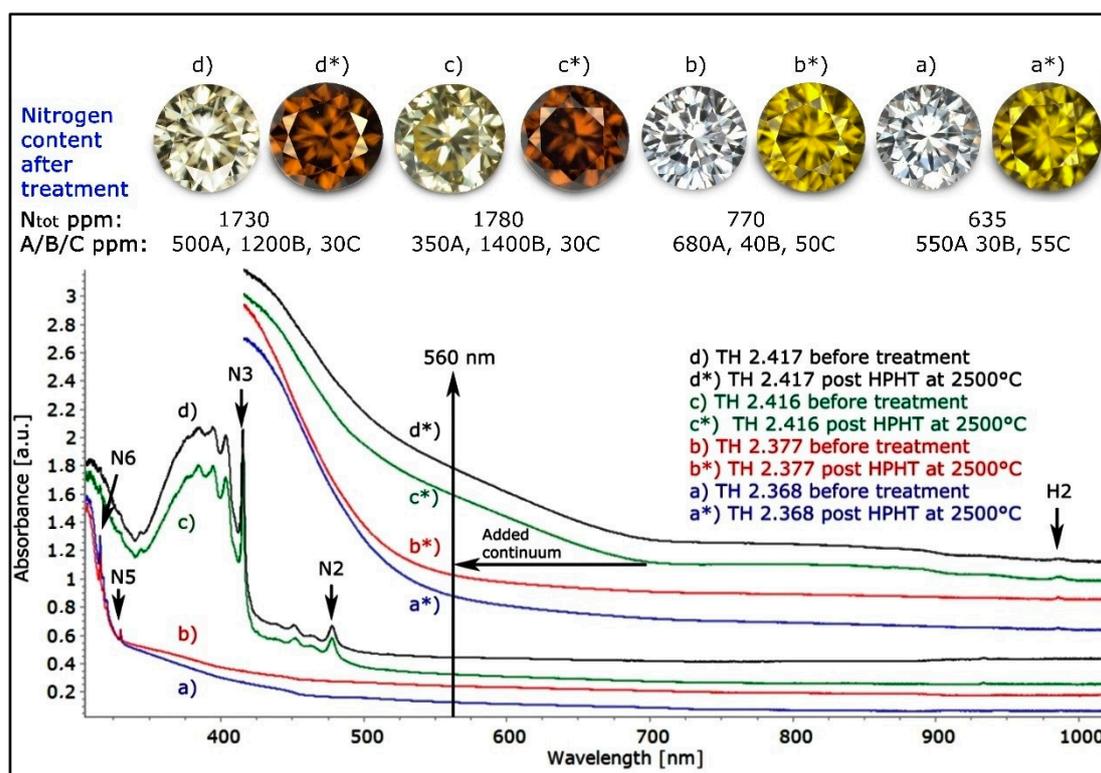


Figure 30. The low temperature UV-Vis-NIR spectra of four cape type IaAB diamonds that were HPHT processed at 2500 °C. Samples TH 2.416 and TH 2.417 were light yellow before the treatment and turned orangey brown by HPHT while the other two diamonds were perfectly colorless before the treatment and turned vivid yellow by HPHT. The only analytical difference between the diamonds was the relative ratio of A to B aggregates and total nitrogen content, which leads in consequence to the much higher N3 concentration in the yellowish samples. After the treatment the diamonds rich in N3 centers developed the additional continuum absorption starting at 700 nm and neither N3 nor N2 is detectable. The spectra have been shifted vertically for clarity.

The result of this evaluation indicated that only the significant difference in the N3 center concentration was responsible for the very different outcome in color. The low temperature UV-Vis-NIR spectra of the samples showed that all four samples developed continuum absorption as expected from the produced C centers. The continuum had a text-book shape of type Ib diamonds for the samples that turned vivid yellow, with barely any absorption increase from 1050 to 560 nm and then a sharp increase at 560 nm to 410 nm (Figure 30, traces a* and b*). In contrast, the continuum of the orangey brown diamonds increased significantly from 700 nm onwards to equally cut-off at 410 nm (Figure 30, traces c* and d*); additionally, there was already a noticeable absorption increase visible from 986 nm onwards because of the H2 center. Besides the continuum absorption created a very noteworthy change induced by the HPHT treatment was the suppression of the N2 center absorption observed in the spectra of samples TH 2.416 and 2.417; while at the position of the N3 absorption ZPL (415.2 nm) the continuum absorption was heading into the cut-off, at 478 nm (N2 ZPL) the continuum absorption was low enough to easily detect the N2 center if there was any left. With the N3 and N2 center being the same defect, the spectra clearly indicate that the HPHT treatment at such high temperature has annealed out much of the N3 center.

This was confirmed by the PL spectra at 360 and 402 nm, which were dominated by the N3 center prior to treatment; after the treatment the N3 center PL was strongly reduced and with it the PL at 933.3 nm. Other than this, the main centers created in the PL spectra of all four diamonds include H3 and NV⁻, but there was one significant difference between the low N3 and the high N3 diamonds: In the spectra of the high N3 diamonds, a very distinct broad PL band centered at approximately 880 nm

was created, with overlaying oscillating peaks with maxima every 25 to 33 nm, centered at 749, 774, 800, 829, 860, 892, and 925 nm (Figure 31). The data leads us to suggest that the brown color in these two diamonds was induced by a new defect formed via the destruction of N3 centers. If this process involves the actual dissociation of N3 into vacancies and nitrogen or aggregation of N3 (N3-V) into possibly larger defects such as N6-2V is not known and needs to be investigated further.

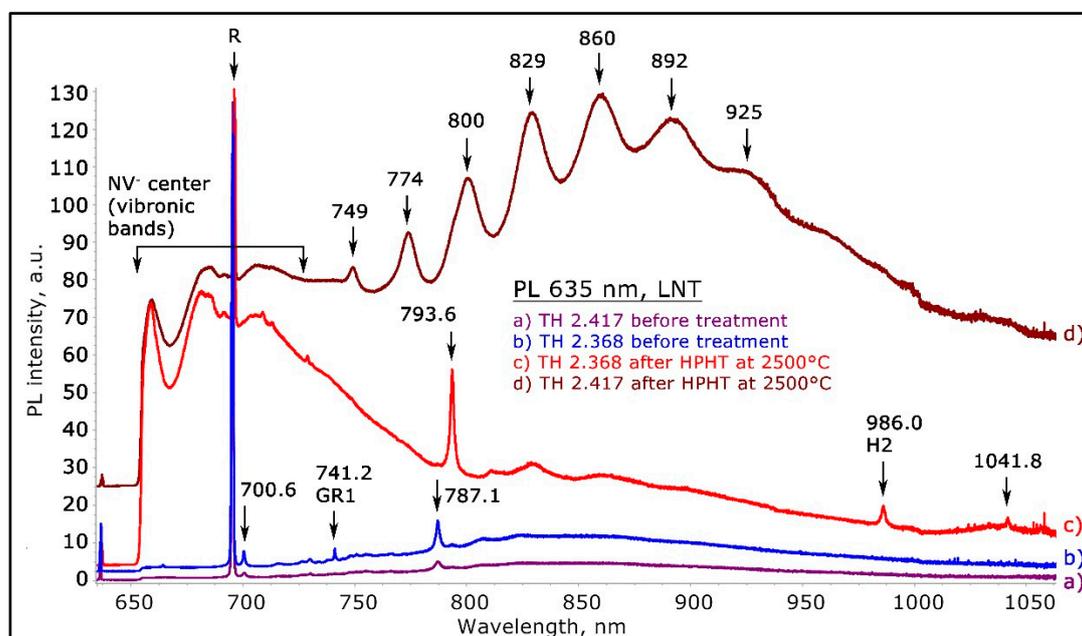


Figure 31. The low temperature PL spectra of two cape type IaAB diamonds that were HPHT processed at 2500 °C, excited by 635 nm laser. Sample TH 2.417 was light yellow before the treatment and turned orangey brown by HPHT while sample TH 2.368 was perfectly colorless before the treatment and turned vivid yellow by HPHT. While both spectra show the formation of significant NV⁻ center post HPHT annealing, the formation of significant PL with rather broad bands every 25 to 33 nm in the more yellow diamond TH 2.417 is significant. This PL feature is published here for the first time and seems related to the defect formed by annealing the N3 center. The spectra have been shifted vertically for clarity.

3.4. Synthetic Brown Diamonds

3.4.1. HPHT Synthetic Brown Diamonds

HPHT synthetic diamonds can be grown in a very limited range of colors besides colorless, including yellow, orangey yellow to brownish yellow and blue. The yellow color originates from the nitrogen present in the growth cell that is incorporated in the diamond structure in form of C centers.

Blue color is induced by adding boron in the growth chamber. The brownish and orangey color of some yellow synthetic diamonds is generally caused by nickel defects. Other colors can only be achieved by post-growth treatment including HPHT, irradiation and annealing and combinations of those treatments; this includes also brown. The HPHT synthetic included in this study (sample TH 2.22) was originally brownish yellow from distinct nickel absorptions overlaid on the C center continuum absorption (Figure 32, trace/image a); the sample was irradiated by 2 MeV electrons and then annealed at 800 °C. After irradiation the color of the synthetic diamond changed to “olive” brown from an overlaid GR1 absorption (Figure 32, trace/image b) and after annealing the stone turned red-brown from very strong NV⁻ center absorption (Figure 32, trace/image c).

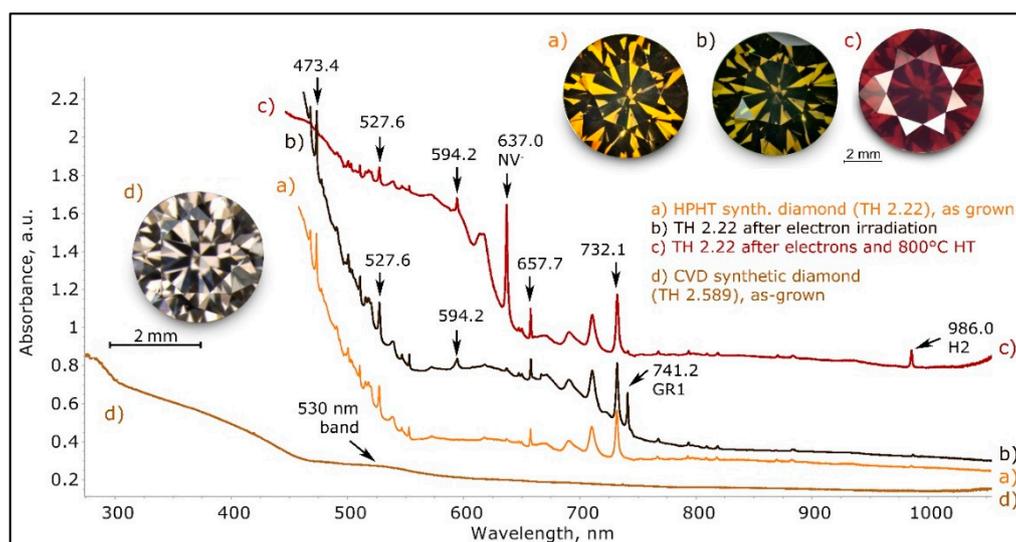


Figure 32. The low temperature UV-Vis-NIR spectra of an olive brown/red brown type Ib > IaA HPHT (High Pressure High Temperature) synthetic diamond (TH 2.22) and a brown CVD (chemical vapor deposition) synthetic diamond (TH 2.589). The olive brown color in the HPHT synthetic diamond is the result from electron irradiation of the originally overly dark yellow stone. The GR1 absorption overlaying the complex spectrum rich in nickel-related absorptions results in the basically brown color (trace b). Heating this stone at 800 °C for 2 h resulted in the deep red brown color, from the newly formed intense NV⁻ center absorption (trace c). Trace (d) shows the spectrum of an as-grown brown CVD synthetic diamond; the brown color is caused by a featureless continuum, just like many type IIa natural brown diamonds; the only overlaying absorptions visible are a weak broad band at 530 nm and a series of very weak sharp peaks (not indexed). While HPHT synthetic diamonds must be treated to appear brown, CVD synthetic diamonds are often grown brown and need HPHT treatment to decolorize them. The spectra have been shifted vertically for clarity.

3.4.2. CVD Synthetic Brown Diamonds

In contrast to HPHT synthetic diamonds, CVD synthetic diamonds can be grown in a larger variety of colors besides colorless, including brown, yellow, blue, gray, violet, and pink orange. Of these colors, brown is the most common one, as most CVD synthetic diamonds are grown as fast as possible, and as a consequence are rich in sp² carbon, dislocations and vacancies. This defective lattice is responsible for the brownish color of these synthetic diamonds; the vast majority of such synthetic diamonds are HPHT treated to eliminate the brown color.

The spectra of brown CVD synthetic diamonds are characterized by a pretty featureless continuum absorption, often with a weak broad band at 530 nm. A series of generally very weak sharp peaks can often be found. In the spectrum of the sample included in this study, the above mentioned broad band at 530 nm plus peaks at 296.6, 301.3, 305.8, 413.4, 414.1, 419.5, 442.9, 446.9, 450.4, 596.0, 603.4, 624.3, 637.0 (NV⁻), 648.3, 736.9 (Si-V⁻) were visible (Figure 32, trace d).

4. Conclusions

Natural brown diamonds of natural non-deformation-related (NDR) color are much rarer than the common brown diamonds with deformation-related (DR) color. Nevertheless, they are of great interest not only concerning their unusual NDR brown color, but also as a link to many otherwise colored diamonds. While DR brown diamonds are the perfect candidates for HPHT treatment, NDR brown diamonds were shown not to react favorably to such a treatment. With five different classes of NDR brown diamonds defined, their properties were clearly found to be very different to the DR brown diamonds. Their brown color is caused by a range of defects and/or inclusions, many of which are not well understood. In the course of this study it was revealed that the color cause of the 1330 nm

defect H-rich diamonds are at least two different types of nickel-related defects, a nickel-nitrogen defect lacking hydrogen being responsible for the 1330 nm defect and all its associated structure and a nickel-nitrogen defect likely involving hydrogen being responsible for the 990 nm series defect and all its associated structure. A very interesting point is that these two defect structures together with the N3 center can be used to explain a vast range of colors of (usually) H-rich diamonds, including greenish yellow to “olive”, brownish yellow to brown, and gray to violet.

From the properties of some of the NDR brown diamonds, such as the “asteriated” H-rich diamonds and certain CO₂ rich diamonds, it is possible that the brown color in these could relate to micro-inclusions rather than to actual color-causing defects.

It was shown that irradiated/annealed as well as HPHT treated diamonds of brown color are known, and there were basically two scenarios in both types of treatments. The first scenario involves the NDR brown diamonds that do neither react positively to irradiation/annealing nor HPHT treatment—hence basically stay the same color as before the treatment—the second scenario covers the actual creation of brown color by either of the two types of treatments. It was shown that CO₂ and Pseudo-CO₂ diamonds remained basically the same brown color that they exhibited before treatment when they were irradiated/annealed or HPHT treated (up to 2100 °C). These diamonds do neither show deformation-related defects that could be modified via HPHT treatment, nor the needed nitrogen to create significant nitrogen-vacancy defects via irradiation and annealing.

An orangy brown color was shown to be created in colorless diamonds by a very high dose of irradiation, preferably by neutrons, followed by annealing at 800 to 1100 °C; the continuum created relates to large accumulations of vacancies that are created besides the well-known single vacancies (GR1/ND1); the defects responsible and in consequence the brown color anneal out at a temperature of 1500 °C. HPHT treatment at very high temperature creates orangey brown color in originally light yellow “cape” diamonds; we suggest that this surprising color modification must be associated with the significant reduction of the N3 center through the HPHT treatment. Either new defects created via dissociation of the N3 center or via further aggregation of N3 centers into more complex nitrogen-vacancy defects could be responsible for the brown color.

Finally, it was shown that brown is not a color typically seen in HPHT synthetic diamonds and can only be created by either irradiation or irradiation/annealing of brownish yellow synthetic diamond. In contrast brown color is the most common one in CVD synthetic diamonds; the color origin of the two types of synthetic diamonds is very different, as one relates to the combination of C center, nickel and irradiation defects while the other relates to the high density of vacancies and dislocations in rapidly grown CVD diamond.

This second part of our brown diamond study concludes the work conducted on this large group of diamonds and demonstrates once again the complexity of brown diamonds and their color origin.

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