HPHT treatment of different classes of type I brown diamonds: before and after

By Thomas Hainschwang, Andrey Katrusha and Heiner Vollstaedt

ABOUT THE AUTORS

Mr. T. Hainschwang (gemlab@adon.li) is research gemologist and director at the GEMLAB gemological laboratory in Vaduz, Principality of Liechtenstein; Prof. Dr. H. Vollstaedt is professor of mineralogy and director of AphroDiamante GmbH - R&D center; Mr. A. Katrusha is PhD researcher at Aphrodiamante GmbH - R&D center and the Institute for SuperHard Materials, Kiev, Ukraine.

Abstract

As part of a work about the classification and color origin of brown diamonds by one of the authors (Hainschwang, 2003), 7 stones belonging to the defined classes were selected and treated by the HPHT process. Each of these diamonds was tested extensively before and after the treatment by standard and advanced gemological methods, including FTIR spectroscopy as well as low temperature Vis/NIR and Photoluminescence spectroscopy. All diamonds except the CO_2 and "Pseudo CO_2" diamonds lost their brown coloration and exhibited various shades of yellow; they exhibited a strengthened luminescence, in some cases also a change of color of the emission. It was found that the spectra of all diamonds except the CO_2 and "Pseudo CO_2" diamonds showed very apparent changes. The FTIR spectra were characterized by the elimination of the amber center, the reduction of the platelet peak and some changes of nitrogen aggregation state after HPHT. A strong increase of N3 and H3 absorption as well as the formation of a distinct H2 center was noted in the Vis/NIR spectra at 77K. The Photoluminescence spectra showed very clearly, that non-negligible amounts of single nitrogen were formed during HPHT, exhibiting very strong NV-centers. The data of a yellow diamond with strong green transmission luminescence of unambiguously natural color origin (exhibiting GR1 damage) was then compared to the data of the treated diamonds and it was found that there can be very distinct similarities between natural and HPHT treated "green transmitters".

Introduction

Diamonds have been artificially colored since a very long time. Untill the late 1990's this was either done by superficial coating, painting or by the creation of lattice defects by irradiation, sometimes followed by annealing. The primary treatment since the late 19th century was irradiation/annealing, by which the color of mainly type Ia and Ib yellowish diamonds can be changed. In this treatment, the high energy particles/radiation displace some carbon atoms and thus create vacancies and interstitials; annealing causes these defects to diffuse through the lattice where they will be mostly trapped by nitrogen to form various nitrogen-vacancy defects, such as the NV^- center with a ZPL at 637nm. The primary radiation treatment results in green coloration, which can be changed to yellow, greenish yellow or orange in type Ia cape diamonds and to pink or purple in type Ib diamonds by annealing at 600-800°C. Some brown diamonds will be of blue (type IIa) to greenish-blue (type Ia) color after irradiation with electrons of ~6 to 10 MeV energy; others just develop green luminescence and some orange color, but they are still mainly brown after the treatment.
In the late 1990's, relatively large amounts of intensely colored yellow to yellow-green diamonds with very strong green luminescence - also visible as transmission - appeared in the market. Such stones, which are frequently termed "green transmitters", were very rarely seen before and are considered to be extremely scarce in nature. Buerki et al. were the first group to postulate in 1998, that these stones were produced by a new treatment: they proposed, that the stones were treated by irradiation followed by very high temperature annealing at stabilizing pressure. In 1999, it has been published by Collins et al., that these findings were most probably false and that these diamonds were treated by high temperature annealing at stabilizing pressure only; the treatment was called the HPHT (**H**igh **P**ressure-**H**igh **T**emperature) treatment and conditions of 1700-2500°C at about 6.5 GPa were reported. Since then, several publications covered the subject of the HPHT treatment; these include papers about the decoloration of type IIa brown diamonds (e.g. Smith et

al., 2000) and the production of green transmitters out of type Ia brown diamonds (Reinitz et al., 2000) by HPHT. It was postulated that the reduction of the brown coloration is caused by the realignment of the distorted crystal lattice; this distortion was (and by some still is) believed to cause the brown coloration of diamonds. During the realignment, vacancies are released, which are trapped by nitrogen in type Ia diamonds and which are mostly annihilated in type IIa diamonds since there is not enough nitrogen present; therefore Ia diamonds will be colored while IIa diamonds turn (near-) colorless after the HPHT treatment. More recently, it has been suggested, that the brown color of diamonds is due to graphitic (Ewels et al., 2001) or amorphous carbon (E. Fritsch, pers. comm. 2002), thus sp2 bonded carbon, which is recrystallized by the HPHT process; the recrystalization causes a release of vacancies and thus the before described changes of color occur.

Experiment

Previous to this present study, a classification of brown diamonds has been established by one of the authors (Hainschwang, 2003). This classification included standard and advanced gemological analysis of 63 brown diamonds preselected out of 900 brown diamonds by FTIR spectroscopy; it also included research about the possible formation of the brown coloration and a close look at certain defects, notably the “amber center”. To support some of the theories and ideas, it was decided to take one or several stones of most of the proposed classes and treat the 7 selected samples by HPHT at 2000°C / 6.5 GPa for 10 minutes. The total HPHT circle lasted 30 minutes. This paper includes a comparison of the data collected before and after the treatment and a comparison to a natural diamond with green transmission luminescence.

Materials and Methods

The seven brown diamonds were analyzed by standard and advanced gemological analysis before and after the HPHT treatment. The diamonds included one brown diamond each of type IaA, IaB, IaA/B, Ib, Ia containing solid CO_2 (Schrauder and Navon, 1993), Ia “Pseudo-CO_2” (Hainschwang, 2003) and one olive-brown stone of type IaA. The color of the stones was observed using 6200 K daylight illumination; the color distribution was analyzed with the stones immersed in methylene iodide and diffuse transmitted light. The diamonds were analyzed with a binocular microscope fitted with crossed polarizing filters to see any strain and extinction patterns. Luminescence to longwave and shortwave ultraviolet radiation was observed, including any observeable phosphorescence after the UV source was shut off.
Advanced analysis included FTIR spectroscopy and VIS/NIR as well as PL spectroscopy.
The IR spectra were recorded with a PerkinElmer Spectrum BXII FTIR spectrometer at resolutions of $4cm^{-1}$ and $2cm^{-1}$. The VIS/NIR spectra covering the range of 400-1000 nm were recorded on an SAS2000 spectrophotometer system with a resolution of 1.5 nm; all spectra were recorded at 77K. The Photoluminescence spectra were also measured with the stones immersed in liquid nitrogen using an SAS2000 Raman system equipped with a 532 nm semiconductor laser and a resolution of 1.5 nm. All these tests were also performed for the natural “green transmitter”.

Results

Visual Appearance

Before

The 7 samples included 6 “regular” brown diamonds and 1 olive-brown stone. Their tones varied from medium to dark.

After

In all except two stones, the brown color was practically eliminated; the treatment did not change the color of the CO_2 and the “Pseudo- CO_2“ diamond considerably. The other stones exhibited a yellow hue after the treatment, some with a greenish and one with a pinkish modifying color.

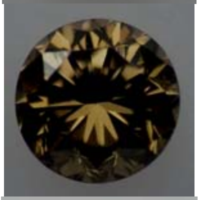
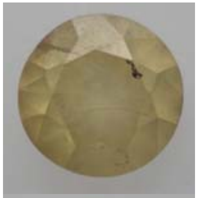
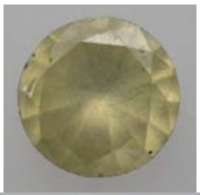
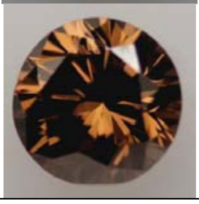
Sample Type (FTIR)	Color before HPHT	Color after HPHT
DUG 7 Type Ib		
DUG 10 Type IaA with double amber center (4070cm^{-1} /4165cm^{-1})		
DUG 18 Type IaA/B, very strong platelets		
DUG 22 IaB, (A very small), high hydro		
DUG 46 Type IaA, near pure		
DUG 3 IaA/B, solid CO2		
DUG 30 IaA/B, "Pseudo" CO2		

Table I. The diamonds included in this study before and after the HPHT treatment. The stones were not repolished after HPHT, therefore the matte surface

Color Distribution

Before

When discussing about brown (and pink) diamonds, most people in the trade will associate all these diamonds with "colored graining"; this graining appears as sharp narrow parallel color bands along octahedral growth directions. Five of the selected brown diamonds exhibited such brown graining of varying strength; the CO_2 diamond showed no grain bands but had its color distributed as an irregular brown color patch; the "Pseudo CO_2" diamond showed half of its color as irregular patchy color and half as strongly developped brown graining.

After

Since the stones were not repolished they showed a burnt skin which did not permit an undisturbed view of the interior of the diamonds; immersion in methylene iodide helped but faint color irregularities could not be seen; anyways, immersion revealed that the graining was strongly reduced and that the little graining which was left had a yellow coloration. The CO_2 diamond did not show any change and after the HPHT run the same irregular brown color patch was present as before the treatment; it was quite interesting to see, that the color distribution of the "Pseudo CO_2" diamond was very different after annealing: before HPHT it was a mix of graining and patchy brown coloration and after HPHT the color was solely patchy brown. The brown graining was thus removed in all cases by the HPHT treatment.

Luminescence to UV Radiation

The defects and changes of nitrogen aggregation, which are caused by the HPHT process, result not only in the formation of yellow to orange coloration, but also in a change of luminescence. This is also the case with the seven samples analyzed in this study: all except the CO_2 and the "Pseudo CO_2" diamond showed a very marked change in luminescence when excited by longwave and shortwave ultraviolet radiation. Interestingly, none of our samples showed the typical strong "pure" green luminescence, which has been described before (e.g., Reinitz et al., 2000). The resulting fluorescence can be explained by the observation of the formation of N3 and H3 in the Vis/NIR spectra compared to the nitrogen content and aggregation state observed in the FTIR spectra.

N° and type	**Before HPHT**		**After HPHT**	
	LW UV	**SW UV**	**LW UV**	**SW UV**
3 (Ia CO_2)	medium yellow	weaker yellow with weak lasting phosph.	same as before	same as before
7 (Ib)	faint reddish orange	weak reddish orange	med. greenish blue	strong chalky yellow
10 (IaA olive-brown)	none	none	faint greenish yellow	inert
18 (IaA/B)	weak blue	faint yellowish blue	medium chalky blue	medium chalky yellow
22 (IaB)	weak chalky blue	faint chalky blue	strong chalky blue, lasting phosphorescence	very strong chalky greenish yellow, lasting phosphorescence
30 (Ia "Pseudo-CO_2")	medium yellow	weak yellow	same as before	same as before
46 (IaA)	faint yellow	none	medium chalky blue	medium chalky greenish yellow

Table II. Luminescence of the samples before and after the HPHT treatment

Infrared Spectroscopy

Infrared spectroscopy is the classical technique to classify diamonds. Mainly the observation of the nitrogen or boron related absorptions in the one phonon region between $400cm^{-1}$ and $1332cm^{-1}$ is used to do this. Pure diamond is transparent from approximately 230nm in the UV all the way to the far-infrared; this transparency is only disturbed by the intrinsic diamond absorptions due to lattice vibrations: these absorptions are found in the infrared between $1500cm^{-1}$ and $2700cm^{-1}$ which forms the two phonon region; the three phonon region extends from $2700cm^{-1}$ to about $3900cm^{-1}$.
For this study, the region from the near infrared to the mid infrared of the 7 type I diamonds were analyzed, i.e. the region from $7200cm^{-1}$ to $400cm^{-1}$, and all changes noted.

Changes of nitrogen aggregation

It was noted in all samples, that the nitrogen had changed its aggregation state to a certain degree; in the type IaA and IaA/B diamonds, the amount of B-aggregates increased while the amount of A aggregated decreased; thus the A-aggregates have formed B aggregates, although such aggregation has been predicted to occur at temperatures of ≥ 2600°C (Kiflawi and Bruley, 2000). The type Ib diamond has been nearly completely transformed into a type IaA diamond by aggregation of the single nitrogen into A-aggregates.
It appears surprising that such changes in aggregation occur after such relatively short HPHT annealing, thus it appears that in the case of these brown diamonds, the nitrogen aggregation must have been enhanced. It may be proposed that the high concentration of dislocations and

other defects in the brown diamonds are the reason for this aggregation at “low” temperature. A similar effect has been described by Collins et al. (1999): it was described, that A-aggregates could be formed in type Ib synthetic diamonds at temperatures as low as 1500°C, when the stones were irradiated prior to heating; the temperatures indicated for the formation of A aggregates out of single nitrogen in untreated synthetic diamonds are in the proximity of 2000°C.

Effects on other defect induced absorptions

It has been described before, that a defect called the “amber center” was eliminated by HPHT treatment; the main peak of this complicated structure was described to be at 4165cm^{-1} in type I brown diamonds by Du Preez (1965); during the extensive research of brown diamonds by Fritsch, Massi, Hainschwang and Notari, it was found that the main peak of this defect (the peak will be further referred to as the “amber center”) was not only found at 4165cm^{-1} but at several different positions varying from 4070cm^{-1} to 4165cm^{-1} (see box A). It was found during the HPHT experiment, that all these peaks were eliminated by the treatment; apparently, the “amber center” is very closely related to the brown coloration of diamonds. During earlier work on the amber center, it was found that it could be correlated either to the presence of C-centers or A-centers of nitrogen; B-centers were found not to be involved in this defect, since pure type IaB brown diamonds do not exhibit the amber center. Also, type IIa diamonds do not show this absorption. The A-aggregate or the neutral single nitrogen impurity combined with the defect, which is responsable for the brown color in diamond, are thus probably causing the amber center absorption.

The reduction of the platelet peak, which can be found in the vicinity of ~1360cm^{-1}, has been reported before (e.g. Reinitz et al., 2000); this peak has been ascribed to a large structure made up of carbon and nitrogen (probably present as impurities), and the shift in position from 1358cm^{-1} to 1380 cm^{-1} has been explained by the variable size of the platelets, which has been measured by Transmission Electron Microscopy (TEM).

Other defects, which were reduced or eliminated, include some of the hydrogen related features like the 3307, 4494, 4667 and 1405 cm^{-1} absorptions. The 1430 cm^{-1} absorption seen in one sample was also reduced. In sample 18, a type IaA/B diamond with a very strong platelet peak, an absorption at 1480 cm^{-1} was formed by the HPHT treatment (Fig. 2). This feature has not been observed in untreated diamonds yet. In sample 7, a pure type Ib diamond before HPHT, the bands seen in the diamond intrinsic at 3474 cm^{-1} and 3360 cm^{-1} were eliminated (Fig. 1).

In the spectrum of the CO_2 diamond, practically no changes were observed. In the “Pseudo-CO_2” diamond, a peak at 2415 cm^{-1} was formed and the broad band around 650-400 cm^{-1} was strengthened. The 2415 cm^{-1} peak could possibly be due to the formation of CO_2 in this diamond; in CO_2 diamonds this peak has been found between 2390 and 2355 cm^{-1}.

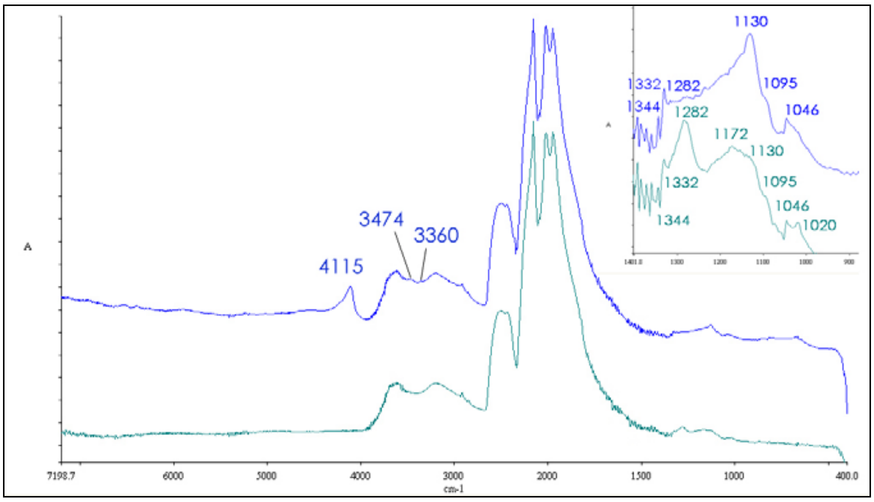


Fig. 1. The FTIR spectrum of Sample 7, a brown type Ib diamond, before (blue trace) and after HPHT (green trace)

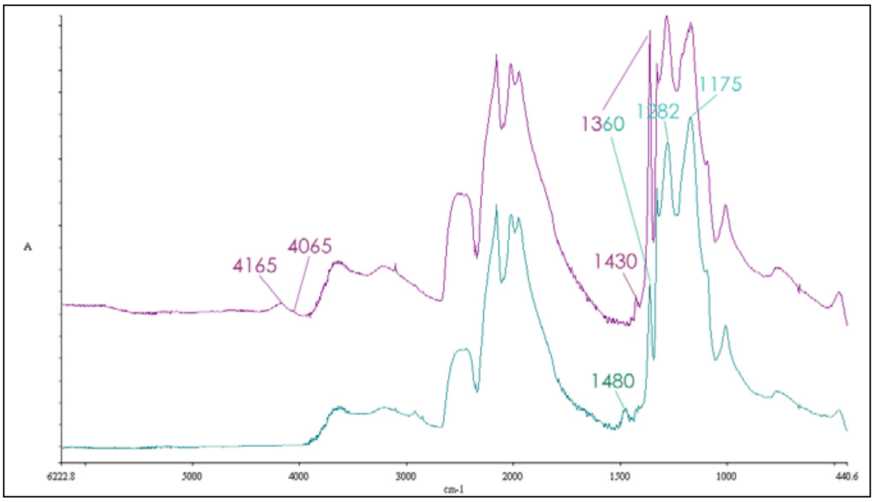


Fig. 2. The FTIR spectrum of Sample 18, a brown type IaA/B diamond, before (purple trace) and after HPHT (teal trace)

Sample		Peak position, cm^{-1}										Type
7	BEFORE				4115		3474, 3360					Ib
7	AFTER				none		none					IaA, some b
10	BEFORE			4165		4065			1430	1405	1370 medium	IaA
10	AFTER			none		none			none	1405	1370 weak	IaA, some B
18	BEFORE			4165				none	1430		1360 strong	IaA/B, A>B
18	AFTER			none				1480	none		1360 weak	IaA/B, A<B
22	BEFORE	4668	4494	4165					1430	1405	1362 strong	IaB, some A
22	AFTER	none	none	none					none	none	1362 weak	IaB, less A
46	BEFORE			4165							1360 medium	IaA
46	AFTER			none							1360 very weak	IaA, some B
30	BEFORE						none		615 weak		1360 medium	IaA/B, A>B “Pseudo CO_2”
30	AFTER						2415		615 medium		1360 weak	No changes Co_2 (?)

Table 3. Observed major changes in the FTIR spectra of the analyzed samples (CO_2 not included: no changes observed)

VIS/NIR Spectroscopy

Background

UV-VIS-NIR spectroscopy is a very useful technique to detect absorptions due to electronic transitions in diamonds of which most occur in the region of 190 to ~1200 nm. Pure diamond is a covalent semiconductor with a large bandgap and thus colorless. The bandgap is reduced by impurities such as nitrogen and boron and electronic transitions become allowed; therefore diamonds with such impurities absorb light in the visible range and can appear distinctly colored. A very large amount of electronic transitions has been described in diamond and the observation of UV-Vis-NIR spectra, especially at low temperature, was found to be a very useful technique to characterize natural, treated and synthetic diamonds. This is also the case for HPHT treated diamonds: many defects are strengthened or created by this treatment, some of which appear rather characteristic for the treated material. The formation of strong H3 and H2 absorptions has been reported in previous publications (e.g. Collins et al., 2000).

Results

The VIS/NIR spectra of the brown diamonds before the treatment were split into the following types:
Ia ⇨ very weak to undetectable N3, very weak H3, 560nm band
Ib ⇨ distinct NV^- center absorptions, 560nm band

CO_2 and "Pseudo CO_2" ⇨ continuous absorption without distinct absorption bands
After the HPHT treatment, weak to strong N3, H3 and H2 absorptions were formed in all samples except the CO_2 and "Pseudo CO_2" diamonds. In the samples with distinct to strong H2 absorption, a peak at 871nm was observed (Fig. 3).

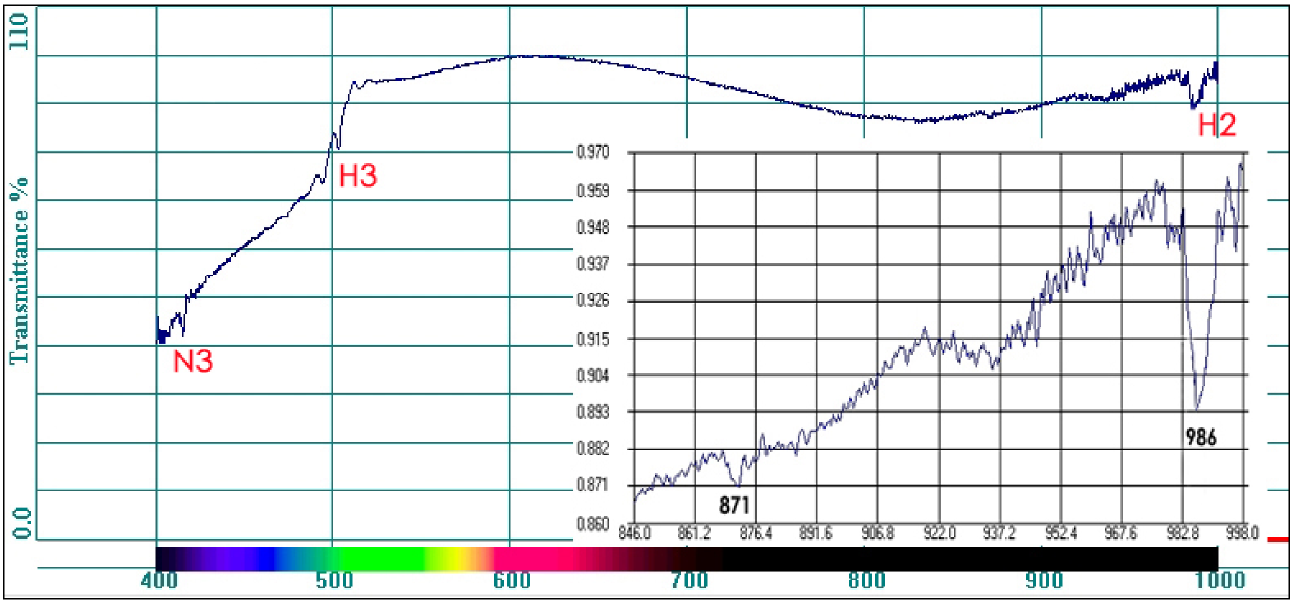


Fig. 3. The Vis/NIR spectrum of Sample 46, a brown type IaA diamond, after HPHT with a typically strong H2 center.

Besides a distinct N3 absorption, the H3 and H2 defects were weak in sample 10, which represents an olive-brown diamond of type IaA. Only a weak H2 center combined with distinct H3 and N3 was present in sample 22, a near-pure type IaB brown diamond.
An interesting "transformation" was observed in sample 7, a pure type Ib brown diamond: the distinct absorptions at 620, 637 and 667nm due to the NV^- center were very strongly reduced while rather strong H3 and and H2 defects were formed; very surprising was the presence of a rather strong N3 peak at 415 nm after the HPHT treatment (Fig. 4)- apparently the N3 aggregates were directly formed out of the C-centers, a phenomenon previously described, but at much higher annealing temperatures of ~2600°C.

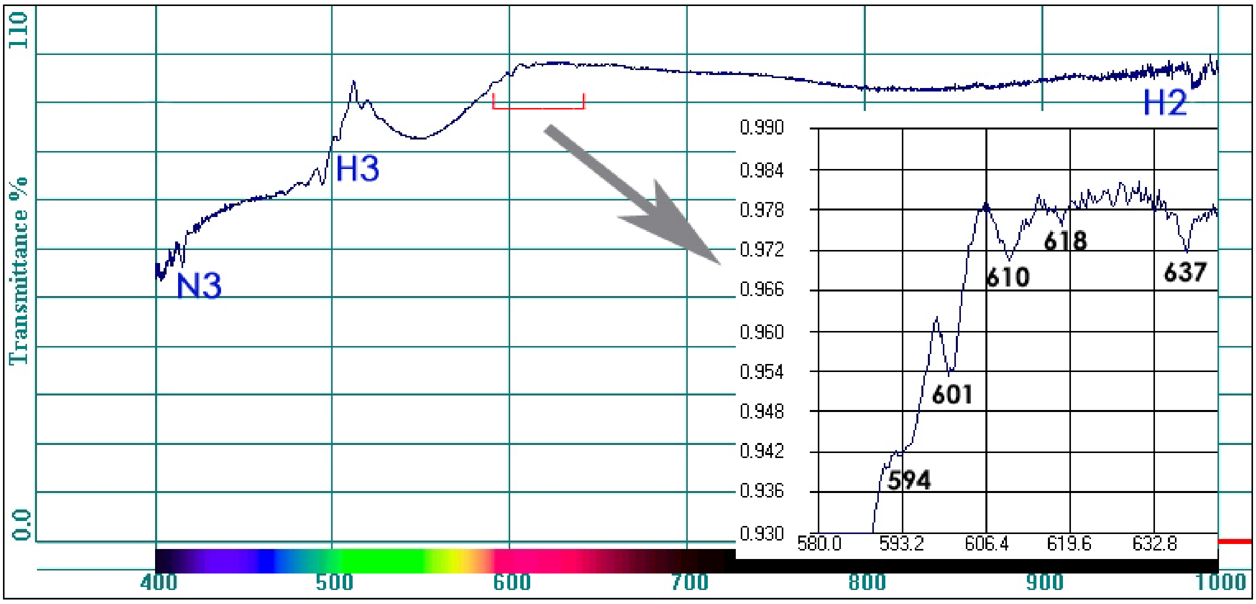


Fig. 4. The Vis/NIR spectrum of Sample 7, a brown type Ib diamond, after HPHT. The spectrum before exhibited only a distinct NV^- center; the aggregation of the single nitrogen produced H3, H2 and very surprisingly distinct N3 absorption.

Sample		Peak position, nm																
7	BEFORE								560					620	637	667		
7	AFTER	415	473	485	494	503	515	525	560	594	601	610	618		637		871	986
10	BEFORE	415 weak				very weak H3			560									
10	AFTER	415			494	503	515										871	986
18	BEFORE	415 weak				very weak H3			560									
18	AFTER	415	473		494	503	515	525	560								871	986
22	BEFORE	415 weak				very weak H3			560									
22	AFTER	415	473	485	494	503	515	525	560									986
46	BEFORE	415 weak				very weak H3			560									
46	AFTER	415	473		494	503	515	525	560								871	986

Table IV. The changes observed in the Vis/NIR spectra of the analyzed diamonds (CO_2 and "Pseudo CO_2" not included: no changes observed)

Photoluminescence Spectroscopy

Background

Before the appearance of HPHT treated diamonds in the late 1990's, photoluminescence (PL) spectroscopy was a rarely used technique in gemology. It was found that PL spectroscopy at low temperature could supply important clues to identify HPHT treated diamonds, thus PL systems became invaluable tools for the analysis of diamonds. Photoluminescence spectroscopy has the advantage that it is much more sensitive to certain defects in diamonds; for example, the smallest amounts of NV- centers and defects due to nickel or nickel-nitrogen can be detected by PL, even when they are far from being detectable by VIS/NIR spectroscopy. Besides, many defects which are not seen in VIS/NIR spectroscopy can be detected by Photoluminescence.

Results

Before the treatment, the emission of the brown diamonds was mostly very weak, when they were excited by the green laser; the only exception was the Ib diamond, which exhibited very strong photoluminescence. The peaks observed in the brown diamonds were mostly described before (Fig. 5), except some of the features present in the CO_2 and "Pseudo-CO_2" diamonds.
Many of these emissions have been ascribed to brown diamonds but not explained so far (see e.g. Smith et. al., 2000). The NV$^-$ center peak at 637 nm was present in most samples, but it was always very weak, except for the type Ib diamond.
After the HPHT treatment, all type Ia samples (except the CO_2 and "Pseudo-CO_2" diamonds) showed PL spectra characteristic for type Ib diamonds with a very strong NV$^-$ emission at 637nm and peaks at 659 and 681nm (Fig. 6); in contrast, the NV$^-$ emissions in sample 7, the Ib diamond, were reduced.
Some other emissions were formed, which have not been described before, such as the 926 nm peak in sample 10 (Fig. 6). Except for the reduction of certain emissions, no dramatic changes were observed in the PL spectra of the CO_2 and "Pseudo-CO_2" diamonds.

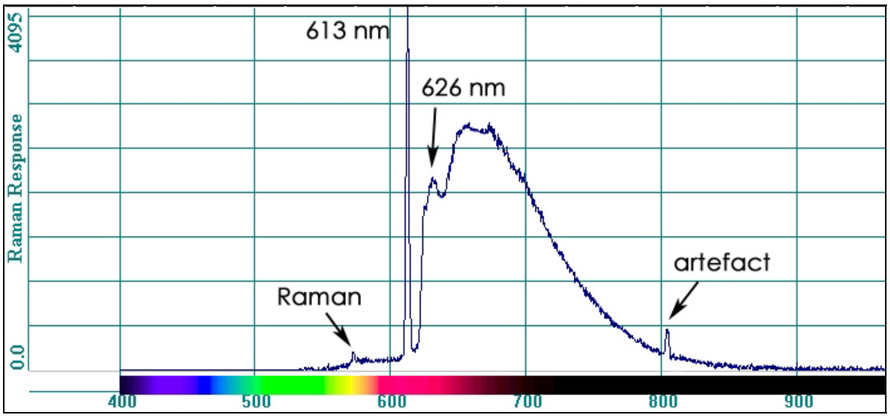


Fig. 5. The PL spectrum of Sample 10, an olive-brown type IaA diamond, before HPHT

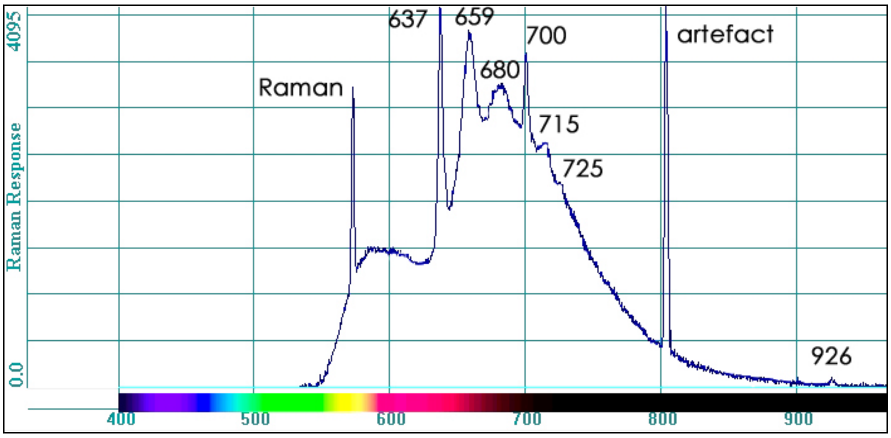


Fig. 6. The PL spectrum of Sample 10 after HPHT. The spectrum indicates a clear type Ib character

Sample		Peak position, nm																				
7	BEFORE			587		600				620		637		659	681		700				
7	AFTER	566	575	587		600	602	605				637		659	681			707			
10	BEFORE								613		626		652			691					
10	AFTER											637 strong		659	681		700		715	725	926
18	BEFORE		575		596				613		626	637 weak									
18	AFTER		575									637 strong		659	681			707			
22	BEFORE		575			600			613	620		637 weak									
22	AFTER		575	588	596		602			620		637 strong		659	681			707			
46	BEFORE		575			600			613			637 weak		659	681						
46	AFTER		575									637 strong		659	681			707			

Table V. The changes observed in the PL spectra of the analyzed diamonds (CO$_2$ and “Pseudo CO$_2$“ not included: no changes observed)

Discussion

The results of the HPHT treatment of brown diamonds has been described before (e.g. Reinitz et al., 2000); the stones included in these works were mostly typical brown diamonds of type Ia or IIa, which either turned greenish yellow or colorless after HPHT. This work, in contrast, included only diamonds, which represent various classes, predetermined by standard and advanced gemological analysis. Some of the observed results were described in these previous papers while others have not been published before.

FTIR spectroscopy

The changes of the IR features were most interesting; aggregation changes of the nitrogen were observed; typically, A aggregates started to transform into B aggregates, while C centers were transformed into A aggregates. The C center – A center aggregation was found to be nearly complete in the type Ib brown diamond while only relatively little of the A centers were transformed into B centers in all analyzed type Ia diamonds. This complete transformation of C centers into A aggregates has been seen in HPHT treated synthetic diamonds by one of the authors (TH). The changes of nitrogen aggregation has limited influence on the observed color changes and mainly the production of single nitrogen as a side product of A to B center aggregation (Kiflawi and Bruley, 2000) may enhance the yellow coloration of the HPHT treated diamonds.

The amber center was one of the main features of interest- its main peak has been described at 4165 cm^{-1} by Du Preez (1965) and recently by other authors (e.g. Hainschwang, 2003). It was noted that the amber center and related peaks were always eliminated by HPHT. Since the amber center peaks were found to be related to the A-center in type Ia and to the C-center in type Ib brown diamonds, the amber center absorption may be caused by these forms of nitrogen "aggregated" with the defect responsible for the brown coloration of diamond. If the brown color is indeed caused by graphitic or amorphous carbon, a combination of this sp2 bonded carbon and the A- respectively the C-center may cause this feature; recrystalisation of the sp2 carbon into sp3 carbon by HPHT treatment will accordingly eliminate the amber center peaks, which would explain our findings.

VIS/NIR spectroscopy

The observed strengthening of the H3 center and the formation of H2 are well known effects of the HPHT treatment. In our samples, weak to strong H3 and H2 were always present, except in the CO_2 and "Pseudo CO_2" diamonds. The formation of H2, which is the negative charge state of the H3 center, is believed to be caused by an electron transfer from single substitutional nitrogen to H3 centers (Buerki et al., 1999); in the case of the HPHT treatment, substantial amounts of single nitrogen appear to be produced as a by-product of the A to B center formation or simply by dissociation of the A-aggregates.

Also clearly visible was the strengthening of the N3 absorption at 415 nm, which was generally weak or even undetectable before the treatment. Most interesting is the fact that the type Ib diamond, which was transformed into a IaA stone, exhibited a rather strong N3 absorption post HPHT treatment; in this case it appears highly improbable, that the N3 aggregates were formed as a side product of A to B aggregation (Kiflawi and Bruley, 1999) since no B-aggregates were formed and it appears as if the N3 was formed directly during the C- to A-center aggregation. Mainwood (1994) suggested that the B-aggregates are formed by a dissociation of A-aggregates into single nitrogen, which then migrates to form the B aggregate. It was then suggested by Kiflawi and Bruley (1999) that the N3 defect is formed as an intermediate product of this aggregation. In this particular stone it may be suggested that a combination of A-aggregate and single nitrogen have led to N3 formation.

The general formation of N3 and H3 has in all stones some influence on the observed color; N3 will add a yellowish tint while H3 will add a greenish hue due to the green luminescence produced by this defect. H2 absorption, if sufficiently strong, will give a green hue to a diamond (Collins, 2000); our samples did not have strong enough H2 absorptions to exhibit green face up color (which is not caused by H3 emission).

Photoluminescence spectroscopy

Photoluminescence has clearly shown that a non-negligible amount of single nitrogen was formed in the type Ia diamonds by the HPHT process. All stones which showed typical "brown diamond PL spectra" had spectra characteristic of type Ib diamonds post HPHT; thus a very strong Ib character in PL, with strong NV^- and weak NV^0 emission, is typical for most of such treated diamonds. We have seen other HPHT diamonds which did not exhibit such an extreme Ib character; such stones are difficult to identify and show spectra very much like natural green transmitters with strong NV^0 absorption at 575 nm and generally a weaker or absent NV^- center with its ZPL at 637 nm (Fig. 8).

In the type Ib diamond, the NV^- center emission was reduced due to the formation of

A-aggregates out of the single nitrogen.

Peaks at 602 and 605 nm and 715, 725 and 926 nm were seen in some samples and have not yet been observed in any untreated or otherwise treated diamonds.

Comparison with a known natural "green transmitter"

We found one diamond of yellow color and strong green luminescence/transmission luminescence, which unambiguously is of natural color: the stone was found to exhibit a 741 nm peak in its Vis/NIR- and photoluminescence spectrum when recorded at 77 K (Fig. 8); This absorption/emission is caused by the neutral vacancy induced by natural and laboratory radiation, and this peak is reduced and consequently eliminated at rather low temperatures of 400 to 800°C, thus cannot be found in an HPHT treated diamond.

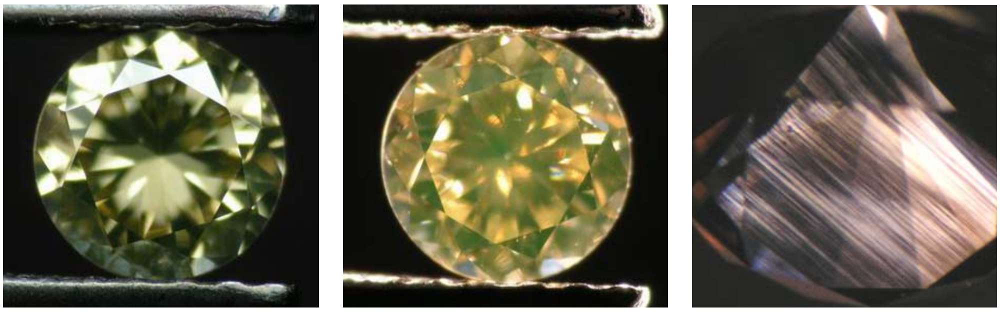


Fig. 7. The natural green transmitter as seen in daylight (left), in transmitted light (center) and between crossed polarizers (right)

The stone was characterized as a very low nitrogen containing type IaA/B diamond with B>>A by FTIR spectroscopy; the diamond exhibited a strong tatami pattern (Fig. 7, right), with very little low order interference color when viewed between crossed polarizers; this pattern is characteristic for type IIa diamonds but can also be found in some low nitrogen type Ia diamonds such as this stone. The Vis/NIR spectrum showed very weak N3 absorptions, strong H3, a weak but distinct GR1 absorption at 741 nm but no H2 center (986 nm). This stands in contrast to the lack of GR1 and the usually present distinct to strong H2 center absorption in HPHT treated type Ia diamonds. The Photoluminescence spectrum exhibited a very distinct emission at 741 nm besides a very strong 575 nm peak due to the neutral NV-center; a comparison with a treated "green transmitter" shows that the PL spectra can be extremely similar; in this case only the GR1 damage absorption differentiates the two spectra (Fig. 8). Unlike the samples analyzed for this study, this treated stone exhibited a very dominant 575 nm emission while the negatively charged NV center peak at 637 nm was extremely weak; in all our samples the opposite was the case, thus 637 nm >> 575 nm. Apparently the ratio of NV^0 to NV^- is not characteristic to distinguish natural and HPHT treated diamonds. The presence of a GR1 damage in such a diamond of natural color is most probably the exception, but if present can be used to prove natural color origin.

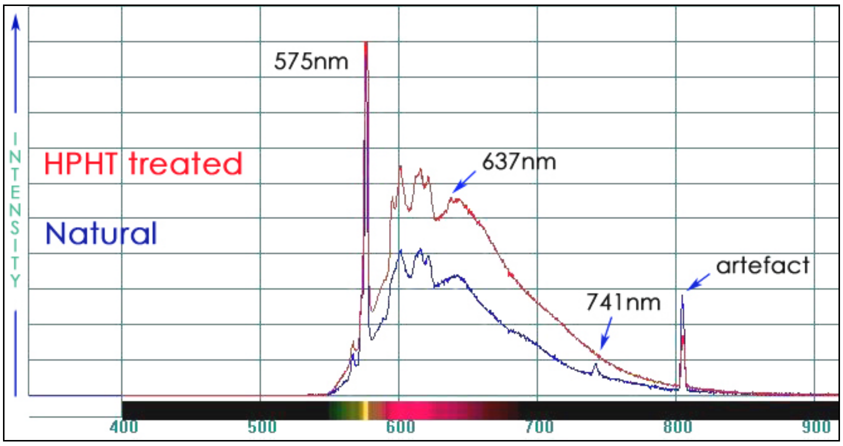


Fig. 8. The PL spectra of a natural (blue trace) and a HPHT treated diamond (red trace) with green transmission luminescence

Conclusions

The present paper has shown that all classes of type I brown to olive-brown diamonds do exhibit a change of color after HPHT annealing. The only exceptions are type I diamonds of the CO_2 and "Pseudo CO_2" classes; such stones stay practically unaffected by the treatment.
The other stones have all a strongly reduced brown color and appear in various shades of yellow, greenish yellow or orangy/pinkish yellow after HPHT.
The reduction of all "amber centers" in the IR spectra is apparent and the defect is thus most probably directly related to the cause of the brown coloration in diamond.
From a gemological standpoint, it can be stated, that a diamond with a type IaA/B infrared spectrum with an apparently unusually weak platelet peak and a "type Ib" PL spectrum with 637 nm >> 575 nm, is highly suspicious of having undergone HPHT treatment. If additionally H2 absorption is visible in the Vis/NIR spectrum, HPHT treatment must be assumed. The presence or absence of the H3 absorption cannot be used as an indication for the HPHT treatment. Peaks at 602 and 605 nm and 715, 725 and 926 nm in the PL spectrum and/or absorptions at 594, 601, 610 and 618 nm in the VIS/NIR spectrum may also be indicative for this treatment, but these defects appear to be rather the exception than the rule. In rare cases, especially at higher annealing temperatures of 2200 to 2400°C, we observed 1344 cm^{-1} peaks due to single substitutional nitrogen together with A-and B-aggregates; the presence of A-, B-, and C-center absorptions in one stone have not yet been observed in natural diamonds and are thus a clear indication for HPHT treatment. By far most HPHT treated "green transmitters" exhibited very strong high order interference colors between crossed polarizers.
Although in the samples treated for this study, the negatively charged NV-center was always clearly dominant in their PL-spectra, this was not true for all stones seen to date and some stones exhibited a faint 637 nm NV^- peak while the 575 nm NV^0 peak was very strong. Since HPHT treated stones without H2 absorption and without other clear indications for the treatment are sometimes seen, it is difficult to define characteristics for the natural origin of a diamond with strong green luminescence and transmission. At this point, it can be stated, that a diamond exhibiting GR1 damage besides the typical characteristics for natural "green transmitters" is most certainly of natural coloration. Other indications for natural origin are:
⇨ strong platelet peak in the IR spectrum.
⇨ No H2 absorption (very weak H2 may be present [Chalain, pers. comm. 2003]).
⇨ Strong 575 nm emission and lack of 637 nm emission in PL (only in combination with other indications).
⇨ Lack of high order interference colors when viewed between crossed polarizers.
Of course, many more diamonds of known natural origin must be analyzed to give conclusive characteristics of such stones.

References

Buerki P.R., Reinitz I.M., Muhlmeister S., Elen S. (1999) Observation of the H2 defect in gem-quality type Ia diamond. Diamond And Related Materials, Vol. 8, pp. 1061 – 1066.

Collins A.T., Kanda H., Kitawaki H. (2000) Colour changes produced in natural brown diamonds by high-pressure, high-temperature treatment. Diamond And Related Materials, Vol. 9, pp. 113 – 122.

Du Preez L. (1965) Electron paramagnetic resonance and optical investigations of defect centres in diamond. A thesis presented to the department of physics in the faculty of science, University of the Witwatersrand, Johannesburg.

Ewels C.P., Wilson N.T., Heggie M.I., Jones R., Briddon P.R. (2001) Graphitization at diamond dislocation cores. Journal Of Physics: Condensed Matter, Vol. 13, pp. 8965 – 8972.

Hainschwang T. (2003) Classification and Color Origin of Brown Diamonds. Diplôme d'Université de Gemmologie (DUG), presented at the University of Nantes/France.

Kiflawi I., Bruley J. (2000) The nitrogen aggregation sequence and the formation of voidities in diamond. Diamond And Related Materials, Vol. 9, pp. 87 – 93.

Kolodzie A.T., Bleloch A.L. Investigation of band gap energy states at dislocations in natural diamonds. Cavendish Laboratory, University of Cambridge, Cambridge, England.

Reinitz I.M., Buerki P.R., Shigley J.E., McClure S.F., Moses T.M. (2000) IDENTIFICATION OF HPHT-TREATED YELLOW TO GREEN DIAMONDS. Gems&Gemology, Vol. 36, No. 2, pp. 128 – 137.

Schrauder M., Navon O. (1993) Solid carbon dioxide in a natural diamond. Nature, Vol. 365, pp. 42 – 44.

Smith C.P., Bosshart G., Ponahlo J., Hammer V.M.F., Klapper H., Schmetzer K. (2000) GE POL DIAMONDS: BEFORE AND AFTER. Gems&Gemology, Vol. 36, No. 3, pp. 192 – 215.

Wilks E.M., Wilks J. (1991) Properties and Applications of Diamond. Butterworth-Heinemann, Oxford, 525 pp.

Zaitsev A.M. (2001) Optical properties of Diamond: a Data Handbook, Springer, Berlin.