

Article

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

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Abstract: For this study, the properties of a large sample of various types of brown diamonds with a deformation-related (referred to as “DR” in this work) color were studied to properly characterize and classify such diamonds, and to compare them to pink to purple to red diamonds. The acquisition of low temperature NIR spectra for a large range of brown diamonds and photoexcitation studies combined with various treatment experiments have opened new windows into certain defect characteristics of brown diamonds, such as the amber centers and naturally occurring H1b and H1c centers. It was determined that the amber centers (referred to as “AC” in this work) exhibit rather variable behaviors to annealing and photoexcitation; the annealing temperature of these defects were determined to range from 1150 to >1850 °C and it was found that the 4063 cm⁻¹ AC was the precursor defect of many other ACs. It is suggested that the amber centers in diamonds that contain at least some C centers are essentially identical to the ones seen in diamonds without C centers, but that they likely have a negative charge. The study of the naturally occurring H1b and H1c link them to the amber centers, specifically to the one at 4063 cm⁻¹. Annealing experiments have shown that the H1b and H1c defects and the 4063 cm⁻¹ AC were in line with each other. The obvious links between these defects points towards our suggestion that the H1b and H1c defects are standalone defects that consist of multiple vacancies and nitrogen and that they are—in the case of brown diamonds—a side product of the AC formation. A new classification of DR brown diamonds was elaborated that separates the diamonds in six different classes, depending on type and AC. This classification had been completed recently with the classification of brown diamonds with a non-deformation-related color (referred to as “NDR”), giving a total of 11 classes of brown diamonds.

Keywords: natural diamonds; defect characterization; optical properties; plastic deformation; Vacancies

1. Introduction

Brown diamonds (Figure 1) make up a considerable percentage of the diamonds produced worldwide, particularly from certain deposits like the Argyle mine in Australia. They represent a large group with variable properties and were—in combination with this work—classified recently [1]. With the color “brown” not being a spectral color, but a mix of different colors (a composite color), it is often quite difficult to define; brown is produced by mixing red and green, orange and blue, purple and yellow, or simply by darkening orange or red, hence mixing red or orange with black. In diamonds, the brown color often exhibits modifying hues, such as yellow, orange, green, and pink. The brown color in most diamonds is associated with post-growth plastic deformation and the defect responsible for this color of such plastically deformed diamonds was identified as large spherical aggregates consisting of 40 to 60 vacancies, so-called vacancy clusters [2–5]. Not all brown diamonds are plastically deformed, though, as there are particularly CO₂ and “Pseudo CO₂” diamonds [6] as well as hydrogen-rich diamonds [7] that owe their brown color to other defects.

Diamonds of all the different types can appear brown, and practically all colored diamonds can show brown as a modifying color.

A classification based on a range of criteria has been established in 2003 [6]; this classification separated brown diamonds into two broad categories, one including diamonds not exhibiting an “amber center” infrared absorption and one including all diamonds exhibiting an “amber center” (referred to as “AC” in this study). This approach defined a total of nine classes, three with AC and nine without AC; it was found that out of the roughly 900 diamond samples tested, about 95% exhibited an AC. The ACs are absorptions caused by electronic transitions—hence not vibrational absorptions—which exhibit their ZPLs (zero phonon lines) in the range between 3462 and 4165 cm^{-1} at room temperature and with structures that extend to approximately 10,500 cm^{-1} [8]. Since they are electronic transitions, they react strongly to temperature and the absorptions become distinctly narrower at a low temperature, by which means it was demonstrated that the ACs consist of a series of ZPLs [8].

Spectroscopically speaking, the brown color in diamonds is caused by an absorption continuum gradually increasing from the NIR to the UV; this continuum is shallow and overlaid only by minor absorptions—if any—such as N3 (ZPL at 415.2 nm), H3 (ZPL at 503.2 nm), and the 560 nm band [6].

The brown color in diamonds can be induced by treatment, although generally such a result is undesired and accidental, since it does not increase the value and/or desirability of the treated diamond; exceptions are orange brown diamonds, which are colors produced purposely by treatments. Treatments resulting in a brown color include irradiation by most commonly electrons or neutrons and irradiation followed by annealing [9], as well as HPHT (high pressure, high temperature) treatment [10].

The vacancy cluster defects responsible for the brown color in diamonds are very stable and anneal out only at temperatures above 1800 °C, with distinct variation between the different diamond types; the defect is more stable in Type II diamonds and anneals out efficiently (i.e., in a few minutes) only at temperatures of 2300 °C or more. As a consequence, the only treatment to eliminate the deformation-related brown color of diamonds is a heat treatment above 1800 °C, conditions in which diamonds are most efficiently kept from sublimating to CO and then CO₂ by applying pressure. Hence, the only way to eliminate the brown color in natural brown diamonds with a plastic deformation-related color is high pressure, high temperature (HPHT) treatment at temperatures typically ranging from 2000 to 2500 °C and pressures between 55 and 85 kbar. This treatment is used to decolorize type IIa brown diamonds, to eliminate the brown component in “olive”-colored type IIb diamonds—turning them blue—and to transform the color of type Ia brown diamonds into various shades of yellow, with or without green or orange color components [11]; here, the green color components are always caused by H3 fluorescence [12]. The treatment can also be used to modify the color of brown type Ib diamonds and type Ib diamonds with color modifiers; all type Ib diamonds will turn pure yellow upon HPHT treatment [13]. It has been shown that the HPHT treatment does not eliminate the brown color in diamonds with a color not related to plastic deformation; here, the only thing that will modify the color is the modification of the nitrogen aggregation with increased treatment temperature (i.e., the creation of C centers (single substitutional nitrogen)), and the increase or formation of 480 nm absorption [14].

Synthetic diamonds of brown color have been very uncommon until the ascent of CVD (chemical vapor deposition) synthetic diamonds, which are often brown in their as-grown state due to their very defective structure. Such brown stones are generally HPHT treated to render them near-colorless to colorless, but recently significant quantities of untreated brown CVD synthetic diamonds mixed in parcels of melee-sized natural brown diamonds have been discovered [15]. Before the time of CVD synthetics, the brown color in an HPHT synthetic was, in the authors’ experience, only obtained by irradiating dark yellow to orange yellow stones.

The purpose of this paper is a detailed characterization of brown diamonds with a deformation-related color, particularly of the defects that can be detected by various spectroscopic methods, plus a newly proposed classification of such colored diamonds. A series of treatment experiments were used to gain more information on a range of spectral features typical of such brown

diamonds. The annealing behavior of naturally occurring H1b and H1c and the ACs at temperatures from 150 to 1500 °C and 1850 °C is presented here for the first time. Another important result from this study is the creation of AC absorption in colorless type Ia diamonds by heavy neutron irradiation followed by annealing at 1000 to 1850 °C.

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 observations were made using a prototype GGTL Mega-DFI luminescence imaging and spectroscopy system that used high intensity UV in the form of 5 different, more or less broad excitation bands (centered at 350, 320, 280, 260, and 220 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 FTIR spectrometer equipped with a thermoelectrically cooled DTGS detector, using a diffuse reflectance accessory as a beam condenser and a 5 \times beam condenser. The spectra were recorded over a range of 8500 to 400 cm^{-1} , with 50 to 1000 scans for each diamond.

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 [16]. 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} band and/or its first harmonic at 2688 cm^{-1} [17], and not on the intensity of the 1130 cm^{-1} band because of possible false results from underlying Y center absorption [18].

Near infrared spectra in 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 detector, in a 15 cm 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.

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 camera, thermoelectrically cooled down to -30 °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 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 brown diamonds were treated by the different treatments applied to the diamonds, including annealing only, 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, 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 the materials that were passed through the accelerator for the cross-linking treatment. Neutron irradiation was performed in a nuclear reactor in Poland with a dose of 1.8×10^{17} neutrons/cm² by mostly fast neutrons of an energy of several MeV (the exact value being unknown). Annealing and post-irradiation annealing have been realized at our laboratory using a Nabertherm LHT 02/17/P470 oven with a maximum temperature of 1750 °C. For the annealing experiments, the diamonds were kept in a reducing atmosphere, to keep the diamonds from burning at conditions above 500 °C. Annealing was performed for the diamonds up to a temperature of 1500 °C. Some samples were treated by HPHT at temperatures ranging from 1850 to 2500 °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; SedKrist GmbH, Seddiner See, Germany; and Suncrest in Orem, Utah, USA.



Figure 1. A variety of differently colored and shaped deformation-related brown diamonds.

2. Materials and Methods

Besides the brown diamond samples collected in the past 20 years by TH (Thomas Hainschwang), 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 75 gem-quality brown and 2 colorless diamonds weighing 0.01 to 61.56 ct were analyzed in detail for this study; 57 samples for this first part of the article and 20 samples for the second part. Samples include all different diamond types and all different categories of brown diamonds, owing their color to deformation-related defects (referred to as “DR”) and owing their color to non-deformation-related defects (referred to as “NDR”). Only diamonds with a dominantly brown color were included, all of them faceted into various shapes with the exception of one rough diamond. The two colorless diamonds were included to represent the neutron irradiation treatment experiments in this study. See Table 1 for details on the diamonds. Besides the diamonds tested specifically for this study, the data of a large selection of pink to red to purple diamonds analyzed in the past were reviewed to gain some insight into the differences and links between pink and brown diamonds; the details of these diamonds are not listed here.

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

Key	Sample	Cut, Weight	Initial Color	Type	N/B Content, ppm (±5%)	IR Characteristics	Treatments Performed
Deformation-related type Ia	TH 2.13	RBC, 0.086 ct	F. yellowish brown	IaB>>A	≈186 tot.; 31 A, 155 B	AC4167, irr. peaks	2 MeV e ⁻ irradiation, HT 800 °C
	TH 2.40	RBC, 0.080 ct	F. olivish brown	IaA>>B	≈186 tot.; 166 A, 20 B	AC 4167/4063, H1b	-
	TH 2.43	RBC, 0.097 ct	F. dk. brown	IaA>>B	≈199 tot.; 180 A, 19 B	AC 4167	-
	TH 2.44	RBC, 0.067 ct	F. yellowish brown	IaB>>A	≈172 tot.; 39 A, 133 B	AC 4167	-
	TH 2.47	RBC, 0.047 ct	F. brown	IaB>>A	≈300 tot.; 29 A, 271 B	AC 4167	-
	TH 2.48	RBC, 0.042 ct	F.dk olive brown	IaA>B	470 tot.; 317 A, 153 B	AC 4167/4063, H1b, H1c	-
	TH 2.50	RBC, 0.125 ct	F. brown yellow	IaAB	12.6 tot.; 1.6 A, 12 B	AC4167	-
	TH 2.52	RBC, 0.101 ct	F.dp. yellow brown	Ib/IaA	81 tot.; 45 A, 36 C	AC 3457/4112/4063, H1b	HT 950 °C, 1050 °C, 1500 °C @2 h
	TH 2.211	RBC, 0.116 ct	Light brown	IaB>>A	358 tot.; 18 A, 340 B	AC 4190/4063	2MeV e ⁻ irr, HT 400–1310 °C
	TH 2.212	RBC, 0.075 ct	F. brown	IaB>>A	98 tot.; 14 A, 84 B	AC 4167/4063	2MeV e ⁻ irr, HT 400–1310 °C
	TH 2.328	RBC, 0.062 ct	F.dk. olive brown	IaA>B	279 tot.; 205 A, 74 B	AC 4167/4063, H1b, H1c	HT 1500 °C/2 h
	TH 2.330	RBC, 0.107 ct	F.dk. brown	IaA>B	330 tot.; 253 A, 77 B	AC 4167/4063, H1b, H1c	HT 950 °C–1500 °C @ 2 h
	TH 2.349	RBC, 0.034 ct	F. dk. olive brown	IaA>B	253 tot.; 140 A, 113 B	AC 4167/4063, H1b, H1c	HT 950 °C–1050 °C @ 2 h
	TH 2.383	RBC, 0.089 ct	F. brown	IaA>B	262 tot.; 159 A, 103 B	AC 4190/4063, H1b	2MeV e ⁻ irr. 2 h, HT 140–1250 °C
	TH 2.384	RBC, 0.095 ct	F. light brown	IaA>>B	99 tot.; 92 A, 7 B	AC 4167	2MeV e ⁻ irr. 2 h, HT 140–1250 °C
TH 2.387	RBC, 0.121 ct	F. brown	IaB>A	59 tot.; 17 A, 42 B	AC 4167	2MeV e ⁻ irr. 2 h, HT 140–1250 °C	
TH 2.388	RBC, 0.099 ct	F. brown	IaAB	254 tot.; 114 A, 140 B	AC 4190/4063, H1b	2MeV e ⁻ irr. 2 h, HT 140–1250 °C	

Table 1. Cont.

Key	Sample	Cut, Weight	Initial Color	Type	N/B Content, ppm (±5%)	IR Characteristics	Treatments Performed
Deformation-related type Ia	TH 2.389	RBC, 0.122 ct	F. brown	IaB>>A	200 tot.; 7 A, 193 B	AC 4167	10MeV e ⁻ irr. 2 h, HT 140–1250 °C
	TH 2.390	RBC, 0.076 ct	F. dk brown	IaB>>A	141 tot.; 19 A, 122 B	AC 4167	10MeV e ⁻ irr. 2 h, HT 140–1250 °C
	TH 2.391	RBC, 0.129 ct	F. dk. brown	IaA>>B	307 tot.; 265 A, 42 B	AC 4167/4063, H1b, H1c	2MeV e ⁻ irr. 2 h, HT 140–1250 °C
	TH 2.392	RBC, 0.110 ct	F. brown	IaA>>B	526 tot.; 477 A, 49 B	AC 4167/4063, H1b, H1c	2MeV e ⁻ irr. 2 h, HT 140–1250 °C
	TH 2.434	RBC, 0.154 ct	Very light brown (N-O)	IaB>A	45 tot.; 10 A, 35 B	AC 4167	-
	TH 2.435	RBC, 0.137 ct	Light brown (X-Y)	IaA>B	175 tot.; 120 A, 55 B	AC 4167	-
	TH 2.436	RBC, 0.146 ct	Light brown (Z)	IaA>B	50 tot.; 28 A, 22 B	AC 4167/4063	-
	TH 2.437	RBC, 0.136 ct	F.lt. brown	IaA>B	59 tot.; 30 A, 29 B	AC 4167/4063	-
	TH 2.438	RBC, 0.129 ct	F. yellowish brown	IaB>>A	93 tot.; 16 A, 77 B	AC 4167	-
	TH 2.439	RBC, 0.154 ct	F. brown	IaA>B	220 tot.; 156 A, 64 B	AC 4167	-
	TH 2.440	RBC, 0.143 ct	F. pinkish brown	IaA>>B	776 tot.; 660 A, 116 B	AC 4167	-
	TH 2.441	RBC, 0.129 ct	F. dk brown	IaA>>B	134 tot.; 129 A, 5 B	AC 4167	-
	TH 2.611	RBC, 0.113 ct	F. brown	IaA>>B	105 tot.; 95 A, 10 B	AC 4167	-
	TH 2.613	RBC, 0.081 ct	V.l. yellowish brown (O-P)	IaA>>B	148 tot.; 125 A, 23 B	AC 4167/4063	-
	TH 2.614	RBC, 0.176 ct	V.l. yellowish brown (O-P)	IaB>A	97 tot.; 30 A, 67 B	AC 4190/4063	-
	TH 2.615	RBC, 0.078 ct	Light brown (Q-R)	IaB>A	89 tot.; 25 A, 64 B	AC 4167/4063	-
	TH 2.617	RBC, 0.129 ct	V.lt. brown (O-P)	IaA>B	78 tot.; 52 A, 26 B	AC 4190/4063	-
	TH 2.619	RBC, 0.152 ct	Light brown (X-Y)	IaB	643 tot.; 643 B	H rich, AC 4200	HT 1500 °C/2 h
	TH 2.620	RBC, 0.110 ct	V.l. brown (O-P)	IaB	40 tot.; 40 B	AC 4200	-
	TH 2.621	RBC, 0.068 ct	F. brown	IaA>B	405 tot.; 265 A, 140 B	AC 4167	-
	TH 2.622	RBC, 0.126 ct	Lt. pinkish brown (S-T)	IaA>>B	976 tot.; 892 A, 84 B	H rich, AC 4167	-
	TH 2.623	RBC, 0.079 ct	Lt. pinkish brown (S-T)	IaA>>B	1049 tot.; 946 A, 103 B	H rich, AC 4167	-
	EUR 001	RBC 0.027 ct	F. yellowish brown	IaB	320 tot.; 320 B	H rich, AC 4200	-

Table 1. Cont.

Key	Sample	Cut, Weight	Initial Color	Type	N/B Content, ppm (±5%)	IR Characteristics	Treatments Performed
Deformation-related type Ib	TH Ib-4	RBC, 0.101 ct	F.dk. olive brown	Ib>>IaA	14 tot.; 1 A, 13 C	AC 4111	HPHT 1850 °C/5 min
	TH 2.51	RBC, 0.154 ct	F. brown	Ib	4.8 tot.; 4.8 C	AC 4111	-
	TH 2.210	Prin, 0.153 ct	F. yellowish brown	Ib	6.2 tot.; 0.2 A, 6.0 C	AC 4111	-
	TH 2.561	RBC, 0.135 ct	F. brown	Ib	2.0 tot.; 2.0 C	AC 4167/4111	-
	TH 2.46	RBC, 0.056 ct	F. dk. olivish brown	Ib	10 tot.; 3.5 A, 6.5 C	AC 4111	HT 1500 °C/2 h
Deformation-related type II	TH 2.332	RBC, 0.090 ct	F. yellow brown	IIa	-	AC 4063/4200	HT 1500 °C/2 h
	TH 2.445	RBC, 0.652 ct	F. yellow brown	IIa	-	AC 4063/4200	-
	TH 2.562	RBC, 0.062 ct	Lt. yellowish brown (S-T)	IIa	-	AC 4063/4200	-
	TH 2.563	RBC, 0.071 ct	F.lt. yellowish brown	IIa	-	AC 4063/4200	-
	TH 2.564	RBC, 0.068 ct	F.lt. brown yellow	IIa	-	AC 4063/4200	-
	TH 2.565	RBC, 0.037 ct	Lt. yellowish brown (S-T)	IIa	-	AC 4063/4200	-
	TH 2.584	RBC, 0.017 ct	F.lt. brown pink	IIa	-	AC 4063/4200	HT 1500 °C/2 h
	TH 2.610	RBC, 0.083 ct	F.lt. grayish yellowish brown	IIb	0.05 (= 50 ppb) boron	-	-
	TH 2.612	RBC, 0.164 ct	Lt. yellowish brown (O-P)	IIa	-	AC 4063/4200	-
	TH 2.616	RBC, 0.090 ct	Lt. yellowish brown (U-V)	Near IIa	<2 tot (A and B)	AC 4063/4200	-
Type Ia colorless (cape type)	TH 2.163	RBC, 0.109 ct	Colorless (E color)	IaA>>B	144 tot.; 136 A, 8 B	-	1.8 × 10 ¹⁷ neutrons/cm ² , HT 1000 to 1500 °C, 2 h/step
	TH 2.290	Plate, 0.080 ct	Colorless (F color)	IaAB	225 tot.; 105 A, 120 B	-	1.8 × 10 ¹⁷ neutrons/cm ² , HT 1000 to 1500 °C, 2 h/step; HPHT 1850 °C/5 min.

e⁻ = electron. Irr = irradiation. HT = annealed. HPHT = high pressure, high temperature treated. AC4167 = very weak AC; AC 4167 = weak AC; AC 4167 = medium AC; AC 4167 = strong AC. A = A center/A aggregate; B = B center/B aggregate; C = C center/single substitutional nitrogen. V.lt. = very light; Lt. = light; F.lt. = fancy light; F. = fancy; F.dp. = fancy deep; F.dk. = fancy dark.

3. Results and Discussion

3.1. Natural Brown Diamonds Colored by Post-Growth Plastic Deformation-Related Defects

3.1.1. Type I Brown Diamonds

A total of 40 type Ia and 5 type Ib diamonds of this category were analyzed in detail for this study. The samples 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 type I brown diamonds with a deformation-related color.

Microscopic Examination

All diamonds exhibited a variety of inclusions, not distinctly different from what one expects in near-colorless diamonds. These include fissures and solid inclusions like various crystals. In immersion the color distribution was found in all samples to be lamellar, consisting of brown and in some cases pink narrow lamellae following the octahedral directions (Figure 2). These lamellae were more or less obvious, but particularly in type Ib brown diamonds they were hardly discernible. When observed between crossed polarizing filters, all diamonds showed very distinct gray to black extinction bands following the brown colored lamellae, plus distinct and bright interference colors, typical for diamonds that have experienced post-growth plastic deformation. The correlation between the color lamellae and lamellar extinction and their orientations as seen between the crossed polarizing filters can be used to verify whether a diamond's color is DR or NDR. An example can be seen in Figure 3, which is a hydrogen-rich type IaB brown diamond; the immersion images shown prove that this stone is colored by DR defects and not by NDR defects. In many of the type Ia DR brown diamonds, the strong light of the LED darkfield in use to observe the diamonds caused a distinct green appearance of the diamonds because of green fluorescence (usually from the H3 defect), an effect that—when strong enough—will result in what is known in the trade as a “green emitter” diamond. In none of the diamonds included in this study the “green emitter” effect was pronounced enough to be visible face up under regular daylight.

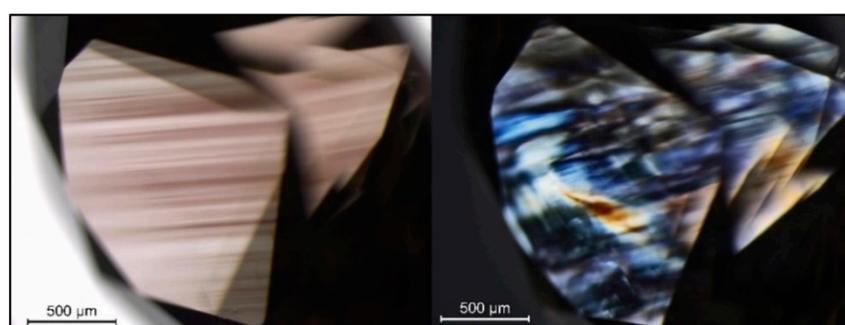


Figure 2. A pinkish brown type IaA>>B diamond (sample TH 2.440) in immersion (left) showing the characteristic plastic deformation-related brown “graining” along (111) combined with some pink “graining”, and the corresponding extinction and interference patterns as shown under crossed polarizing filters.

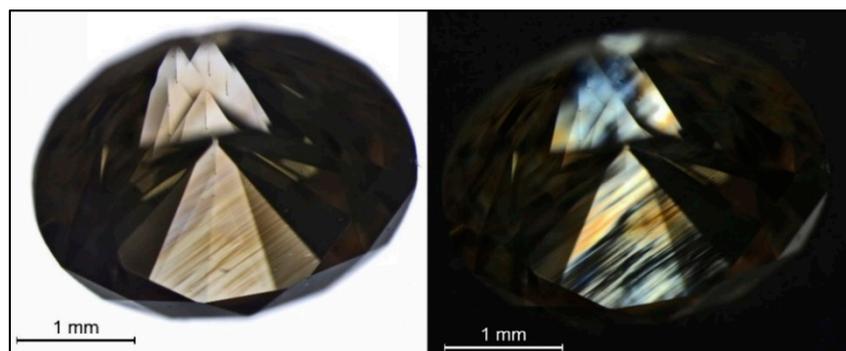


Figure 3. A brown hydrogen-rich type IaB diamond (sample TH 2.619) that clearly shows its color being caused by deformation-related brown color lamellae (left, immersion) along the octahedral crystal directions; the characteristic extinction patterns following the brown lamellae (“graining”) can be seen on the right (immersion, crossed polarizers).

The hydrogen- and nitrogen-rich type IaA>>B samples included in this study were found to be of mixed cuboid-octahedral growth by fluorescence imaging as demonstrated; when verified under crossed polarizing filters, the strain and extinction patterns on one hand follow the (111) brown graining, and on the other hand are influenced by the cuboid and octahedral sectors, which cause additional strain themselves (Figure 4). When comparing the immersion images and the fluorescence images, it was apparent that the brown color lamellae traverse both octahedral and cuboid sectors uninterrupted, which is direct proof that the deformation is post-crystal growth.



Figure 4. A brown hydrogen-rich type IaA>>B diamond (sample TH 2.622) that clearly shows its color being caused by deformation-related brown color lamellae (left, immersion) along the octahedral crystal directions, the color lamellae traversing the cuboid growth sectors that were visualized by fluorescence imaging (see Figure 21 below); the characteristic extinction patterns following the brown lamellae (“graining”) can be seen on the right, but additionally to the (111) extinction, some additional extinction/strain patterns can be seen from the strain caused between the different growth sectors (immersion, crossed polarizers).

Infrared and Near-Infrared Spectroscopy

The infrared spectra of the plastically deformed type Ia brown diamonds included in this study characterized them as diamonds with a usually rather low nitrogen and hydrogen content, with a low aggregation state (hence mostly type IaA), particularly for the darker-colored diamonds, while the lighter-colored specimens were very variable in nitrogen aggregation, from IaA to IaB (Figures 5 and 6). The nitrogen content ranged from ≈ 78 to ≈ 526 ppm ($\pm 5\%$), and only samples containing significant concentrations of hydrogen were found to contain more nitrogen, with the highest concentration having been determined at ≈ 1049 ppm in an unusual diamond being both H-rich as well as plastically deformed. Hydrogen-rich DR brown diamonds are rare, and in most DR brown diamonds the hydrogen

is detectable, but only weakly. The nitrogen concentration was found to have no influence whatsoever on how dark or light a brown diamond was.

The purely brown type Ib diamonds analyzed all had very low nitrogen contents between ≈ 2 and ≈ 10 ppm, with the one sample that represents the more saturated deep yellow brown group (TH 2.52) being distinctly higher in nitrogen with ≈ 82 ppm total nitrogen content. With exception of that higher nitrogen Ib diamond, none of them showed any Y center one-phonon absorption. The Y center with its main absorption at 1145 cm^{-1} is an extremely common absorption that occurs together with the X center (main absorption at 1332 cm^{-1}) in natural type Ib diamonds—particularly in yellow to orange stones [18]. In none of them, with the exception of sample TH 2.52, hydrogen was detectable; the explanation for that is found in the fact that the Y center is directly associated with hydrogen in type Ib diamonds, while the C center is not [17,19]; hence, pure type Ib diamonds without the Y center do never contain IR active hydrogen.

The spectra of all samples, type Ia and type Ib, show amber center (abbreviated with “AC” in the text) absorptions, with either one, two, or more ZPLs (Figure 5).

The Room Temperature IR Spectroscopy of the Amber Centers

In type Ia diamonds with at least some A aggregates detectable, the following AC ZPLs were found in the room temperature IR spectra: 4065 and 4165 cm^{-1} with small 3520 and 2760 cm^{-1} peaks detectable in samples with intense 4165 cm^{-1} AC absorption (Figure 5, traces a, b, and c).

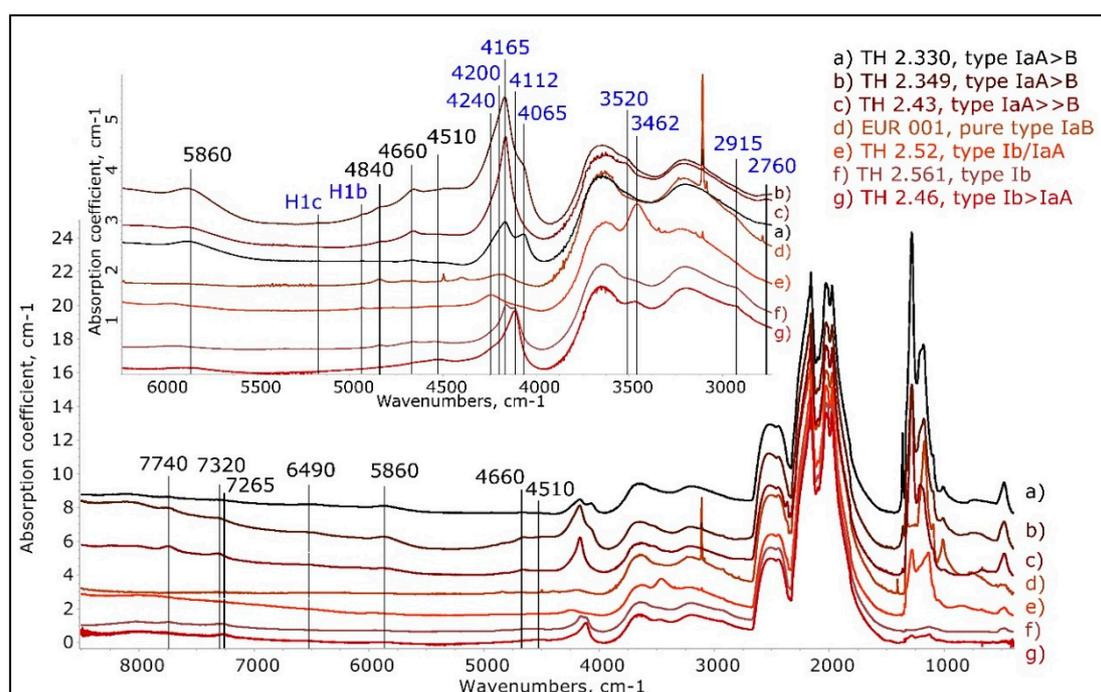


Figure 5. Representative normalized infrared spectra showing the different types of amber centers (ACs) in brown diamonds, recorded at room temperature. Type Ia diamonds show either an AC with the main absorption at 4165 cm^{-1} or a “double AC” having a double band at 4165 and 4065 cm^{-1} (traces a, b, and c), with weak bands at 3520 and 2760 cm^{-1} when the 4165 cm^{-1} AC is strong; in the spectra of type Ib diamonds, there is either a single main band at 4112 cm^{-1} or a double band at 4165 and 4112 cm^{-1} , sometimes with a 3462 cm^{-1} and a 2915 cm^{-1} AC (traces e, f, and g); in some type Ib DR brown diamonds, a band at 4240 cm^{-1} is distinct; it is unclear whether it is another AC zero phonon line (ZPL) or a component of the 3462 cm^{-1} AC (traces e and g). The spectra were shifted vertically for clarity.

As expected from earlier work [6,8], the amber center absorption is most intense in dark samples of type IaA, while it is weak when the color is light and/or the content of the A aggregates is low compared to the content in B aggregates (Figure 6). In the pure type IaB brown diamonds included in this study, the ACs described above were absent and instead a weak band at 4200 cm^{-1} was found (Figure 5, trace d). Some spectra were observed with the 4065 cm^{-1} AC and the second AC at 4190 cm^{-1} instead of 4165 cm^{-1} ; these were samples with significantly more B aggregates than A aggregates, and the shifted position is interpreted as a combination of two bands, the 4165 cm^{-1} AC and the 4200 cm^{-1} AC. From the underlying asymmetry of the 4165 cm^{-1} absorption in the spectra of many diamonds studied, it can be concluded that the 4200 cm^{-1} AC is underlying many of the 4165 cm^{-1} AC ZPLs.

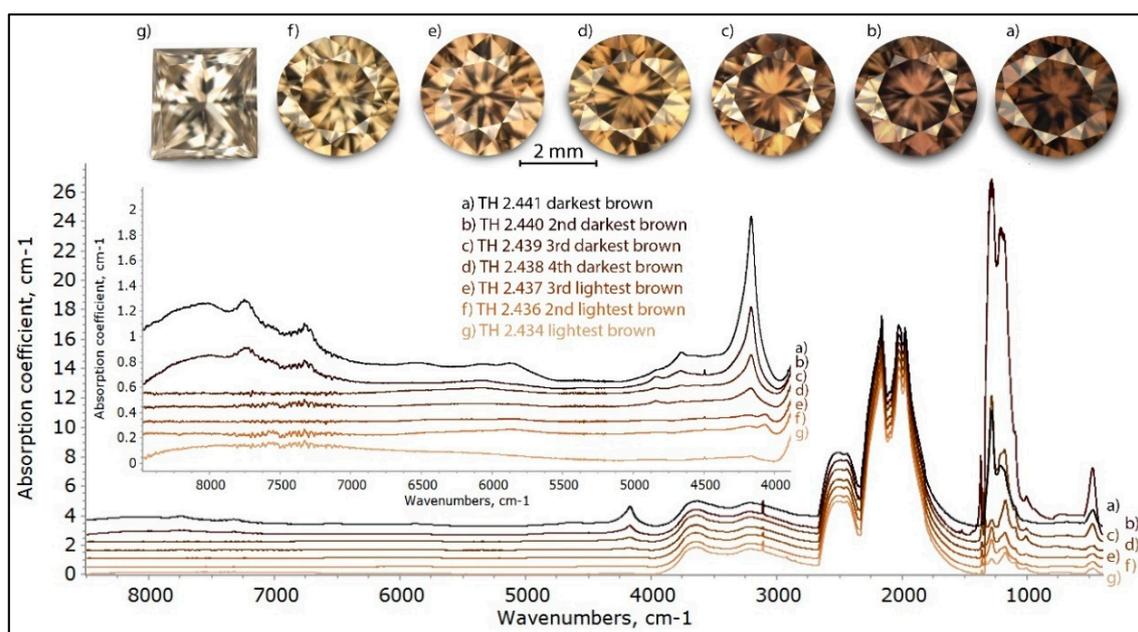


Figure 6. The normalized infrared spectra of a color suite of diamonds with a deformation-related brown color. It can be seen that in these type Ia diamonds, the intensity of the AC absorption correlates well with the darkness of the brown color; the lightest brown diamonds have the weakest AC while the darkest brown diamonds have the strongest AC absorption. The spectra were shifted vertically for clarity.

All type Ib DR brown diamonds except sample TH 2.52 showed a very distinct AC absorption with a broadened and asymmetrical ZPL visible at 4112 cm^{-1} at RT (room temperature), sometimes a 4165 cm^{-1} AC (Figure 5, traces f and g), plus a ZPL at 3462 cm^{-1} . In the spectra of many of the type Ib diamonds, a somewhat broader absorption at 4240 cm^{-1} was visible, which always occurred together with the 3462 cm^{-1} AC; at room temperature, the AC of sample TH 2.52 exhibited almost exclusively these two absorptions, with a weak band at 4065 cm^{-1} (Figure 5, trace e). Additional, often hidden bands at 2790 , 2880 , and 2915 cm^{-1} were detected in some of the spectra in type Ib DR brown diamonds; they always occurred in combination with the AC at 3462 cm^{-1} . This band could only be properly visualized by subtraction of the intrinsic diamond absorptions (Figure 7).

A link between these absorptions could be excluded since in the spectrum of sample TH 2.52 a distinct band at 3462 cm^{-1} band could be seen together with the possibly associated band at 4240 cm^{-1} , but the bands at 2880 and 2915 cm^{-1} were absent. Furthermore, the same was true for more than half of the 27 type Ib diamonds (of various brownish colors), showing obvious signs of plastic deformations that were tested during the PhD thesis of TH [19], which all exhibited IR spectra with the band at approximately 3462 cm^{-1} . In every one of them the band at 3462 cm^{-1} was associated by the 4240 cm^{-1} band, but in contrast, the bands at 2880 and 2915 cm^{-1} were present in less than half of those diamonds.

Looking at the detail of the spectra it was found that the 2880 and 2915 cm^{-1} bands appeared to correlate with the bands at 4510 and 4540 cm^{-1} . The data indicates that these bands at 2880 and 2915 cm^{-1} represent at least two more AC ZPLs.

It must be noted that the 3462 cm^{-1} absorption should not be confused with the 3475 cm^{-1} absorption present in the spectra of high nitrogen and hydrogen type IaA>>Ib diamonds of mixed cuboid-octahedral growth [20]. The two absorptions may look similar but are totally unrelated, and besides the slightly different position, the 3475 cm^{-1} absorption also has a distinctly lower FWHM.

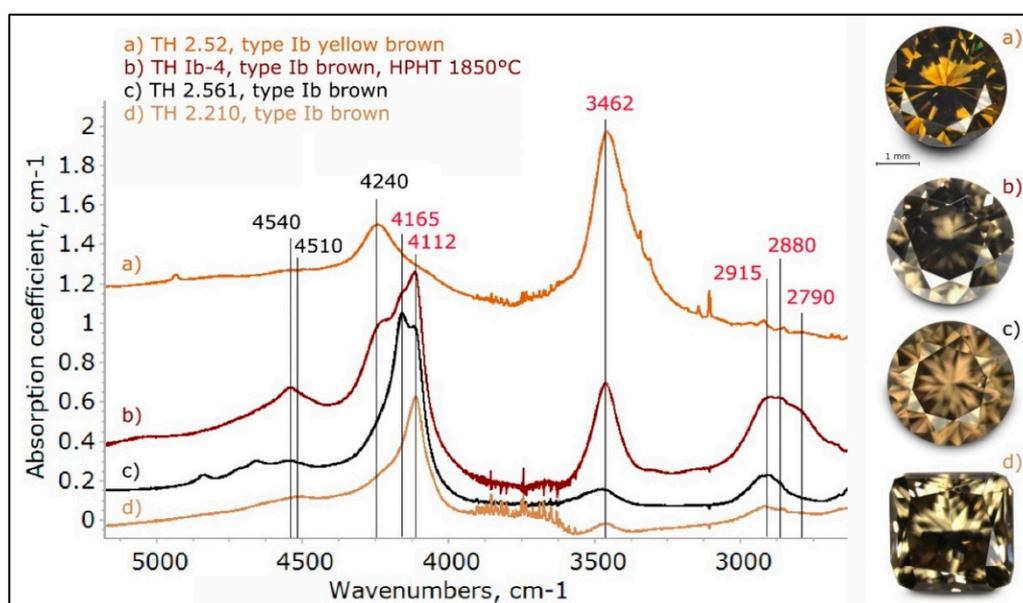


Figure 7. The normalized near infrared spectra of type Ib DR brown diamonds after subtraction of the intrinsic diamond absorptions. All of the spectra show the 3462 cm^{-1} AC ZPL and its likely vibronic component at 4240 cm^{-1} ; this graph demonstrates that the bands between 2915 and 2790 cm^{-1} do not relate to the 3462 cm^{-1} absorption. Instead, it is indicated that these bands are additional ACs, and that the bands at 4540 and 4510 cm^{-1} are likely vibronic components of these ACs. The spectra were shifted vertically for clarity.

Low Temperature NIR Spectra of the Amber Centers

The NIR spectra recorded at 77 K of the various ACs from 4000 cm^{-1} can be seen in Figure 8 and a complete view showing the entire vibronic structure of the different ACs can be seen in Figure 9. In spectra with a simple 4165 cm^{-1} AC, the ZPL was found to only sharpen and shift to 4167 cm^{-1} at a low temperature. In the spectra where both a 4165 cm^{-1} AC and a 4065 cm^{-1} AC were present, both ZPLs got sharper and shifted to 4167 cm^{-1} and 4063 cm^{-1} , while a new ZPL at 4092 cm^{-1} was detectable (Figure 8, traces a and b). For the type Ib diamonds with an isolated AC at 4112 cm^{-1} at RT, this absorption sharpened, shifted slightly to 4111 cm^{-1} , and several ZPLs appeared at 4063 cm^{-1} , 4136 cm^{-1} , and 4167 cm^{-1} (Figure 8, traces c, d, and e). The 4240 cm^{-1} absorption sharpened somewhat in the diamond with a dominant 4240 cm^{-1} /3462 cm^{-1} feature (Th 2.52), but otherwise remained pretty much unchanged in all other samples, and hence maintained the same intensity and FWHM. This indicates that the peak is unlikely another AC ZPL, but rather a feature associated with the 3462 cm^{-1} AC. The NIR spectrum recorded at 77 K of Sample TH 2.52 was unusual as the low temperature caused several ACs to appear in significant intensity, namely the ACs at 4063 cm^{-1} , 4092 cm^{-1} , and 4111 cm^{-1} .

Our low temperature setup did unfortunately not permit to include the range to 2600 cm^{-1} , hence we were unable to resolve the true shape of the 3520 cm^{-1} , 3462 cm^{-1} , 2915 cm^{-1} , 2880 cm^{-1} , and 2760 cm^{-1} bands and see how they behaved at 77 K. For the rest of this study, the AC ZPL positions

will be indicated at LNT (liquid nitrogen temperature), with the exception of the bands measured only at RT (3520 cm^{-1} , 3462 cm^{-1} , 2915 cm^{-1} , 2880 cm^{-1} , and 2760 cm^{-1}).

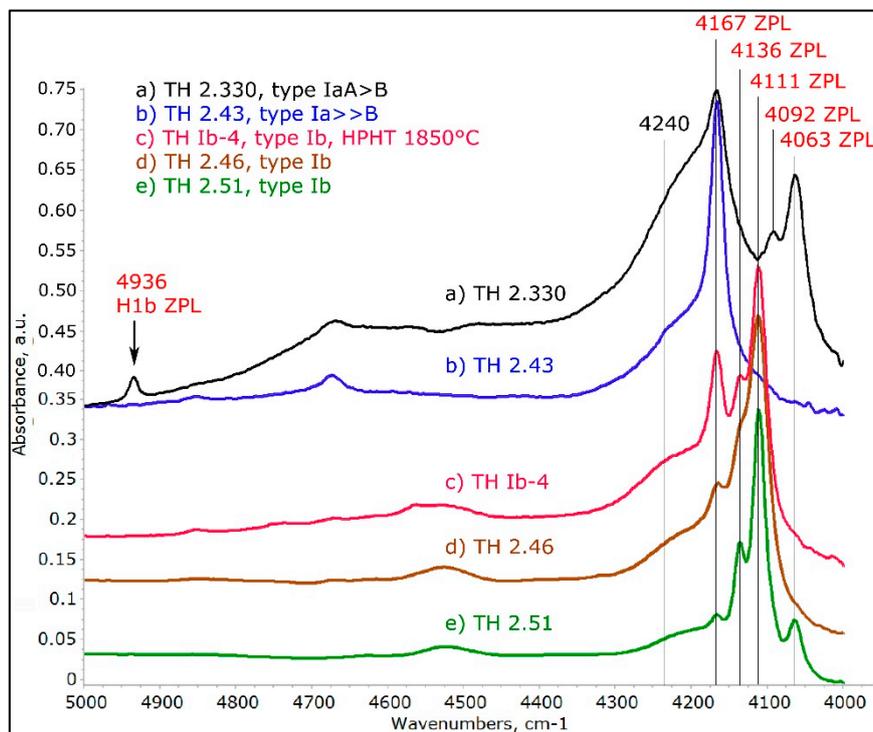


Figure 8. A detailed view of the AC ZPLs when recorded at 77 K. A total of 5 ZPLs can be seen and the band at 4240 cm^{-1} is very likely identified as a vibronic component, since it does not sharpen significantly. A distinct H1b center can be seen in spectrum (a); when present in diamonds not associated with any type of irradiation/annealing, this peak is always associated with the AC at 4063 cm^{-1} . The spectra were shifted vertically for clarity.

The 4136 cm^{-1} absorption appears unique to type Ib diamonds. Curiously, the 4063 cm^{-1} as well as the 4167 cm^{-1} absorptions were detected in sample TH 2.51, and a rather strong 4167 cm^{-1} AC absorption was detected in combination with a 4111 cm^{-1} AC absorption in sample TH 2.561, which both are—according to their one-phonon IR absorption—very low nitrogen pure type Ib diamonds with aggregated nitrogen undetectable. While one could interpret this as nitrogen possibly not at all involved in these defects, it is more likely that extremely low nitrogen concentrations are sufficient to create detectable signals of the ACs. While aggregated nitrogen was undetectable in the IR spectrum of the given samples, the N3 and H3 centers were detectable by PL spectroscopy. This means that at least some A and B aggregates must have been present, although most of the A aggregates could have been used up in the H3 defects. The concentration of nitrogen aggregates was well below 1 ppm, otherwise we would have been able to measure it by FTIR spectroscopy. With the 4167 cm^{-1} and 4111 cm^{-1} ACs being absent or weak in DR type IIa and IIb diamonds, nitrogen clearly seems to play a role in the defect structure, but from the above observation it appears reasonable to suggest that very low nitrogen concentrations are sufficient to create significant AC absorption. It also seems reasonable to assign the 2760 cm^{-1} , 3520 cm^{-1} , 4063 cm^{-1} , 4092 cm^{-1} , and 4167 cm^{-1} ZPLs to vacancy defects containing A aggregates. The ACs only detected in diamonds containing C centers with ZPLs at 2790 cm^{-1} , 2880 cm^{-1} , 2915 cm^{-1} , 3462 cm^{-1} , 4111 cm^{-1} , and 4136 cm^{-1} are either related to C center-containing vacancy defects, or the more likely possibility is that they represent different charge states of the ACs with ZPLs at 2760 cm^{-1} , 3520 cm^{-1} , 4063 cm^{-1} , 4092 cm^{-1} , and 4167 cm^{-1} . Since the C center acts as an electron donor, it can cause the change of the charge states of the defects as, for example, they form H2 $(\text{N-V-N})^-$ in H3 $(\text{N-V-N})^0$ -containing diamonds through this mechanism.

Only the 4200 cm⁻¹ band appeared to be the ZPL of an AC related to the B aggregates; in contrast to the other ACs absorptions measured at LNT, the 4200 cm⁻¹ AC sharpened less distinctly at 77 K.

Only some bands clearly relate to a specific AC ZPL, others can only be tentatively assigned to a specific ZPL since there appears to be significant overlap between many of the structures associated to the different ACs (Table 2).

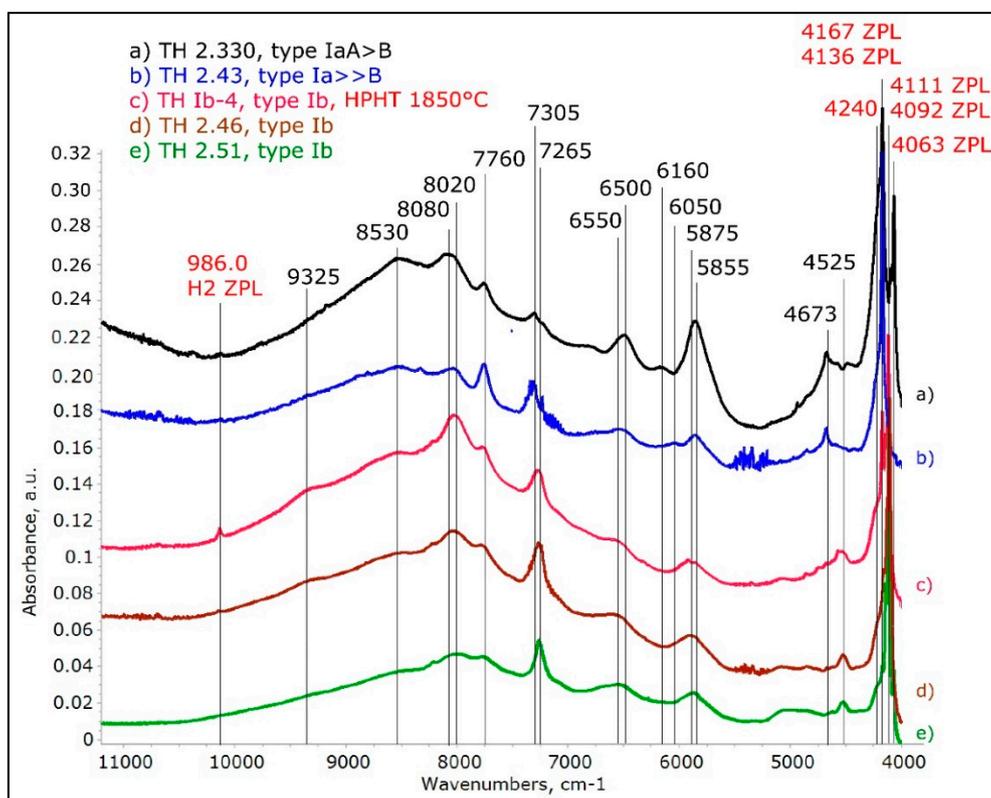


Figure 9. The NIR spectra of the different AC absorptions recorded with the samples at 77 K. The spectra confirm which ones of the absorptions are ZPL's and which ones are not, and the significant sharpening and splitting of the absorptions reveal much more details about the ACs than the spectra at room temperature. The spectra were shifted vertically for clarity.

Table 2. The different AC ZPLs and tentative details of their associated structure and spectral features.

ZPL	Likely Associated Structure and other Associated Spectral Features (LNT)						
4200 (LNT)	4854 (ZPL?), 5115	5990, 5890, 5770	6700	7919 (ZPL?)	8115	8410	8810
4167 (LNT)	4673	5855	7305	7760	8020	8530	
4136 (LNT)	Too weak to determine associated structure						
4111 (LNT)	5875	7265	8020	8530	9325		
4092 (LNT)	Too weak to determine associated structure						
4063 (LNT)	5875	7305	8080	8530			
3520 (RT)	Too weak to determine associated structure						
3462 (RT)	4240	5850	7960				
2915 (RT)			4525				
2880 (RT)			4525?				
2790 (RT)	Too weak to determine associated structure						
2760 (RT)	Too weak to determine associated structure						

The Photoexcitation Behavior of the Amber Centers

The photoexcitation experiments performed during this study and during the PhD thesis of TH have shown that excitation with 360 nm light causes certain ACs to increase while others decrease. This at first sight random phenomenon was found to be most prominent in type Ib diamonds, but to some degree detectable in all diamonds with ACs. A detailed look at as many samples as possible, including the ones of this study and all samples (including non-brown diamonds with ACs) included in the PhD thesis of TH and the ones used for an irradiation study currently performed by the authors, has shed more light on the photoexcitation behavior of the ACs.

The conclusions drawn from this work are that the 4167/4111/4063 cm^{-1} ACs decrease in the IR spectra that do not show the 3462 cm^{-1} /2790 cm^{-1} AC features. The 4167/4111/4063 cm^{-1} ACs increase whenever the beforementioned features are present in the spectra; while the 4167/4111/4063 cm^{-1} ACs increase, the 3462 cm^{-1} /2790 cm^{-1} AC peaks decrease or even disappear. Illuminating the samples by wavelengths >400 nm for a short time restores the original appearance of the ACs.

Another result from the photoexcitation experiments was obtained from sample TH 2.52, the type Ib/IaA yellow brown diamond with—besides a faint 4063 cm^{-1} AC—only the 4240 cm^{-1} and 3462 cm^{-1} bands detectable at RT: photoexcitation caused the 3462 cm^{-1} to reduce significantly, while two distinct ACs at 4100 (a mix of the 4111 cm^{-1} AC and the 4092 cm^{-1} AC as determined at 77 K above) and 4063 cm^{-1} appeared; the 4240 cm^{-1} feature did not change during this experiment. This again is indicative that the 4240 cm^{-1} absorption is not a ZPL, but a vibronic component of another center, likely the 3462 cm^{-1} AC.

Naturally Occurring H1b and H1c Centers in Brown Diamonds with Amber Centers

As seen in Figure 8 (trace a) and Figure 5 (trace a, b, and e), type I DR brown diamonds can exhibit natural H1b and the H1c centers; these defects are known in any diamond that contains aggregated nitrogen after irradiation and annealing from 550 °C to about 1400 °C [21]. In the brown diamonds they are only detectable in type I diamonds that contain aggregated nitrogen and that exhibit IR spectra that show the 4063 cm^{-1} AC; in most of them only a very weak H1b peak can be found, H1c is rare. Years back we believed that the peak detected in such stones was just part of the vibronic structure of the 4063 cm^{-1} AC, but a range of tests have led to the conclusion that the defect responsible is indeed H1b; this has been further confirmed when samples were found with detectable H1c absorption. A detailed analysis of a series of DR brown diamonds with H1b and of some with both H1b and H1c has shown that there is no indication whatsoever for natural or artificial irradiation and annealing in such diamonds; their spectroscopic data does not vary in any specific way from other type Ia DR brown diamonds. Clearly, in such brown diamonds the H1b and H1c defects are formed while plastic deformation creates high densities in dislocations and vacancies. One could speculate that aggregated nitrogen—A aggregates in H1b, B aggregates in H1c [21], combined with an extended vacancy defect, consisting of at least several vacancies—results in these defects. In irradiated diamonds, monovacancies but also extended vacancies are induced by irradiation; monovacancies combine with A and B aggregates to form H3 and H4, but their formation does not at all correlate with the formation of H1b and H1c; the 595 nm defect has been suggested to correlate with the formation of H1b and H1c, and currently the cause of this defect is unknown [21]. The brown diamonds with H1b and H1c do not exhibit the 595 nm defect, hence one might wonder if H1b and H1c actually relate in any way to the 595 nm defect. A more complex vacancy defect must be involved in the H1b and H1c defects; however, it cannot be the large vacancy cluster, because of the high thermal stability and inertia of the vacancy cluster defect. The annealing behavior of the different ACs, including the 4063 cm^{-1} AC and the related H1b and H1c defects, was therefore verified during this study, see results below.

The Annealing Behavior of the Amber Centers and Naturally Occurring H1b/H1c

While all ACs and natural H1b in brown diamonds have been shown to anneal out by HPHT treatment from about 2000 °C [19], limited and incomplete data on the annealing behavior of the ACs at a lower temperature is available [22], while no data on the behavior of natural H1b at a lower temperature have been published, and no data whatsoever on the annealing behavior of natural H1c have been published so far. Therefore, some samples with IR spectra representing the different ACs and samples with H1b and H1c were annealed up to 1500 °C in this study, and some were treated by HPHT at 1850 °C up to 2250 °C.

These high temperature annealing experiments have shown that heating diamonds with ACs at 4167/4063/4092 (LNT) to 1500 °C annealed out the 4063 cm^{-1} and 4092 cm^{-1} AC while the 4167 cm^{-1} AC increased distinctly (Figure 10). In the samples used for this specific experiment (TH 2.328 and TH 2.330), in the spectra measured at room temperature, the 4167 cm^{-1} AC ZPL increased by a factor of 3.5 after two hours of heating at 1500 °C while the 4063 cm^{-1} peak disappeared; at 77 K, the 4063 cm^{-1} AC was barely detectable or undetectable and the 4092 cm^{-1} AC was undetectable. These diamonds also exhibited weak but clearly visible H1b and H1c absorptions prior to the annealing, and both annealed out at 1500 °C (Figure 10). To determine the precise annealing behavior of the ACs in diamonds showing both the 4167 cm^{-1} and 4063 cm^{-1} ACs, sample TH 2.330 was heated from 950 to 1350 °C in 100 °C steps and from 1350 °C to 1500 °C in 50 °C steps, for two hours at every step. This treatment has shown that neither the AC nor H1b and H1c were affected up to a temperature of 1050 °C; from 1150 °C onwards the 4063 cm^{-1} AC got weaker, until it disappeared at 1500 °C, while the 4167 cm^{-1} AC increased, until it was strongest at 1500 °C. H1b and H1c started to increase from 1150 °C to 1250 °C, when their intensity was found to be 4 to 5 times that of their intensity in the unheated state; then both decreased until they were both undetectable at exactly 1500 °C. Hence, it was shown that the temperature when the 4063 cm^{-1} AC and H1b H1c completely anneal out is identical. The exact annealing behavior appears to correlate to when the 4063 cm^{-1} AC starts to decrease in intensity, and H1b and H1c increase significantly; the H1b and H1c defects in these brown diamonds could be interpreted as a side product of the transformation of the 4063 cm^{-1} AC into the 4167 cm^{-1} and/or 4111 cm^{-1} AC. This interpretation is supported by the fact that the H1b and H1c absorptions in the brown diamonds do not increase in intensity before 1150 °C. In the artificially irradiated diamonds of type I studied for various research projects by our laboratory, the common behavior of H1b and H1c is that they are detected between 600 and 750 °C and that these increase to different temperatures, somewhere between 1100 and 1200 °C, when they typically start to decrease and anneal out between 1400 °C and 1500 °C. The situation looks somewhat different for very heavily irradiated diamonds, like one of the samples included here (TH 2.163): in such stones, H1b might be detected at temperatures as low as 550 °C and an H1c at 600 °C, and the temperature when these centers are completely annealed out are significantly higher: for this sample, at 1500 °C, the H1b absorption decreased by a factor of 62, while the weak H1c absorption increased by a factor of 3; hence the annealing temperature is >1500 °C.

All this said, this data might simply mean that these brown diamonds that exhibit H1b and H1c had been exposed naturally to temperatures between 1050 and 1100 °C during and after plastic deformation. It must be added that, while in artificially irradiated diamonds with the disappearance of H1b and H1c an array of new absorptions may be created, no new absorptions whatsoever appear in the spectra of brown diamonds with naturally occurring H1b and H1c. Their spectra—from the UV to the NIR, absorption and luminescence—remain essentially unchanged with annealing up to 1500 °C, with some minor exceptions such as the NIR features covered here and some PL features discussed later in this paper. It seems clear from this data that the H1b and H1c defects in natural DR brown diamonds is the same defect as the one induced by irradiation and annealing, but that it is simply induced by deformation-related vacancy defects that combine with aggregated nitrogen through natural annealing. All observations made here also allow it to question the direct correlation between the 595 nm defect and H1b/H1c. The H1b/H1c defect in irradiated/annealed diamonds might

simply be standalone defects resulting from irradiation-induced multi-vacancies combining with A and B aggregates upon annealing, hence very similar to what is suggested here for brown diamonds.

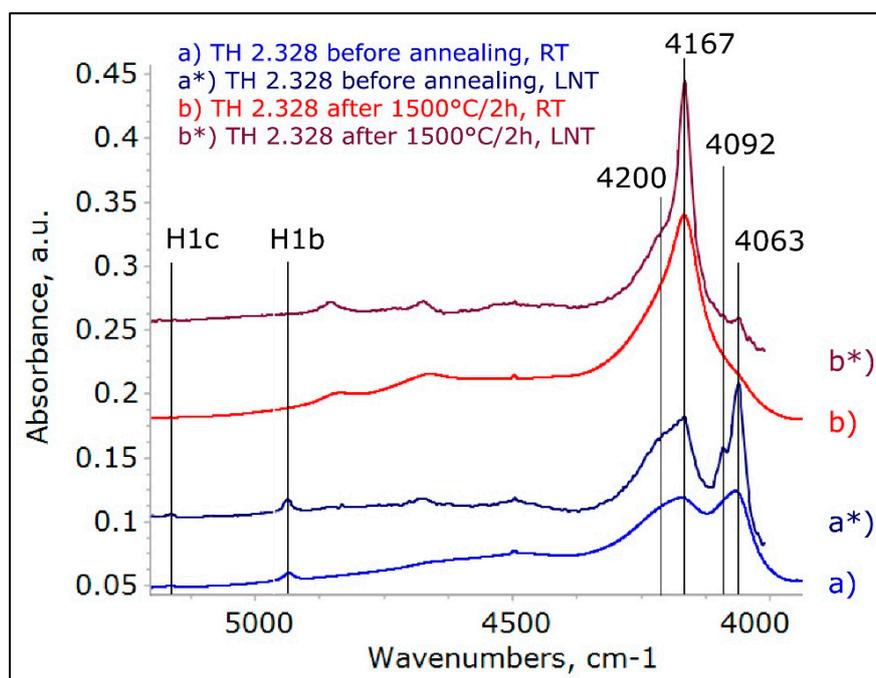


Figure 10. The NIR spectra (at 77 K) of a diamond exhibiting both the DAC ($4167/4063\text{ cm}^{-1}$) as well as H1b/H1c before (a/a*) and after annealing to $1500\text{ }^{\circ}\text{C}$ for 2h (b/b*). It is obvious that the $4063/4092\text{ cm}^{-1}$ component is annealed out while the 4167 cm^{-1} ZPL increases distinctly after the annealing experiment. H1b and H1c are also annealed out under these conditions. The 4200 cm^{-1} band is apparently unaffected. The spectra were shifted vertically for clarity.

When annealing a type Ib DR brown diamond with distinct ACs to the higher temperatures of $1850\text{ }^{\circ}\text{C}$ we found the same results as described above concerning the ACs at 4063 cm^{-1} , 4167 cm^{-1} , 4093 cm^{-1} and 4111 cm^{-1} ; no consistent annealing behavior for the 3462 cm^{-1} AC could be determined, since it appears to behave randomly, intensifying in one sample while in a another one it decreased. What seems clear is that the band centered at 2790 cm^{-1} can be induced by treatment at $1500\text{ }^{\circ}\text{C}$ to $1850\text{ }^{\circ}\text{C}$, since it was usually detectable in heated stones, but was also found in the spectra of several untreated samples.

In diamonds with only the 4167 cm^{-1} AC detectable, annealing to $1500\text{ }^{\circ}\text{C}$ did not affect the AC at all, and neither did heating to $1850\text{ }^{\circ}\text{C}$. In type Ib diamonds with the 4111 cm^{-1} AC, annealing for two hours at $1500\text{ }^{\circ}\text{C}$ caused a reduction in the intensity of the 4111 cm^{-1} ZPL by about 30%, while if a small 4167 cm^{-1} AC was present the 4111 cm^{-1} AC was not affected at all; in type Ib DR brown diamonds with more complex ACs composed of 4063 cm^{-1} , 4111 cm^{-1} , and 4167 cm^{-1} , the 4112 cm^{-1} AC remained unaffected even at temperatures as high as $1850\text{ }^{\circ}\text{C}$. In sample TH 2.52, the type Ib/IaA sample with the IR spectrum dominated by $4240\text{ cm}^{-1}/3462\text{ cm}^{-1}$ bands at RT and strong 4111 , 4092 cm^{-1} , and 4063 cm^{-1} ACs only after photoexcitation or at LNT, annealing at $950\text{ }^{\circ}\text{C}$ to $1050\text{ }^{\circ}\text{C}$ caused a decrease of the 3462 cm^{-1} absorption by approximately 20%; the other ACs remained unaffected, and so was H1b. At $1500\text{ }^{\circ}\text{C}$, the 4063 cm^{-1} AC annealed out and so did the associated 4092 cm^{-1} AC, a new AC absorption at 4165 cm^{-1} appeared and both the 4111 cm^{-1} and 4136 cm^{-1} absorptions increased.

These results show that the 4063 cm^{-1} AC is clearly the least stable of all the ACs since it is affected by heating as low as $1150\text{ }^{\circ}\text{C}$ —distinctly lower than the value of $1700\text{ }^{\circ}\text{C}$ published earlier [22]—and that the 4167 cm^{-1} and the 4111 cm^{-1} ACs are the most stable of all the ACs as they remain essentially

unaffected by heating to 1850 °C, except for likely some charge-related modifications occurring for the 4111 cm⁻¹ AC. Since annealing out the 4063 cm⁻¹ AC results in a distinct increase or formation of the 4167 cm⁻¹ AC and when the 4111 cm⁻¹ AC is present also in an increase in the 4111 cm⁻¹ AC and the associated 4136 cm⁻¹ AC; it seems reasonable to suggest that the 4167 cm⁻¹ and 4111 cm⁻¹ AC form out of the 4063 cm⁻¹ AC, hence the 4063 cm⁻¹ AC appears to be a precursor of the those ACs.

HPHT treatment at 2000 to 2250 °C performed on selected type I DR diamonds has shown that all AC absorptions described in this chapter are annealed out under such conditions; the effective annealing temperature is somewhere between 1850 and 2000 °C, which is consistent with the earlier published values [22]. A summary of the various ACs, their annealing behavior and their possible interpretations can be found in Table 3.

Table 3. The ZPL positions of the ACs, their annealing behavior in type I DR brown diamonds, and their possible interpretations.

ZPL LNT	ZPL RT	Annealing Behavior	Possible Interpretation
4200	4200	Anneals out at >1850 °C	Multi-vacancy defect involving the B center
4167	4165	Without 4063 cm ⁻¹ AC: anneals out at >1850 °C. With 4063 cm ⁻¹ AC: increases from 1150 °C to 1500 °C while 4063 cm ⁻¹ AC decreases, then anneals out at >1850 °C	Multi-vacancy defect involving the A center
4136	-	Anneals out at >1850 °C	Likely different charge state of one of the defects causing the ACs at 4167/4092/4063
4111	4112	When dominant it reduces by 30% at 1500 °C, anneals out at >1850 °C. When accompanied by 4063 cm ⁻¹ AC then unaffected until it anneals out at >1850 °C	Likely different charge state of one of the defects causing the ACs at 4167/4092/4063
4092	-	Decreases from 1450 °C, anneals out at 1500 °C	Multi-vacancy defect
4063	4065	Decreases from 1150 °C, anneals out at 1500 °C	Multi-vacancy defect—precursor defect of the 4167 cm ⁻¹ AC and the 4111 cm ⁻¹ AC
n/a	3520	Anneals out at >1850 °C	Multi-vacancy defect involving the A center
n/a	3462	Anneals out at >1850 °C	Likely different charge state of one of the defects causing the ACs at 4167/4092/4063
n/a	2915, 2880, 2790	Anneal out at >1850 °C	Likely different charge states of one of the defects causing the ACs at 4167/4092/4063
n/a	2760	Anneals out at >1850 °C	Multi-vacancy defect involving the A center

The Behavior of the Amber Centers upon Electron Irradiation and Annealing up to 1050 °C

Irradiation of type I DR brown diamonds with ACs by 2 to 10 MeV electrons and annealing up to 1050 °C has shown that the 4167/4063 ACs decrease in intensity in type Ia diamonds by simple electron irradiation while the 4167/4111/4063 ACs increase in most type Ib diamonds; in some type Ib samples either the ACs remained unchanged or appeared to decrease very slightly, particularly stones in which only the 4167 cm⁻¹ AC was detected. Annealing up to 1050 °C—the maximum temperature before some of the ACs are affected by the heat in untreated diamonds—continuously restored the intensity

of the ACs to their original level in type Ia diamonds, and in Ib diamonds the ACs either returned to their original level or stayed at an intermediate level. It must be stressed out that no new ACs that were absent prior to irradiation were formed, only the ones present were modified.

Amber Centers induced by Treatment

The hypothesis that the different amber centers are basically all closely related complex vacancy based defects generally associated with nitrogen and that there appears to be a direct link between the amber center formation and the formation of natural H1b and H1c defects in type I DR brown diamonds must lead to the question whether it could be possible to create the amber centers by an irradiation treatment process. Having seen that regular commercial irradiation by relatively low doses of electrons had an influence on already existing amber centers, but that it did not induce new amber centers led us to conclude that possibly a much higher vacancy density would be needed to create an amber center-like defect. To verify this idea, a series of originally colorless type Ia diamonds—all belonging to the cape series—have been irradiated by a very high dose of neutrons (1.8×10^{17} neutrons/cm²) and in consequence turned opaque black. The diamonds were then annealed at different temperatures up to 2000 °C and the effects on their color and spectra were analyzed, with a particular focus on the IR and NIR spectra.

To our positive surprise, the results of these treatment experiments have shown that heavy neutron irradiation followed by annealing indeed created absorptions that with high probability are identical to the ACs. After annealing at 1000 °C, a weak peak at 4063 cm⁻¹ was created and after 1500 °C weak absorptions at 4167 cm⁻¹ and 4111 cm⁻¹ were detected, associated by a band at 3462 cm⁻¹ and a very weak band at 2915 cm⁻¹ (Figure 11, traces b and d). The reduction of the 4063 cm⁻¹ absorption while the 4167 cm⁻¹ band was formed at 1500 °C is identical to what we have seen happening when diamonds with a 4063 cm⁻¹ AC were annealed to 1500 °C.

After HPHT treatment at 1850 °C a much stronger 3462 cm⁻¹ band was formed and at the same time the band at 2915 cm⁻¹ increased strongly as well (Figure 11, trace f). Photoexcitation experiments have confirmed that the absorptions behave the same as the ACs in DR brown diamonds, with the 3462 cm⁻¹ band decreasing while the 4167 cm⁻¹ and the 4111 cm⁻¹ bands increased (Figure 11, traces c and e). Furthermore when the NIR spectrum recorded at 77 K was analyzed, a distinct sharpening and associated increase was noticed for the 4167 cm⁻¹ and 4111 cm⁻¹ absorptions while the 4063 cm⁻¹ feature that could not be resolved at RT was detectable again (Figure 11, trace g). The shift between RT and LNT of these three absorptions was identical to the one observed for the ACs in DR brown diamonds. When diamonds with these treatment-induced absorptions were treated by HPHT at 2000 °C, all the described features were annealed out, which—again—is consistent with the behavior of the ACs. High-resolution IR spectra of the treated diamonds have shown that, even after 2 h at only 1500 °C, 4 ppm of C centers were detectable and that 8 ppm of the C center were formed after annealing at 1850 °C for 5 min. This explains why many of the AC absorptions that were created by heavy neutron irradiation and annealing at 1500 and 1850 °C are identical to the ACs that only occur in the spectra of C center containing natural, untreated DR brown diamonds. The dissociation of the aggregated nitrogen into single nitrogen at such a “low” temperature—normally the C center cannot be detected in the IR spectra of HPHT-treated type Ia diamonds with treatment temperatures below 2100 °C—is clearly related to the heavy neutron irradiation the diamonds were exposed to and the associated density of induced vacancies. Vacancies are known to enhance the aggregation—and dissociation—of nitrogen since the vacancies create new diffusion channels within the diamond lattice [23].

In conclusion, the absorptions formed by heavy neutron irradiation and annealing correspond to the naturally occurring ACs in position, shape, photoexcitation behavior, low temperature behavior, and stability to high temperature. It seems reasonable to suggest that the absorptions created are indeed treatment-induced ACs.

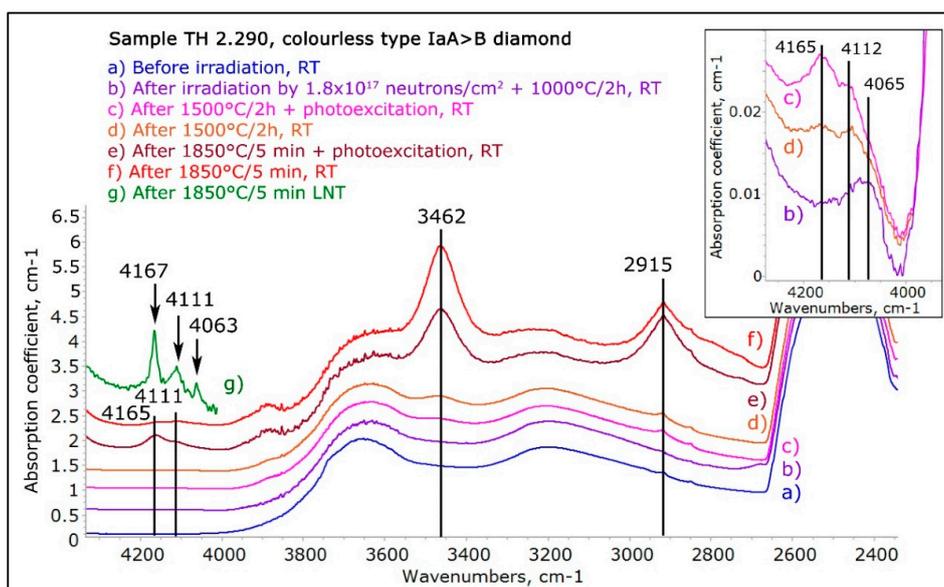


Figure 11. The IR/NIR spectra showing the evolution of an originally colorless type IaA>B “cape series” diamond before neutron treatment (trace a), after heavy neutron irradiation and annealing for 2h at 1000 °C (trace b), after 2h at 1500 °C (trace d), after 2h at 1500 °C with photoexcitation (trace c), after 1850 °C for 5 min (trace f) after 1850 °C for 5 min with photoexcitation (trace e), and, finally, the low temperature NIR spectrum after 1850 °C for 5 min (trace g). At 1000 °C, a weak 4065 cm⁻¹ absorption was formed, After 1500 °C, weak 4165 and 4112 cm⁻¹ absorptions were apparent plus the absorption at 3462 cm⁻¹ appeared and a hint of the 2915 cm⁻¹ absorption was detectable; photoexcitation caused the 3462 cm⁻¹ band to decrease while the 4165 cm⁻¹ peak increased. After 1850 °C, the spectral features detected after annealing at 1500 °C became distinctly stronger, but their behavior remained identical. The spectrum recorded with the diamond at 77 K shown in trace g demonstrates the distinct increase, sharpening and peak shifting of the three peaks at low temperature. The peak shapes, positions, photoexcitation, and low temperature behavior are all identical to what has been described for the ACs, and hence it appears highly likely that what was created are indeed treatment-induced ACs. The spectra were shifted vertically for clarity.

UV-Vis-NIR Spectroscopy

The UV-Vis-NIR spectra of all the studied samples showed the continuum absorption increasing steadily from the NIR to the UV, which is so typical of brown diamonds, both type Ia and Ib (Figure 12). Overlaying the continuum many of the spectra exhibited a relatively weak broad band centered at 560 nm, which corresponds to the broad band responsible for the pink color in diamonds, combined with a band centered at about 390 nm and that consists of two components in type Ia diamonds, namely at 394 and 386 nm (Figure 12, trace c). Most commonly, a weak N3 and a weak H3 absorption was observed in the spectra of the type Ia brown diamonds (Figure 12, trace b and c)—being usually the responsible defects for the blue fluorescence (N3) and in most cases for the green fluorescence (H3). Besides these, a handful of weak absorption features were found, none of which had any significant influence on the color. Only certain hydrogen-rich type IaB DR brown diamonds showed significantly different spectra, in which the continuum was overlaid by a broad band centered at 580 nm, a ZPL at 500.2 nm with broad vibronic bands similar to H3, and a ZPL at 406.4 nm with a broad vibronic structure similar to N3 (Figure 12, trace e).

Truly brown type Ib diamonds, being the rarest of all brown diamonds, also showed the well-described vacancy-cluster related continuum absorption in their UV-Vis-NIR spectra, but instead of the spectral features described above they show a distinct NV⁻ center absorption with its ZPL at 637.0 nm (Figure 12, trace a).

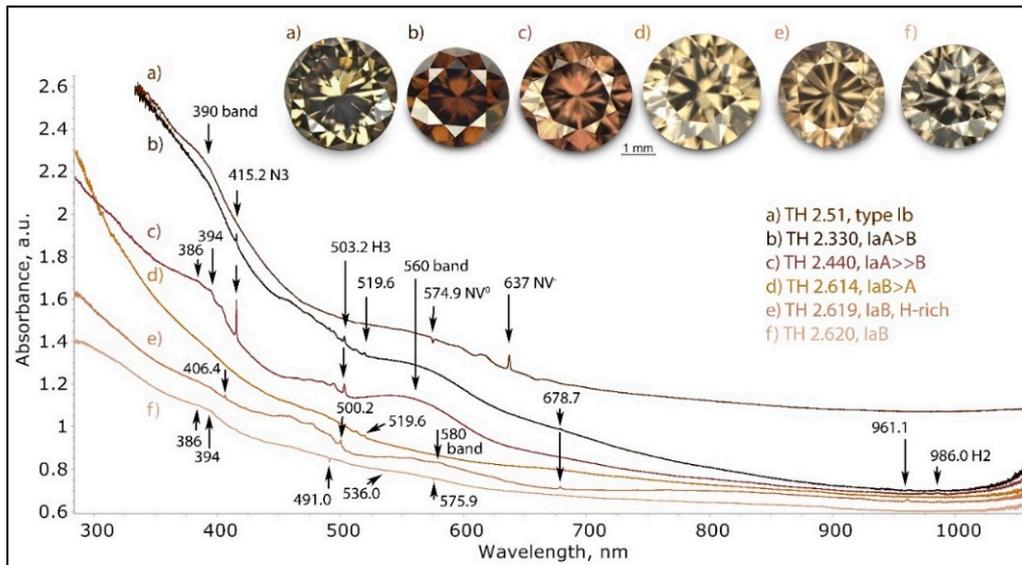


Figure 12. The range of UV-Vis-NIR spectra of type I brown diamonds with a plastic deformation-related color is shown in this graph. The brown color itself originates in all cases mainly from the continuum absorption that is relatively flat and steadily increasing from the NIR to UV. Since the indexed overlaying absorptions are all comparatively weak, they have only a limited influence on the color. A notable exception is the 560 nm band, which causes a pink hue added to the brown. The spectra were shifted vertically for clarity.

This study confirmed that the lightness/darkness of the brown color directly correlate with the steepness of the absorption continuum, with an important point being that the continuum has a relatively consistent inclination over the visible spectral range (Figure 13). If the continuum becomes significantly steeper somewhere between 550 and 600 nm, the color becomes more saturated and will shift towards orange or yellow.

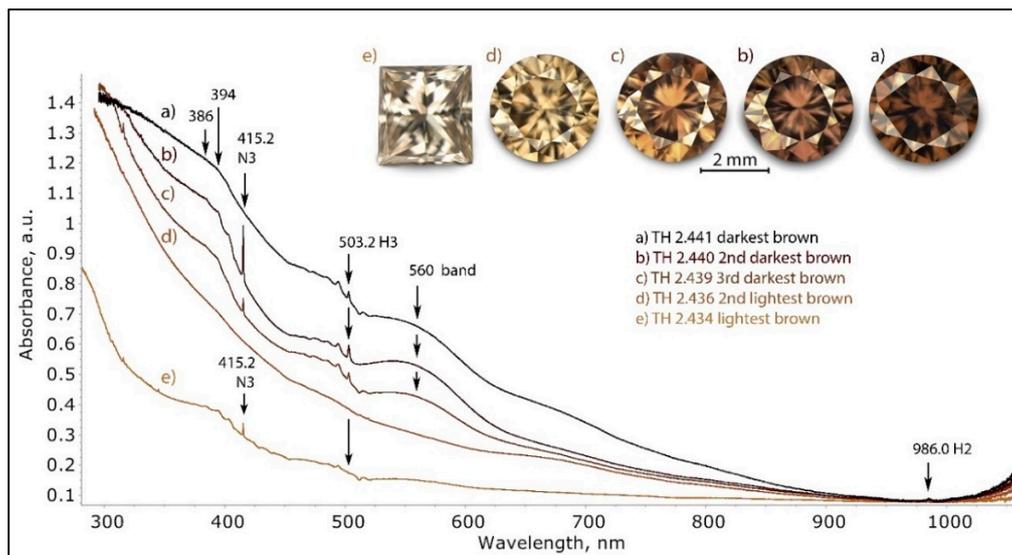


Figure 13. The UV-Vis-NIR spectra of stones from the color suite shown in Figure 7 demonstrate that the darkness of the brown diamonds is represented by the steepness of the absorption continuum. The spectra shown are the most common type of UV-Vis-NIR spectra, with a characteristic continuum, weak N3 and H3 absorption and often a detectable 560 nm band. The spectra were shifted vertically for clarity.

Photoluminescence Spectroscopy

The DR type Ia brown diamonds showed a range of PL spectra, of which some were very common and others much rarer. The most common type of PL data is shown in Figures 14 and 15, even though they represent rather extreme cases for certain defects. The most commonly dominating PL defects detected in such diamonds are the H3 center with its ZPL at 503.2 nm, the 617.6/626.3 nm defect and its associated vibronic band at 720 nm [24], the 490.8 nm defect, the 576.0 nm defect—often with a weaker peak at 575.5 nm—the 612.5 nm defect, N3 (ZPL 415.2 nm), and H4 (ZPL 495.9 nm). Very often detected but rarely intense are defects with the ZPLs at 406.1 nm, 412.1 nm, 422.8, 494.3 nm, 500.1 nm, 535.9 nm, 537.5 nm, 578.1 nm, 578.9 nm, NV⁻ (ZPL 637.0), 710.3 nm, 768.0 nm, 787.1 nm, 793.6 nm, and 925.4/926.2 nm doublet. Only detectable in diamonds with low nitrogen content were peaks at 566.0, 566.7, and 567.6 nm and distinct GR1 PL (Figure 16).

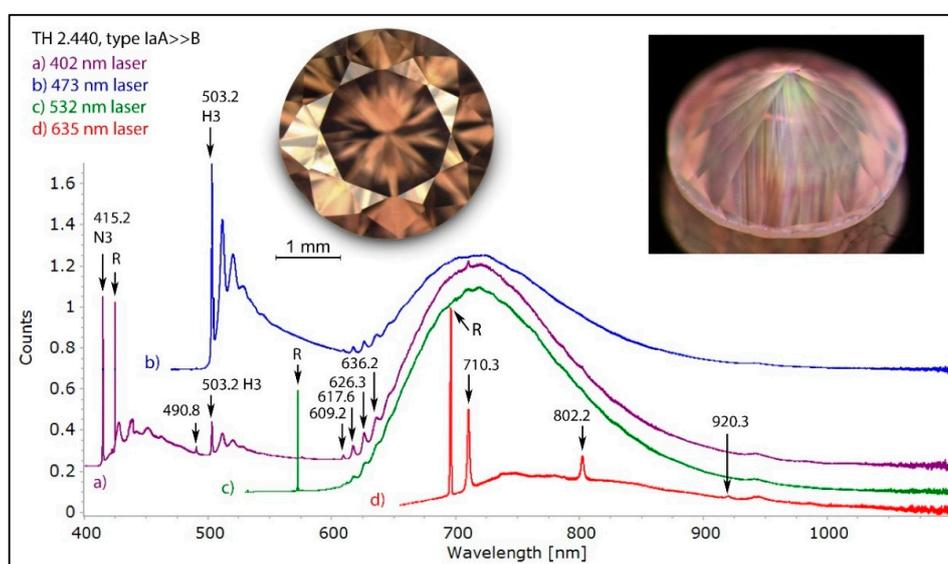


Figure 14. The low temperature PL spectra of a pinkish brown type IaA>>B diamond with a deformation-related color, recorded with four different lasers. Besides the omnipresent H3 defect and the 490.8 nm defect, the most characteristic band seen in most of such diamonds is the 617.6/626.3 nm defect with its associated broad vibronic band centered approximately at 720 nm. This defect is responsible for the pink fluorescence seen in the diamond under DFI 340 nm excitation (photo inset, right). The spectra were shifted vertically for clarity.

The 617.6/626.3 nm defect seems to be unique to DR type Ia brown diamonds with appreciable nitrogen content, since it was absent in the low nitrogen DR brown diamonds and also in the type II DR brown diamonds. Further, in the experience of the authors, this defect is unknown in colorless and any otherwise-colored diamonds. De Weerd and Collins have concluded in their 2007 paper [24] that the 617.6 and 626.3 nm lines were not ZPLs, but vibronic bands, based on their observation that the peaks did not weaken distinctly at higher temperature. In our experiments it was obvious that the two peaks (and the other associated vibronic peaks) started to decrease very rapidly when increasing the temperature and that they were undetectable at RT, while the 720 nm band remained unchanged (Figure 17). Further, these peaks showed variable intensity depending on the laser excitation (Figure 14), a behavior typical of certain ZPLs, such as the S1, S2, and S3 centers. Both the shape of the two peaks and their behavior have led to our conclusion that the two peaks represent the ZPLs of the 720 nm vibronic band. The 617.6/626.3 nm center appears to be the only defect detected by PL spectroscopy that is unique to DR type Ia brown diamonds. Many of the other defects listed above are typical for such brown diamonds, yet they are not unique to them and can—in the experience of the authors—be found in other diamonds that have undergone plastic deformation, in any color, including colorless.

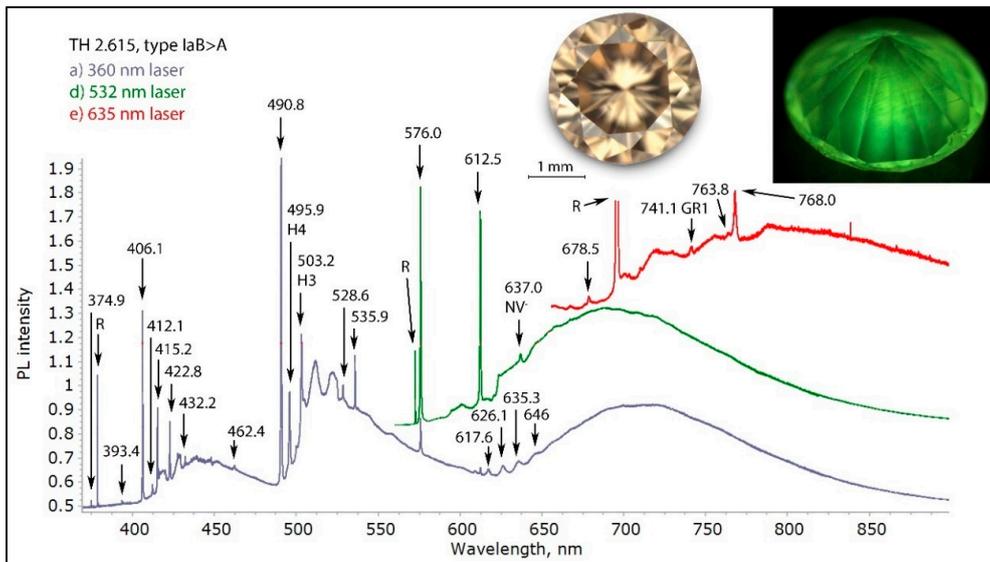


Figure 15. The low temperature PL spectra of a brown type IaB>A diamond with a deformation-related color, recorded with three different laser excitations. Interesting in this diamond is that the blue component of the fluorescence is not mainly caused by the N3 center, but by the 406.1 nm defect. This defect is very common in DR brown diamonds, but rarely as intense as seen here. The other very typical defects for DR brown diamonds are 490.8, H4, H3, 535.9, 576.0, 612.5 and the 617.6/626.1 nm center. While in most brown diamonds the H3 defect is responsible for the commonly observed green fluorescence, in this diamond the 490.8 nm defect is dominantly responsible for the green fluorescence seen in the photo (inset, right). The spectra were shifted vertically for clarity.

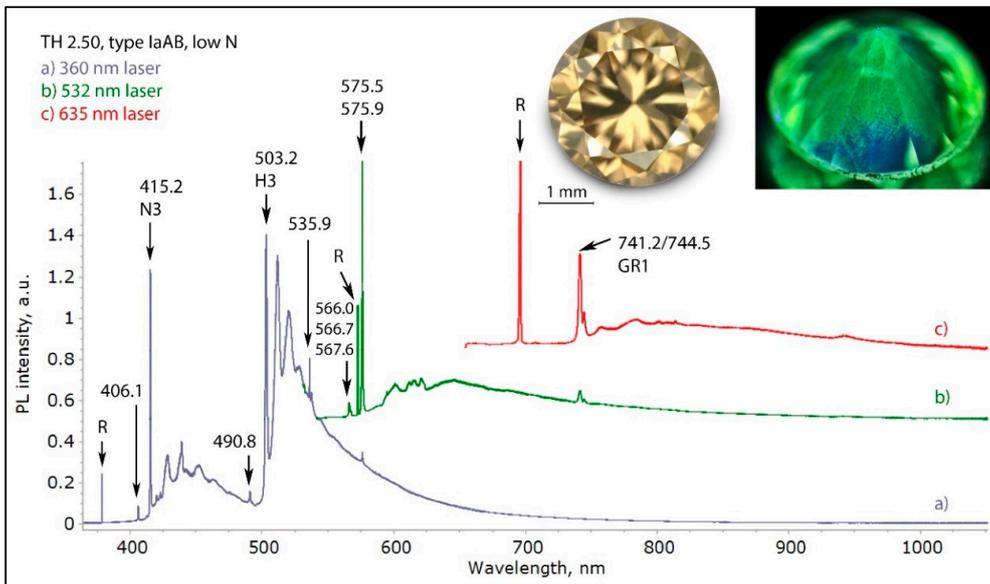


Figure 16. The low temperature PL spectra of a brown-yellow low nitrogen type IaAB diamond with a deformation-related color, recorded with three different laser excitations. While many of the defects observed are the same as the ones observed in higher nitrogen containing brown diamonds, some defects are notably absent with the most noteworthy being the 617.6/626.1 nm center. In this diamond, the H3 and N3 defects are responsible for the green and blue fluorescence seen in the photo (inset, right). This type of spectrum is similar to what can be seen for many type IIa diamonds. The spectra were shifted vertically for clarity.

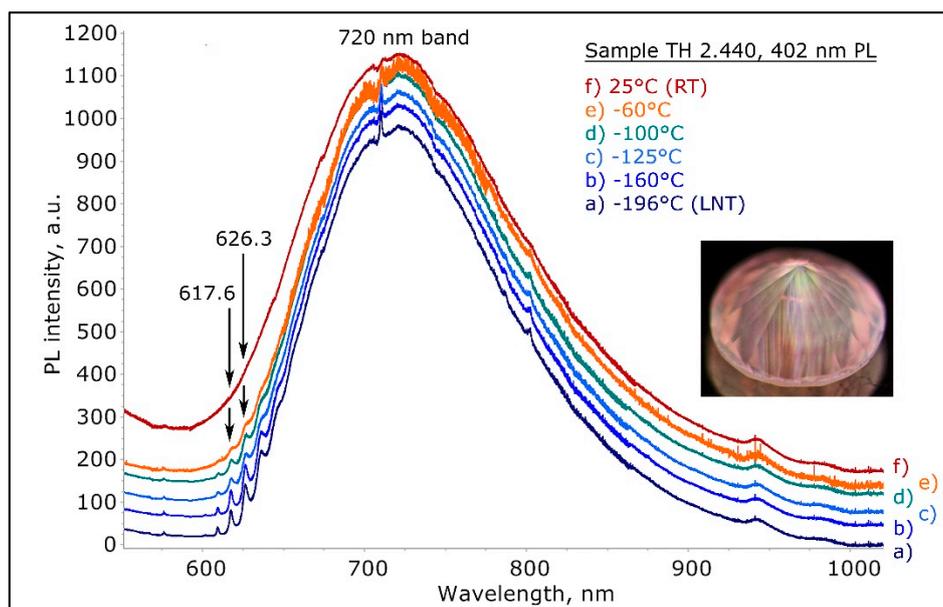


Figure 17. The 402 nm PL spectra of the pinkish brown type IaA>>B diamond shown in Figure 14, recorded at various temperatures from room temperature to $-196\text{ }^{\circ}\text{C}$ (LNT) and normalized to the intensity of the 720 nm band. The shape and behavior of the 617.6/626.3 nm peaks are indicative that these features represent zero phonon lines and not vibronic components. The correlation of these two ZPLs with the broad 720 nm band led us to suggest that they are the ZPLs of the defect responsible for the 720 nm band, hence the 720 nm band is the vibronic component. The spectra were shifted vertically for clarity.

The PL spectra of the type Ib DR brown diamonds were very different from type Ia stones: their spectra were generally dominated by NV^0 and NV^- centers (ZPL's at 574.9 nm and 637.0 nm respectively), with distinct H3 (ZPL 503.2 nm) and very weak N3 (ZPL 415.2 nm) center PL (Figure 18); a weak peak at 565.7 nm was present in some of the spectra as well, which is characteristic for the vast majority of type Ib diamonds [13]. Most of the type Ib DR brown diamonds were found to be pure type Ib without any aggregated nitrogen detectable via IR spectroscopy; the high vacancy density in such diamonds combined with the C centers results in the dominant NV center PL. The presence of N3 and H3 indicates that some aggregated nitrogen must be present, even though a good portion of the A aggregates are surely bound in the H3 centers and thus not visible in the IR spectra. The very weak N3 PL in contrast requires the presence of at least some B centers, even though the concentration is certainly extremely low, and below the detection limit of IR spectroscopy. Interestingly, sample TH 2.561, a pure type Ib diamond with only 2 ppm of C centers, was characterized by PL spectra with a very dominant H3 center and only minor NV^0 and NV^- ; furthermore, N3 was easily detected by PL. This stone was shown to exhibit distinct 4111 cm^{-1} and 4167 cm^{-1} ACs in its IR spectrum, which already indicated the presence of aggregated nitrogen. Since the aggregated nitrogen could not be found in the IR spectra, it must be assumed that all the aggregated nitrogen was bound by the ACs and by the H3 defect, and hence became undetectable by IR spectroscopy.

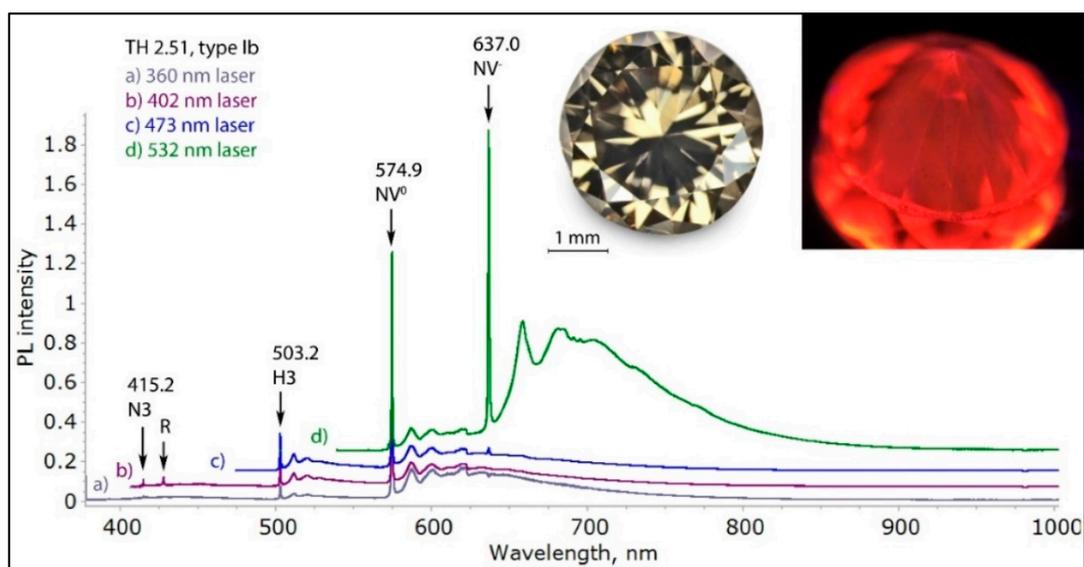


Figure 18. The low temperature PL spectra of a very rare brown low nitrogen type Ib diamond with a deformation-related color, recorded with four different laser excitations. The spectra of such diamonds are always dominated by NV^0 and NV^- centers, combined with the H3 defect. In this diamond, the NV^0 defects are responsible for the red orange fluorescence seen in the photo (inset, right). The spectra were shifted vertically for clarity.

The Behavior of PL Defects upon Annealing

While the annealing behavior of most PL defects of DR brown diamonds by temperatures used during the HPHT treatment (2000–2500 °C) are relatively well known, their behavior at lower temperatures are not well studied and only some data on LPHT (low pressure, high temperature) treatments has been published for type Ia diamonds [22]. Therefore, annealing experiments up to 1500 °C were performed to check the stability of the PL defects in DR type I brown diamonds. Of all the common defects detected in this study, only a few were consistently affected in the samples that were treated. The least stable defect besides GR1—which anneals out at 800 °C—is the 612.5 nm defect; this defect was either annealed out completely or reduced by >95% at 1500 °C. The H4 center was found to reduce in intensity by about 75%, and finally the 406.2 nm defect reduced by 40% at 1500 °C. Some of the other defects behaved irregularly, in some cases they reduced significantly in other cases they remained unaffected; these include the 422.8 nm defect, the 490.8 nm defect, and the NV^- center. In type Ib diamonds, none of the defects were affected by annealing at the highest temperature.

DFI Fluorescence Imaging and Spectroscopy

Using a standard 365 nm (LW) and 254 nm (SW) fluorescence lamp many the brown diamonds—particularly the darker ones—only exhibited a rather weak fluorescence, being typically blue, green, or orange in color under LW and blue, green, or yellow under SW when discernible, otherwise they appeared practically inert. The lighter-colored diamonds were the most fluorescent ones while the darkest ones were the least fluorescent ones. This phenomenon is likely related to the high density of vacancy clusters present in such stones, and an associated suppression of fluorescence in an overly defective structure.

Under the powerful UV excitations of the Mega-DFI system, the diamonds all exhibited distinct fluorescence, with variable colors and distribution, depending on the excitation wavelength. When tested with the different excitations available, the most common PL that could be seen was green, blue, or mixes of green and blue under all excitations >240 nm, while the PL was always blue to green blue under the excitations <230 nm (Figure 19). Much more rarely a pink to orange red PL under the

longer excitation wavelengths was observed, while such samples showed a blue PL under the shortest wavelengths (Figure 20).

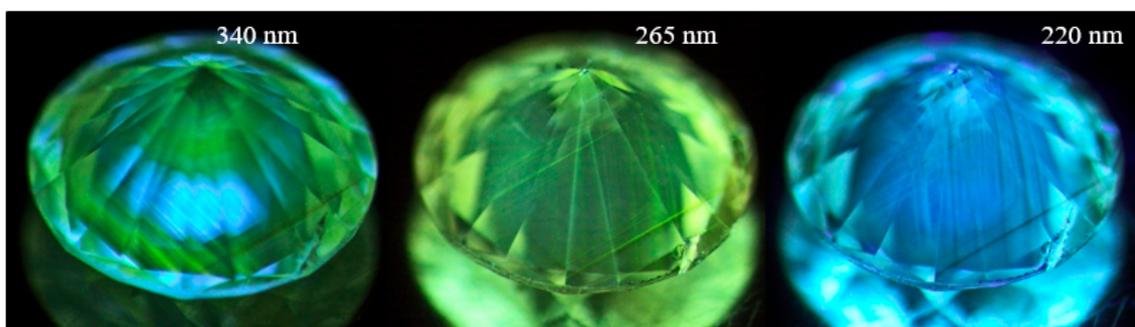


Figure 19. A light brown type IaA>B diamond (sample TH 2.435) under three different UV excitations of the DFI system. The images clearly show the defect distribution along the deformation-related slip planes along (111).

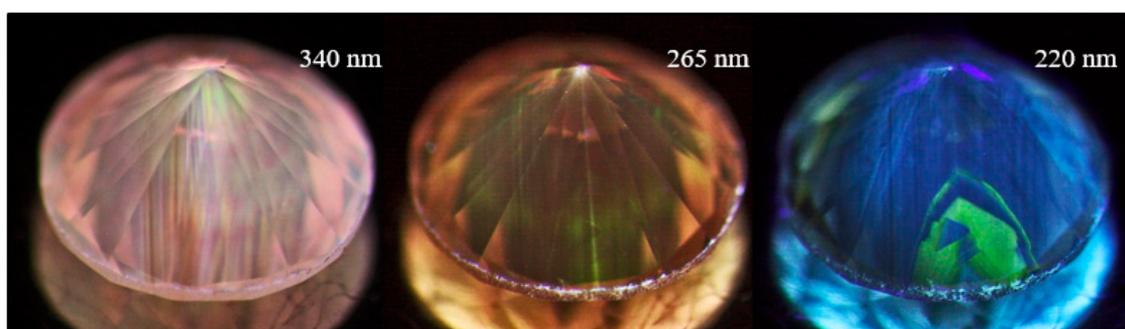


Figure 20. A pinkish brown type IaA>>B diamond (sample TH 2.440) under three different UV excitations of the DFI system. The images clearly show the defect distribution along the deformation-related slip planes along (111). At 340 nm, the main defect visible as pink PL is the 617.6/626.3 nm defect; the green H3 PL can be seen under all excitations, and at 220 nm the N3 defect is dominant.

The 340 nm excitation, which is most comparable to LWUV, excited mostly either green, blue, or pink fluorescence in the type Ia diamonds, often mixed with each other (Figure 19). The causes of the different visually observed fluorescent colors were verified by the spectrometer that is part of the Mega-DFI system and it was found that green PL in type Ia DR brown diamonds can be caused by the following defects: H3 (503.2 nm ZPL, by far most common), the 490.8 nm defect (common), H4 (495.9 nm ZPL, rather rare), and S3 (496.6 nm ZPL, unusual, only in cuboid growth sectors). The blue fluorescence generally thought to be uniquely caused by the N3 center in diamonds can be caused by the N3 center (415.2 nm ZPL, most common), but in some diamonds included in this study it was also caused by the 406.1 nm defect (Figure 15). Theoretically it could also be caused by 412.1 nm and 422.8 nm defects, but no example with these features intense enough to visually influence the observable PL were found. The pink to red fluorescence in type Ia DR brown diamonds almost always relates to the 617.6/626.3 nm defect (Figures 14 and 15), but in certain cases an orange to pink luminescence was caused by a dominant 576.0 nm defect that, whenever dominant, occurred together with an unusually intense 535.9 nm defect.

While by far most of the DR brown diamonds were characterized as being of very dominantly octahedral growth, it was obvious from the typical growth patterns—often exhibiting a “Mercedes star” pattern—that the type IaA>>B nitrogen and hydrogen-rich DR brown diamonds were of mixed cuboid-octahedral growth (Figure 21).

In the majority of type Ib DR brown diamonds, the fluorescence was orange to orange-red from the NV^0 center (574.9 ZPL); this fluorescence was found to be distributed in a much more homogenous manner than in type Ia DR brown diamonds, and there was hardly any particular sectoring or distribution visible (Figure 22). One sample (TH 2.561), a pure type Ib diamond with the lowest measurable nitrogen content of all diamonds studied (≈ 2 ppm of C centers), surprisingly exhibited a purely yellowish green H3 fluorescence under all excitations of the DFI system (Figure 23). With the H3 center consisting of the A aggregate combined with a vacancy it appears obvious that the diamond should contain mainly A aggregates instead of C centers; one would expect the vacancy to combine with the C center and result in NV centers and consequently orange to red PL. A closer look at the diamond showed other indications that aggregated nitrogen should be present, such a rather strong 4167 cm^{-1} AC. The only way one can explain that absence of aggregated nitrogen in the IR spectrum is that all the A aggregates available were bound to the H3 and the 4167 cm^{-1} AC defects. Nonetheless, this does not explain why the vacancies bound to these A aggregates instead of the C centers; the energy required to combine the vacancy with an A aggregate may be lower, which would explain the observed features.

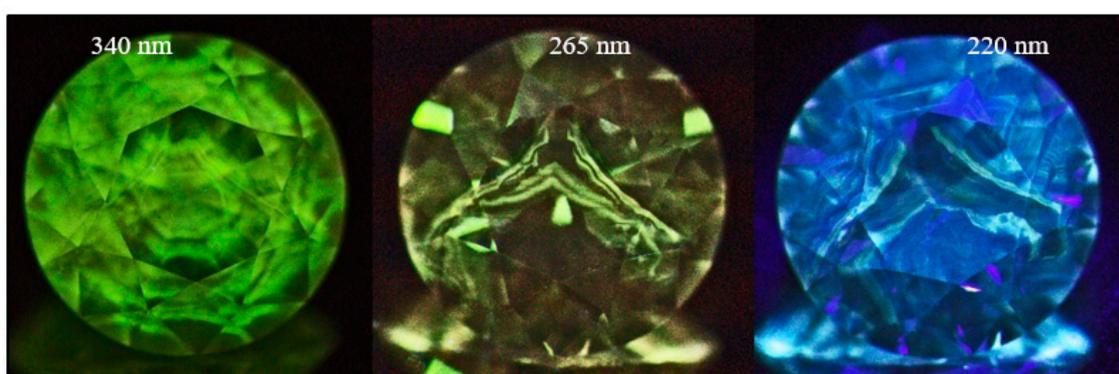


Figure 21. A DR brown hydrogen- and nitrogen-rich type IaA>>B diamond (sample TH 2.622) under three different UV excitations of the DFI system. The images clearly show the typical “Mercedes-star” pattern visible in mixed cuboid-octahedral growth diamonds. In this diamond, the defects were distributed along the cuboid sectors and along the DR slip planes. Along the cuboid sectors, the S3 defect can be detected, while within the deformation-related slip planes the H3 defect is found. At 340 nm, the main defect visible as green PL is the H3 defect while under 265 nm excitation it is the S3 defect; at 220 nm, the N3 defect combined with the S3 center are dominant.

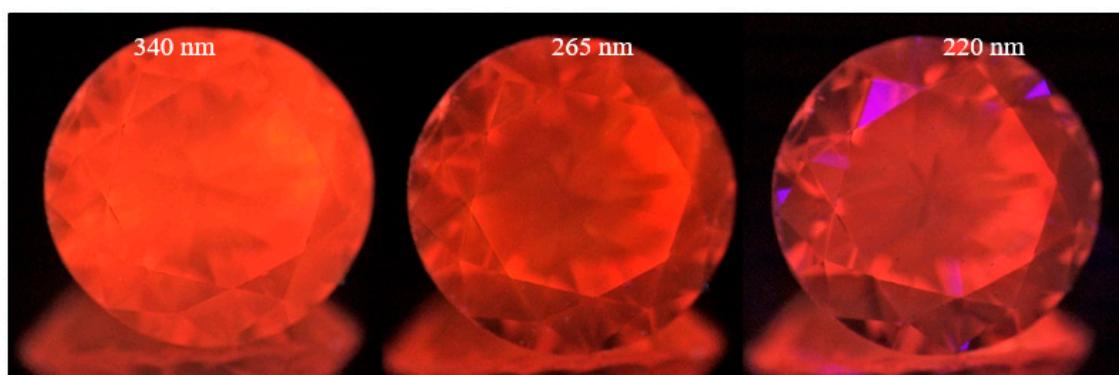


Figure 22. A pure type Ib brown diamond (sample TH 2.51) under three different UV excitations of the DFI system. The NV^0 center is responsible for the luminescence under all excitations, and the distribution of the defects is much less obvious than in other deformation-related samples. Photos: Dr. Thomas Hainschwang.

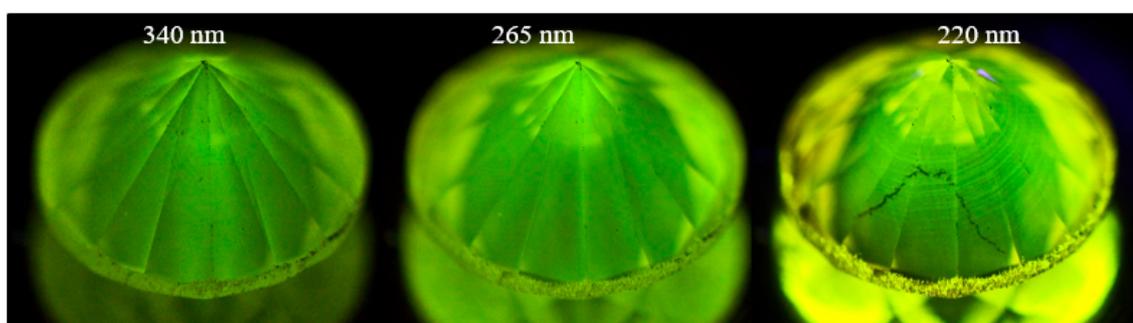


Figure 23. A pure type Ib brown diamond (sample TH 2.561) under three different UV excitations of the DFI system. The yellowish green PL is caused by the H3 defect, even though according to the IR spectrum the stone did not contain measurable A aggregate nitrogen.

3.1.2. Type II Brown Diamonds

Ten type II diamonds—nine type IIa and one type IIb—were part of this study. They ranged in color from brown to pinkish brown to yellow brown, and they showed a wide range of fluorescent responses, hence covered what one can typically find in type II diamonds. The only sample missing in the selection was a stone with distinct NV center fluorescence, but samples analyzed in the past have been used to fill in the data for such diamonds.

Microscopic Examination

Just like type I DR brown diamonds, the type II counterparts exhibited brown-colored lamellae along the (111) directions when they were viewed in immersion, and extinction (= double refraction) along the same directions when they were viewed in immersion and crossed polarizing filters. These lamellar patterns were identical in the tested type IIa and IIb diamonds. Together with the extinction, strain-related interference colors were apparent in some of the tested diamonds, but far less than what could be seen in many type I DR brown diamonds. The extinction patterns in the type II diamonds were generally finer and more regularly intersecting than the often more chaotic and coarse patterns in type I diamonds, and represented what is typically referred to as a “tatami pattern” in the trade (Figures 24 and 25).

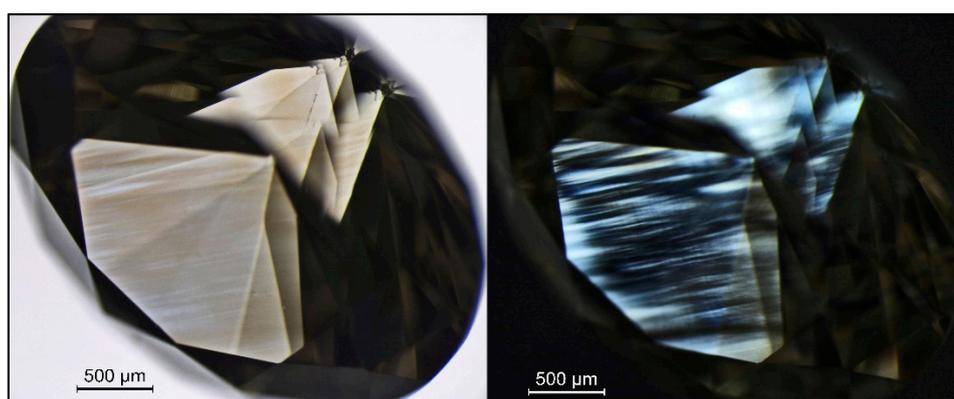


Figure 24. A brown type IIa diamond (sample TH 2.612) in immersion (left) showing the characteristic plastic deformation-related brown “graining” along (111), and the corresponding extinction patterns as shown under crossed polarizing filters (right).

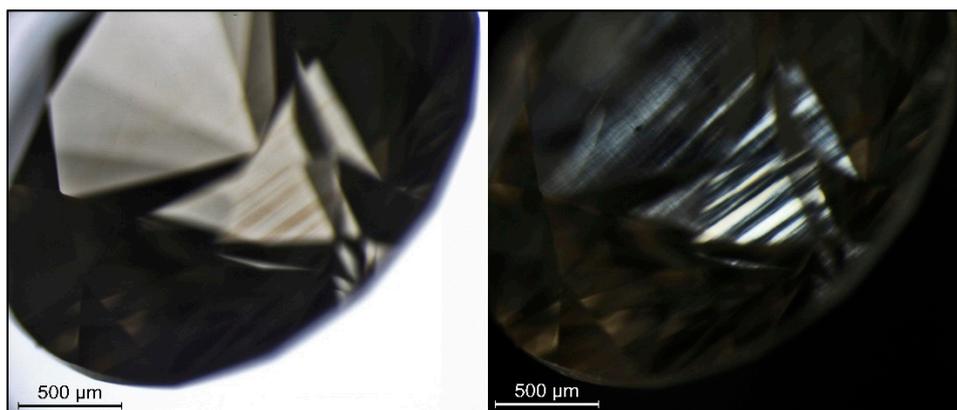


Figure 25. A brown type IIb diamond (sample TH 2.610) in immersion (left) showing the characteristic plastic deformation-related brown “graining” along (111), and the corresponding extinction patterns as shown under crossed polarizing filters (right), equal to what is seen in type IIa diamonds.

Infrared and Near-Infrared Spectroscopy

As per definition, none of the type IIa diamonds showed any measurable traces of nitrogen-related absorptions in the IR spectra; hydrogen was also undetectable. The type IIb diamond showed—also per definition—weak boron-related absorption, the strongest of which being a relatively sharp peak at 2800 cm^{-1} . The spectra of type IIa DR brown diamonds exhibited very weak AC absorption at 4063 cm^{-1} and a broader band at 4200 cm^{-1} . Verifying the laboratory’s database, it was found that virtually all type IIa brown diamonds ever analyzed at the laboratory did exhibit a weak to very weak 4063 cm^{-1} AC. With the 4063 cm^{-1} AC being the least stable in type Ia and Ib diamonds, it was of great interest to see how this AC behaved in type II diamonds, and therefore heat treatment at 1500 °C for two hours was also performed on type IIa DR brown diamonds. The experiment revealed that the AC in the tested type IIa DR brown diamonds was not modified by annealing at these conditions; the 4063 cm^{-1} AC remained unaffected. Comparing the behavior between type I and type IIa diamonds, a possible explanation for this differing annealing reaction could be the absence of nitrogen; this could implicate that in order to form the 4167 cm^{-1} and/or the 4111 cm^{-1} ACs out of the 4063 cm^{-1} AC nitrogen needs to be available. From this it could be concluded that the 4063 cm^{-1} AC defect might possibly not contain nitrogen.

In most low temperature NIR spectra of the analyzed type II DR brown diamonds, a sharp ZPL at 7878 cm^{-1} ($= 1269.2\text{ nm}$) was detected; heating at 1500 °C reduced the intensity of this absorption by 80%. In the type IIb diamond, a similar ZPL was found slightly shifted, at 7868 cm^{-1} (1271.0 nm), at LNT. In the NIR spectrum of the pink brown sample (TH 2.584), a ZPL at 4847 cm^{-1} and one at 7497 cm^{-1} were detected; the peak at 4847 cm^{-1} was found to anneal out after 2 h at 1500 °C .

UV-Vis-NIR Spectroscopy

As with type I brown diamonds, the color of type II DR brown diamonds is the result of the relatively flat and steadily increasing continuum from the NIR to UV.

With nitrogen-related absorptions, such as N3 and H3, typically absent, the only features overlaying the continuum were a broad band at 675 nm, and for the very unusual samples with the 597.9 nm PL (see PL section for details), a broad band at 550 nm and a double band at 385/396 nm was found (Figure 26); the 550 nm band caused the pinkish color seen in the diamond shown in image d in Figure 26. This 550 nm–385/396 nm spectrum is identical to what is seen for any type IIa diamond of pinkish brown color, with exception of the rare cases when the NV^0 center causes a pinkish color in such diamonds [25,26].

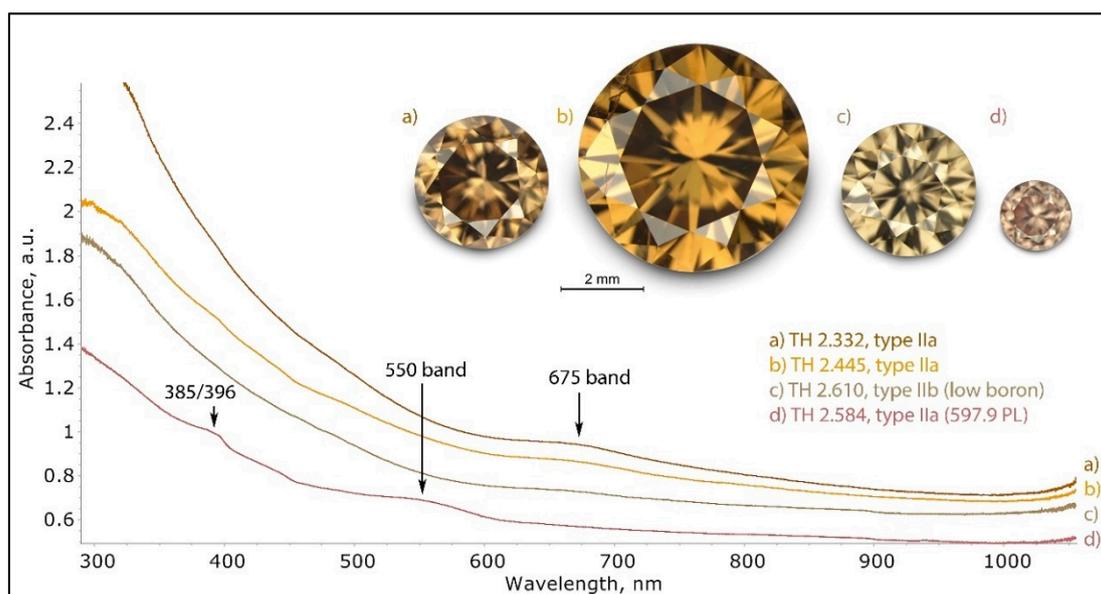


Figure 26. The different UV-Vis-NIR spectra of brown type II diamonds, recorded at 77 K. As with type I brown diamonds, the color of such stones is the result of the relatively flat and steadily increasing continuum from the NIR to UV. With nitrogen-related absorptions, such as N3 and H3, typically absent, the only features overlaying the continuum are a broad band at 675 nm, and for the very unusual samples with the 597.9 nm PL, a broad band at 550 nm and a double band at 385/396 nm can be seen, which is basically a regular UV-Vis-NIR spectrum for any pink brown type IIa diamond. The spectra were shifted vertically for clarity.

Photoluminescence Spectroscopy

The PL spectra of type IIa diamonds were found to be very variable, since many type IIa diamonds are simply type I diamonds with a very low nitrogen content. Hence, many defects found in type I diamonds are also found in type IIa diamonds. In consequence, the PL spectra shown in Figure 17 above of a low nitrogen type Ia diamond is a typical example of spectra as they also occur for many type IIa diamonds. Besides 406.1 nm, N3, H3, 490.8 nm, 535.9 nm, H4, 576.0 nm, and 612.5 nm, which can typically be found in the PL spectra of both type Ia and type IIa diamonds, some features are mainly found in the spectra of low nitrogen type Ia and “nitrogen-free” type II diamonds, including type IIb. These include 417.2 nm, 431.1 nm, 3H (503.5 nm ZPL), 558.3 nm, 566.0 nm, 566.7 nm, 567.6 nm, 578.9 nm, 649.5 nm, distinct GR1 (741.2/744.6 nm ZPL), 802.2, and 814.2 nm. Some of these features are seen in Figure 27, the PL spectra of the only type IIb DR brown diamond included in this study; as a general rule, a non-type-sectored type IIb diamond will not exhibit any nitrogen-related PL centers, such as it is the case for this specific stone. Interestingly, the few truly brown type IIb diamonds that we have seen so far always exhibited very similar spectral data like the sample included in this study, with the 417.2 nm defect being the consistent one present in all the spectra. Only samples appearing “olive” or blue with a brownish tinge that we have tested in the past exhibited the PL centers typical for gray to blue type IIb diamonds, such as the 479.9 nm, 517.6 nm, 648.1 nm, and 776.4 nm defects.

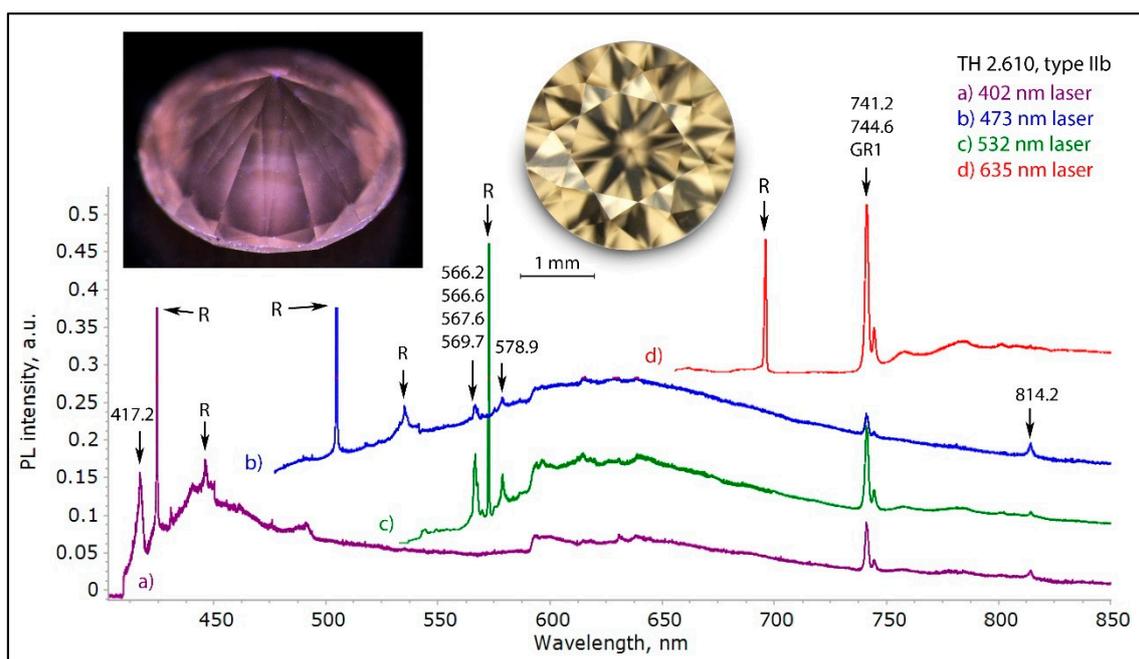


Figure 27. The photoluminescence spectra of a rare type IIb brown diamond, recorded using four different lasers. With many of the features being characteristic of low nitrogen Ia or type II diamonds, the asymmetric and somewhat large band at 417.2 nm is only rarely found in type IIa diamonds but is very common in type IIb diamonds. The spectra were shifted vertically for clarity.

Some rare type IIa DR brown diamonds can exhibit PL spectra characterized by mainly NV centers and other radiation induced defects; such stones have been tested prior to this study, but no stones are directly included here; the PL features typically seen include 388.8 nm, 470.0 (TR12), H3, 550.8 nm, NV⁰, NV⁻, and GR1. Often, such stones are of mixed pink and brown color.

In very large parcels of small (<0.02 ct) pinkish brown diamonds we have encountered four highly unusual nickel-rich type IIa DR pinkish brown diamonds with distinct orangey red PL, not related to the NV centers; the series of PL spectra characteristic for these diamonds, recorded from sample TH 2.584, are shown in Figure 28. Besides the 417 nm PL peak described above and a distinct doublet at 882.9/884.6 nm—a well-known nickel-related defect assigned to Ni_i⁺ [27]—the spectra were found to be very unusual with all other PL features unknown in our PL database. This very rare orangey red PL was found to originate from three very sharp and intense ZPL's at 559.7 nm, 584.5 nm, and 597.9 nm, with their associated vibronic sidebands that range all the way to 850 nm and which are centered at approximately 650 nm. After some research into these spectral features, it was discovered that these types of spectra are reminiscent of what has been described in the cathodoluminescence spectra of natural type IIa diamonds that have been implanted by nickel and oxygen ions and annealed to 1650 °C [28]. Nonetheless, it was confirmed by the authors of [28] that the spectra of their research were not identical to the ones included here and the lack of features such as H3 and/or NV centers are highly indicative that no artificial irradiation and annealing were involved; while annealing at 1650 °C would anneal out all irradiation-related features, H3 and/or NV centers would clearly form during such a treatment and survive the annealing.

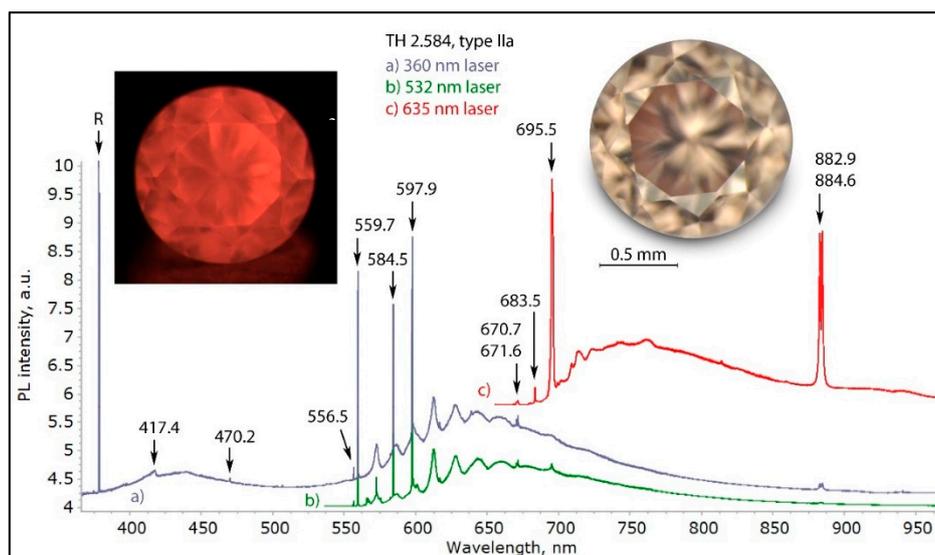


Figure 28. The photoluminescence spectra of a highly unusual pink brown type IIa diamond with orangy red luminescence not originating from the NV^0 center, but from the 559.7, 584.5, and 597.9 nm defects, excited using three different lasers. These are nickel-containing natural type IIa diamonds, as is apparent by the presence of the 882.9/884.6 nm Ni_i^+ doublet; the 584.5 and 597.9 nm defect(s) can possibly be attributed to oxygen or nickel defects. The spectra were shifted vertically for clarity.

We have heated the sample included here at 1500 °C for two hours to see whether the treatment would modify the PL of the diamond, but it had no effect whatsoever. The UV-Vis-NIR data also suggests that the diamonds might be naturally colored, since the continuum absorption with the 550 nm band combined with the double absorption at 385/396 nm is in no way different to a regular type IIa pink brown diamond. The results from the NIR spectroscopy performed for the stone that was heated at 1500 °C shows at least that this sample has for sure not been heated above 1400 °C, since an NIR peak at 4847 cm^{-1} was found to anneal out after 2 h at 1500 °C. In conclusion, these unusual diamonds remain puzzling, but combining all data it is highly likely that these diamonds are naturally colored and untreated.

DFI Fluorescence Imaging and Spectroscopy

As mentioned above, the PL of type II diamonds can be very variable because of the fact that type II does not mean that a stone is strictly nitrogen-free, but only that nitrogen cannot be detected by infrared spectroscopy. As a consequence, the PL imaging is rather diverse, and a range of different colors and color distributions can be observed, depending on the defects present. As a general rule it can be stated that the fluorescence intensity in a type II diamond is lowest when the density of PL active defects is lowest and/or when the brown color of the diamonds is the darkest. In diamonds with excessive PL active defects the fluorescence intensity decreases, because of the resulting imperfection of the diamond lattice. Equally, when a diamond is very rich in DR defects, such as vacancy clusters, the defective lattice causes a suppression of fluorescence. A highly defective diamond lattice gives rise to many alternative pathways for de-excitation of the UV-excited electrons, and not all of these result in fluorescence. Energy transfers that lead to this so-called fluorescence quenching are well known in diamonds very rich in aggregated nitrogen, which fluoresce much weaker than stones much lower in nitrogen, even though the stones with much higher nitrogen content are much richer in N_3 centers than the lower nitrogen samples. Therefore, high nitrogen type IaAB yellow “cape” diamonds barely show any N_3 -related blue fluorescence while relatively low nitrogen type IaAB near colorless “cape” diamonds typically fluoresce much stronger. This energy transfer occurs from the N_3 center to the A aggregate [29], possibly also the B aggregate [30].

As a consequence, the most intense fluorescence was found in lightly colored “near-type IIa” diamonds, stones in which the IR spectrum does not definitely define them as IIa, but neither definitive nitrogen-related absorptions can be defined, hence stones with a nitrogen content of <2 ppm. Such stones appear very similar to type Ia DR brown diamonds when tested under the various excitations of the DFI system, such as seen in Figure 29; the shown diamond exhibited green fluorescence from the H4 and 490.7 nm defects and blue fluorescence from the 406.1 nm and the N3 defects, similar to many type Ia DR brown diamonds.

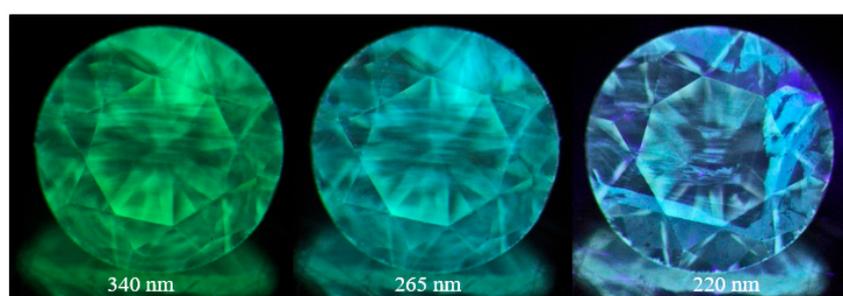


Figure 29. A light yellowish brown near type IIa diamond (sample TH 2.616) under three different UV excitations of the DFI system. The green PL is caused by the 490.7 nm and H4 defects, the blue PL by the 406.1 nm and the N3 defects.

Orange to pink/red fluorescence does occur very rarely in type IIa DR brown diamonds, and generally this relates to the NV^0 center [26]. While such diamonds have been tested by us during this study, no such sample is included here. The diamonds that are included are very unusual pinkish brown diamonds with a distinct pink to orange red PL under the various excitations used (Figure 30); while it appeared obvious that these should be luminescent from the NV^0 center, the spectra of the emission identified it as the 559.7, 584.5, and 597.9 nm defects and their associated vibronic sidebands; these defects are possibly linked to oxygen or nickel.



Figure 30. A pink brown type IIa diamond (sample TH 2.584) under three different UV excitations of the DFI system. The pink to orange red PL is caused by the possibly oxygen- or nickel-related 559.7, 584.5, and 597.9 nm defects.

3.2. Comparison of DR Brown with DR Pink to Red to Purple Diamonds

As mentioned in the microscopic examination and UV-Vis-NIR spectroscopy sections above, there is an obvious link between brown DR diamonds and pink to red to purple diamonds. With brown diamonds often exhibiting both, brown and pink color lamellae, and often showing spectral features in their UV-Vis-NIR spectra that are characteristic of pink diamonds, the obvious question must be what the differences between the two clearly related color groups are. For this reason, a series of pink diamonds were specifically analyzed for this study and the data of large numbers of pink to purple to red diamonds analyzed in the past at our laboratory was reviewed and included. Pink diamonds do not exhibit the characteristic UV-Vis-NIR continuum absorption responsible for the brown color

but instead they exhibit a broad absorption band centered at 550 to 560 nm, often with a band at 390 nm, which consists typically of two components at 385 and 396 nm. Their infrared spectra lack the distinct AC absorptions but very weak ACs at 4063 cm^{-1} , 4167 cm^{-1} , or 4200 cm^{-1} can be detected in some of the type Ia stones. Besides type IIa brown diamonds, type Ia pink to purple diamonds are the only diamonds for which we have occasionally detected an isolated 4063 cm^{-1} AC, even if only weak. In contrast to brown diamonds, none of the pink to purple diamonds with the 4063 cm^{-1} AC showed any H1b and/or H1c center absorption.

To see how the weak ACs in pink to red to purple diamonds reacted to heat, five type Ia pink diamonds were heated to $1500\text{ }^{\circ}\text{C}$ for two hours; interestingly, none of the weak ACs changed with the annealing, including the 4063 cm^{-1} AC that was shown to be so noteworthy unstable in DR brown diamonds from temperatures as low as $1150\text{ }^{\circ}\text{C}$. On the note of heat treatment, the behavior of certain type IIa DR brown diamonds to HPHT treatment should be noted, since stones of pinkish brown color may turn pink when HPHT treated at lower temperature of $<2000\text{ }^{\circ}\text{C}$ [11,31], and then turn colorless or yellowish when HPHT treated in a second step at $>2000\text{ }^{\circ}\text{C}$ [31].

Clearly, the nature of the defect responsible for the pink color—even though certainly similar to the vacancy cluster—cannot be the same as the one in DR brown diamonds. Pink diamonds lacking any brown graining do not show the complex DR PL spectra that are so characteristic for brown diamonds. With the exception of the H3 and H4 center, deformation-related defects appear absent in the PL spectra, even though the color origin is clearly deformation-related. The question thus remains, what defects can be created by post-growth plastic deformation in a way that both pink and brown color lamellae can be present at the same time? There is no significant difference other than this lack of IR and PL active deformation-related defects, both DR brown and pink diamonds can be type IIa, both type Ia DR brown and pink diamonds are relatively low in nitrogen, low to very low in hydrogen and can show any kind of nitrogen aggregation state, with often B>A in pink diamonds and A>>B in more purple diamonds. It seems obvious that both brown and pink to red to purple diamonds have the same formation conditions; the difference between the color groups is thus not their growth condition, but the post-growth conditions. As post-growth plastic deformation is the process responsible for these colors, the conditions of plastic deformation must be significantly different to cause one or the other color. A multi-step deformation process is the only way to explain both pink and brown color lamellae in the same stone. From the annealing behavior of the amber center, which has shown that the 4063 cm^{-1} AC is the least stable AC and anneals out at $1500\text{ }^{\circ}\text{C}$ to form both the 4165 cm^{-1} AC or the 4111 cm^{-1} AC (if C centers are available) and from the creation of the different ACs via heavy neutron irradiation and annealing, it seems logical to conclude that the pink to red to purple color is likely caused by plastic deformation at lower temperatures while the brown color is likely caused by plastic deformation at higher temperatures. Two or more different plastic deformation events at significantly different temperatures would thus be a logical way of explaining the occurrence of pink and brown color lamellae in the same diamond.

3.3. Treated Brown Diamonds with Originally DR Brown Color

A series of type Ia brown diamonds was included in this work, which had been electron irradiated and annealed. While some of the stones showed an obviously modified color—being yellow to greenish yellow after irradiation and annealing—some stones remained essentially brown during the entire process. The reason for this was generally the starting color of the diamond: when the color was comparatively light, then the resulting color was as desired (greenish blue after irradiation, yellow to greenish yellow after annealing) (Figure 31), but when the color was somewhat darker, the resulting colors were brownish or even dominantly brown (Figure 32). The explanation for this is the combination of the original color with the diamond type and the nitrogen content, plus the energy of the electrons and the dose used: it is difficult to distinctly modify an overly dark brown color with the defects induced by irradiation and annealing. The treatment does not change the originally occurring UV-Vis-NIR absorption continuum caused by the vacancy clusters, and GR1, H3, or H4 are

generally not strong enough to mask the brown color. The nitrogen type and concentration are of importance since it is much easier to create significant H3 absorption compared to H4; in consequence it is far more efficient to create yellow color in diamonds with significant concentrations of A aggregates than in pure or nearly pure type IaB diamonds. The two examples shown in Figures 31 and 32 were both diamonds with mainly B aggregates; the main differences between the two was the depth of the brown color, with sample TH 2.211 being significantly lighter than sample TH 2.212, and that the lighter stone had three times higher nitrogen concentrations than the darker diamond. As a consequence, the treatment worked nicely for the lighter diamond, while the darker one remained essentially brown at each step of the treatment.

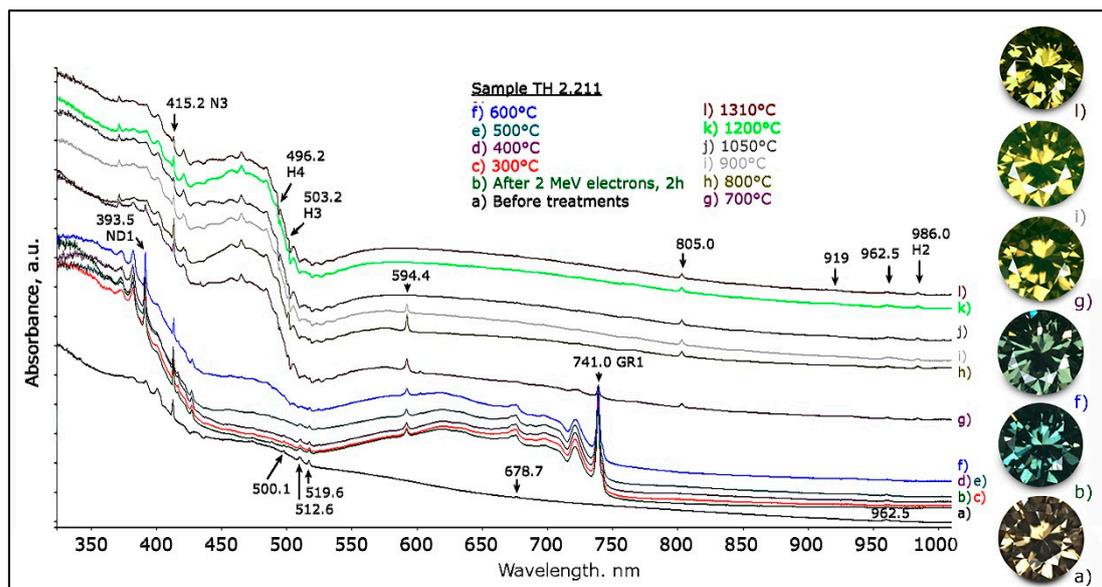


Figure 31. The evolution of the color and the UV-Vis-NIR spectra of a light brown diamond (sample TH 2.211) after 2 h of 2 MeV electron irradiation and stepwise annealing from 300 °C to 1310 °C. The stone showed the desired color changes from brown via greenish blue to greenish yellow, by formation of GR1 from irradiation and H4 plus H3 via the annealing.

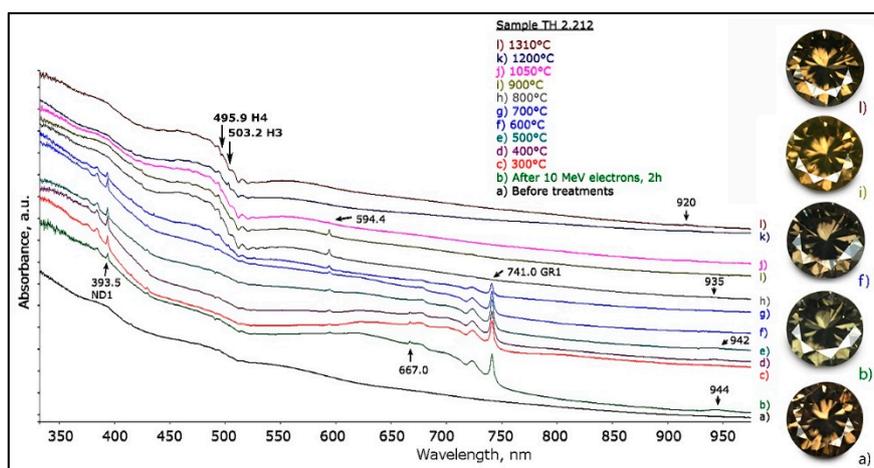


Figure 32. The evolution of the color and the UV-Vis-NIR spectra of a darker brown diamond (sample TH 2.212) after 2 h of 10 MeV electron irradiation and stepwise annealing from 300 °C to 1310 °C. The stone showed some color changes but remained essentially brown, because neither GR1 nor H4 or H3 had a strong enough influence on the distinct continuum absorption.

Other examples of diamonds that turn brown by treatment include DR type Ib deep yellow-orange to olive diamonds; these may appear mainly brown after simple irradiation, or turn orange brown after annealing. Here the brown hue is caused by combination of the strong continuum absorption from the C center and deformation-related vacancy clusters with the absorptions induced by irradiation and annealing (ND1, GR1, and NV⁻) [19].

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

In contrast to the original classification proposed in 2003 [6], the new classification puts the group of brown diamonds into two main groups, deformation-related (DR) brown diamonds and non-deformation-related (NDR) brown diamonds. In this first part of this study the classification of the DR brown diamonds is presented, in the second part the classification of the NDR brown diamonds will be presented. The DR brown diamonds are subdivided into type I and type II, and from here into type Ia, type Ib, type IIa, and type IIb. The type I diamonds are further divided by their typical amber centers, which leads to a total of six different classes of DR brown diamonds (see Table 4 for details and properties).

Table 4. The newly elaborated classification of natural, untreated DR brown diamonds.

Deformation-Related (DR) Brown Diamonds						
Main type	Type I			Type II		
Sub type	Type Ia		Type Ib	Type IIa	Type IIb	
Main AC (RT)	4167 cm ⁻¹ AC	4167/4063 cm ⁻¹ ACs	4111 cm ⁻¹ AC	4111/4063/3462 cm ⁻¹ ACs	None or very weak	None
Other characteristic IR features	None	May exhibit H1b and H1c	No Y center present	Higher C center content, Y center, may show H1b	None	None
Characteristic PL features	617.6/626.3 nm, 612.4 nm		H3, NV ⁰ , NV ⁻	565.7, H3, NV ⁰ , NV ⁻	Various	417.2
Characteristic UV-Vis-NIR features	Absorption continuum from NIR to the UV, 560 nm band		Absorption continuum from NIR to the UV, NV ⁻ center	Steeper absorption continuum from NIR to the UV, weak NV ⁻ center	Absorption continuum from NIR to the UV	
Class name	4167 AC DR brown diamond	4167/4063 DAC DR brown diamond	4111 AC Ib DR brown diamond	4111/4063/3462 TAC Ib brown diamond	IIa DR brown diamond	IIb DR brown diamond

4. Conclusions

In the first part of this study, we have given a full characterization of DR brown diamonds of all types and presented a re-worked classification of this group of diamonds. The extensive amount of data obtained from the diamonds studied and from diamonds studied for other projects, such as our diamond irradiation project, has led to significant advances in the comprehension of some of the characteristics of brown diamonds and on the link between pink to red to purple and brown diamonds. Particularly important is the data on the amber center and the naturally occurring H1b and H1c defects found in untreated DR brown type I diamonds as well as the detailed PL characterization of DR brown diamonds. The re-worked classification still divides diamonds into such that exhibit IR spectra with amber centers, and such that do not show any amber centers, but it puts the entire group into two major classes, one being with a deformation-related (DR) brown color and one being with a non-deformation-related (NDR) brown color. The DR brown diamonds were finally divided into six different classes, four with ACs and two without ACs.

The detailed study of the ACs and the natural H1b and H1c centers by a range of methods, including low temperature NIR spectroscopy and photoexcitation, and the analysis of the behavior of these features upon annealing, electron irradiation, and finally electron irradiation and annealing, have given a much deeper insight into these defects. The various ACs were found to be closely related

defects, most likely involving multiple vacancies and nitrogen, with the 4063 cm^{-1} AC being the precursor of the 4167 cm^{-1} group of ACs and very likely also the 4111 cm^{-1} group of ACs; there are indications that the 4063 cm^{-1} AC does not contain nitrogen but this must be investigated in more detail. The defect structure of the 4167 cm^{-1} AC proposed in an earlier study [8] seems an unlikely candidate to explain this complex group of defects, and defects involving more complex vacancy accumulations seem more likely. It is suggested that the naturally occurring H1b and H1c centers in brown diamonds are side products of the transformation of the 4063 cm^{-1} AC into the 4167 cm^{-1} and/or 4111 cm^{-1} AC hence have a clear link to deformation-induced multi-vacancy defects.

The link between DR pink to red to purple and brown diamonds was elaborated and a mechanism involving post-growth plastic deformation at different temperatures was suggested that could explain the occurrence of the different colors; in this mechanism, it is suggested that the brown color occurs when the plastic deformation occurred at a higher temperature while the pink to red to purple color occur when the plastic deformation occurred at a lower temperature. This is consistent with the conclusions drawn in earlier publications [32]. Such a mechanism would be perfectly suitable to explain the presence of both pink and brown color lamellae in one and the same diamond, by assuming that the post-growth plastic deformation process did not only occur in one single event, but in two or multiple events at significantly different temperatures.

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