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CLASSIFICATION AND COLOR ORIGIN OF BROWN DIAMONDS

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Abstract

Natural diamonds of brown color, including modified brown colors such as pinkish, olivish, yellowish and orangish brown were examined. The gemological, spectroscopic and microscopic properties of 63 brown diamonds, preselected out of 900 diamonds by FTIR spectroscopy, were determined.
9 different groups, some of which have apparently different color origins, were found and a classification based on spectral, gemological and microscopic properties has been established; most interesting for this classification was the observation of the defect induced one phonon region and the NIR region between 4000 cm^{-1} and 7200 cm^{-1}. The NIR region revealed differences which characterize many of the brown diamonds; this includes peaks at various positions between 4065 cm^{-1} and 4165 cm^{-1} which all appear to be related to the defect which is responsible for the brown coloration in diamonds. The absorption found at 4165 cm^{-1}, which is the most common one, has been described before and is the strongest absorption of the so-called amber center (ac) (DuPreez, 1965). Thus the classification was divided into two groups, one including the classes "exhibiting an amber center" and one with the classes "exhibiting no amber center". The group with amber center consists of 3 classes while the group without amber center consists of 6 classes.

The 3 classes with amber center were characterized as follows:

1) Typical brown (type Ia) ⇨ 4165 cm^{-1} peak, brown graining
2) Double amber center (type Ia + Ib) ⇨ 4165/4065 cm^{-1} peak, brown and olive graining
3) "Regular" type Ib ⇨ 4115 cm^{-1} peak, quite homogeneous color distribution

The 6 classes without amber center were characterized as follows:

4) "Orange-brown" group (type Ia+Ib) ⇨ No ac, Brown color modified by orange, only little graining if any
5) Typical brown, type IaB pure ⇨ No ac, brown graining
6) "Extreme" type Ib ⇨ No ac, high single N content, no graining
7) Type IIa ⇨ No ac, practically no 1 phonon absorption, often little or no graining
8) Solid CO$_2$ ⇨ No ac, 2390 and 645cm^{-1} absorptions, color patchy distributed
9) "Pseudo-CO$_2$" ⇨ No ac, lack of 2390 and 645 cm^{-1} absorptions, color patchy with sometimes some graining

Under crossed polarizing filters all stones except the CO$_2$ and "Pseudo-CO$_2$" diamonds showed strong anomalous double refraction with various amounts of strain, one "Extreme" type Ib diamond showed no strain.
It was attempted to find an explanation for the origin of the brown color of the different types by analyzing the amber center further and treating diamonds of the different groups by HPHT (High Pressure High Temperature) treatment; it was found that 5 groups appear to have very similar color origins while the remaining four groups seem to have different color origins.

1. Introduction

Brown diamonds are the most abundant colored diamonds in the earth crust. The color "brown" can be composed of various different hues and thus, is very complex. In most natural brown diamonds, the color appears to be mostly confined to sharp narrow parallel color planes, the so-called "colored graining". Until recently, the generally accepted theory for the brown coloration stated, that distortion of the crystal lattice (➔ slip systems along octahedral planes) caused by plastic deformation of the diamonds after the growth was the reason for the continuous absorption of light along the whole range of the visible spectrum (Wilks and Wilks., 1991). Doubts about this theory arose from the fact that colorless diamonds with very apparent lattice distortions exist. Perfect examples are type IIa colorless diamonds, which indeed appear to be highly strained. Also, various experiments with the High Pressure High Temperature (HPHT) treatment have shown, that the strain pattern observed before the treatment of brown diamonds did not change noticeably after the treatment (Smith et al., 2000). One would expect, that a "healing" of lattice distortions would reduce strain considerably. Thus, a more recent theory concludes, that graphitization (creation of sp2 bonded carbon) within the diamond lattice (made of sp3 bonded carbon), formed at diamond dislocation cores, is responsible for the brown coloration (graphitization with temperature, sp3 to sp2 conversion) (Ewels et al., 2001). Even more recent is a theory, which indicates that the color is not due to graphitization, but due to amorphous carbon (also sp2 bonded C) in micro domains (E. Fritsch, pers. comm. 2002). HPHT treatment would, according to this latest theory, recrystallize the amorphous sp2 bonded carbon to sp3 bonded carbon (diamond). Therefore the brown coloration would be reduced. Certain results following HPHT treatments are neither explained by the first nor by the second theory, thus, possibly a variety of color origins must be assumed.

The amazing variety of results obtained by the HPHT treatment of brown diamonds and the generally complex and little understood subject of brown diamonds lead us to undertake this present study.

2. Materials and Methods

For the present study about 900 faceted natural brown diamonds (sizes of 0.04 ct to 4.2 ct), including modified colors such as olivish brown, orangish brown, pinkish brown and yellowish brown, were analyzed by FTIR spectroscopy. Out of these 900 diamonds, a total of 43 "special cases" and 20 typical brown diamonds were selected by their IR spectrum.

These 63 stones were tested by standard gemological methods for fluorescence and phosphorescence to longwave and shortwave ultraviolet radiation; then the diamonds were analyzed with a binocular microscope fitted with crossed polarizing filters to see any strain patterns (sometimes with the diamond immersed in methylene iodide). The inclusions were observed by standard microscopy techniques using different lighting conditions. The color of the diamonds was described using 6200K daylight fluorescent lamps. To distinguish the slight color modifiers, comparison stones such as pinkish brown, olivish brown, yellowish brown and orangish brown diamonds were used. The color is described with a different, but more appropriate color language than usual:

Descriptions were made by using tone-(sometimes saturation)-modifying color(s)-dominant color(s). Saturation has little importance in the description of truly brown diamonds, since brown will never be highly saturated. A highly saturated "brown" will be orangish, yellowish or reddish. So higher saturations are only possible in strongly modified brown colors such as orange-brown or yellow-brown.

For the depth of color (tone), the following terms were used:

light • medium light • medium • medium dark • dark • very dark
Browns with strong modifying colors showing a saturated color are termed: deep
"Deep" describes a medium dark to very dark color with strong saturation.
The hue is described as follows: minor modifying color•major modifying color•minor dominant color•major dominant color
modifying colors are called: orangish, yellowish, olivish, pinkish, brownish
dominant colors are called: orange, yellow, olive, pink, brown
Olive is not a pure color, but a mix of brown, green and yellow. Nevertheles, "olive" is used as a color term in this work; some laboratories like GIAGTL use descriptions like "brownish yellow green" for such diamonds. Here it was decided to use the term "olive", since olive diamonds are a truly separate group and not even related to green and yellow green diamonds.

Examples: -a dark brown diamond with a strong yellow component and a weak olive component will be called: deep olivish yellow-brown.
-a medium brown diamond with a weak orange and a weak olive component (orange stronger than olive) will be called:
medium olivish orangish brown.

To avoid the influence of cut when it was tried to find relations between certain spectral features and the depth of color, the comparison of the depth of color was made with the diamonds table down; thus for this application the stones depth of color was established through the pavilion (in the same manner as "colorless" diamond color-grading).
The color distribution was observed by immersion microscopy using methylene iodide and diffuse transmitted light. All photomicrographs were taken by the author with an Olympus Camedia 5050 digital camera with 5 megapixels and a special adaptor for the microscope (with magnifications of 30 to 420x).
The 63 samples were then analyzed by advanced gemological testing.
IR spectra in the range 7200 to 400 cm^{-1} were recorded with a PerkinElmer Spectrum BXII FTIR spectrometer equipped with a DTGS detector, using a beam condenser, with accumulation of 100 to 1000 scans at a resolution of 4 cm^{-1} to 2 cm^{-1}. For some stones, the sample chamber was flooded with gaseous nitrogen to reduce the CO_2 and H_2O artefacts in the IR spectrum. Photoluminescence spectra were recorded with the diamonds cooled in liquid nitrogen (LN, -196°C [77K]) on an Adamas Advantage SAS2000 Raman spectrometer (resolution 1.5 nm) using a 532 nm semiconductor laser with integration times of 100 to 15'000 msec.
VIS/NIR spectra of selected stones were analyzed with the Adamas Advantage SAS2000 VIS/NIR spectrometer (equipped with an integration sphere) in the range of 400-1000 nm at room temperature and at 77K, with a resolution of 1.5 nm and 100 to 400 scans.
The cathodoluminescence images of selected brown diamonds were observed and recorded using a Jeol 5800 scanning electron microscope at the SEM facility of the IMN (Institut des Materiaux Jean Rouxel Nantes) at the University of Nantes, France.

3. Results

3.1. Visual Appearance

The 63 samples covered nearly the whole range of colors, which are found in so-called brown diamonds. These include browns modified by olive, pink, yellow and orange plus a nearly "pure" olive color. The only color, which we were unable to find, is a brown with a modifying blue color (type IIb diamond).
The observation of the minute color differences was difficult and all descriptions were made using reference stones. Especially in lightly colored brown diamonds it is

extremely difficult to observe and identify the modifying colors present. A modifying olive color, for example, is nearly impossible to see in a light brown diamond.

3.2. Color Distribution

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 planes (Fig. 1).

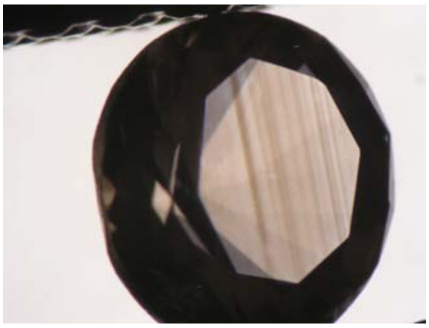


Figure 1. Brown graining (20x)

As expected, the distribution of color in our diamonds was mostly irregular, but in contrast with most previous publications, the color is not in all cases confined to the sharp narrow parallel color bands (graining). Since all diamonds included in this study were preselected by their IR spectra, we could see, that the 20 brown diamonds termed "typical" by their characteristic IR spectrum did indeed have their color confined to graining, whereas in the 43 "special cases" a portion showed a distinctly different color distribution. We were able to observe the following color distributions:

1) Color confined to sharp narrow parallel bands ("graining") along one (111) plane (octahedral) (e.g. sample 53, fig. 2)

Figure 2. Graining in one {111} direction

2) Color distributed as graining, in two {111} (octahedral) directions forming either a rhombus or square in the center (e.g. sample 25, fig. 3 (left)) or a pattern of small rhomboid figures (e.g. sample 47, fig. 3 (right))

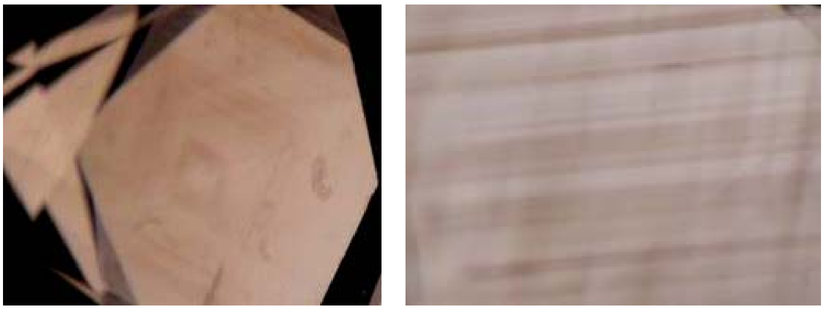


Figure 3. Graining in two {111} directions

3) Patchy irregular color distribution (e.g. sample 62, fig. 4)

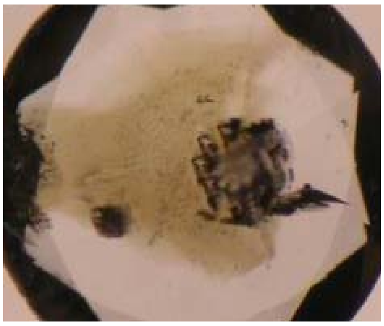


Figure 4. Patchy coloration

4) Near homogeneous color (e.g. sample 51, fig. 5)

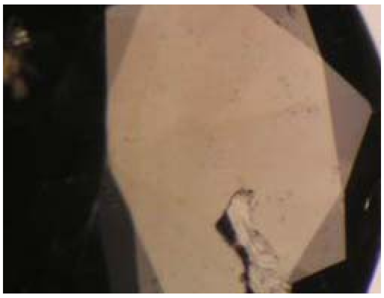


Figure 5. Near homogeneous color

5) Diffuse irregular parallel bands in two sets at 120°/60° (e.g. sample 28, fig. 6)

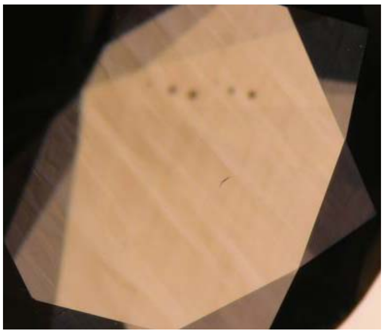


Figure 6. Unusual diffuse color bands

6) Color distributed around a cuboid shape phantom (e.g. sample 50, fig. 7)

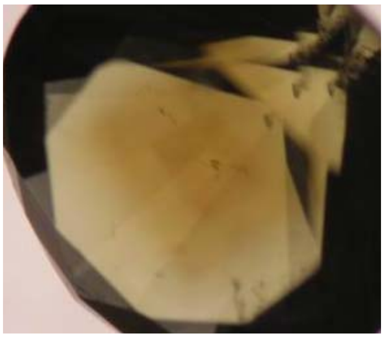


Figure 7. Color distributed in a cuboid shape

7) Color partly patchy or homogeneous, partly graining (e.g. sample 5, fig. 8)

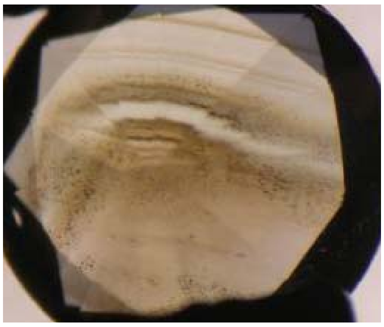


Figure 8. Graining and homogeneous color

8) Homogeneous color with some overlaying graining (e.g. sample 6, fig. 9)

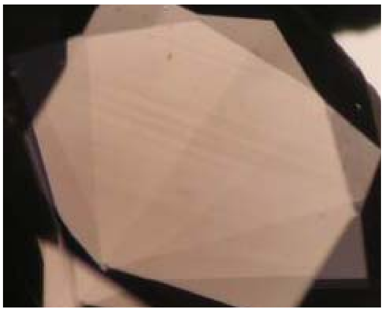


Figure 9. Graining in one {111} direction which appears to overlay near homogeneous color

The graining was observed in brown, pink, olive and in two stones in a greenish gray color. The most frequently observed pattern was brown graining in a (near-) colorless "matrix". By far most brown diamonds observed showed this typical "colored graining". Around 98% of our 800 samples had their color distributed as graining while only about 1% exhibited a patchy coloration and 1% showed the other above described color distributions.

3.3. Luminescence to UV Radiation

Fluorescence to longwave and shortwave irradiation and phosphorescence after the excitation source was shut off showed a variety of results.
The 20 diamonds belonging to the "typical group" generally exhibited weak yellow, blue or greenish blue to chalky yellow, blue or greenish blue glow, which appeared stronger under LW than under SW UV. The color of the fluorescence frequently appeared "yellowish blue" or grenish blue" and was indeed difficult to describe. Phosphorescence was not observed in these stones.
The 43 "special" diamonds exhibited various luminescent responses. A part of this group showed the same response as the "typical" diamonds, whereas the other part was distinctly different. The following emissions were observed in the 43 "special" brown diamonds:

1) Yellowish blue, blue to greenish blue luminescence, similar to "typical" group (12 stones)
2) Yellow luminescence with lasting yellow phosphorescence, LW fluorescence stronger than SW, LW phosphorescence weaker than SW (11 stones, 2 of them without noticeable phosphorescence)
3) None (inert) (11 stones)

4) Chalky blue luminescence (4 stones)
5) Reddish orange emission (3 stones)
6) Orangy yellow emission (1 stone)
7) Strong yellowish green fluorescence (1)

The strength of the luminescent glow was generally faint to weak, except for the group exhibiting the yellow fluorescence with phosphorescence- these diamonds exhibited a medium to medium strong emission, which was irregularly distributed. Also, near-pure IaB diamonds showed a medium-strong (blue) glow and the H3 center in diamond #11 causes a strong yellowish green fluorescence. The strength of the blue fluorescence in some of the analyzed brown diamonds followed the grain bands.

3.4. Observations with magnification

3.4.1. ⇨Inclusions

The observation of the internal features present in the diamonds revealed, that there are basically three types of characteristic inclusion-scenarios present:

1) Fractures ("feathers") and relatively "large" crystals (Fig.10)

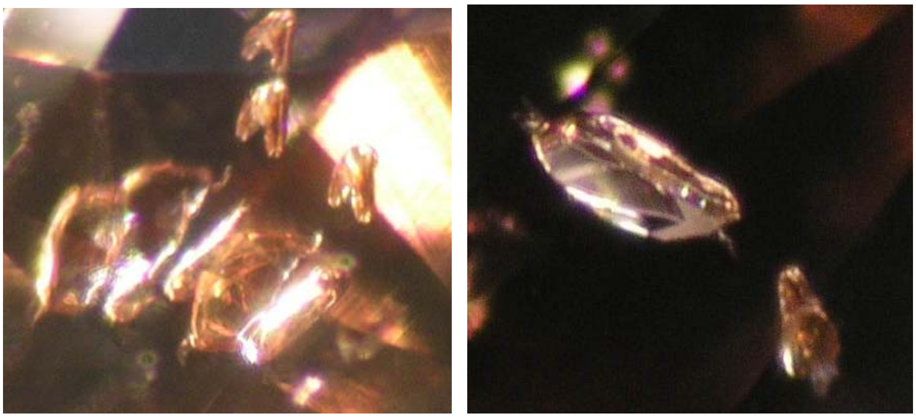


Figure 10. Crystals in a type Ia diamond

2) Large amounts of tiny reflective flakes (some with hexagonal outline) often associated with very fine needle-like inclusions (Fig. 11)

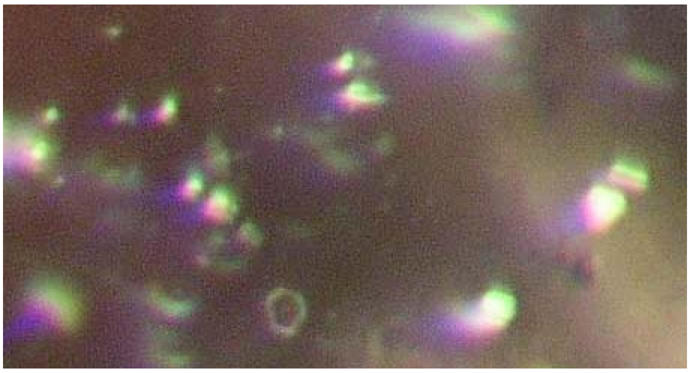


Figure 11. Reflecting particles, one with a clearly hexagonal shape

3) Tiny particles forming a phantom (Fig. 12)

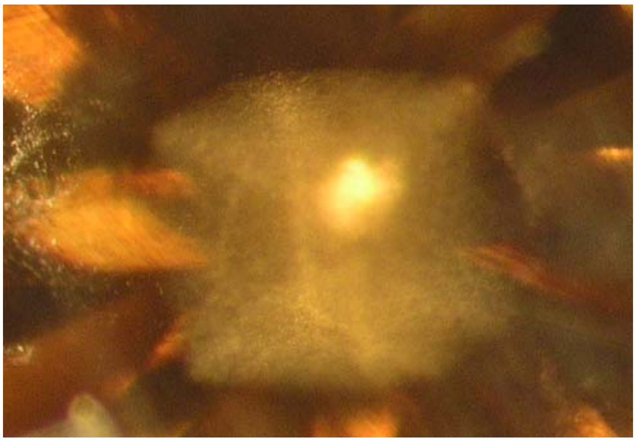


Figure 12. A cuboid phantom formed by tiny particles

The first type was observed in all of the 20 "typical" brown diamonds and some of the "specials"; by far most of these stones only contained feathers and crystals were rather rare. The second type was only seen in the "special" diamonds-it was limited to the diamonds with yellow fluorescence and lasting phosphorescence. The third type is very rare and has only been seen in some type Ib brown diamonds.

3.4.2. ⇨Pattern observed under crossed polarizing filters

Although diamonds are isotropic, they frequently exhibit anomalous double refraction (ADR), when observed under crossed polarizing filters. It has been reported, that especially brown diamonds are always highly strained (Shigley and Fritsch, 1993). Such strain will manifests itself as interference colors when a stone is viewed under crossed polarizing filters (Fig. 13). ADR can be seen as tatami and banded extinction patterns with usually the above mentioned interference colors (Smith et al, 2000). This indicates that these diamonds are not perfectly isotropic.

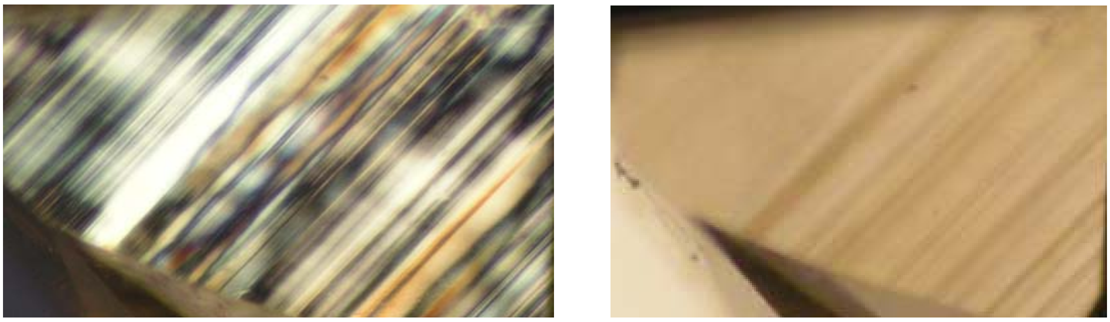


Figure 13. Strain clearly distributed along olive-brown graining (left, 30x, crossed polarizers, right, 30x, immersion)

Strain of various degrees has been observed in all 63 brown diamonds except the stones with the yellow fluorescence/lasting phosphorescence. The strain pattern was generally clearly distributed along the brown graining (e.g. sample 12, Fig. 13). In some cases, the strain was quite random though and appeared as a mottled, curved and twisting pattern (Fig. 14) without an apparent orientation.

Figure 14. Mottled strain in a dark brown diamond

The tatami pattern has been described as a characteristic feature in type IIa diamonds; it has a crosshatched appearance (parallel lines appearing as two sets intersecting each other at angles of ~120°/60°) and resembles the pattern of a Japanese straw mat- thus the name "tatami" (Koivula, 2000). Of the four type IIa diamonds included in this study, only one exhibited prominent tatami strain (Fig. 15), all others showed mixed strain patterns.

Figure 15. The "tatami" strain pattern in a type IIa diamond

3.5. Infrared Spectroscopy

As mentioned above, the 63 brown diamonds studied in this work were preselected out of 800 brown diamonds by infrared spectroscopy.

3.5.1. Background

Diamonds are divided into different types based on the presence or absence and form of nitrogen in the lattice as well as the presence of boron. Nitrogen, boron and hydrogen are the most common impurities, which substitute carbon atoms in the diamond lattice. Nitrogen, boron and hydrogen vibrations can be detected by infrared spectroscopy; for the diamond classification, the one phonon region between 400 and 1332 cm^{-1} is analyzed. The absorptions in this region define the impurity present and the state of the nitrogen. Hydrogen is detected as sharp peaks in the region between 2800 and 8600 cm^{-1} and an as an absorption at 1405 cm^{-1}.
The definitions of the different types:
Type I ⇒ contains nitrogen
    Type Ia ⇒ contains aggregated nitrogen
    Type Ib ⇒ contains single substitutional nitrogen (unaggregated nitrogen)
Type II ⇒ does not contain nitrogen
    Type IIa ⇒ does not contain any measurable amounts of nitrogen or boron
    Type IIb ⇒ contains boron but no (or only very little) nitrogen impurities
Type Ia diamonds are subdivided into IaA, IaB and IaA/B; A= A-aggregates (two neighbored N atoms), B= B-aggregates (four N atoms surrounding a vacancy).
Type Ib diamonds are often accompanied by smaller amounts of A-aggregates and

sometimes absorptions due to positively charged single nitrogen can be detected. Diamonds are believed to form initially as type Ib (i.e. single nitrogen containing). Heat during the growth causes single nitrogen atoms to diffuse through the lattice and to form aggregates. At lower temperatures or shorter periods of heating, A-aggregates form. Higher temperatures or longer periods of heating can form B-aggregates. Unlike the previous theory, that B-aggregates are formed by aggregation of two A-aggregates, today it is generally believed that the B-aggregates are formed by a dissociation of A-aggregates into C-centers (single nitrogen) and re-aggregation into B-centers. A by-product of this aggregation process seems to be the N3 aggregate, which consists of 3 nitrogen atoms surrounding a vacancy and which causes the 415 nm absorption and the associated pale yellow color (Cape series absorptions). The platelets (a large structure mainly consisting of carbon and nitrogen), which are characterized by an absorption at about ~1360 cm^{-1} are believed to be produced by the release of carbon interstitials during the A to B center aggregation. The platelets are then converted into dislocation loops and voidities (an octahedral defect containing molecular nitrogen) (Kiflawi and Bruley, 2000).

Brown diamonds are usually mixed type IaA/B or sometimes type IIa. Since type IIa diamonds are virtually nitrogen-free, it was concluded that brown diamonds do not owe their color to a nitrogen-related absorption.

3.5.2. Results

It was noticed quickly, that the majority of the analyzed stones showed an additional infrared absorption besides the expected intrinsic diamond, nitrogen and hydrogen features: this is the strongest peak of the so-called amber center, first described by Du Preez (1965); the center is a complicated structure in the NIR region (Shigley and Fritsch, 1993); the position of this main peak is at 4165 cm^{-1}. Thus the selected “typical” stones are all type IaA/B diamonds with regular brown graining and a peak at 4165 cm^{-1} (the term “amber center” will be used for the 4165 cm^{-1} absorption in this work). The 43 “special cases” include extreme “typical” brown diamonds (e.g. “pure” types➡IaA, IaB) and stones, which have apparent differences from the expected IR spectra.

Since many of the stones were very small, most spectra had to be recorded with the beam perpendicular to the table, measurements through the girdle were very difficult: since it was attempted to resolve the peaks in the NIR between 7200 and 4000 cm^{-1}, we were unable to keep the stones in the proper position with “Bluetack” without creating artefacts due to the “Bluetack”. One artefact created is precisely positioned in the region of the main amber center peak, with a maximum at 4334 cm^{-1}, and thus interferes with this feature. Thus, the accumulations were performed having relatively little energy available; due to this fact, the S/N ratio was not good enough in the NIR when this region was highly enlarged and plenty of artefacts due to interference were created. To avoid this, one stone of each group was prepared by polishing a very large culet, creating two parallel faces (table and culet); this is the preferred case to record spectra. In fact, the energy throughput obtained during the accumulation of the spectra was in the order of 10 to 50x higher when there was a large culet present; these spectra had excellent S/N ratio.

The following “typical” and “special” spectra have been defined within the three groups of “diamonds with amber center”, “diamonds with modified amber center” and “diamonds without amber center”:

3.5.2.1. Diamonds with amber center

”Typical” brown diamonds

After the observation of hundreds of IR spectra of brown diamonds, the term “typical brown diamonds” has been defined for stones with regular brown graining and the 4165 cm^{-1} absorption in the infrared portion of the electromagnetic spectrum. About 90% of the analyzed stones were of this “class”. The 4165 cm^{-1} peak alone has only been observed in type Ia diamonds with variable amounts of A and/or B aggregates (Fig. 16). The spectrum below (recorded with 1000 sample scans at 4 cm^{-1} resolution) shows a representative pattern for the regular brown diamonds; it is a type IaA/B diamond with very dominant A-aggregates and very little hydrogen (visible as the 3107 cm^{-1} absorption [Davies et al, 1984]).
In most cases, the strength of the “amber center” was directly correlated to the depth of color. For some stones, this rule could not be applied-they showed a darker color than expected for the strength of the 4165 cm^{-1} absorption (e.g. sample 48)

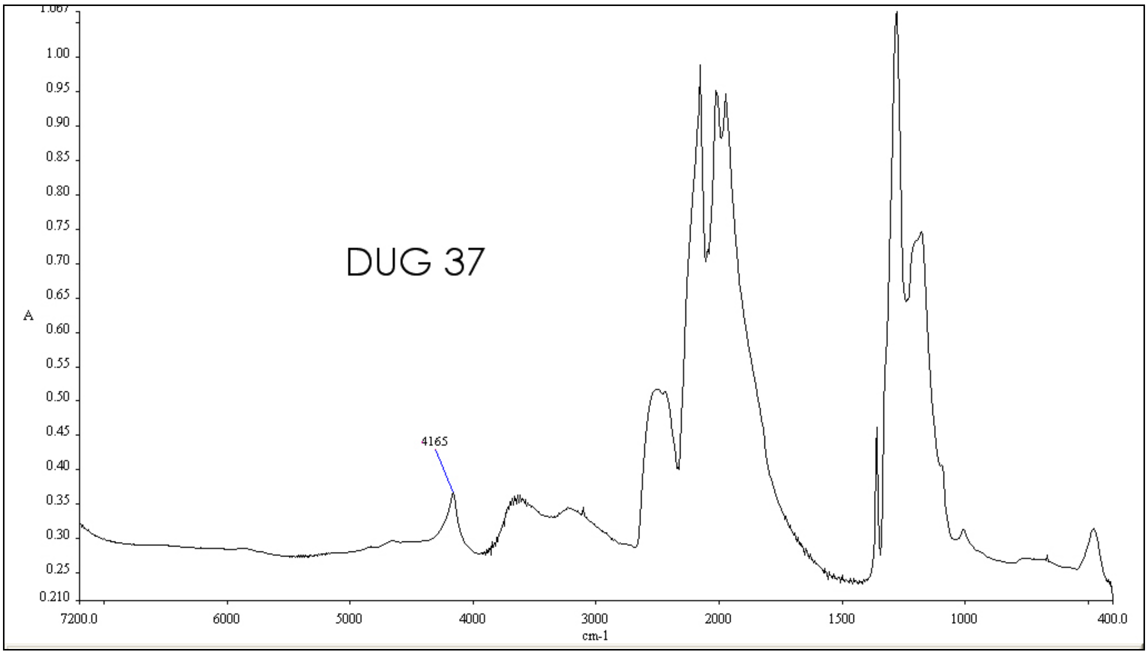


Figure 16. A very strong 4165 cm-1 amber center peak in a dark brown diamond of type IaA/B, A>>B

➨Pure or near pure type IaA diamonds with amber center

The properties and spectra of pure or near pure type IaA diamonds were analyzed separately. These stones do not differ markedly from the “regular” brown diamonds except that they often exhibit only little luminescence because the dominating A-aggregates behave as a luminescence poison. It was remarked at some point, that the (near) pure type IaA generally showed stronger amber center peaks than the other type Ia diamonds. Consequently, the dark to very dark brown diamonds were all predominantly type IaA. The spectrum below (Fig. 17) was recorded with 1000 sample scans at 4 cm^{-1} resolution with the sample chamber flooded with gaseous nitrogen (to reduce noise due to atmospheric water and CO_2 vibrations)

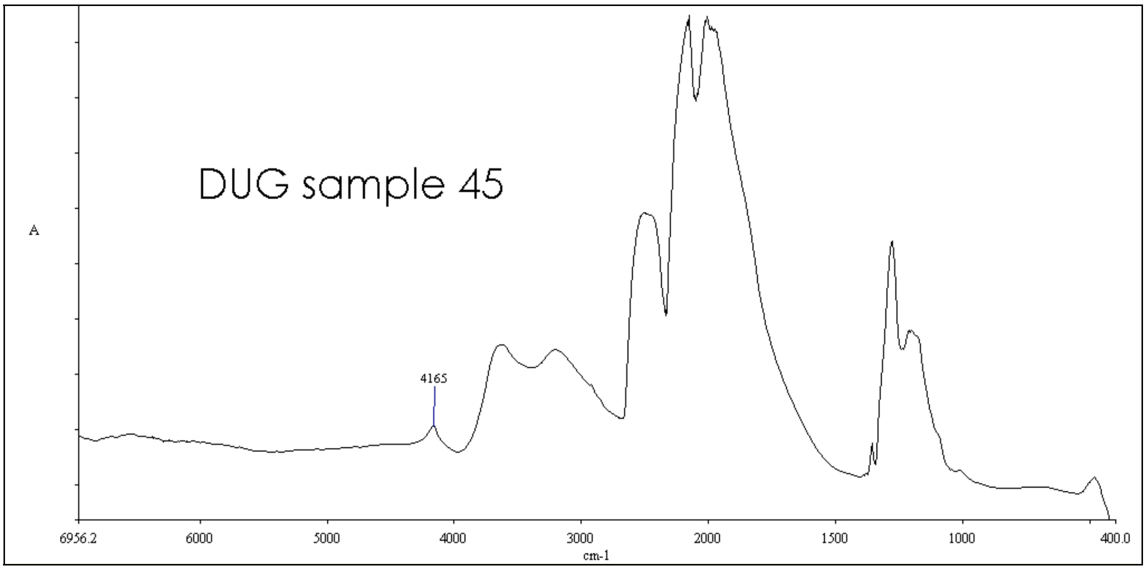


Figure 17. The distinct amber center in a near pure type IaA diamond

➡Near pure type IaB diamonds with amber center

(Near) pure type IaB diamonds were also studied separately. Except a potentially stronger luminescence, initially no difference to the "typical" group was found; a closer look at this group showed though, that all diamonds with strongly predominant B-aggregate absorptions never showed strong 4165 cm^{-1} absorption, but it was always present (Fig. 18); also, diamonds with very little A-aggregate absorption were never of dark to very dark color; they were all in the light to medium brown color range. This phenomenon will be further analyzed later, in the section where results are correlated.

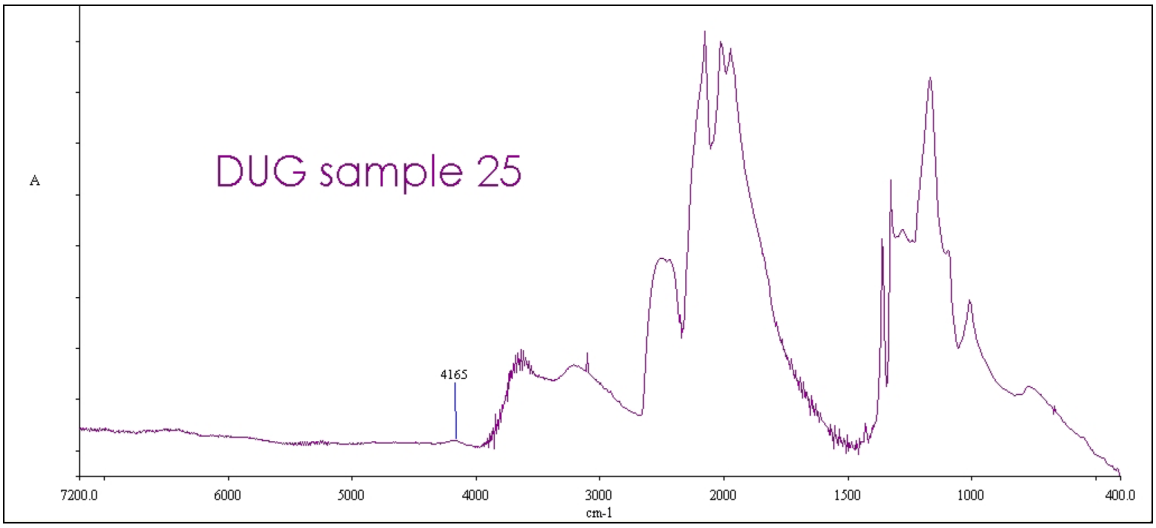


Figure 18. The amber center appears relatively weak in this near pure type IaB diamond

3.5.2.2. Diamonds with modified amber center

Besides the regular amber center peak, several stones with peaks in the vicinity of the 4165 cm^{-1} feature were found. These differed clearly in position and are described below:

➨Ia and Ib diamonds with a "double amber center" (which consists of the 4165 cm^{-1} absorption and an adjacent peak at 4065 cm^{-1})

In some diamonds we have found an additional absorption in the vicinity of the 4165 cm^{-1} amber center; the position of this adjacent peak has been established to be at 4065 to 4070 cm^{-1}. An apparent relation between color and the 4065 cm^{-1} peak was found: all stones with this feature exhibited an olive modifying color. This combination of absorptions has been observed in type Ia and Ib diamonds. The only stone of type Ib had a nearly "pure" olive color. This stone showed a strong and near-pure 4065 cm^{-1} absorption with only a very small 4165 cm^{-1} feature accompanying it (see Fig. 20). Since the olive color was found to be confined to grain bands in various diamond types, the olive color seems to be independent from the form of nitrogen, but is possibly correlated to a type Ib character of the diamonds. It is likely that the olive color has a similar origin like brown and pink; this idea is supported by the fact, that all three colors normally appear as graining and can appear simultaneously in the same stone. The first spectrum below (Fig. 19) is from a type IaA/B (with A~B) diamond with a dominant 4065 cm^{-1} peak. The stone's color was described as "dark olivish brown". The spectrum was recorded with 1000 scans at 4 cm^{-1} resolution. The double peak described here will be referred to as "double amber center" in this work. We were unable to find a direct and clear correlation between the strength of the 4065 cm^{-1} peak and the depth of the olive color, although it seems that diamonds with a pronounced olive color also have a stronger 4065 cm^{-1} peak.

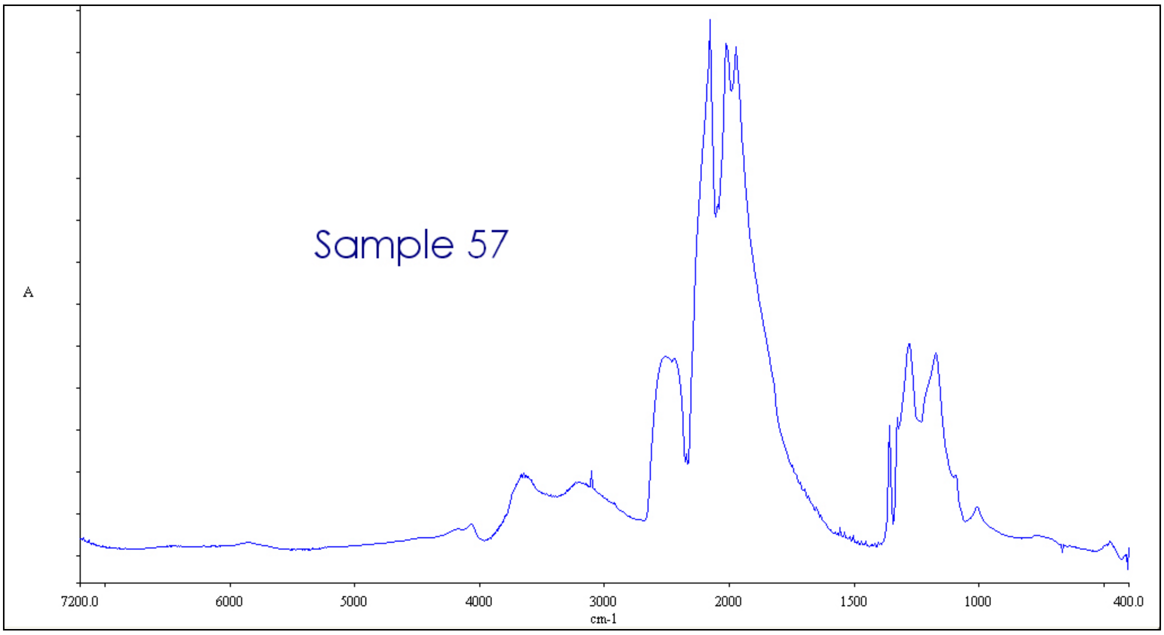


Figure 19. The spectrum of sample 57, an olive brown diamond of type IaA/B, A~B, shows a double peak at 4065 cm^{-1}/4165 cm^{-1}

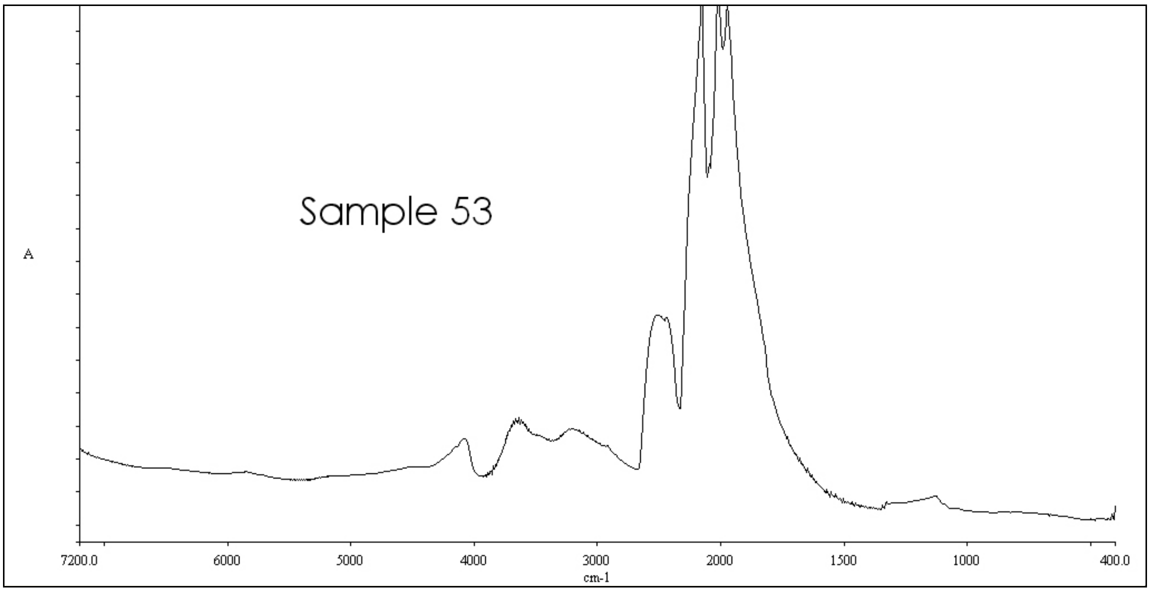


Figure 20. The IR spectrum of a "pure" olive diamond of type Ib; the peak at 4065cm^{-1} is clearly dominant

➡Ib diamonds (excluding olive diamonds)

Natural brown diamonds of type Ib (i.e. containing mainly single substitutional nitrogen) have been found to be extremely rare. Out of the 900 analyzed diamonds, we only found 5 diamonds of this type. The stones do not belong to the "dark or deep orange" group, which commonly shows a type Ib spectrum. The colors observed can indeed be categorized as a common brown, except for sample 61, which exhibited a strong modifying orange to red color. This stone represents a special case in and of itself and no known comparison or reference could be established. The spectrum below appears to be typical for regular medium brown type Ib diamonds; these diamonds show a quite strong absorption at 4115 cm^{-1} which appears not to be directly related to the color of the diamond; besides a small peak in the diamond intrinsic absorption at ~3455 cm^{-1} can be seen (Fig. 21). The single nitrogen absorption complex between 1344 cm^{-1} and 1130 cm^{-1} is generally not very strong and intense peaks at 1130 cm^{-1} are extremely uncommon.
The spectrum was recorded with 1000 sample scans at 4 cm^{-1} resolution.

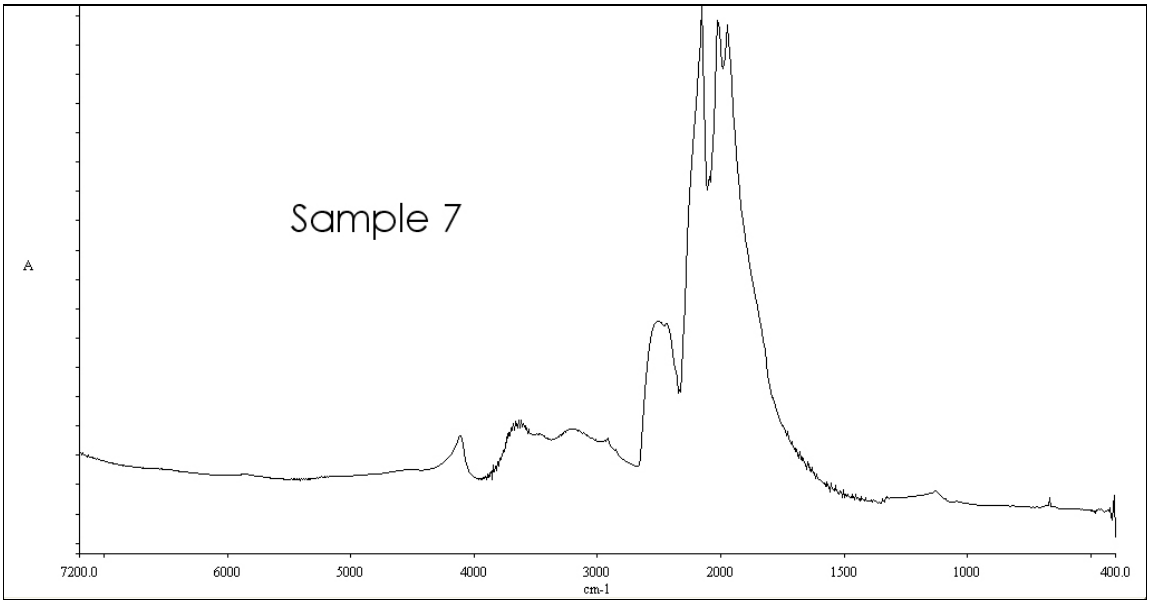


Figure 21. The IR spectrum of a type Ib diamond of "regular" medium brown color; a peak at 4115 cm^{-1} is obvious

Type Ib "extreme" (sample 50)

The following IR spectrum (Fig. 22) represents the exception rather than the rule. The amount of single nitrogen in this stone is extraordinarily high and additional absorption features than the ones found in "regular" type Ib brown diamond were found. Sample 50 is a type Ib/aA diamond with a very strong absorption at 3455 cm^{-1}, a peak at 4934 cm^{-1} and a strange "amber center" at 4238/4065 cm^{-1}. The color of this stone was described as "dark olivish orangish brown". Once again, we see the 4065 cm^{-1} peak in a stone with an olive color modifier. The peak at 4934 cm^{-1} is surprising, since it corresponds to the H1b defect, which is due to the combination of the A aggregates and the 594 nm defect; it is thought to be only caused by irradiation followed by annealing to high temperatures. Thus we cannot rule out, that this stone has been treated.
The spectrum below was recorded with 250 sample scans at 4 cm^{-1} resolution with the sample chamber flooded with gaseous nitrogen (to reduce noise due to water and CO_2 absorptions)

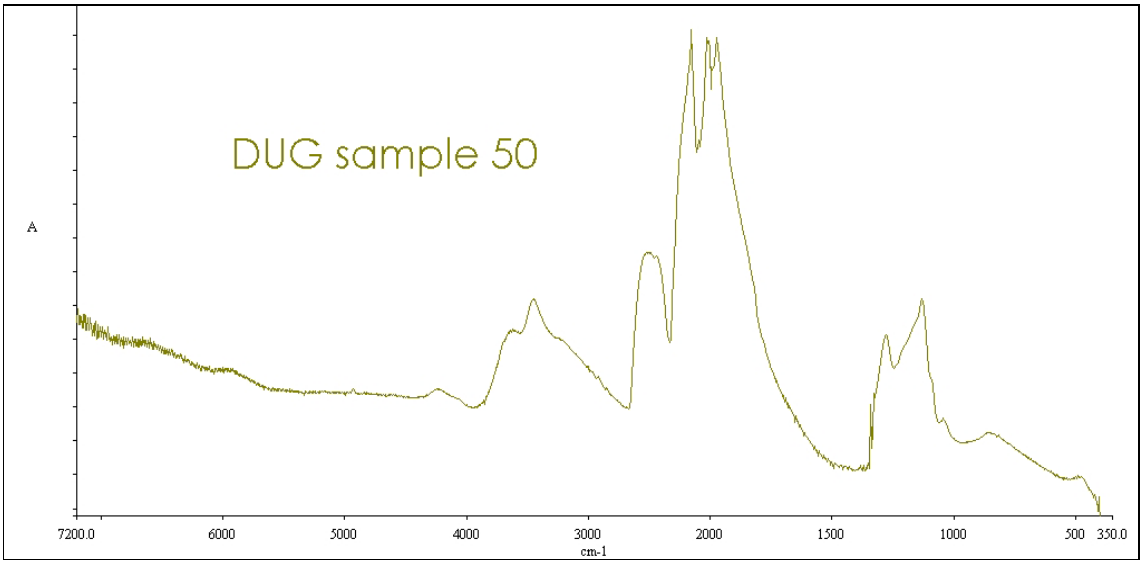


Figure 22. Besides the high N^0 content, this sample shows an unusual curve shape between 4500 cm^{-1} and 3000 cm^{-1}

3.5.2.3. Diamonds without amber center

Only very few brown diamonds without noticeable absorption in the ~4000 to 4500 cm^{-1} region were found:

➡Type Ia diamonds without amber center

Interestingly we have only found one type Ia diamond (not belonging to the CO_2 or "Pseudo-CO_2" groups) without the 4165 cm^{-1} amber center (Fig. 23), although in earlier observations of brown diamonds far less of them were found to contain this peak (E. Fritsch, pers. comm. 2002). Although the 800 analyzed stones were supplied from various sources, the fact that the Argyle mines in Australia produce by far most brown diamonds found in the market today makes it quite possible that the majority of the stones originated from this mine. Some of the Indian suppliers have also indicated, that this was the case, although such statements can never really be confirmed. Thus there might be a correlation between origin and the amber center. The stone we found was indeed not really a brown diamond, but a brown orange diamond with strong green transmission fluorescence caused by a strong H3 center.

More diamonds of a brown coloration without the amber center absorption were found, but these all were part of the brownish orange to orange brown color series; it appears that such stones nearly never contain this feature; these diamonds are often associated with "canary yellow" diamonds and are frequently of type Ib or mixed Ib/IaA; since apparently such stones do have a different color origin, which is more likely related to the canary diamond color origin, we excluded the "orange" group of this study and only this single stone will be described more closely.

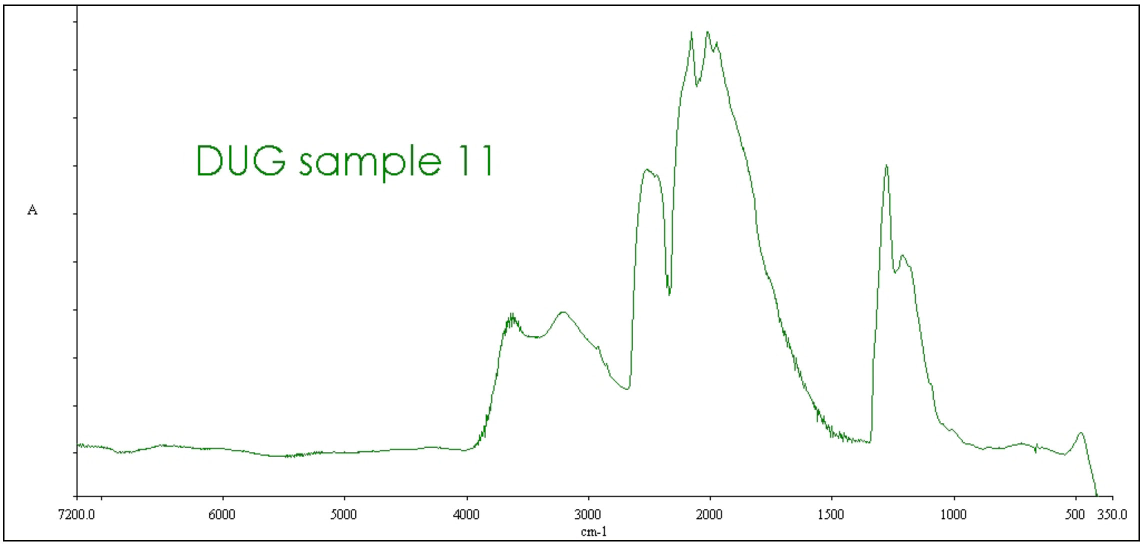


Figure 23. Typical for the "orange-brown series" is the lack of the amber center

➡Type IIa diamonds

Since the vast majority of the analyzed diamonds were small, we could only find 4 stones, which were essentially nitrogen-free, and these were larger stones (0.65 to 3.01ct). It is a fact that type IIa diamonds are often quite large. The reason for this is unknown. Three of the type IIa stones had a quite intense orangish yellow brown to yellow brown color. This color is surprising and it could be questioned if there are other reasons for the yellow color than nitrogen or that there might be a form of nitrogen, which is not detected by infrared spectroscopy. The fourth stone (sample 63) exhibited a regular medium dark brown color. The spectrum in Fig. 24 was recorded from a yellow-brown type IIa diamond with 1000 sample scans.

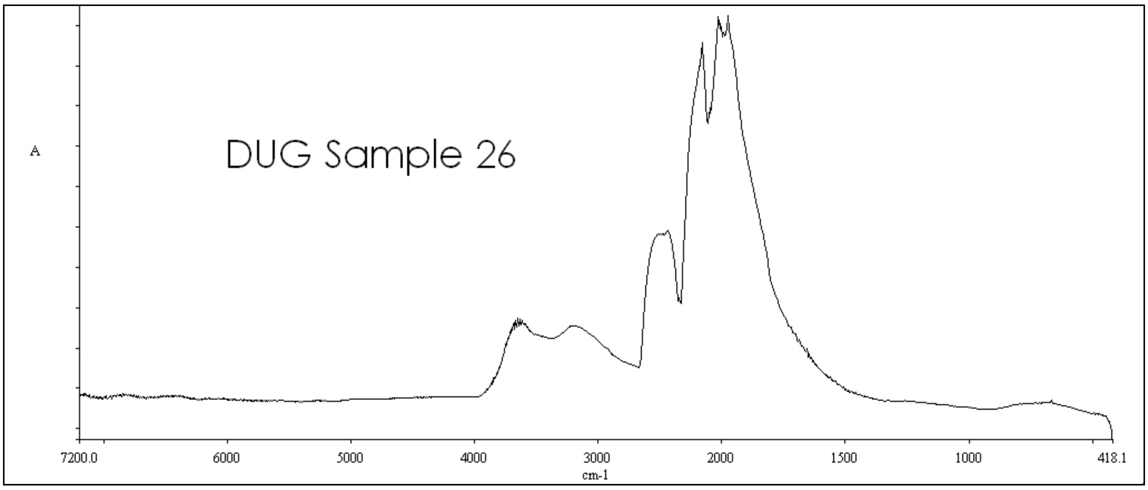


Figure 24. The relatively featureless IR spectrum of a yellow-brown type IIa diamond

➨Solid CO_2 containing diamonds.

After scanning the first 100 samples, 3 stones with very unusual IR spectra were observed (Fig. 25). This spectrum shows additional peaks at 2390 cm^{-1} and at 645 cm^{-1}. These features were found in one single publication where they were attributed to solid carbon dioxide (CO_2) present as inclusions in diamond (Schrauder et Navon, 1993). The solid state has been used to explain the offset of the peaks from the absorptions caused by gaseous CO_2 (666 cm^{-1} and 2360/2338 cm^{-1}). All CO_2 containing diamonds were type IaA and IaA/B diamonds, and the 1 phonon region between 1332 cm^{-1} and 1000 cm^{-1} appeared very unusual and distorted in the IaA/B CO_2 diamonds. The spectrum below was recorded with 500 sample scans at 4 cm^{-1} resolution.

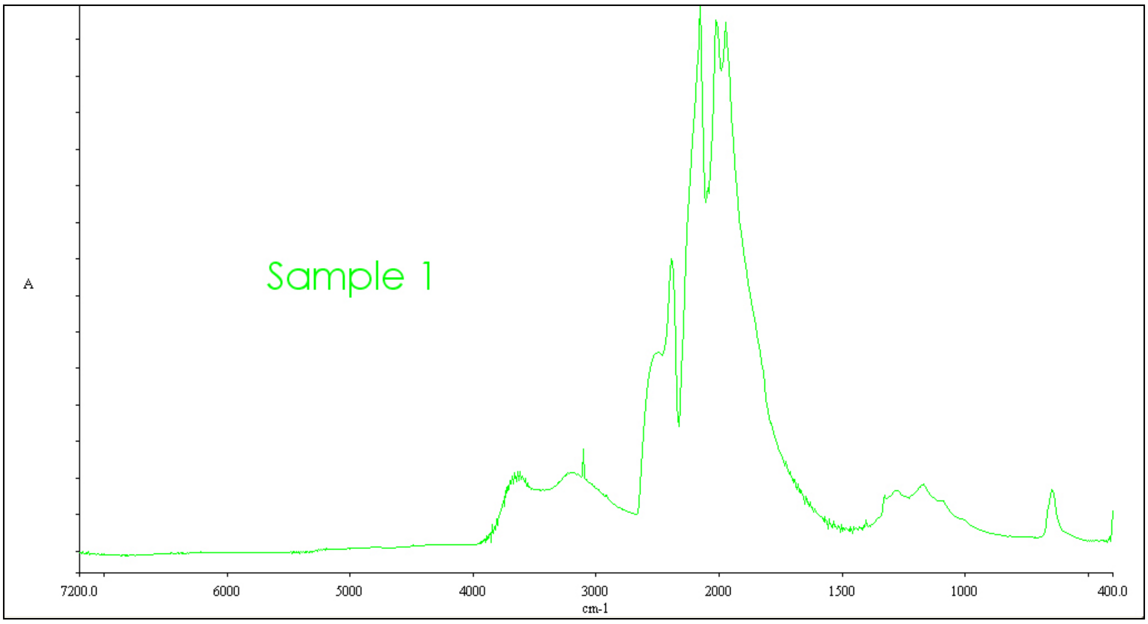


Figure 25. The IR spectrum of this CO_2 diamond lacks the amber center and shows two extra peaks at 2390 cm^{-1} and 645 cm^{-1} plus a distorted one phonon region between 1300 cm^{-1} and 1000 cm^{-1}

➨"Pseudo-CO_2" diamonds

Other diamonds with the distorted 1 phonon region were found, but which did not show the strong absorptions at 2390 cm^{-1} and 645 cm^{-1} (Fig. 26). Instead, the 2390 cm^{-1} feature was missing and only a quite weak peak at approximately 615-620 cm^{-1} was found. It was assumed, that these diamonds might represent diamonds which contain CO_2 in a minor concentration; since they lack the CO_2 absorptions, we termed them "Pseudo-CO_2" diamonds.
The spectrum below (Fig. 24) represents one of these "Pseudo-CO_2" diamonds; quite clearly, the one-phonon nitrogen region is unusually shaped but the major peaks at 2390 cm^{-1} and 645 cm^{-1} are missing. As in CO_2 diamonds, the amber center at 4165 cm^{-1} was absent. All other properties were identical to the properties observed in the CO_2 diamonds. Note: the small sharp features seen at 666 cm^{-1} and around 2360/2338 cm^{-1} are artefacts due to atmospheric CO_2.

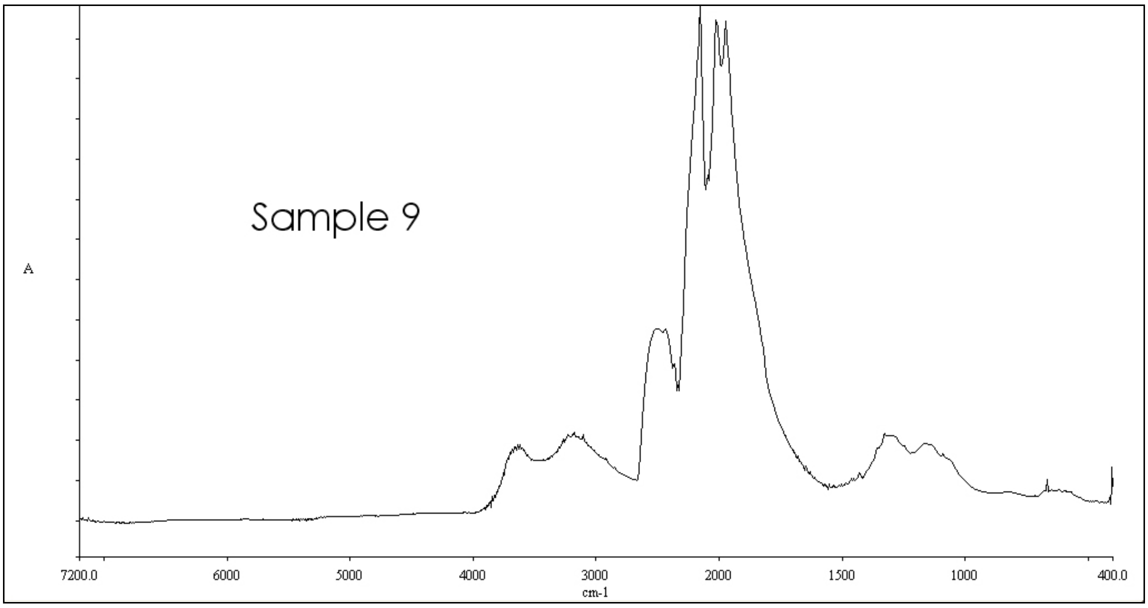


Figure 26. This "Pseudo-CO_2" diamond lacks the amber center; the 1-phonon region is unusual, but the 2390 cm^{-1} peak is missing and instead of the very apparent 645 cm^{-1} feature, a broad peak between 615-620 cm^{-1} is present

Type Ib "extreme" (sample 61- "Monster")

The second type Ib "extreme" diamond (sample 61) shows a spectrum unlike anything ever seen before (Fig. 27). It's single nitrogen absorption at 1130 cm^{-1} is nearly as strong as the intrinsic peaks of the diamond. This is something we have not even observed in high nitrogen synthetic diamonds. Besides this, the spectrum contains various absorptions that have not been described before; this includes several peaks in the NIR region plus a "forest" of absorptions between 3307 and 2910 cm^{-1}. This complex can be tentatively ascribed to "new" CH-vibrations since a number of absorptions in this region are known to be due to hydrogen. (Fritsch et al., 1993; Zaitsev, 2000). Additionally, multiple peaks between 1535 and 1352 cm^{-1} were found which are apparently related to the peaks between 3307 and 2910 cm^{-1} (combination bands, bending and stretching vibrations). Thus they can most probably be ascribed to hydrogen as well. The color of this stone was described as "deep red-orange-brown". The spectrum below was recorded with 250 sample scans at 2 cm^{-1} resolution with the sample chamber flooded with gaseous nitrogen (to reduce noise due to water and CO_2 absorptions).

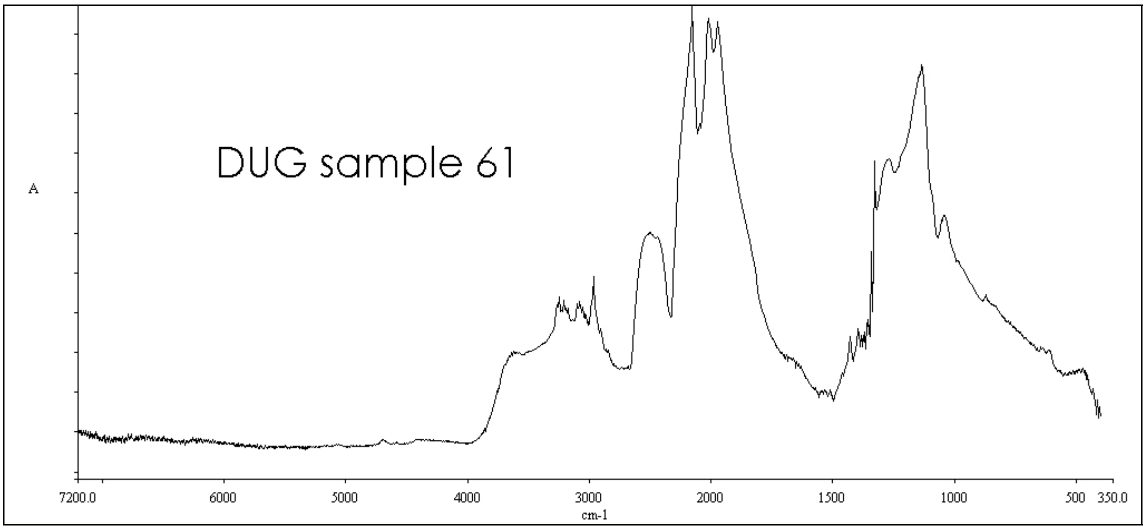


Figure 27. The spectrum of the deep red orange brown diamond is characterized by an extremely high N content and many undescribed absorptions, probably due to C-H vibrations, between 3500-3000 cm^{-1} and 1500-1350 cm^{-1}

3.5.3. Discussion

Infrared spectroscopy was found to be a most useful technique to analyze brown diamonds. A surprising variety of results was found and based on these, various groups were defined. The differences in the region between 4000 cm^{-1} and 4500 cm^{-1} were found to be useful to form these groups. Besides this, the one-phonon region was closely examined and all this tried to be correlated with the color of the brown diamonds.

The presence of a peak in the vicinity of 4000 to 4500 cm^{-1} in by far most type I brown to olive diamonds is most interesting and most probably closely correlated with a defect causing the brown to olive coloration, since it has not yet been observed in other colors.

Besides this, our findings of the solid CO_2 containing diamonds and the "Pseudo-CO_2" diamonds as well as type Ib stones with a regular brown coloration and the Ib "extremes" must be highlighted.

3.5.4. Peak Table: FTIR spectra

Sample #: 4=CO2; 30="Pseudo-CO2"; 12=double amber center; 22=type IaB; 17=very strong platelets; 6=type Ib; 28=type IIa; 49="regular brown" diamonds; 56=others
Darker grey columns = main "amber-center" peaks; Light grey columns=approximate values of the complex amber center structure in the NIR

N-A=nitrogen A aggregates; N-B=nitrogen B aggregates; N-C=nitrogen C centers; plate="platelets" (large carbon-nitrogen structure); H=hydrogen; ac=amber center;

cm^{-1}		4495 H	4320	4165 az	4065 az*	3270	3230 H	3180 N-C	3106 H	2784 H	2390 co2	1430 N3?	1405 H	1360 plate	1344 N-C	1332 N-B	1282 N-A	1215 N-A	1170 N-B	1130 N-C	1100 N-B	1062	1046 N-C	1035 x	1025 x	1010 N-B	870	820	770 N-B	750 N-B	645 CO$_2$	620	560	480 N-A
1	6450, 6213, 5850, 5716, 5110, 4780, 4693, 4560	x							x		x		x			x	x		x	x	x										x			
2		x				3281	x	x	x		2371	x				x	x		x	x	x										x			
3									x		2401		x			x	x	1235	x	x	x										x			
4		x							x		2402						x	x			x										x		x	x
51						x	x	x 3143	x		x	(x)	(x)			(x)	x		x		1094							807			650-585			
52							x	x 3143	x		x		(x)	(x)		(x)	x		x		x		(x)			x	940				x			x
5	6460, 6360, 6213, 6040, 5850, 5716, 5140, 4860, 4710, 4687											x		x		x	x	1250	x	x	x	x						x				615		
8		x				x	x	3142	x			x				x	x	1235	x	x		x						x				615		x
9		(x)				x	x	x	x			x		x		x	x	50-35	x	x	x	x					x	x				x	x	
30		x				x	x	x	x			x	x	x		x	x		x		x							x				x		
6	6500, 6280, 6140, 6040, 5850, 5720, 5200, 4840, 4710, 4520			4115		3455								x	x	(x)	x			x	x	x	x	x	x	1018		x						
7				4115		3455	3360								x	(x)	x			x	x	x	x	x	x	1018	x	x						
50	6400, 6140, 5955, 4934, 4835,	4530		4234	x	3455									x	(x)	x			x	x		x				x	x						(x)
54		4530		4115		3455										(x)	x			x	x		x					x						x
26	Type IIa diamonds																																	
27																																		
28																																		
63																																		
10	6450-6500, 6214, 6130, 5850, 5720, 5340, 5200, 4931, 4800, 4711, 4440	x sh		x	x		x		x	x		x	x	1391		1372	x	x			x					945				727				x
12		x br		x	x				x					x		x	x	x	x		x					x			x	x				x
13		x sh		x	x				x			x	x	x		x	x		x		x					x			x					x
14		x sh		x	x				x				x	x		x	x	1240	x		x									x				x
21		x br		x	x									x		x	x		x		x					x			x					x
24		x br		x	x									x			x	x			x					x								x
53	6500, 6278, 5850,5718, 5200,4840, 4710	x br		(4143	x	3452									x	(x)				x	1094		x					x						
57		x sh		x	x		(x)		x				x	x		x	x		x		x					x			x					x
58		x br		x	x		(x)		(x)					x		(x)	x	x	(x)		x					x			720?					x
59		x br		x	x												x	x	(x)		(x)		(x)											x
60		x br		4180	x				(x)			x		x		x	x	x			x					x			x					x
16	6500, 6278, 6140, 5850, 5200, 4840, 4710, 4667, 4396			x					x			x		x		x	x		x		x					-945			x				x	x
17		x		x					x					x		x	x	1240	x		x					x			x					x
18		x		x					x			x		x		x	x		x		x					x			x					
19		x		x					x			x	x	x		x	x		x		x		x			x			x					x
20	6500, 6280, 6140, 5850, 5200, 4840, 4720, 4667, 4396	x		x					x					x		x	x		x		x					x			x					
22		x		x									x	x		x	x		x		x					x			x					x
23		x		x					x				x	x		x	x		x		x					x			x					
25		x		x					x			x		x		x	x		x		x					x			x					
55				x								x		x		x	x		x		x					x			x					

cm^{-1} nm		4495 H	4333	4165	4065 az*	3270	3230 H	3180 N-C	3106 H	2784 H	2390 co2	1430 plare	1405 H	1360 plate		1332 N-B	1282 N-A	1215 N-A	1170 N-B	1130 N-C	1100 N-B	1062	1046 N-C	1035 x	1025 x	1010 N-B	870	820	770 N-B	750 N-B	645 CO_2	620	560	480 N-A
31	6500, 6214, 6140, 6060, 5850, 5720, 5200, 4840, 4667, 4557, 4530, 4515, 4396			x	x									x			x	x	(x)		x	x	x											x
32				x								x	x	x		x	(x)		x		x					x			x					
33				x					x					x		x	x		x		x		x			x			x					x
34				x										(x)			x	x			(x)					(x)								x
35				x										x			x	x								x			720?					x
36				x					x					x		x	x	x	x		x		x			x			x					x
37				x										x			x	x	x		(x)					x			x					x
38				x										(x)			x	x			(x)					(x)				692?				x
39				x										x			x	x			(x)					x			720?					x
40				x					x				(x)	x		x	x		x		(x)		x			x			x					(x)
41				x										x		(x)	x		x		x					x			x					x
42				x					x				(x)	x		x	x		x		(x)		(x)?			x			x					
43				x					x			x		x		x	x		x		(x)					x			x					x
44				x										x		(x)	x		x		(x)					x			x					x
45				x										x			x	x	(x)		(x)					(x)								x
46				x										x			x	x			(x)					(x)								x
47				x										x			x	x	(x)		(x)					x			720?					x
48				x					x					x		x	x		x		x					x			x					(x)
49				x					x				(x)	x		(x)	x		x		(x)					x			x					x
11			x														x	x			x					x								x
15	6500, 6214, 6140, 6060, 5850, 5720, 5200, 4840, 4667, 4557, 4530, 4515, 4396	x		x					x				x	x		x	x		x		x					x			x					x
29			4280	x					x					x		x	x		x		x					x				x				x
56				x					x								x	x	(x)		(x)													x

3.6. VIS/NIR Spectroscopy

The spectra of some selected diamonds were recorded at room temperature (~25°C) and at liquid nitrogen temperature (-196°C).

3.6.1. Background

UV-VIS-NIR spectroscopy is a very useful technique to detect absorptions due to electronic transitions in diamonds. Depending on the instrument, the range of 190 to 1100 nm can be covered, although for diamonds, the most important absorptions can be found in the range of 400 to 1000 nm. These include absorptions due to nitrogen (e.g. N3 aggregates- the 415.2nm "cape" absorption), nitrogen-vacancy induced absorptions (e.g. the 637 nm NV^- and 575 nm NV^0 absorptions), absorptions due to radiation damage (e.g. 594.2 nm and 741.2 nm [GR1, neutral vacancy]), some hydrogen absorptions and others. A very large number of absorptions has been described, the cause of which is not always known (e.g. the 560 nm band in pink diamonds). Cooling to very low temperatures sharpens by far most absorption bands. This is often done by immersing a diamond in liquid nitrogen (-196°C = 77 K) or rarely in liquid Helium (-269°C, 4 K). With this method, absorptions bands, which are practically indetectable at room temperature, can be made strong and sharp enough for detection (e.g. very weak absorptions at 741 and 815 nm in sample 28). Brown diamonds generally only show a continuous absorption over the whole range of the spectrum with sometimes a weak broad band at 560 nm. This relatively continuous absorption is responsible for the brown coloration. The spectra of these stones do not generally show strong sharp absorptions, even when cooled in liquid nitrogen. Weak absorptions due to N3 aggregates at 415.2 nm and very weak H3 complexes (503 nm) can be generally be detected in brown diamonds. Since some olive coloration is often incorporated in the color of brown diamonds, we provide some information on the spectra of olive diamonds.

"Pure" olive diamonds, such as sample 53, have very similar absorption spectra like brown diamonds, with a relatively continuous absorption over the whole range of the spectrum, with weak broad bands centred at ~425 nm and 600 nm; the resulting transmission window centred around 520 nm causes the additional green hue of these stones. Dominantly type Ib olives show distinct NV^- absorptions sometimes with extremely weak H3 centres. Type Ib/aA olive diamonds show both NV^- and H3 absorptions. Interestingly, the mixed brown-olive colored diamonds we found for this study were of type Ia, some with an Ib character, but never dominantly type Ib.

3.6.2. Results

At room temperature all stones showed the expected continuous absorption (with some broad bands) over the whole range of the spectrum (in our case i.e. 400-1000 nm). A weak H3 complex was observed in most stones when the spectra were recorded at LN_2 (=Liquid Nitrogen) temperature and in many stones a rather feeble N3 absorption could be resolved.

The type Ib brown diamonds and the IaA diamond with strong green transmission fluorescence were exceptions- they exhibited strong and sharp absorptions due to the NV^- center and the H3 center respectively.

The following spectra are representative for the analyzed diamonds:

Type Ia

The type Ia diamonds showed a continuous absorption, often with a weak H3 complex and a broad band at ~560 nm. In many of the stones, a very weak absorption at 415.2 nm due to the N3 aggregates was found. The spectrum below is characteristic for "typical" brown diamonds. Recorded at 77K, N3 becomes visible and a very weak H3 complex can be seen (Fig. 28).

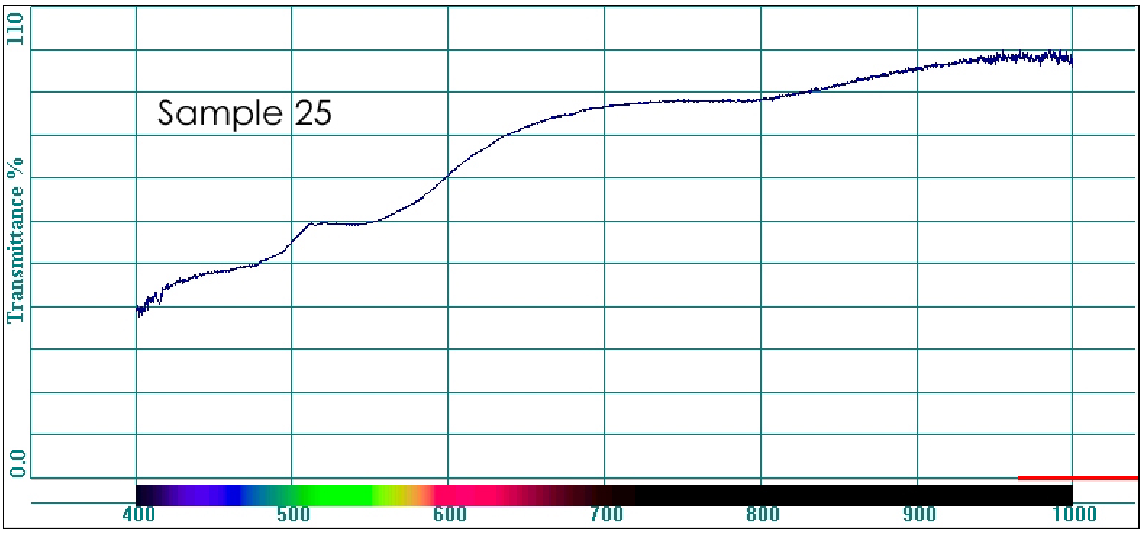


Figure 28. The low temperature VIS/NIR spectrum of this near pure type IaB diamond shows weak N3, H3 and a broad band centered at 560 nm

Type Ia with green transmission luminescence

One diamond exhibited a strong H3 center and resulting strong green luminescence (Fig. 29); this luminescence was strong enough to affect it's face up appearance: a distinct greenish glow was always visible besides the brown-orange bodycolor. This low temperature spectrum shows distinct similarities with those of the HPHT treated type Ia brown diamonds that mostly turn yellow with strong green transmission luminescence.

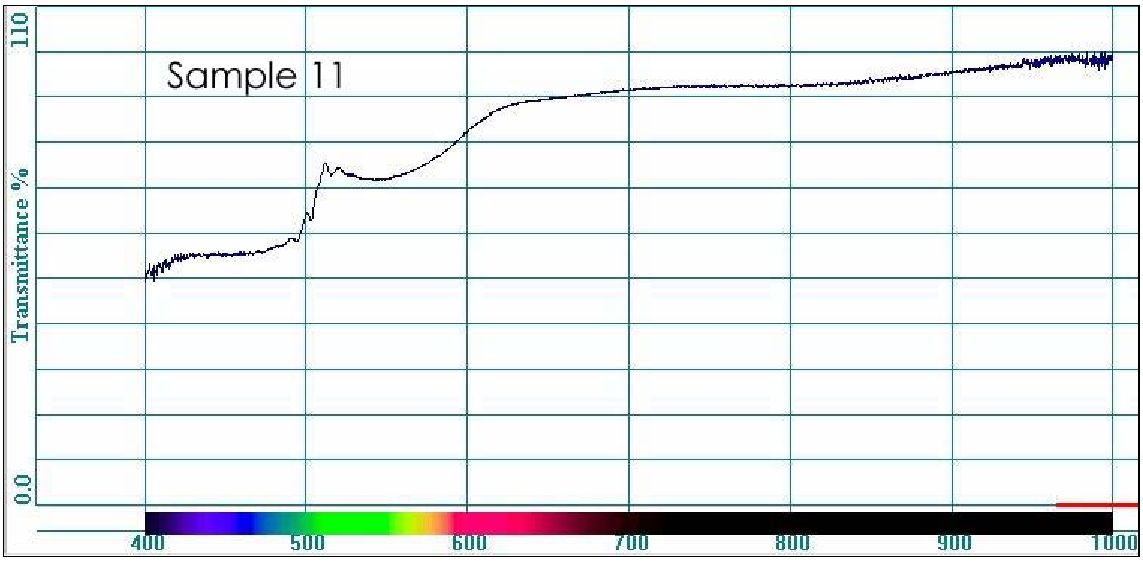


Figure 29. Recorded at 77 K, this spectrum of a diamond of brown-orange color is characterized by a strong H3 defect which causes a strong green luminescence in the stone

Such treated stones do usually exhibit a weak to strong H2 absorption at 986 nm (Fig. 30); this absorption was not detected in this naturally colored stone, although it has been reported in a known untreated green transmitter by Chalain, (2003). The reported stone, in which a very weak H2 absorption was visible, showed a strongly greenish face-up appearance; a treated stone of such color would most certainly show a much stronger H2 center, since the greener colors appear to be only produced at temperatures ~ 2100°C. As part of this study, one stone of each class of brown diamonds was treated by the HPHT process at 2000°C and 6.5 GPa and some of the results are presented below in this work; the low temperature VIS/NIR spectra of all the treated Ia brown diamonds (except the CO_2's) showed weak to distinct H2 absorption, although none of the stones showed an apparent green face-up color. Below the spectrum of sample 46 post HPHT treatment is shown (Fig. 30). The stone appears medium yellow and the spectrum is highly distinct for an HPHT treated stone, exhibiting absorptions at H2 and 871 nm. A natural stone will with very high probability never have a such easily visible H2 feature, since the conditions in nature do not permit the formation of enough single nitrogen (N^0) due to annealing; this N^0 appears to be necessary to act as an electron donor to form H2, which is the negatively charged state of H3 (Collins et al, 2000). The strong disintegration of A-aggregates into C-centers occurs at higher temperatures than in nature, and thus, generally the required C-centers are not present in natural stones and they lack H2 or show it only as a microscopic defect (K.Iakoubovskii, pers. comm. 2001).

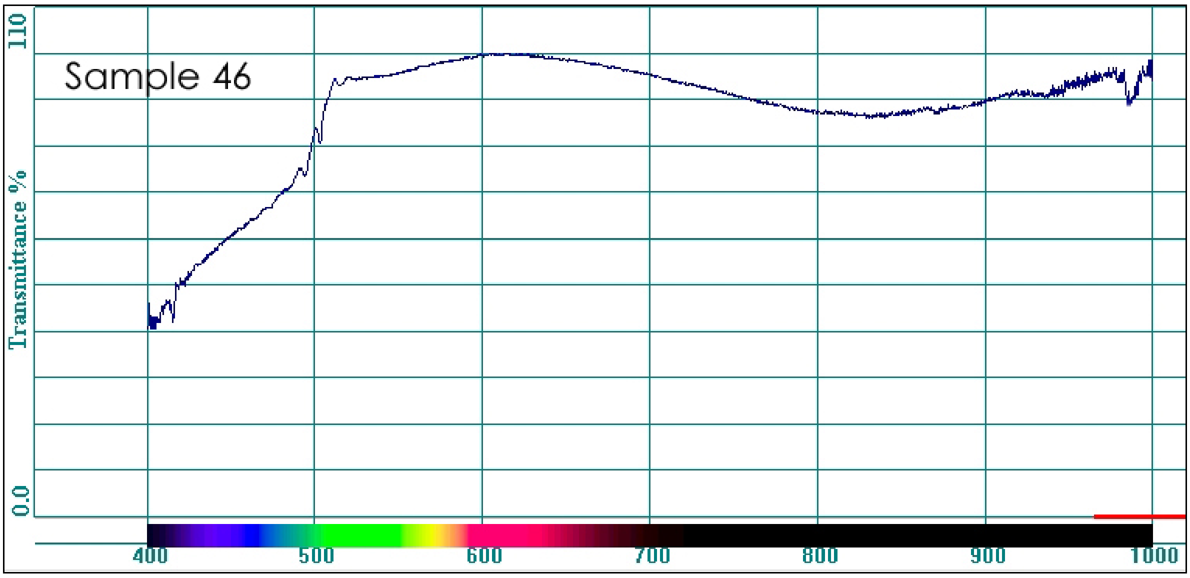


Figure 30. This spectrum of a near pure type IaA diamond was recorded after HPHT treatment at 2000°C / 6.5 GPa and shows new absorptions at 871 nm, 986 nm (H2) and relatively strong H3; N3 was strengthened as well.

Type Ia, CO_2 and "Pseudo- CO_2"

These diamonds showed a continuous absorption over the whole spectral range without any apparent absorption bands (Fig. 31).

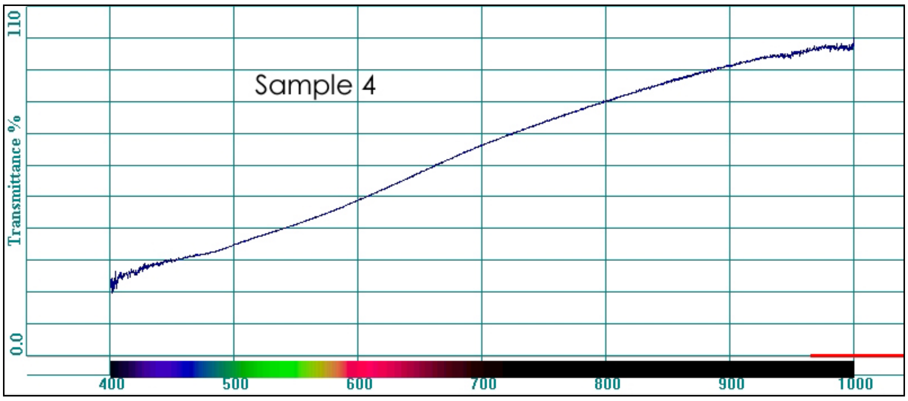


Figure 31. A featureless rise in transmission is characteristic for all CO_2 and "pseudo-CO_2" diamonds

Type Ib

Besides an extremely weak H3 complex and a broad band at ~560 nm and ~770 nm, the "regular" type Ib samples and one "extreme" type Ib diamond (sample 50) showed a distinct absorption at 637 nm due to the negatively charged nitrogen vacancy (NV^-) plus adjacent sidebands at 620 and 665 nm (Fig. 32). This defect is caused by (natural and artificial) radiation and annealing: irradiation causes vacancies, which diffuse through the lattice under the effect of heat. The vacancy is trapped by the single nitrogen and then forms the NV^- defect. These absorptions were clearly visible only at 77 K.

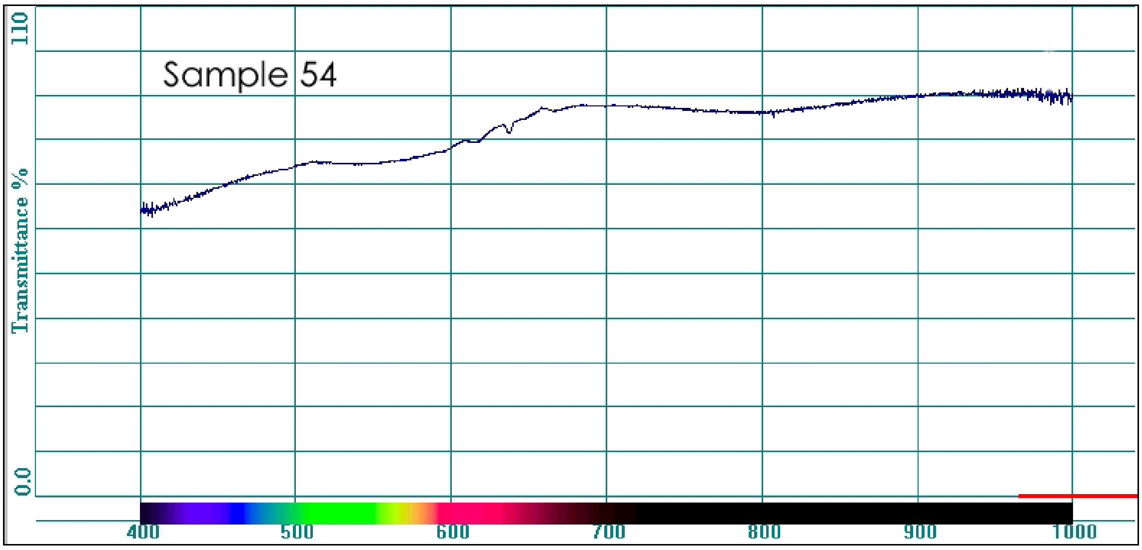


Figure 32. All type Ib brown diamonds-except sample 61- exhibited distinct NV^- centers with associated sidebands

Type Ib "monster" (sample 61)

This tiny stone (1.9 mm Ø) indeed deserves the attribute "monster"; besides the extremely uncommon infrared spectrum the VIS/NIR spectrum contributed even more to the confusion: the spectrum below (Fig. 33), recorded at 77K, showed several unknown absorptions besides a distinct H2 center at 986 nm (the negative charge state of the H3 center). These include distinct absorptions at 766, 828, 880 and 905 nm, accompanied by weak peaks at 734, 750, 790, 808, 867, 930 and 940 nm. None of these absorptions have been described in the literature so far, and no reference could be found. Similar absorptions with some overlapping positions were found in yellow diamonds with extremely high hydrogen content, thus it appears that they are closely related to hydrogen impurities.

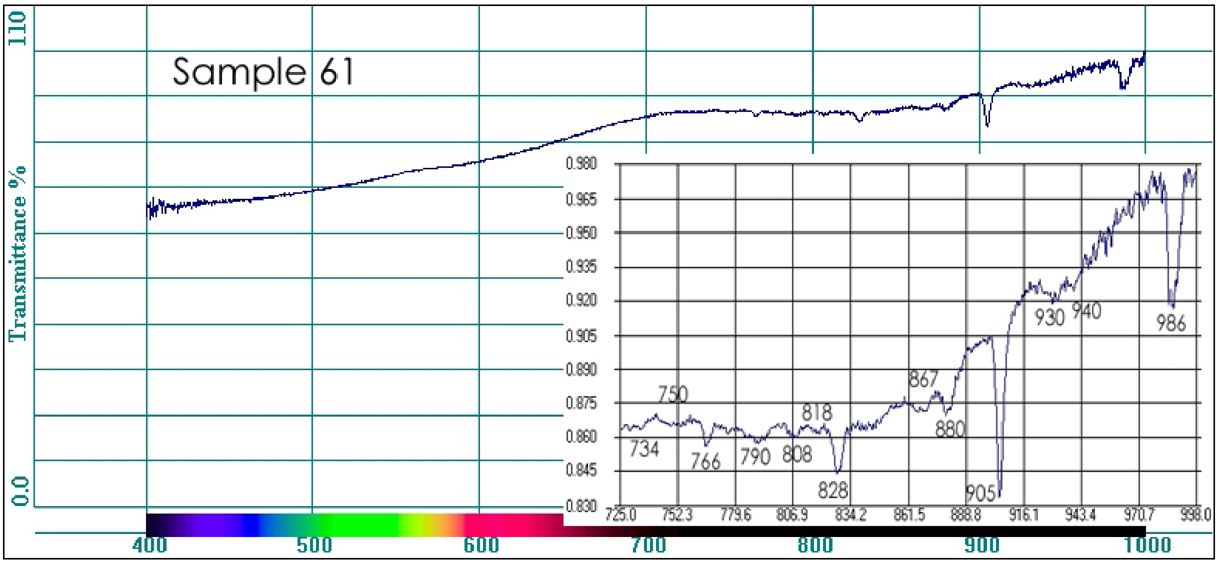


Figure 33. The spectrum of the small red orange brown diamond is characterized by numerous unknown absorptions between 734 nm and 986 nm (H2); recorded at 77 K

Type IIa

Besides a continuous absorption, the four type IIa diamonds showed a weak broad band centred at ~670 nm. The spectrum below (Fig. 34) was recorded at liquid nitrogen temperature.

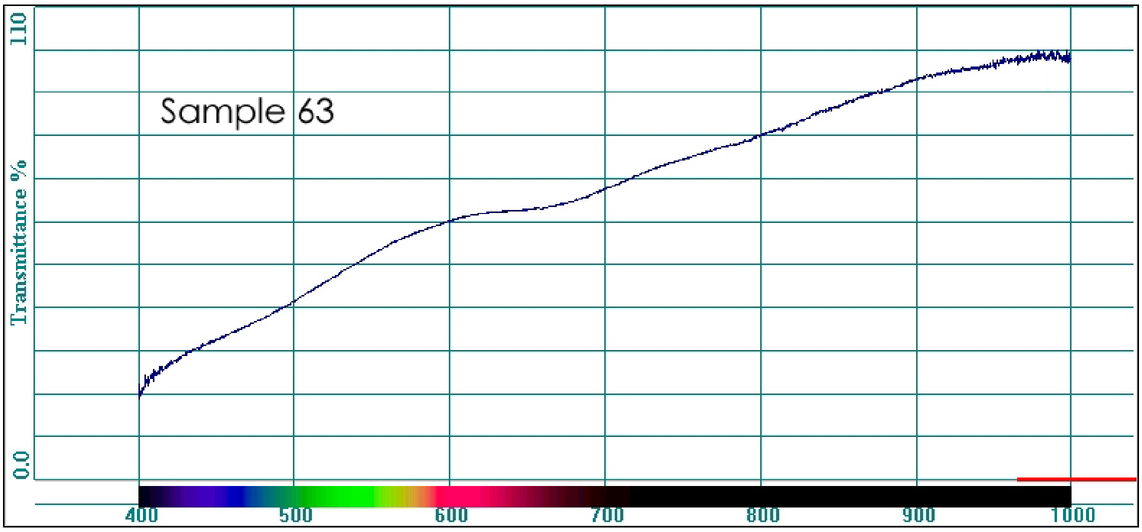


Figure 34. The LN temp. spectrum of a medium dark brown diamond of type IIa; besides a broad band at ~670 nm the spectrum is featureless

An exception was sample 28, which showed two weak absorptions at 741.2 nm and 815 nm besides the broad band at 670 nm (Fig. 35). These absorptions were only resolved at 77K. The peak at 741.2 nm can be attributed to radiation damage and is termed GR1; the absorption at 815 nm has been described as being present in irradiated type IIb diamonds (Zaitsev, 2001).

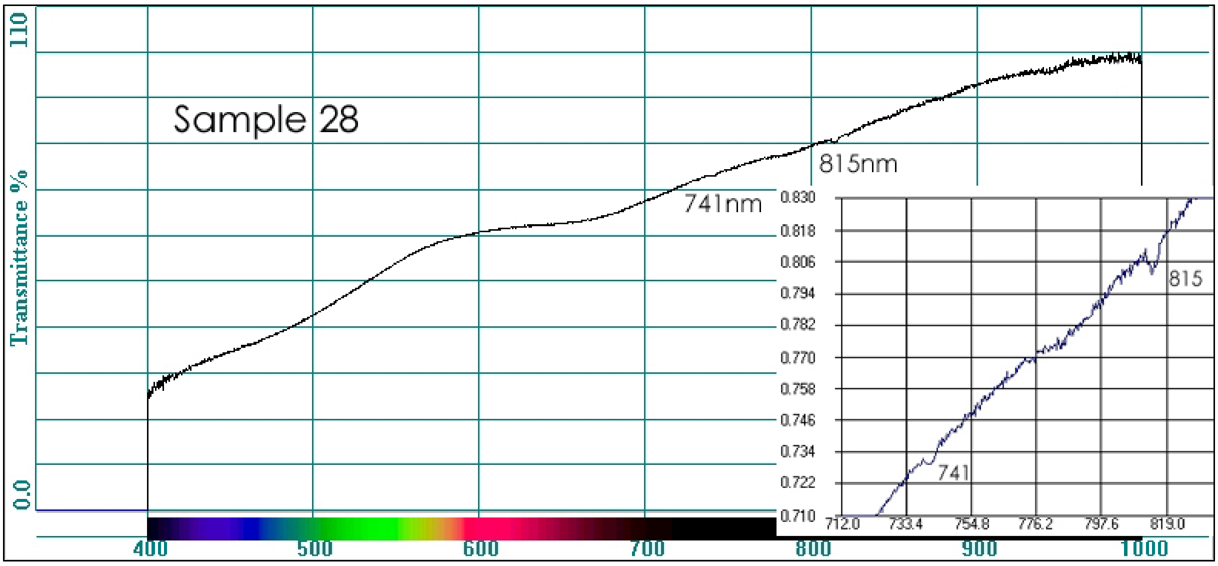


Figure 35. Besides the band at 670 nm, this spectrum of an extraordinary yellow-brown type IIa diamond exhibits weak absorptions due to radiation damage at 741 nm and 815 nm. Recorded at 77K

Olive diamonds VS brown diamonds

As mentioned above, pure olive diamonds were always found to be type Ib or type Ib/aA; their VIS/NIR spectrum appeared very similar to the brown diamond spectra with a relatively continuous absorption. There is a broad band centred at ~600 nm and one at approximately 425 nm. As mentioned before, the resulting transmission window centred around 520 nm causes the additional green hue of these stones. At low temperature, distinct but weak NV$^-$ defects (with its ZPL at 637 nm) were found and in some stones extremely weak H3 was detected (Fig. 36). A second type of olive diamonds is just briefly mentioned and represents very high nitrogen/hydrogen containing diamonds which often exhibit a chameleon behaviour (thermochroic and sometimes photochroic color change) (Fig. 37)

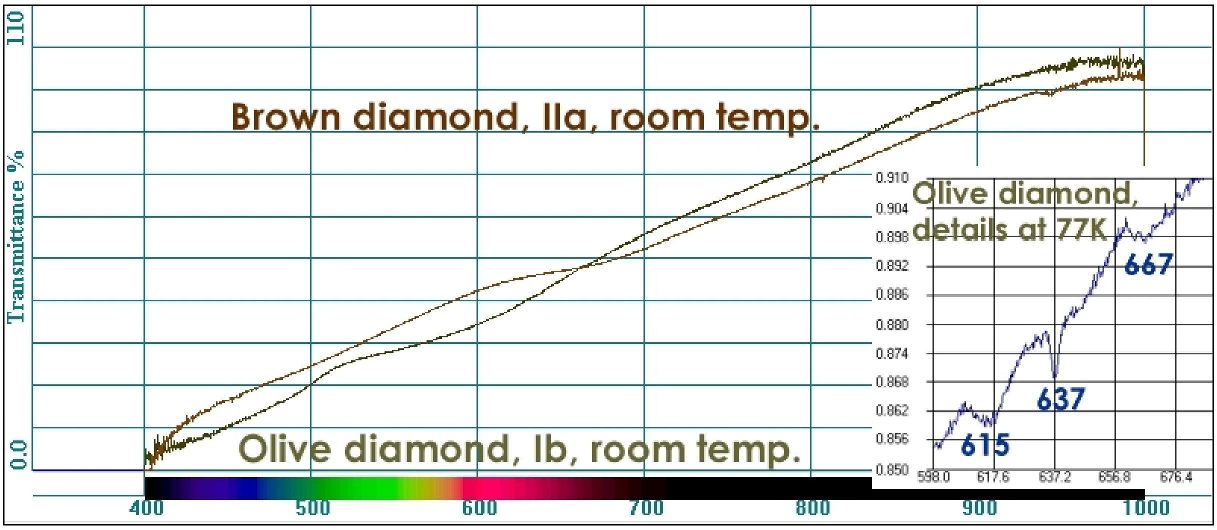


Figure 36. The comparison of the room temperature spectra of an olive and a brown diamond. Inset the spectral details of the olive diamond, recorded at 77K.

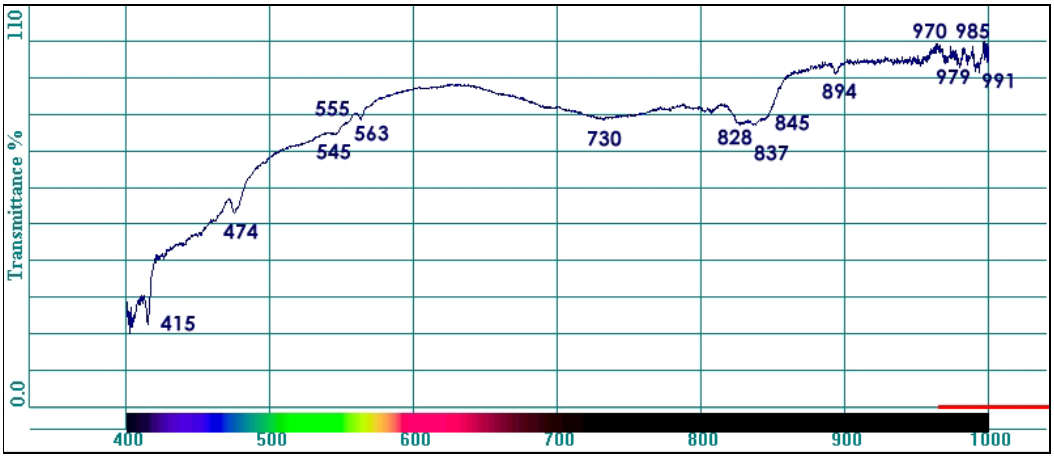


Figure 37. The spectrum of a type Ia olive diamond with very high nitrogen and hydrogen content with a weak chameleon behavior

3.6.3. Summary

The VIS/NIR spectroscopic analysis of the brown diamonds incorporated in this study has shown that the majority of brown diamonds shows a broad band centered at 560 nm (causes pink color nuances) in combination with very weak N3 and H3 centers (cause yellow+orange nuances). The type IIa diamonds only showed a broad band at 670 nm except sample 28 (Fig. 35), which exhibited weak absorptions due to primary radiation damage. The type Ib diamonds showed a broad band at ~560 nm combined with relatively strong NV$^-$ centers or in one case a spectrum for which no reference was found with many peaks in the NIR region.
The VIS/NIR spectra are especially useful for the comparison of brown diamonds before and after HPHT treatment and aid in the detection of many of such treated stones.

3.7. Photoluminescence Spectroscopy

Photoluminescence spectra of all 63 diamonds were recorded at 77 K and some also at room temperature.

3.7.1. Background

The technique of photoluminescence (PL) spectroscopy has been found to be extremely sensitive to certain defects. Many of them are not detectable with VIS/NIR spectroscopy but can be easily detected by PL - spectroscopy. As an example, the tiniest traces of NV$^-$ centers in type IIa diamonds can be detected by this technique. In PL, an intense beam of monochromatic radiation, usually a laser, excites the diamonds. In the excited state the diamond will emit radiation of lower energy (higher wavelength) than the excitation source; for example a diamond excited by a 532 nm laser will emit radiation >532 nm. Defects such as the NV$^-$ center do behave as luminescent centers, thus they will be apparent as defined peaks in PL spectra. The interpretation of unknown PL features is very difficult.

3.7.2. Results

The luminescent response to the 532 nm laser used was generally weak; thus rather long integration times of 5 to 15 sec had to be used to measure PL spectra. Only a few stones such as the “regular” type Ib diamonds produced sufficient emission with short excitation times. At room temperature, usually only the broad band emissions of

the diamonds were observed, except the Raman peak at 1332 cm^{-1} plus some of the stronger emission features. To resolve most of the weaker sharp emission peaks, the samples had to be cooled to LN_2 temperature.
Our 63 samples showed mainly known PL emissions like the ones described by Smith et al. (2000). Many of these defects have only been described, but not attributed. Thus all type Ia brown diamonds showed similar PL spectra, except the diamonds with "CO_2" and "Pseudo-CO_2" IR spectra: these samples showed several as of yet unknown peaks in the NIR region between 700 and 900 nm. The type Ib stones had spectra with very strong peaks due to NV^- centers. The spectra of the type IIa diamonds were typical and showed similar patterns as mentioned by Smith et al. (2000). Note that the peak visible at 805 nm in most PL spectra shown is an artefact (filter-luminescence).

Type Ia:

The regular brown diamonds all showed very similar PL spectra with various known centers besides NV centers. Most of these have been described but not assigned. As observed they are simply declared as "present in natural brown diamonds". Fig. 38 represents a typical low temperature PL spectrum of a type Ia brown diamond.

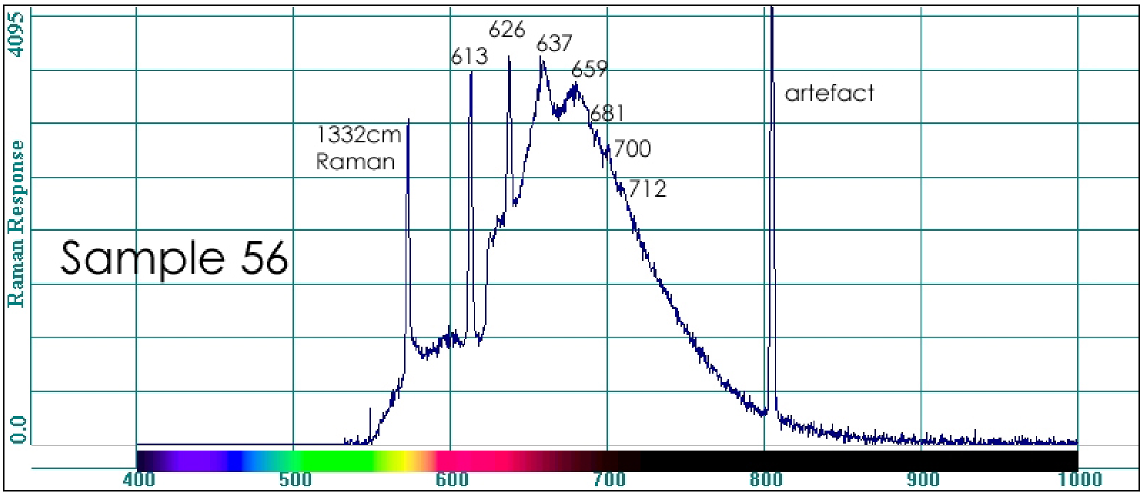


Figure 38. The PL spectrum of a type IaA brown diamond, recorded at 77 K

Ia with "double amber center":

The "double amber center" diamonds were not too unusual either; typically they showed a dominant 613 nm emission and only weak other features. Fig. 39 shows the spectrum of an olivish brown diamond with a "double amber center" in its IR spectrum.

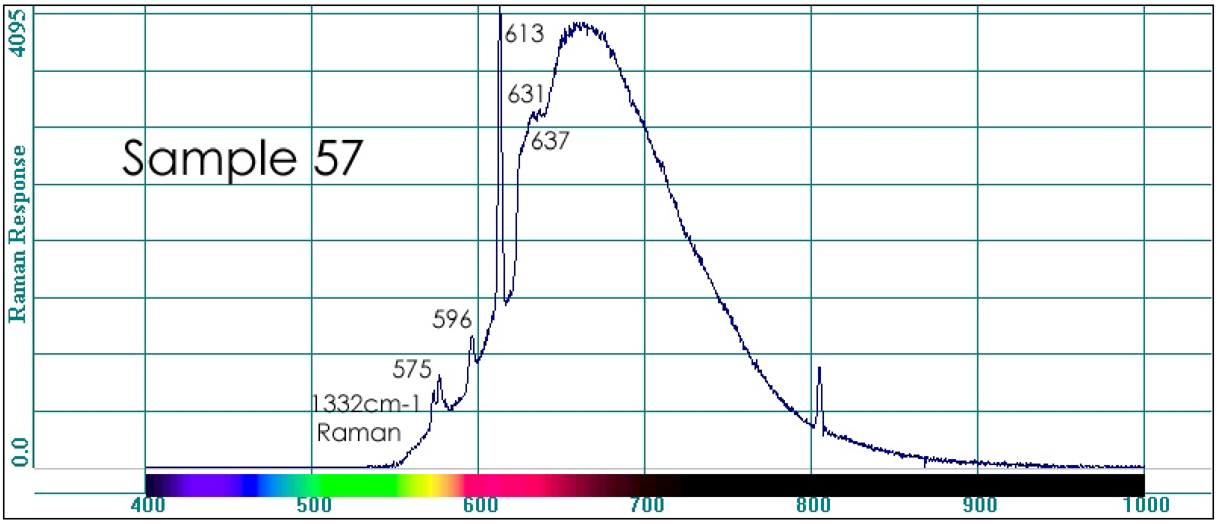


Figure 39. The low temperature PL spectrum of an olivish brown diamond

Type Ia, solid CO_2 (Fig. 40) and “Pseudo-CO_2” (Fig. 41):

The PL spectra of the CO_2 and “Pseudo-CO2” diamonds were more unusual; besides some differences in the 540 to 700 nm region, there were several peaks visible in the NIR part of the spectrum (Fig. 40); as far as we are aware, these have not been described yet. It must be noticed that four of the ten analyzed CO_2 diamonds lacked these NIR emissions. Three of the stones CO_2 and one a “Pseudo-CO_2” diamond.

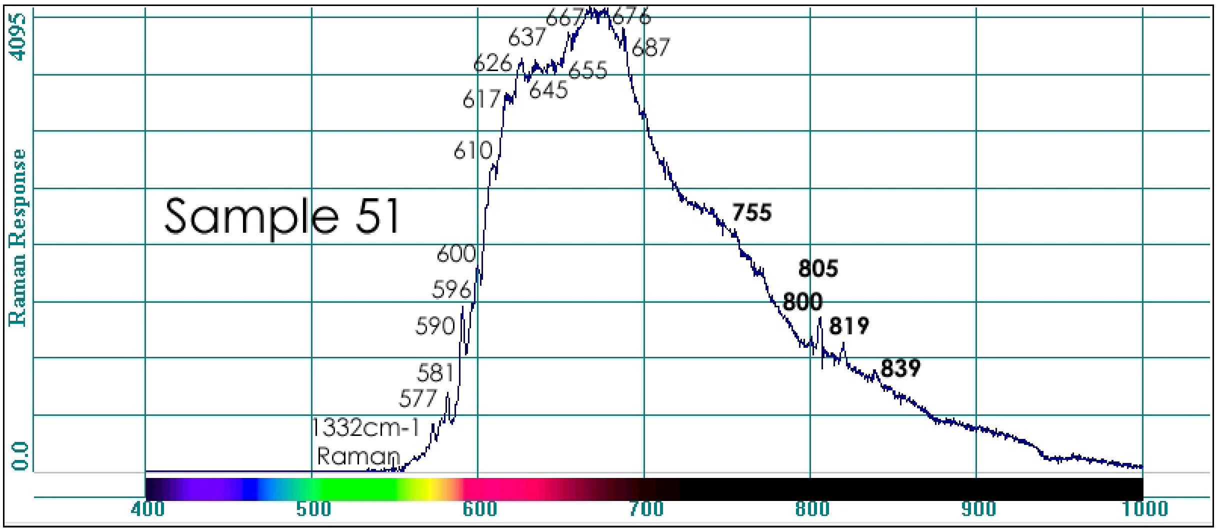


Figure 40. A PL spectrum of a CO_2 diamond with unknown emissions between 755 and 839 nm (recorded at 77 K)

Type Ia, “Pseudo-CO_2”

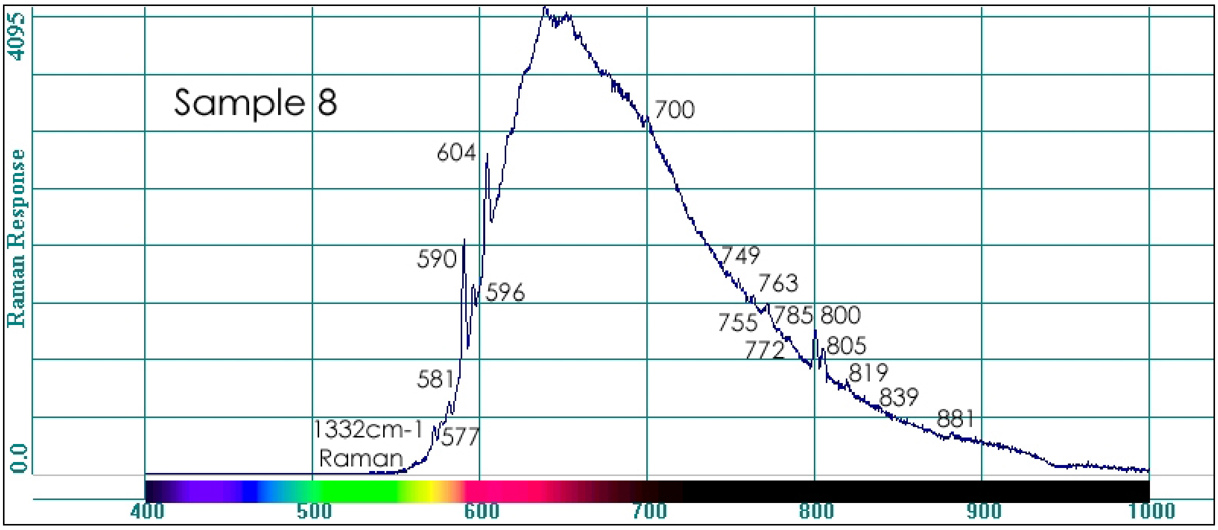


Figure 41. The low temperature PL spectrum of a “Pseudo-CO_2” diamond
with unknown emissions between 749 and 881 nm

Type IIa:

The PL spectra of two of the three IIa diamonds were as expected, except that neutral NV centers (575 nm) were absent. The 637 nm negatively charged NV center was quite weak as well. Thus, the nitrogen content of these stones appears to be extremely low. One stone, sample 28, showed a distinct peak at 741 nm, termed GR1, caused by natural radiation (Fig. 42). The GR1 absorption was barely visible in the VIS/NIR spectrum at 77 K.

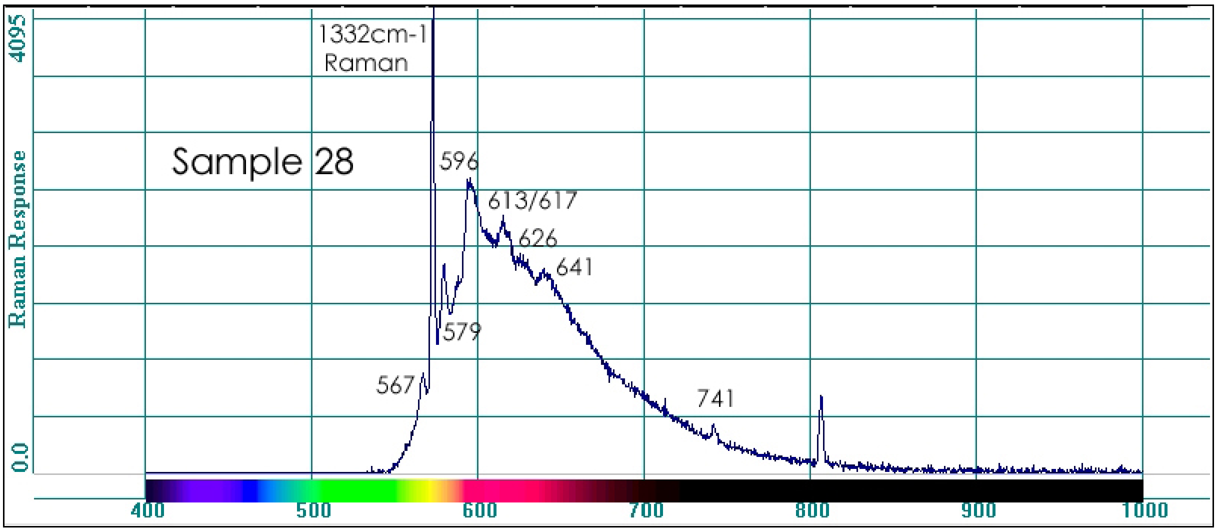


Figure 42. GR1 absorption (741 nm) in an unusual type IIa diamond of yellow-brown coloration

Type Ib (olive and brown):

The “regular” type Ib brown diamonds exhibited strong Photoluminescence (Fig. 43). A very strong NV^- center with additional peaks was typical for these stones. The spectra of brown and olive Ib diamonds did not differ. The below spectrum was recorded from an olive diamond of type Ib; it must be noticed that the PL of all “regular” brown Ib diamonds was much stronger than in all type Ia brown diamonds.

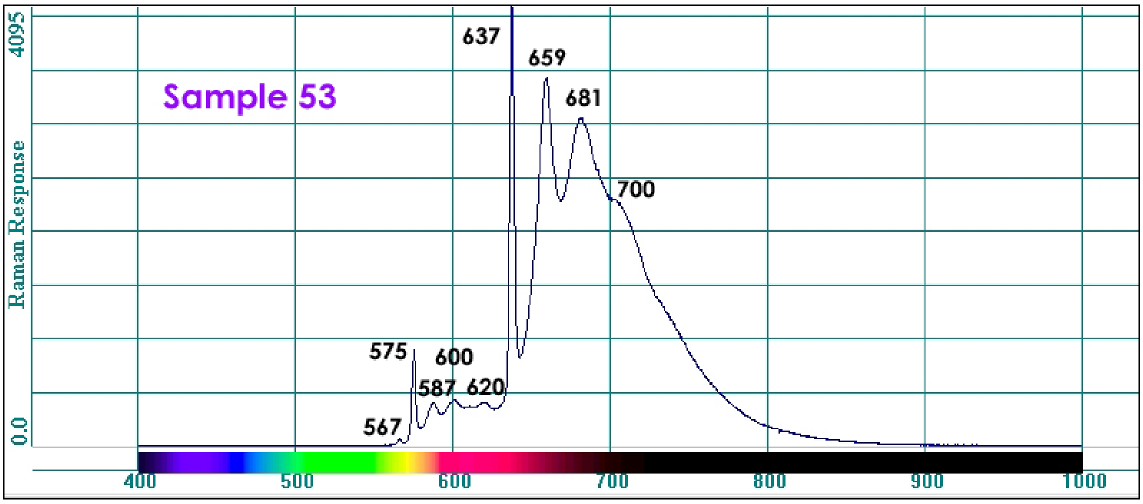


Figure 43. A typical PL spectrum for type Ib brown and olive diamonds;
such spectra are characterized by strong NV centers

Type Ib ("Monster"):

This most unusual stone showed an NV^- center plus very weak emissions at 828.5 and 905.2 nm. These are in agreement with the absorptions seen in the VIS/NIR spectrum. Due to the extremely small size, it was difficult to get an acceptable low temperature spectrum, and the one seen below (Fig. 44) was the best out of several attempts.

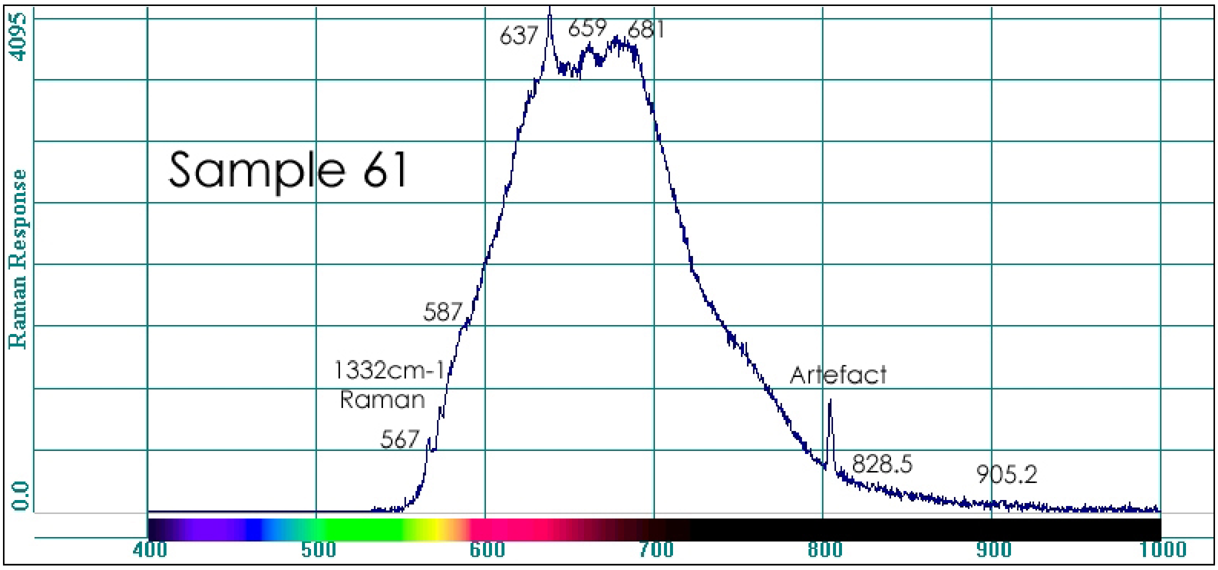


Figure 44. Very weak emissions at 828.5 an 905.2nm and an NV^- center were seen in this "extreme" type Ib stone

3.7.3. Discussion

The PL spectra were found to be of relatively little value for this work; too many rather weak PL emissions were found in our 63 samples and except for the CO_2 / "Pseudo-CO_2" and the type Ib diamonds, the spectra were not characteristic. The CO_2 and "Pseudo-CO_2" spectra were characterized by unknown emissions between 700 and 900 nm and the type Ib stones by very strong NV centers and much stronger PL than all other brown diamonds; most of the 63 diamonds exhibited very weak PL and it was difficult to obtain acceptable spectra.
The PL spectra have some diagnostic features when analyzing stones for HPHT treatment; the combination of PL, FTIR and VIS/NIR spectra is in by far most cases conclusive in the distinction between natural and HPHT treated diamonds.

3.7.4. PEAK TABLE: PHOTOLUMINESCENCE AT 77K, 532 NM LASER

Sample #: 4=CO2; 30="Pseudo-CO2"; 12=double amber center; 22=type IaB; 17=very strong platelets; 6=type Ib; 28=type IIa; 49="regular brown" diamonds; 56=others

GUB (NAT)=described but not assigned in HPHT article Smith et al 2001-NAT: only observed before HPHT; NV-/0=nitrogen vacancy center;
BD=brown diamond; H=hydrogen; Ni=nickel; LON=Lonsdaleite; GR1=General Radiation 1; X=describe, not assigned

nm	**559 GUB**	**567 GUB**	**575 NV^0**	**577 BD-AC**	**581 X-AC**	**587 BD-GUB**	**590 X**	**596 GUB-NAT**	**600 GUB-NAT**	**604 BD**	**610**	**613 GUB-NAT**	**615 X**	**617 NV-**	**620 NV-GUB**	**626 X NV/**	**631**	**637 NV-**	**641**	**645 X**	**652 X**	**655**	**659 GUB**	**667 X**	**676**	**681 GUB**	**687 BD**	**691 X NI?**	**700 H?**	**712 LON ?**	**741 GR1**	**749**	**755**	**763**	**772**	**785**	**800**	**819**	**839**	**881**
1				x	x		x		x		x			x		x		x		x		x					x													
2					x		x			x									x		x			x	x		x		x						x		x	x		
3				x	x		x	x	x		x			x	x	x		635	x			x					x			x?										
4				x	x		x	x	x		x			x		x		636		x		x		x	x		x													
51				x	x		x	x	x		x			x		x		636		x		x		x 670	x		x			x			x				x	x	x	
52				x	x		x		x		x			x		x		x		x		x					x													
5	562	569		x	x		x	x		x						x		634?	x			x		x	x	x	x		x	x				x	x	x	x	x	x	
8				x	x		x	x		x	x				x			x			x		x		x	x	x	x	x			x	x	x	x	x	x	x	x	x
9	x			x	x	x	x	x		x	x		x						x			x		x		x	x	x	x				x				x	x	x	
30				x	x		x			x										x		x		x	x		x	x	x	x?		x?	x?	x?			x	x	x	
6						x			x						x			x					x			x			x											
7						x			x						x			x					x						x											
50		x				x			x									x					x			x			x											
54			x			x			x						x			x					x			x			x											
26	x	x		579	584			x				x		x				x	x																					
27	x	569		579				x				x						x																						
28		x		579				x				x		x		x			x												x									
10												x				x	x				x							x												
12			x					x				x		x		x				x			x			x														
13			x					x				x						x					x			x														
14			x					x				x		x				x					x						x											
21			x					x	x			x		x		x		x	x?	(x)			(x)																	
24					x			x				x				x		x			650		x			x														
53		x	x			x			x						x			x					x			x			x											
57			x					x				x					x?	x																						
58			x					x				x			x	x		x					x																	
59					x				x									x																						
60			x					x	x?			x?		x?																										
16			x						x					x		x		x																						
17			x						x			x		x		x		x												710?										
18			x					x				x		x		x		x																						
19			x					x				x		x		x		x												710?										
20			x						x			x		x	x	x		(x)(			x																			
22			x						x			x	x		x			(x)																						
23			x						x			x				x		x			x																			
25			x						x			x		x	x	x?		(x)																						
55			x						x					x	x	x		x																						

nm	560	567 GUB	575 NV^0	577 BD-AC	581 X-AC	587 BD-GUB	590 X	596 GUB-NAT	600 GUB-NAT	604 BD	610	613 GUB-NAT	615 X	617 NV-	620 NV-GUB	626 X NV/	631	637 NV-	641	645 X	652 X	655	659 GUB	667 X	676	681 GUB	687 BD	691 X NI?	700 H?	712 LON ?	741 GR1	749	755	763	772	785	800	819	839	881
31			x	x				x				x				x		x					x		x	x														
32			x	x						x				x	x							x																		
33			x						x					x		x		x																						
34		x	x	x		x			x			x						x				x			x				x											
35			x			x						x		x		x		x					x																	
36			x			x			x					x		x		x					x																	
37			x			x			x			x		x		x		x					x																	
38	x		x					x	x			x		x		x		x					x																	
39			x	x								x		x		x		x					x																	
40			x						x			x		x		x				x																				
41			x					x	x			x		x		x		x					x																	
42			x						x																															
43			x			x			x					x		x		x		x			x																	
44			x			x			x			x		x		x				x			x																	
45			x						x			x		x		x		x					x			x														
46			x						x			x						x					x																	
47			x						x			x		x		x		x		x																				
48			x						x			x		x		x		x		x																				
49			x						x			x		x		x		x																						
11		x	x						x			x			x			x																						
15			x				(x)		x			(x)		x		x		(x)		x?																				
29			x									x		x		x		x																						
56												x				x	x	x					x			x		x?	x	x?										

3.8. DUG sample 61: FTIR, VIS/NIR, PL peak tables

FTIR SPECTRUM, 7200-400 cm^{-1}, 1000 scans at 2 cm^{-1} and 4 cm^{-1} resolution

N-A=nitrogen A aggregates; N-B=nitrogen B aggregates; plate="platelets" (large carbon-nitrogen structure); H=hydrogen; ac=amber center; O-B=oxygen-boron vib (?);

cm^{-1}	7040, 6982, 6742, 6689, 6630, 6548, 6506, 6417, 6403, 6253, 6234, 6217, 6145, 6133, 6081, 5996, 5972, 5942, 5852, 5668, 5176, 5157, 5090, 5028, 4697, 4624, 4591, 4537, 4429, 4413, 4345, 4324, 4209, 4154	3307, 3274, 3267, 3251, 3233, 3210, 3195, 3181, 3154, 3143, 3138, 3102, 3082, 3071, 3052, 3040, 3031, 3024, 3012, 3002, 2983, 2971, 2964, 2948, 2941, 2931, 2910, 2867, 2851, 2796, 2783, 2741, 2687	1460	1431	1401	1396	1383	1374	1361	1357	1352	1344	1332	1282	1220	1135	1095	1046	870	639	610	480

The IR positions between 7040 and 5157 cm^{-1} are only approximate and some of the peaks may be artefacts due to interference (the stone has not been prepared by a large culet, thus the S/N ration in the mentioned region is not very good). Most certainly, a forest of peaks occurs in this region, but the positions may vary to a certain degree.

VIS/NIR SPECTRUM AT LIQUID NITROGEN TEMPERATURE

nm	734	750	766	790	808	828	867	880	905	930	940	986
												H 2

PHOTOLUMINESCENCE AT LIQUID NITROGEN TEMPERATURE

GUB (NAT)=described but not assigned in HPHT article Smith et al 2001-NAT: only observed before HPHT; NV-/0=nitrogen vacancy center;
BD=brown diamond; H=hydrogen; Ni=nickel; LON=Lonsdaleite; GR1=General Radiation 1; X=described but not assigned

nm	567	587	637	659	681	828	905
	GUB	BD-GUB	NV-	GUB	GUB		

3.9. Cathodoluminescence

The cathodoluminescence of some selected stones was observed using a Jeol 5800 Scanning Electron Microscope; the diamonds with regular octahedral brown graining clearly exhibited cathodoluminescence along the grain bands, as expected (Fig. 45).

More interesting was the luminescence of a type IIa diamond (sample 28) and of the CO_2 diamonds when they were excited by the electron beam of the SEM. Also interesting was the CL of some of the type Ib diamonds.

The strength and distribution of the CL of the CO_2 diamonds was in no way related to the distribution of the brown color as it is the case for regular brown diamonds. The CL was very intense in some parts and inert in others; it was partly distributed along tentatively octahedral growth directions and partly along irregular zones (Fig. 46); the stones appeared to have grown in highly stressful environment and the highly inhomogeneous CL distribution is reminiscent of a broken/cemented stone.

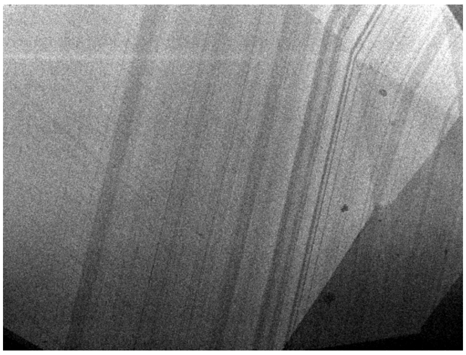


Figure 45. CL along octahedral growth (sample 12)

Figure 46. Irregular and step-like CL in a CO_2 diamond (sample 52)

The type IIa diamonds showed regular CL, except sample 28, which exhibited a spectacular CL distributed along irregular brown color bands (Fig. 47); this color distribution and CL is unique to this sample and cannot be explained at this time but is also reminiscent of a broken/cemented stone.

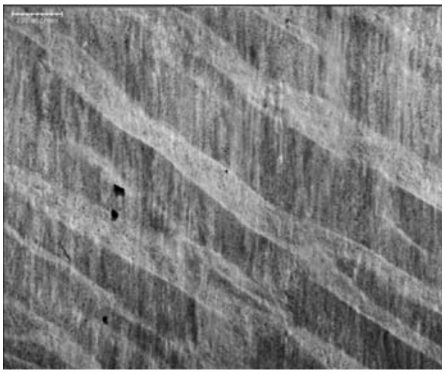


Figure 47. Most unusual CL along color bands in a type IIa diamond (sample 28)

The two extreme type Ib diamonds were also observed under the SEM; both stones, which contain a phantom cloud in their center, exhibited very weak CL; sample 61 was nearly inert and showed only very little CL along a previously fractured part which has completely healed. Sample 50 showed unusual quite regular CL, which was interesting to observe but which cannot be explained at present.

The cathodoluminescence showed quite clearly that the extreme Ib's and the CO_2's appear to have a different formation than the regular brown diamonds.

4. Correlations of the results

A close look at the above results shows that correlations between IR spectra, PL spectra, color distribution, luminescence and even inclusions exist. Based on these correlations, a classification of brown diamonds could be established.
The list below shows the data of the analyzed stones. The list is not based on the final classification but on the initial groups, which were formed mainly by their characteristic IR spectra.
We did not take the PL and VIS/NIR spectra into consideration when establishing the list of properties. It appears, that the IR spectra are much more important when classifying these diamonds. Thus the IR type plus important IR features were compared to color, color distribution, UV-fluorescence/phosphorescence and inclusions.
To demonstrate the correlations more visually two photo-tables were designed: In the first table, the face-up color and the strain pattern between crossed polarizers of 52 selected diamonds are shown.
The second table contains photographs of the color distribution of 27 selected samples (representing all types observed). The color distribution was photographed with the stones immersed in methylene iodide; in this table, pictures of characteristic luminescence patterns and inclusions are shown for stones in which these features appear characteristic.
Additionally, the above features were compared to the luminescent pattern of some stones when they were excited by an electron beam (cathodoluminescence). These pictures were recorded in black and white since the camera in the electron microscope could not record in color.

4.1. Table of Properties

sample #	weight ct	type (FTIR), IR features	color	color distribution	inclusions	LW UV	SW UV
1	0.098	IaA/B?, deformed 1 phonon absorption, solid CO_2	medium yellowish brown	half homogeneous brown, half pink-cl-brown zoned	very fine needles, reflective flakes	medium yellow* with weak lasting phos.	medium yellow* with stronger lasting phos.
2	0.060 **missing**	IaA/B?, deformed 1 phonon absorption, solid CO_2	deep olivish orange brown	strong orange-brown, pink, dark grey-brown zoning	lots of very fine needles and reflective flakes	medium yellow*	medium yellow*
3	0.068	IaA/B?, deformed 1 phonon absorption, solid CO_2	medium dark brown	homogeneous brown (patchy zones,darker-lighter)	very fine needles, reflective flakes	medium yellow*	weaker yellow* with weak lasting phos.
4	0.075	IaA (with some B), solid CO_2	medium pinkish brown	irregular patchy color, some brown and pink graining, colorless zones	very fine needles, reflective flakes	medium yellow* with faint lasting phos.	weaker yellow* with weak lasting phos.
51	0.034	Type IaA/B?, deformed 1 phonon absorption, solid CO_2	medium pinkish brown	pink and brown patchy coloration, relatively homogeneous	lots of very fine needles and reflective flakes	medium-strong yellow* with weak lasting phos.	medium yellow* with medium lasting phos.
52	0.053	Type IaA/B?, deformed 1 phonon absorption, solid CO_2	medium dark olivish brown	brown patchy coloration	very fine needles and reflective flakes, xtls, large xtl (ID?)	medium yellow* with faint lasting phos.	weak yellow* with weak lasting phos
62		Type IaA, solid CO_2	light brown	brown patchy coloration	lots of very fine needles and reflective flakes	medium yellow* with faint lasting phos.	weak yellow* with weak lasting phos
5	0.061	IaA/B?, deformed 1 phonon absorption, "pseudo CO_2"	deep olivish orangish brown	half homogeneous brown (patchy), half brown-yellow-colorless zoned	lots of reflective flakes	medium yellow* with faint lasting phos.	weaker yellow* with weak lasting phos.
8	0.081	IaA/B, deformed 1 phonon absorption, "pseudo CO_2"	medium yellowish orangish brown (intense color)	partly near colorless, "peach" colored graining	very fine needles, reflective flakes (distributed along graining planes)	medium yellow*	weaker yellow* with weak lasting phos.
9	0.064	IaA/B?, deformed 1 phonon absorption, "pseudo CO_2"	deep pinkish orangish brown	homogeneous peach brown (patchy) with some graining	lots of reflective flakes	medium yellow*	weaker yellow* with weak lasting phos.
30	0.063	IaA/B?, deformed 1 phonon absorption, "pseudo CO_2"	dark orange brown	areas of brown graining, areas of brown color patches/broad bands	lots of reflective flakes	medium yellow*	weak yellow*
6	0.126	Ib, 4114cm very strong	medium dark pinkish brown	homogeneous brown with very little pink graining	feathers	faint reddish orange	weak reddish orange
7	0.147	Ib, 4114cm very strong	medium dark-dark brown	homogeneous (patchy) brown very little graining	A very fine needle, feathers	faint reddish orange	weak reddish orange
50	0.054	Type Ib/aA, v. strong 3456cm, 4934cm Strange "amber center" at 4238/4065cm	dark orangish olive-brown	orange color zones concentrated around the phantom, some "grey" graining	phantom (cuboid), twinning wisps	none	none
54	0.054	Type Ib very strong 4114cm	medium pinkish brown	pink graining	feathers, small crystals	faint orange	weak orange
61	0.035	Type Ib, extremely high nitrogen content, most bizzare spectrum	deep red-orange-brown	orange-brown zoning around the phantom	particles and needle like inclusions, phantom (cuboid)	inert	inert
26	0.650	IIa	medium (orangish) brown-yellow, intense color	faint yellow-brown graining	feathers	none	none
27	0.830	IIa	medium brown yellow	no graining found	feathers	none	none
28	0.921	IIa	medium (orangish) brown-yellow, intense color	broad parallel color bands-two sets intersecting eachother at approx. 60/120°	feathers	none	none
63	3.09	IIa	medium dark orangish brown	very little and faint graining, large color patch	feathers	none	none

sample #	weight ct	type (FTIR), IR features	color	color distribution	inclusions	LW UV	SW UV
10	0.137	IaA with very strong 4065/weak 4160 (double amber center)	dark olive brown	olive-brown graining	very fine dust like reflective particles, some needles	none	none
12	0.074	IaA/B with double amber center	medium dark yellowish olivish brown	olivish brown graining (one grain band very thick)	feathers	none	none
13	0.067	IaA/B with double amber center	medium light yellowish olivish brown	olivish brown graining	feathers	weak blue	faint blue
14	0.059	IaA/B with double amber center	med. light yellowish brown	brown graining	feathers	none	none
21	0.084	IaA/B, A>>B, double amber center	medium dark olivish brown	regular brown graining	feathers	none	none
24	0.079	IaA, double amber center	medium dark olivish brown	faint brown graining	many fine particles, crystals	none	none
53	0.129	Type Ib olive, very strong 4065cm	deep olive	olive graining	none	faint orangy yellow	faint orangy yellow
57	0.057	Type IaA/B, double amber, 4065>4165	dark olivish brown	olive- and brown graining	feathers, pinpoints	faint yellow	none
58	0.044	Type IaA/B, double amber center	dark olivish brown	brown and olive graining	feathers	none	none
59	0.057	Type IaA near pure, double amber center	medium dark olive brown	olive and brown graining, an olive color patch..,	none	faint orangy yellow	none
60	0.049	Type IaA/B, double amber, 4065>4165	medium dark olive brown	olive and brown graining, strong	feathers	weak chalky blue	none
16	0.060	IaA/B, A<<B, very strong platelets	medium dark pinkish brown	very regular brown graining	crystals	weak blue	faint yellowish blue
17	0.074	IaA/B, very strong platelets	medium brown	very regular brown graining	feathers	weak blue	faint yellowish blue
18	0.076	IaA/B, very strong platelets	medium yellowish brown	very regular brown graining	feathers	weak blue	faint yellowish blue
19	0.072	IaA/B, very strong platelets	medium light yellowish brown	weak but very regular brown graining	feathers	weak blue	faint yellowish blue
20	0.080	IaA/B, A<<B, 4838cm	medium dark brown	regular brown graining	feathers	weak yellowish blue	faint yellowish blue
22	0.066	IaB, (A very small), high hydro	medium dark brown	very regular brown graining, cubic shape	tiny particles	weak chalky blue	faint chalky blue
23	0,072	IaB, (A very small), high hydro	medium yellowish brown	very regular brown graining, square shape	feathers	weak chalky yellowish blue	faint chalky yellowish blue
25	0.147	IaB, nearly pure	medium pinkish brown	very regular brown and pink graining, square shape	feathers, crystals	medium chalky blue	weak chalky blue
55	0.048	Type IaB near pure	medium light brown some green transmission	pink and brown graining, barely visible	feathers	medium chalky blue	weak chalky blue

sample #	weight ct	type (FTIR), IR features	color	color distribution	inclusions	LW UV	SW UV
31	0.102	Type IaA, little B, double amber	medium light olivish brown	olive and brown graining,weak	none	faint yellow	none
32	0.102	Type IaB, little A, 1430	medium light pinkish brown (some green transmission)	brown graining, cubic shape	feathers, crystals	medium chalky yellow blue with faint lasting yellow phos.	same as LW but weaker
33	0.110	Type IaA/B, A=B	med. dark brown (some green transmission)	brown graining with some patchy areas	feathers	weak yellow	same as LW but weaker
34	0.106	Type IaA	med. dark brown (some green transmission)	brown graining	feathers	weak yellow	same as LW but weaker
35	**missing**	Type IaA, very little B					
36	0.118	Type IaA/B	dark brown	brown graining	feathers	faint yellow	none
37	0.103	Type IaA/B, A >>B	dark orangish brown	orangish-brown graining	feathers	none	none
38	0.098	Type IaA	very dark brown	brown graining	none	none	none
39	0.065	Type IaA, little B	very light yellowish brown	brown graining	feathers, some pinpoints	weak yellow	same as LW but weaker
40	0.077	Type IaA/B, B>A	light yellowish brown	brown graining	feathers, crystals	weak-medium chalky yellow	same as LW but weaker
41	0.078	Type IaA/B	medium light brown	brown graining	none	faint yellow	none
42	0.068	Type IaA/B, A<<B	medium yellowish brown (some green transmission)	brown graining, cubic shape highly reflective graining	highly reflective graining, crystals	weak yellow	same as LW but weaker
43	0.055	Type IaA/B, A=B	medium brown	brown graining, one band rel. broad	crystals	weak-medium chalky yellow	same as LW but weaker
44	0.064	Type IaA/B	medium yellowish brown	brown graining	none	weak yellow	same as LW but weaker
45	0.066	Type IaA, little B	medium yellowish brown	V-shaped brown graining, rel. broad	feathers	weak yellow	same as LW but weaker
46	0.055	Type IaA, near pure	medium brown	brown graining	feathers	faint yellow	none
47	0.068	Type IaA, little B	medium pinkish brown	pink and brown graining, very strong	feathers	none	none
48	0.063	Type IaA/B, A<B	medium dark brown	brown graining, cubic shape	feathers, crystals	faint-weak yellow	same as LW but weaker
49	0.070	Type IaA/B, H	medium dark brown	brown graining	lots of twinning wisps, needles	faint yellow	none
11	0.058	IaA without amber center	deep greenish brown-orange	some graining in a homogeneous background	feathers	strong green	same as LW but weaker
15	0.072	IaA/B, A=B	medium brown	very regular brown graining	small particles	weak blue	faint yellowish blue
29	0.151	Type IaA/B with faint amber center	light brown	faint brown graining	none	medium blue	weak blue
56	0.050	Type IaA near pure	medium brown	brown graining	crystal, two elongate needles	faint orangy yellow	none

Sample

30=CO_2 30="Pseudo-CO_2" 28=type IIa 6=type Ib 17=very strong platelets

22=type IaB 49="regular brown" diamonds 12=double amber center (4165/4065cm^{-1}) 56=others

***The fluorescence of these stones appears irregular**

4.2. Correlation between IR features and color

We found some apparent correlations between the color of the samples and their infrared spectra. The most obvious correlation was noticed when comparing the depth of color with the IR spectra: it was found, that in type Ia diamonds the strength of the 4165cm^{-1} amber center peak (when present) correlated directly with the apparent depth of color (Fig. 49). This was true for most but not all stones. The depth of color was compared through the pavilion of the stones to avoid the influence of the cut. On the color suite below (Fig. 48), the stones are in order of the strength of their amber center (sample 38➔strongest peak, sample 29➔weakest peak). The correlation appears to work quite nicely, except that samples 33 and 43 are too dark for the apparent strength of their 4165cm^{-1} feature. After thinking about some other reason for its deeper color, it was found that these two diamonds contained more B-aggregates than A aggregates; only the lightest sample had a similar B vs A aggregate ratio, all others contained much more A than B aggregates. See the underneath section “nitrogen VS color” for the findings concerning this phenomenon. Below, the color suite with brown diamonds from dark to light with their IR spectra (normalized to their intrinsic diamond peaks).

Figure 48. A color suite of diamonds from light to very dark brown color, through the pavilion and face-up

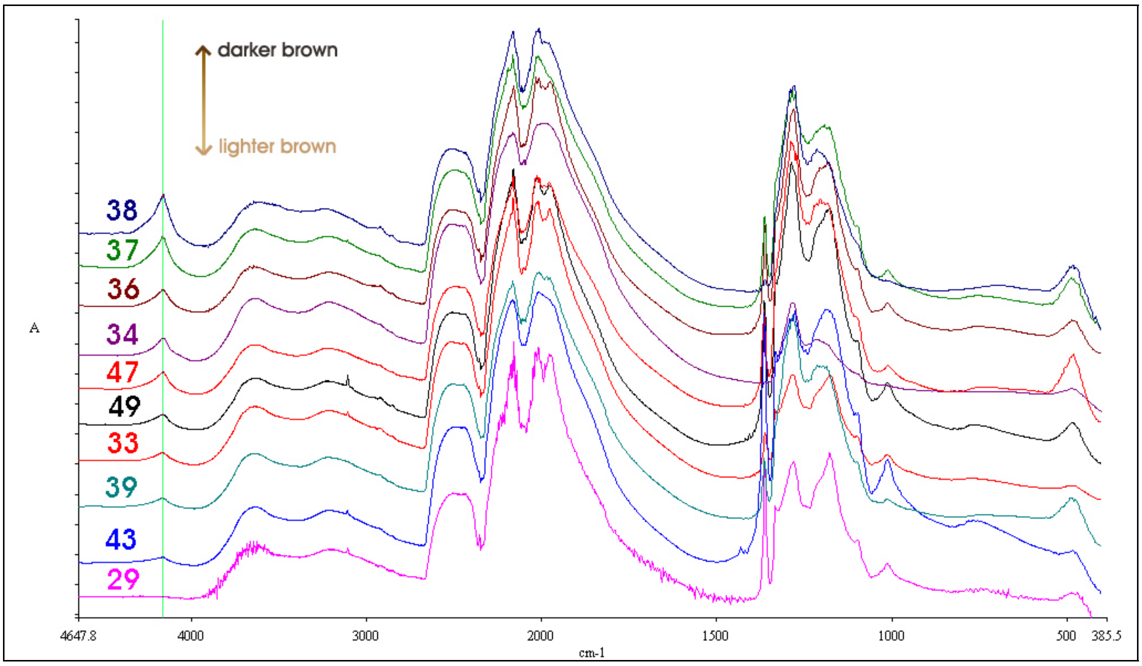


Figure 49. The normalized IR spectra correlating to the above color suite

Another very apparent correlation was mentioned earlier: all type Ia brown diamonds with a tint of olive exhibit a peak just besides the 4165 cm^{-1} amber center. The position was defined as 4065 to 4070 cm^{-1} and the resulting 4165 cm^{-1}/4065 cm^{-1} "doublet" was called "double amber center" (Fig. 51).

Here, a direct correlation between the amount and/or depth of the olive color with the strength of the 4065 cm^{-1} peak was difficult. Since some pure olive colors show only the 4065 cm^{-1} absorption, there appears to be such a correlation. Interestingly, type Ib "pure" olive diamonds sometimes show the peak at 4065cm^{-1} very strongly and sometimes a peak at 4115 cm^{-1} (typical for Ib "browns") instead. Some even show unusual double peaks consisting of the 4115 cm^{-1} feature and a peak at 4234 cm^{-1}. These are more yellow stones though.

Anyway, in all olive-browns, which we have seen until now, the doublet was always found at 4065 cm^{-1}/4165 cm^{-1}.

Even in the "extreme" type Ib diamond (sample 50), which had a modifying olive color, a 4065 cm^{-1} peak was visible besides a strong peak at 4234 cm^{-1}. Thus this peak was visible in any type of diamond as soon as the slightest olive color was apparent. Underneath the comparison of olive to olivish brown diamonds (Fig. 50) with their IR spectra (Fig. 51) is shown.

Figure 50. A color suite of olivish brown to olive diamonds, face up and through the pavillion

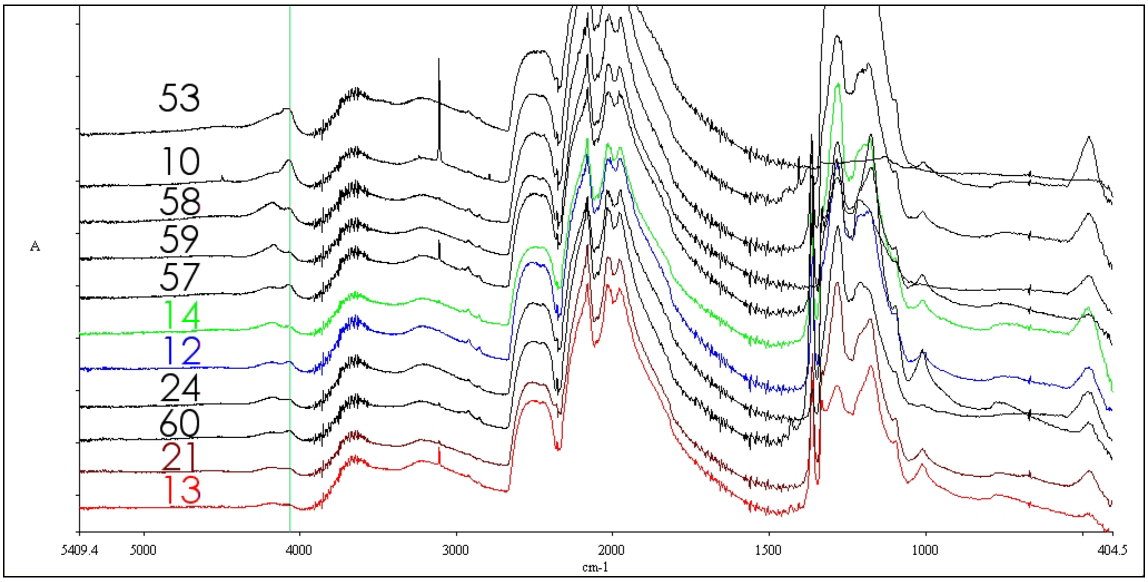


Figure 51. The normalized IR spectra correlating to the "olive-brown" color suite

It has been suggested by Schrauder et Navon (1993), that a close correlation between the depth of color of solid CO_2 containing diamonds and the strength of the peaks observed at 2390 cm^{-1} and 645 cm^{-1} exists; for color variations within one diamond, this may well be the case; our observations show, that this is not the case when several samples are compared to one another: sample 62, for example, shows strong peaks at the mentioned positions but only very light brown coloration whereas sample 51 shows only very weak peaks but a medium brown color (Fig. 52). It appears reasonable to assume though, that variations of the depth of color within one stone correlate directly with the strength of the two absorption assigned to solid CO_2 (as suggested by the above authors). Thus the global depth of color of several carbon dioxide containing stones cannot be defined by these absorptions.

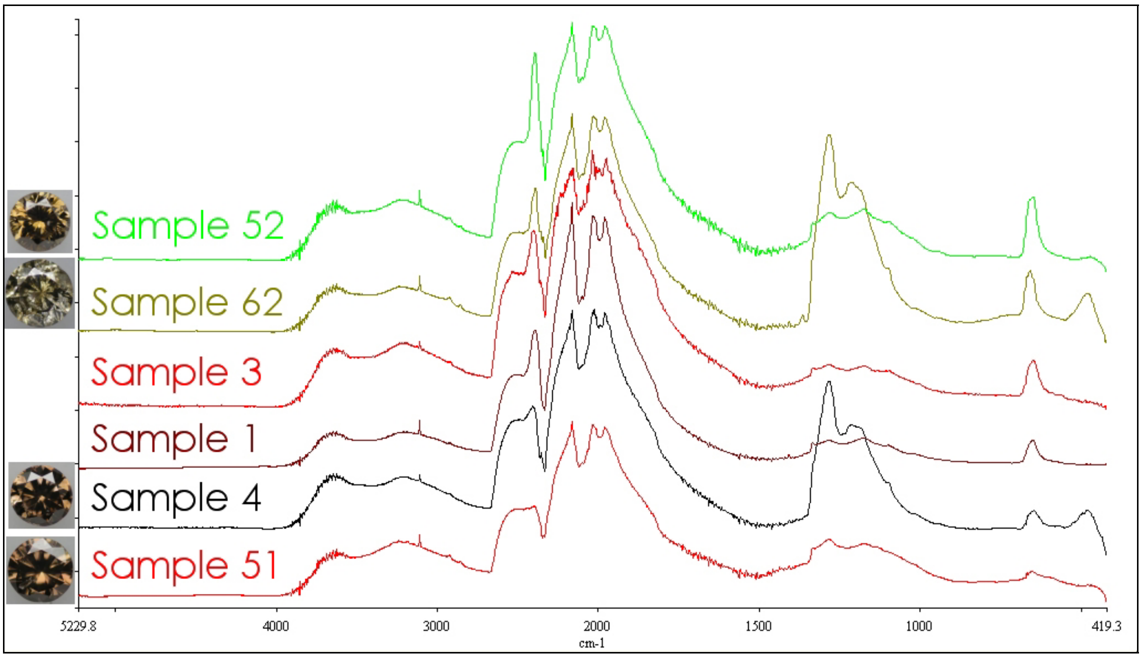


Figure 52. The IR spectra compared to the face up color of solid CO_2 containing diamonds

4.3. Nitrogen VS. color

The amount of nitrogen appears to play very little or no role in the coloration of type Ia brown diamonds. The depth of color was in no way correlated with the amount of nitrogen. Very dark stones with very low or practically no nitrogen (type IIa) were seen while very light stones with very high concentrations also exist.

Only in the extremely rare truly brown type Ib diamonds, the depth of color directly correlates with the strength of the 1344 cm^{-1} and 1135 cm^{-1} IR-absorptions due to single substitutional nitrogen. Why these stones appear brown instead of yellow or orange is one of the important questions arising from this work.

We had to advance quite far into this work, until we stopped only thinking about the presence or strength of the type Ia vs. Ib vs. IIa one-phonon absorptions (mainly due of nitrogen), but started to look at the ratio of A vs. B aggregates. And indeed, the analyzed samples showed a strong correlation between the A aggregates and the strength of the 4165 cm^{-1} amber center peak: it was found, that no matter how strong or weak the 1282 cm^{-1} peak (plus its 1215 cm^{-1} side peak) due to the A-aggregates of nitrogen, there was a very defined amber center present, as long as the amount of B-aggregates was small or even none (seen as the 1175 cm^{-1} peak plus its 1010 cm^{-1} side peak) (Fig. 53). The analyzed type IIa brown diamonds exhibited no amber center.

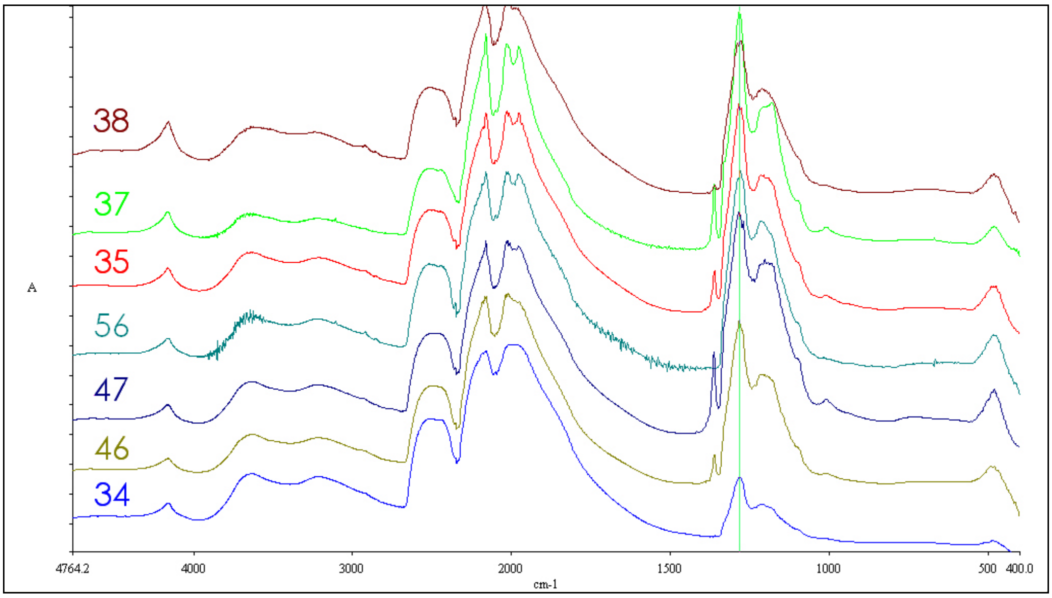


Figure 53. The IR spectra of diamonds with strongly dominant A-aggregates with very distinct 4165 cm^{-1} features

As soon as the B-aggregates dominated, the amber center peak decreased in size considerably (Fig. 54). Unfortunately, we have only one reference-spectrum of a pure type IaB brown diamond; this stone indeed showed only the slightest trace of the amber center; it can be considered to be practically absent. This pure IaB diamond was relatively light brown, but according to its color, an easily visible amber center would normally be expected; and as expected, a type IaA/B diamond of A>B of equally light coloration was compared and found to contain a very easily visible amber center. Diamonds of the intermediate type IaA/B with A≤B showed amber centers with strengths between the two "extremes". As seen above, the strength of the 4165 cm^{-1} was in all cases directly related to the depth of color, except in the stones containing a larger amount of B-aggregates; the close observation of the A to B center ratio has shown, that the strength of the amber center correlates well with the depth of color in all diamonds with stronger A-aggregate absorptions and that this fact becomes less and less true the more B-centers are present in a stone. The amber center appears to be formed by a defect and the A-aggregates, it appears that this defect does not form an IR active center with the B-aggregates.

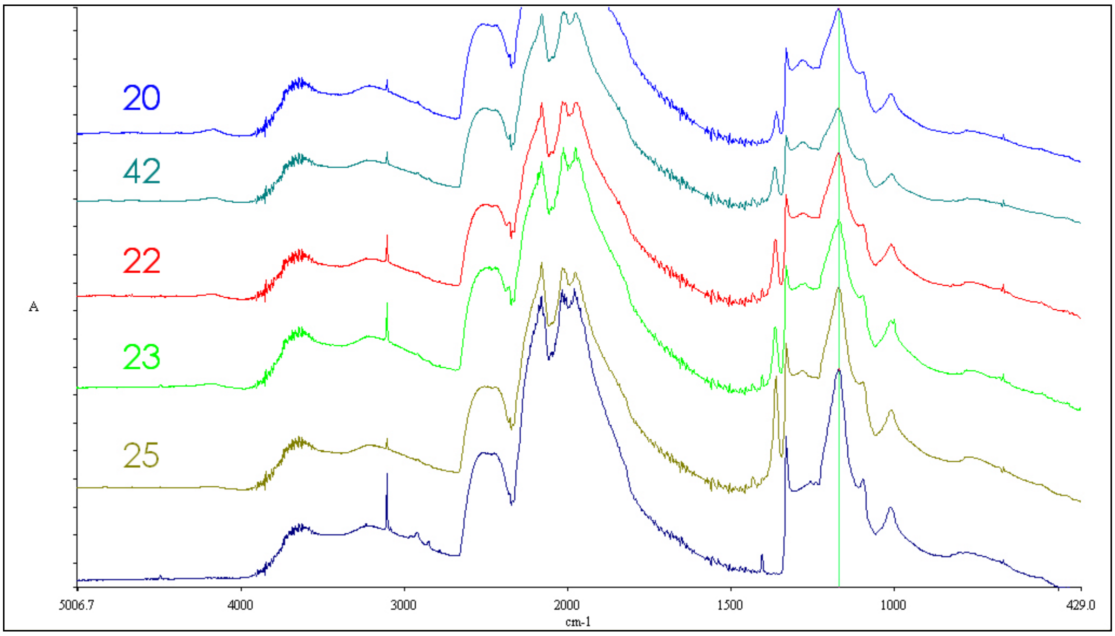


Figure 54. The IR spectra of diamonds with strongly dominant B-aggregates with weak to missing 4165 cm^{-1} features

4.4. IR type/features VS. color distribution

It was found, that all "typical" brown diamonds (i.e. type Ia with the 4165 cm^{-1} amber center) had the classical sharp parallel color bands known as "brown graining"; quite often, some pink graining was found distributed within the brown graining (e.g. sample 47). This regular brown graining was also present in all extreme type Ia's, i.e. in type IaA, type IaB and type IaA/B with very intense platelet peaks.

All diamonds, type Ia and Ib, with the double amber center (i.e. the 4065 cm^{-1}/4165 cm^{-1} absorptions) exhibited brown and olive colored graining. The "regular" type Ib brown diamonds (i.e. sample 6, 7 and 54) showed a very homogeneous color. Some graining present in two stones appeared to be "overlaid" on the already present even brown coloration.

The two "extreme" type Ib stones (sample 50 and 61) had their color distributed in a concentric fashion along a phantom in the center of the diamonds; in sample 50 the zoning followed the cuboid sectors of the diamond; in sample 61 the distribution was less regular but also along the cuboid growth sectors.

The diamonds with the CO_2 IR spectra (termed "CO_2" and "Pseudo CO_2" based on presence or absence of the strong 2390 cm^{-1} peak) showed a patchy brown coloration. Some of these stones (mainly "Pseudo CO_2") featured graining or broad bands besides the patchy zones, and one stone (sample 51) had a homogeneous color distribution.

The four type IIa diamonds included in this study exhibited various forms of color distribution: sample 26 showed even coloration with very slight brown graining, sample 27 was completely homogeneous and sample 28 exhibited an extremely unusual distribution of it's color: the color was present as two sets of broad irregular parallel brown-yellow bands, something we have never observed before in any stone of any color. These bands appeared very different from the known "graining" pattern. Sample 63 had very slight graining but otherwise appeared completely homogeneous.

4.5. IR type VS. UV luminescence

Typically, type IaB diamonds showed a much stronger fluorescence to LW/SWUV than type IaA diamonds. The emission is often clearly distributed along the octahedral graining direction. This appears to be due to a highly localized distribution of the N3 aggregates around regions of plastic deformation (Kanda et al., 1999); the same appears to be true for the H3 center, which causes green emission in diamonds (Hofer, 1998)

A-aggregates tend to play a role as a luminescence poison, thus quench the blue N3 emission. This occurs because of an energy transfer to the A-aggregates (Zaitsev, 2001). The amount of A-aggregates seems to be unimportant in the group of CO_2 containing diamonds- no matter what aggregation state was present, the stones all glowed rather strongly yellow to greenish yellow to UV radiation, with a lasting afterglow when the UV source was shut off. The yellow luminescence appeared very irregular in all these stones except sample 51, and the pattern closely followed the color distribution. Sample 11, which is a near pure type IaA diamond with a moderate nitrogen content, had a strong green emission due to the H3 center; this is surprising since the A aggregates are expected to quench such luminescence. The type Ib diamonds do generally not exhibit UV luminescence, although the lighter brown type Ib's exhibited a faint reddish-orange fluorescence under LWUV and a weak reddish-orange fluorescence under SWUV.

4.6. IR type VS. inclusions

There was one apparent correlation between inclusions and IR features: all “CO_2” and “Pseudo-CO_2”-diamonds contained very small reflective particles. These particles became visible when the stones were tilted back and forth, illuminated from above with a fibre optic light source. Some of them appeared to have a hexagonal outline, but most did not show a clear form and were rather irregular and rounded. Besides these particles, most of these stones showed extremely fine needle-like inclusions. These features where so fine, that they were just visible under darkfield illumination and high magnification. It was not possible to resolve the nature of these “needles”, i.e. if they were produced by lined-up particles or if they were indeed needles. Octahedral diamond crystals were found as inclusions in some of the stones. Another feature, which was only found in two extreme type Ib diamonds (sample 50 and 61), were dust and needle-like particles forming a phantom. In all other diamond types (i.e. “typical” type Ia and all type IIa diamonds), solid inclusions were rather seldom encountered; when present, these were usually rounded colorless crystals, most probably enstatite or olivine. The most common features in the majority of brown diamonds where unhealed fractures and cleavages.

4.7. Inclusions VS. color distribution

In the “CO_2” and “Pseudo-CO_2”-diamonds, the small particles were distributed along the color bands and patches; it appeared that indeed no particles were present in the “near-colorless” areas of these stones and in regions with “regular” brown graining. As described above, in the type Ib diamonds, which featured a phantom in the center, color distribution and inclusions where closely related

4.8. Color and color distribution VS. strain pattern

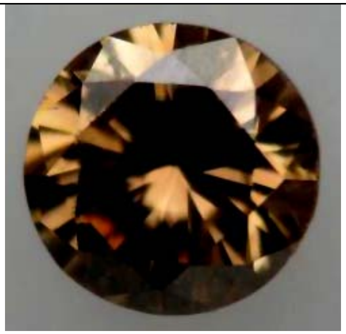
It has been mentioned before, that the depth of color of brown diamonds is directly correlated to the intensity of the strain pattern when viewed between crossed polarizing filters (Hofer, 1998). It was suggested, that high order interference colors such as orange and red are present in darker brown diamonds, while lighter brown diamonds exhibit mainly gray blue and some orange interference colors. The observations made in this work quite clearly show, that this correlation cannot be made as easily. Neither the color (Fig. 55) nor the amount of colored graining do correlate to the intensity of the strain patterns, since strain can be due to several causes, e.g. colored and colorless graining and inclusions. For example, one type IIa diamond (sample 63) with very little observable graining exhibited rather strong interference colors. Also a good example is sample 5, a “Pseudo-CO_2” diamond with half of its color confined to very strong graining; this diamond does not exhibit any strain pattern due to plastic deformation. It can be agreed, that most dark diamonds showed higher order interference colors than light stones, but this cannot be applied to all diamonds. The banded/linear extinction patterns, if present, were found to be clearly related to the amount of graining and they always followed the graining. These extinction patterns were not always accompanied by interference colors.

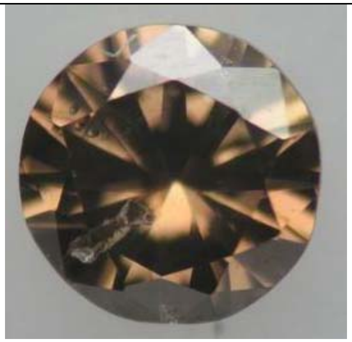
(1) (2) (1) (2)

Figure 55. The strain pattern of the light brown diamond (2) is apparently much stronger than the more linear pattern of the medium dark brown diamond (1)

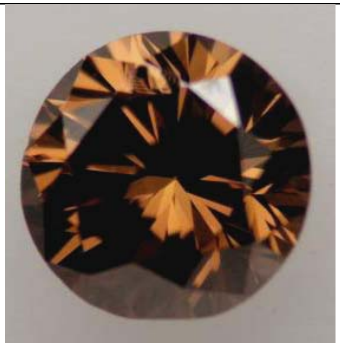
4.9. Picture Table: Color appearance, Pattern between crossed polarizers

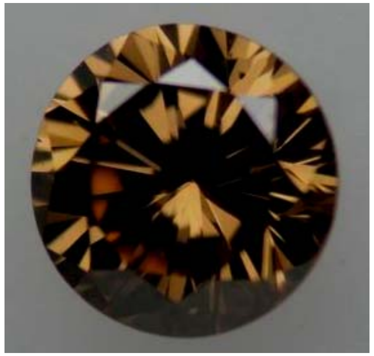
The following table was created to visually demonstrate the face up appearance of the studied diamonds and to compare the colors of the stones with their IR type. This has its importance, since clear spectroscopic differences can be found depending on slight color differences. Also the strain pattern between crossed polarizers is shown for many stones, since this is characteristic for by far most brown diamonds and cannot be properly described by words. The strength of the strain pattern has been associated with the depth of the brown coloration (Hofer, 1998); the side-by-side comparison in this table clearly shows, that this correlation does not exist. The pictures were recorded through a Nikon SMZ660 gemological microscope with an Olympus Camedia 5050 digital camera using a special microscope adapter. Some of the pictures showing the strain patterns were taken with the stones immersed in methylene iodide.

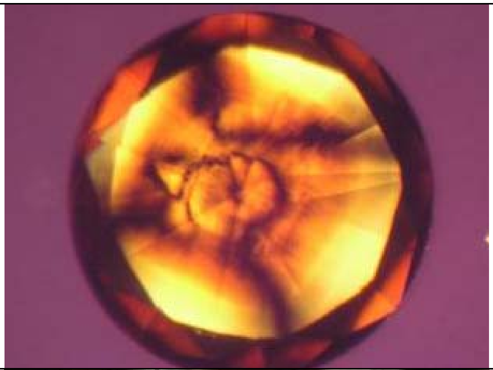
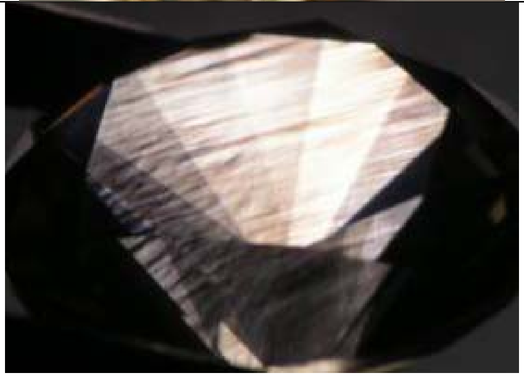
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
1	Type IaA/B; solid CO_2 medium yellowish brown		No signs of strain (equal to sample 4)
3	Type IaA/B; solid CO_2 medium dark brown		No signs of strain (equal to sample 4)

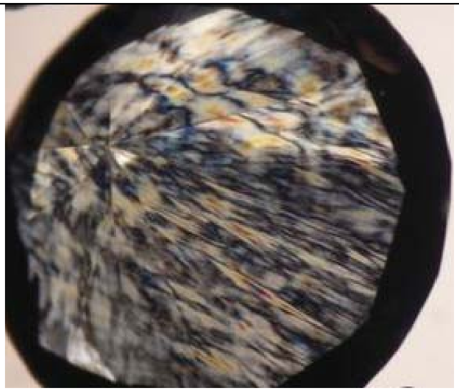
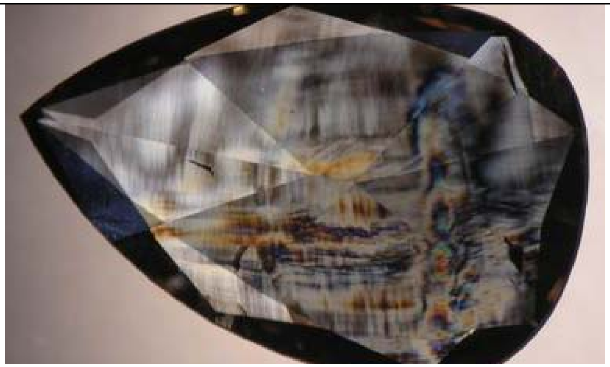
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
4	Type IaA; solid CO_2 medium pinkish brown		 No signs of strain
51	Type IaA/B?; solid CO_2 medium pinkish brown		No signs of strain (equal to sample 4)
52	Type IaA/B?; solid CO_2 medium dark olivish brown		No signs of strain (equal to sample 4)

#	FTIR Color description	Color appearance	Pattern between crossed polarizers
62	Type IaA; solid CO_2 light brown		No signs of strain (equal to sample 4)
5	Type IaA/B?; "Pseudo-CO_2" deep olivish orangish brown		No signs of strain (equal to sample 4)
8	Type IaA/B?; "Pseudo-CO_2" medium yellowish orangish brown (intense color)		No signs of strain (equal to sample 4)

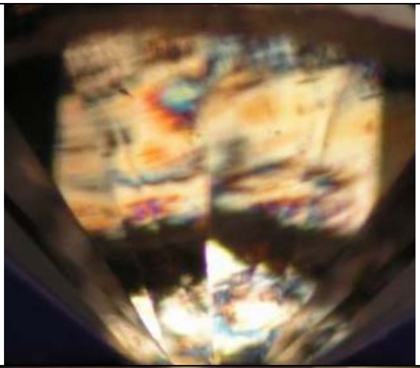
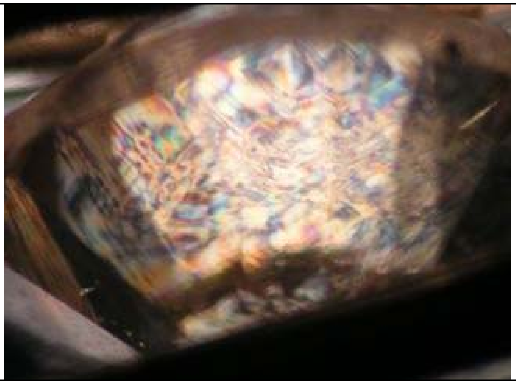
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
9	Type IaA/B?; “Pseudo-CO_2” deep pinkish orangish brown		No signs of strain (equal to sample 4)
30	Type IaA/B?; “Pseudo-CO_2” dark orange brown		No signs of strain (equal to sample 4)
6	Type Ib; very strong 4114 cm^{-1} peak medium dark pinkish brown		

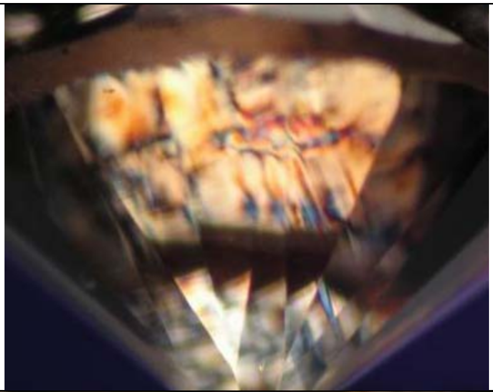
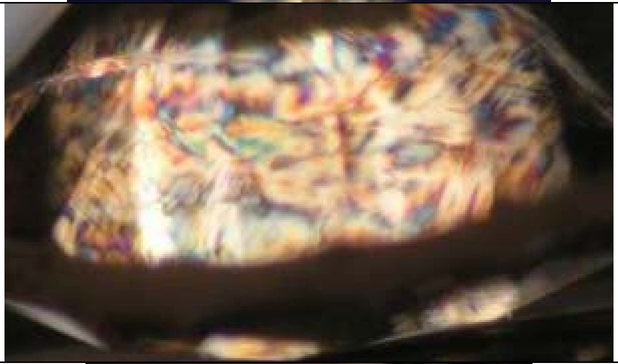
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
7	Type Ib; very strong 4114 cm^{-1} peak medium dark-dark brown		
50	Type Ib/aA; very strong 3456 cm^{-1} peak, 4934 cm^{-1}, 4238/4065 cm^{-1} peaks dark orangish olive-brown		
54	Type Ib; very strong 4114 cm^{-1} peak medium pinkish brown		

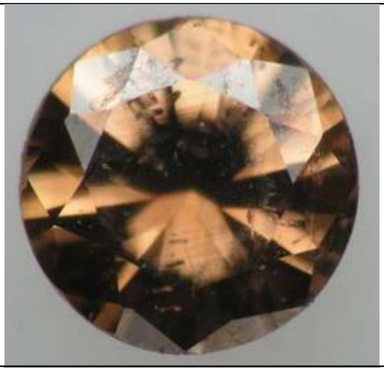
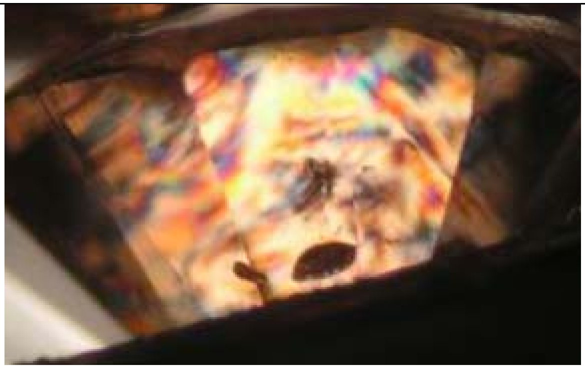
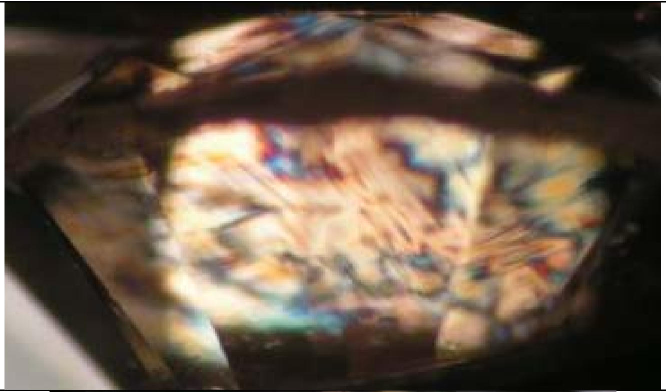
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
61	Type Ib MONSTER deep red-orange-brown		
26	Type IIa medium (orangish) brown-yellow, intense color		
27	Type IIa medium brown yellow		

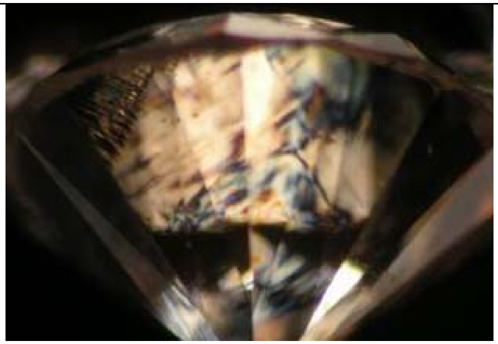
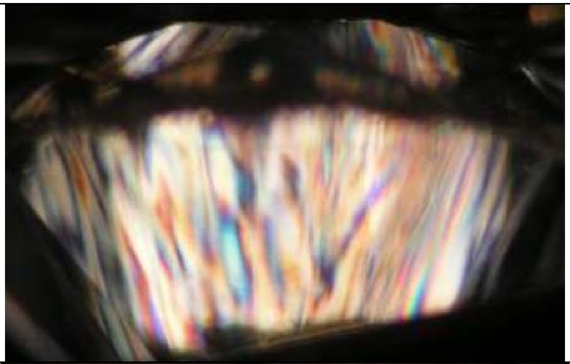
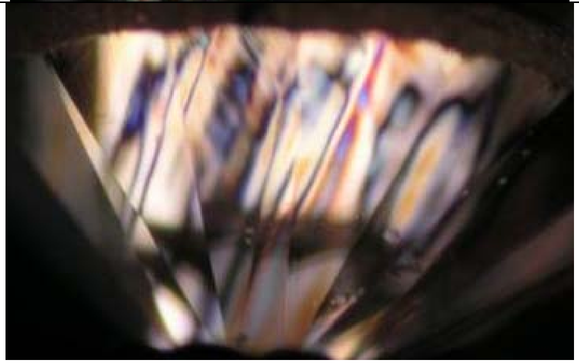
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
28	Type IIa medium (orangish) brown-yellow, intense color		
63	Type IIa medium dark orangish brown		
12	Type IaA/B "Double amber center" medium dark yellowish olivish brown		

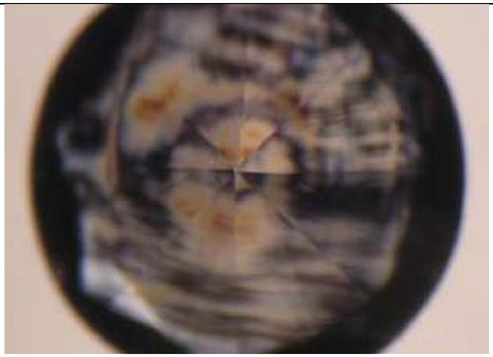
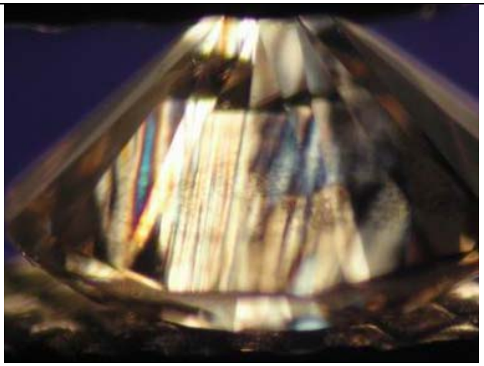
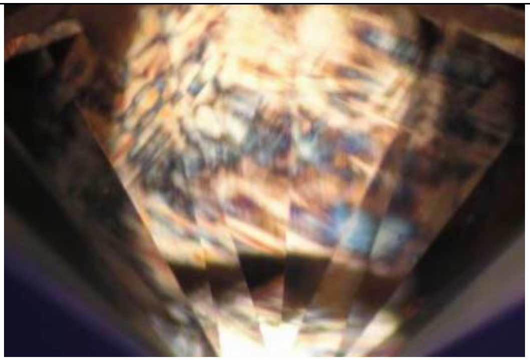
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
53	Type Ib, near pure 4065 cm^{-1} peak deep olive		
13	IaA/B with double amber center medium light yellowish olivish brown		
21	IaA/B, A>>B, double amber center medium dark olivish brown		

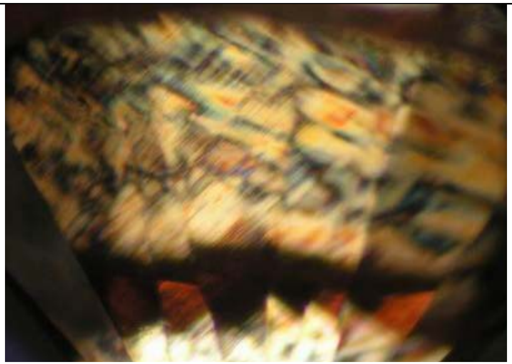
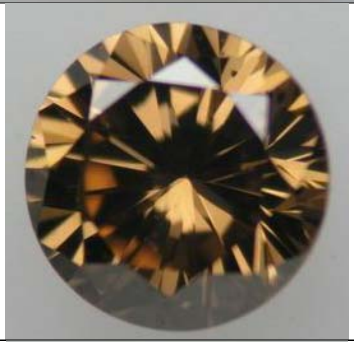
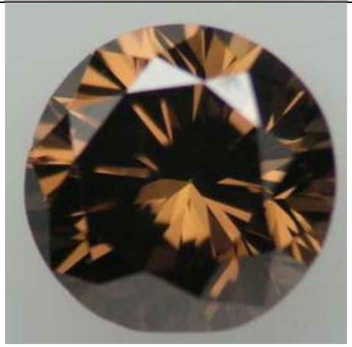
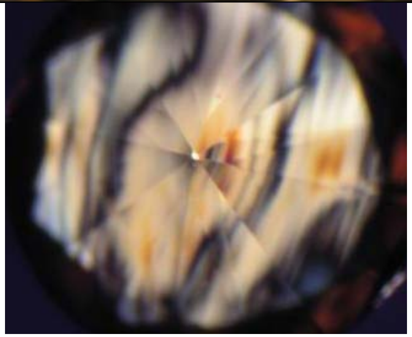
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
24	IaA, double amber center medium dark olivish brown		
59	Type IaA near pure, double amber center medium dark olive brown		
25	Type IaB medium pinkish brown		

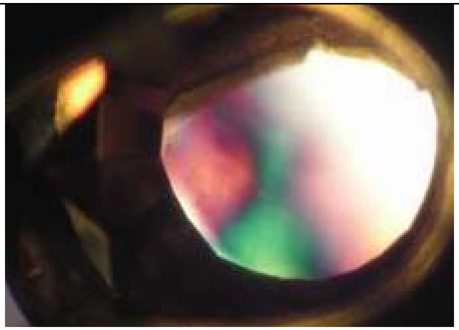
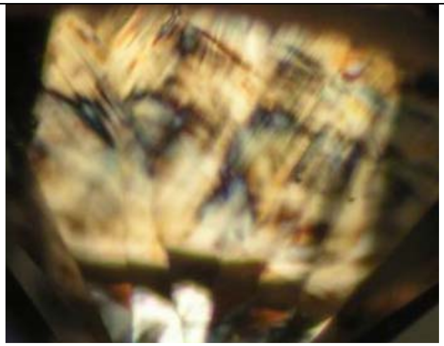
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
20	IaA/B, A<<B, 4838 cm^{-1} medium dark brown		
23	IaB, (A very small), high hydro medium yellowish brown		
55	Type IaB near pure medium light brown some green transmission		

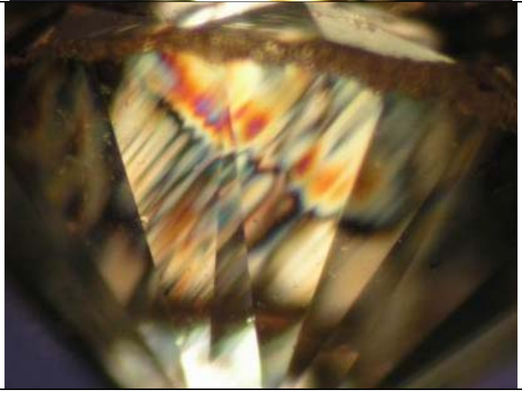
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
16	IaA/B, A<<B, very strong platelets medium dark pinkish brown		
17	IaA/B, very strong platelets medium brown		
19	IaA/B, very strong platelets medium light yellowish brown		

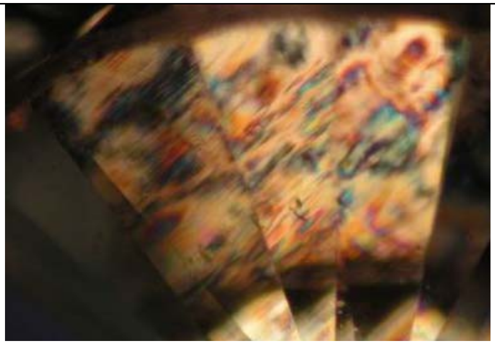
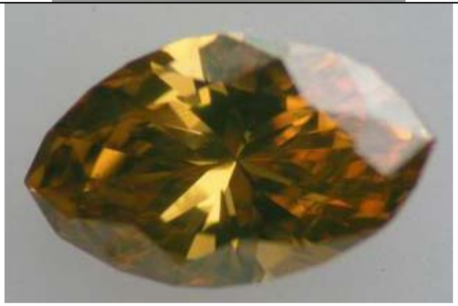
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
42	Type IaA/B, A<<B medium yellowish brown (some green transmission)		
45	Type IaA medium yellowish brown		
47	Type IaA medium pinkish brown		

#	FTIR Color description	Color appearance	Pattern between crossed polarizers
48	Type IaA/B, A<B medium dark brown		
31	Type IaA, little B, double amber medium light olivish brown		
32	Type IaB, little A, 1430cm^{-1} medium light pinkish brown (some green transmission)		

#	FTIR Color description	Color appearance	Pattern between crossed polarizers
33	Type IaA/B, A=B med. dark brown (some green transmission)		
34	Type IaA med. dark brown (some green transmission)		
36	Type IaA/B dark brown		

#	FTIR Color description	Color appearance	Pattern between crossed polarizers
37	Type IaA/B, A >>B dark orangish brown		
38	Type IaA very dark brown		
40	Type IaA/B, B>A light yellowish brown		

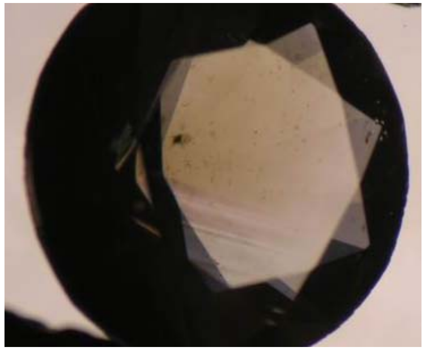
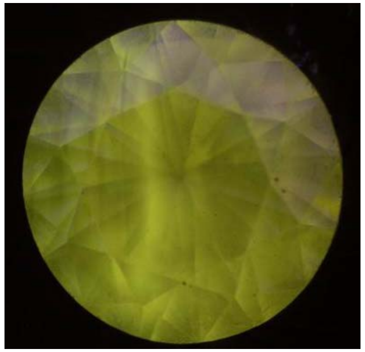
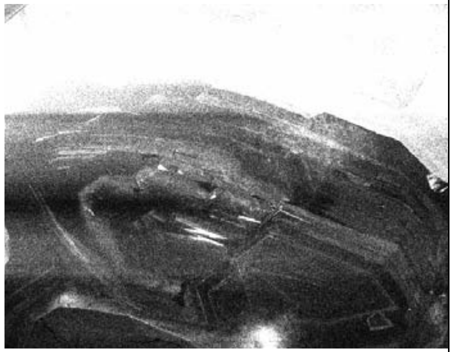
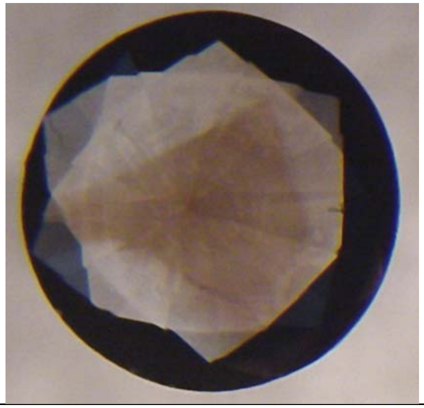
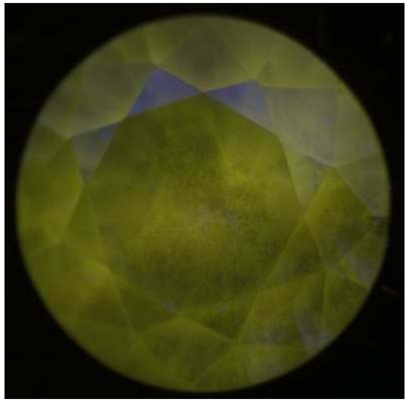
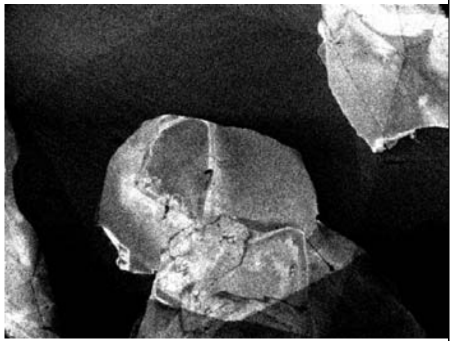
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
41	Type IaA/B medium light brown		
43	Type IaA/B, A=B medium brown		
44	Type IaA/B medium yellowish brown		

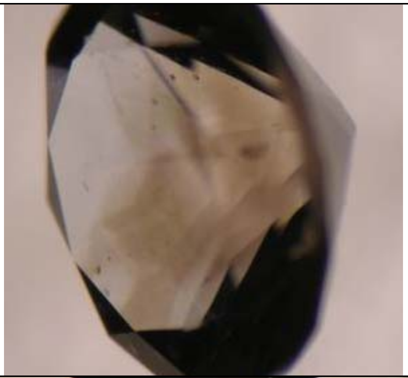
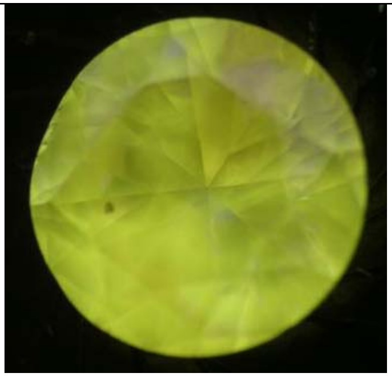
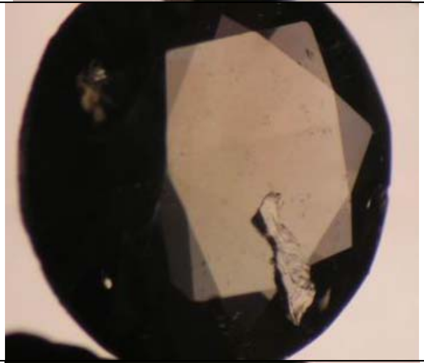
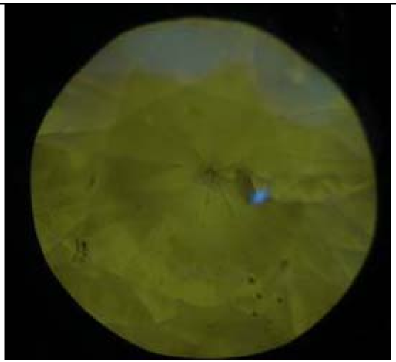
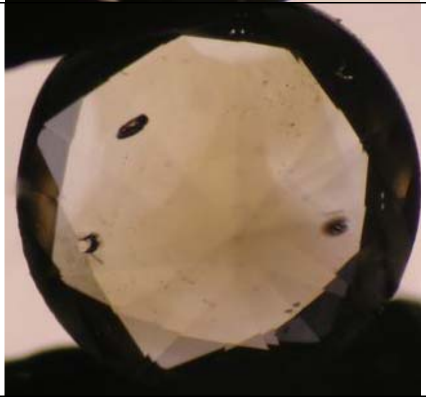
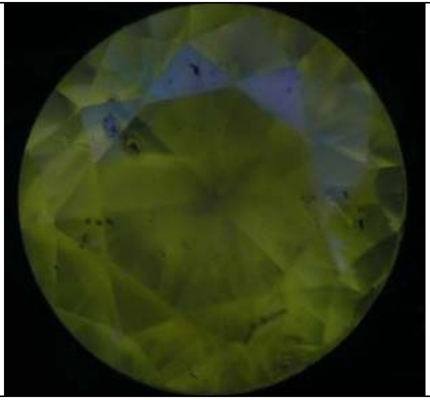
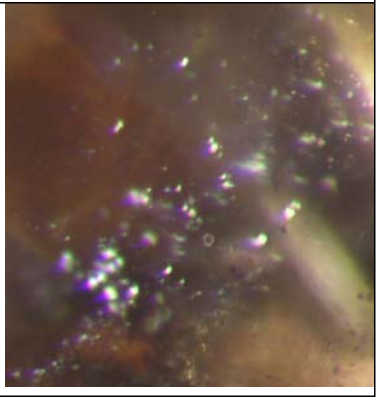
#	FTIR Color description	Color appearance	Pattern between crossed polarizers
49	Type IaA/B, H medium dark brown		
11	Type IaA; no amber center deep greenish brown-orange		
15	IaA/B, A=B medium brown		

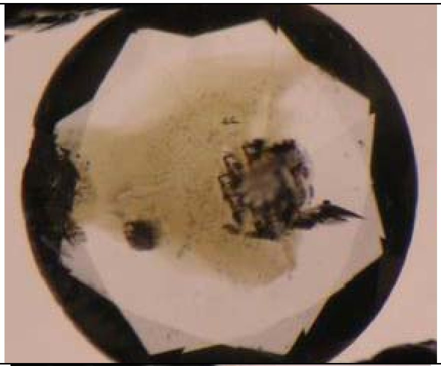
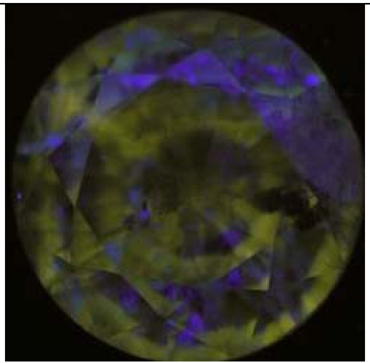
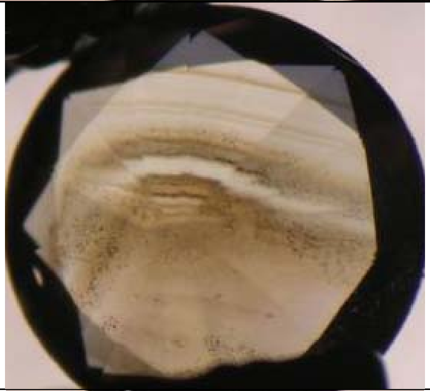
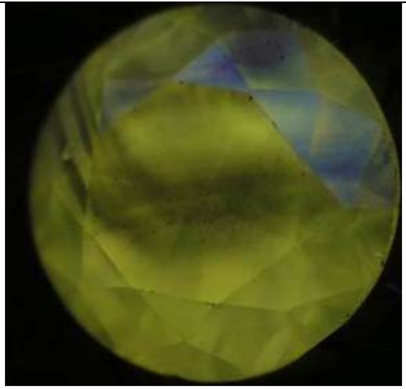
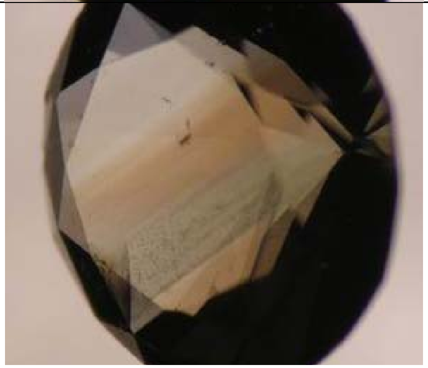
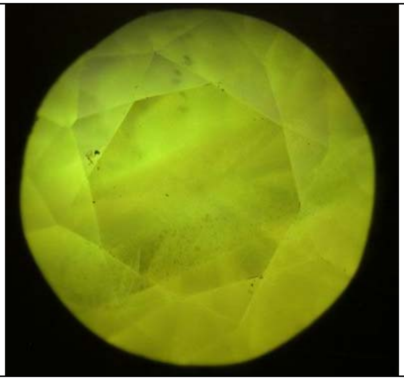
Sample # 62=CO2 30="Pseudo-CO2" 6=type Ib 22=type IaB 12=double amber center (4165/4065cm^{-1}) 28=type IIa 17=very strong platelets 49="regular brown" diamonds 56=other

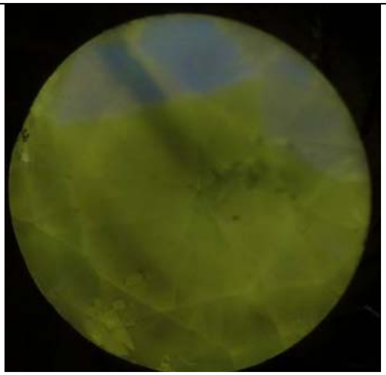
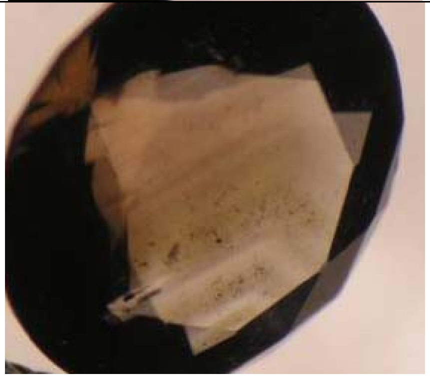
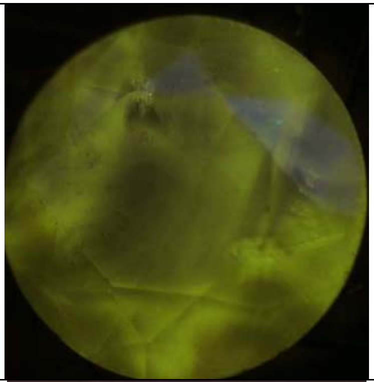
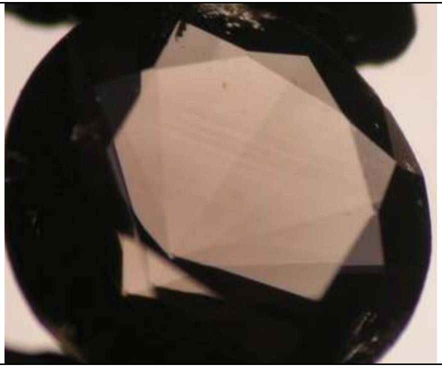
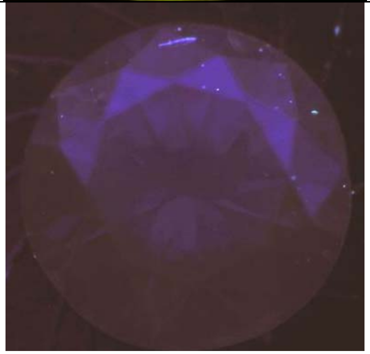
4.10. Picture Table: Color distribution, LW luminescence, Cathodoluminescence, Internal features

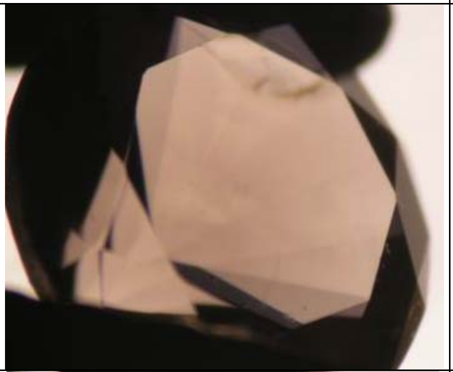
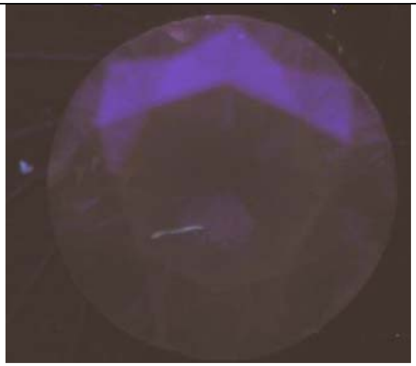
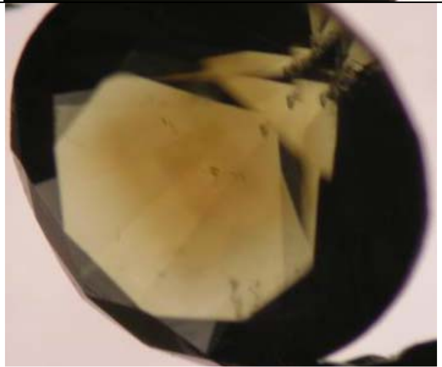
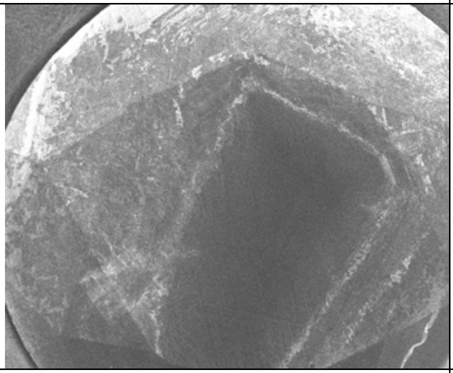
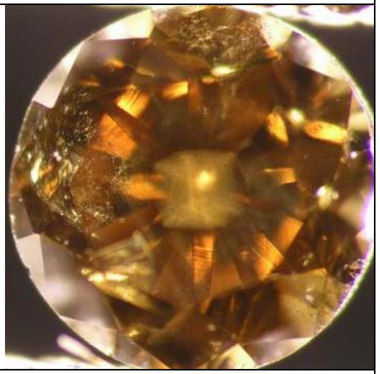
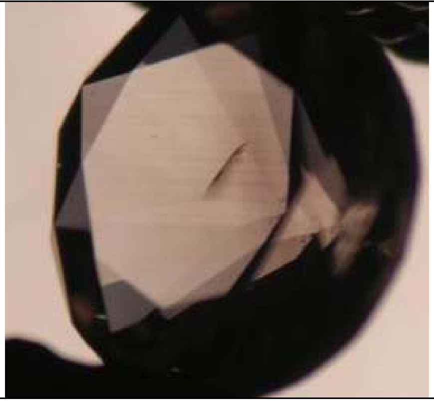
In this table the correlations between IR features, color distribution, LW luminescence, cathodoluminescence and internal features are shown visually. It was found, that by these observative techniques, many of the brown diamonds can be categorized as suggested in chapter 5. The pictures of the color distribution were recorded with the stones immersed in methylene iodide using the same camera setup as described above. For the pictures magnifications of 5-60x were used. The cathodoluminescence images were recorded (in black and white) by the camera in the Jeol 5800 SEM of the IMN at the University of Nantes, France, and are shown with 20 to 30x magnification.

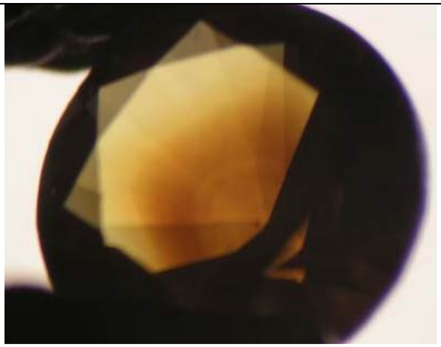
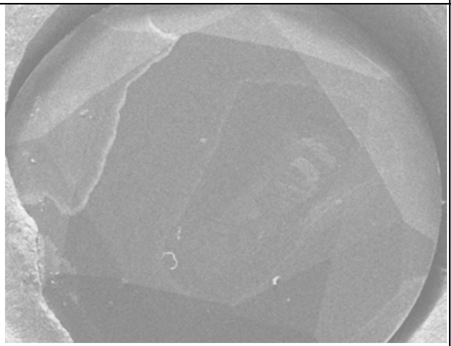
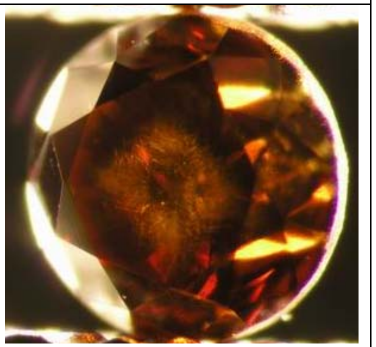
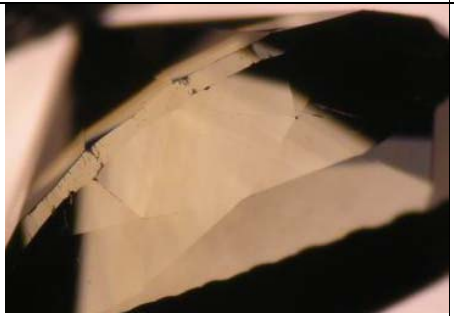
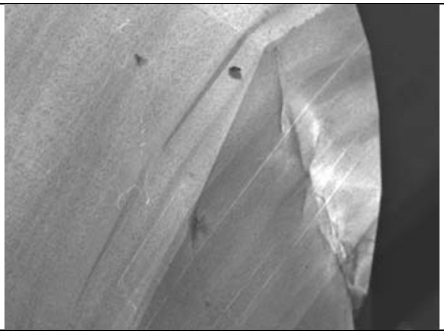
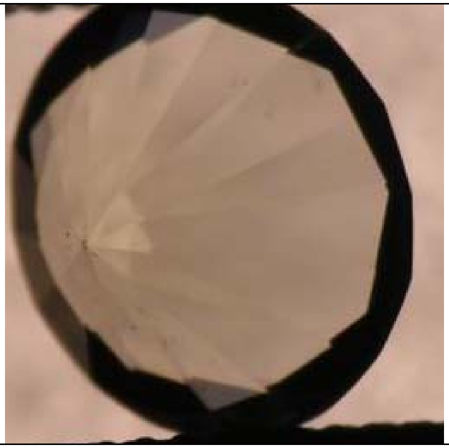
#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
1	Type IaA/B? Solid CO_2				
3	Type IaA/B? Solid CO_2				

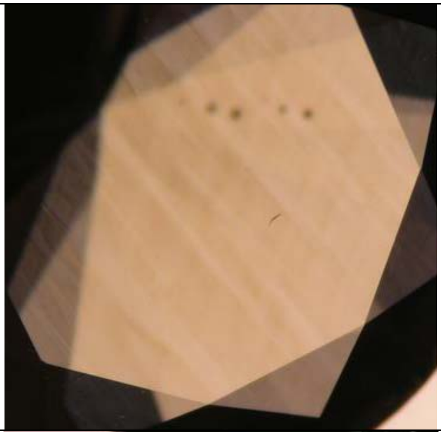
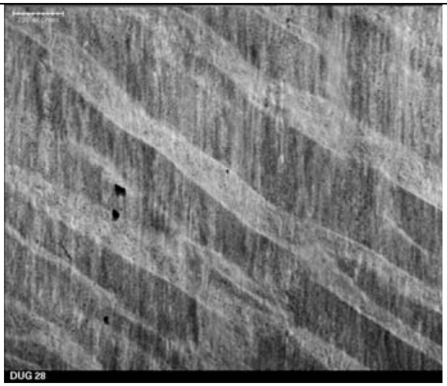
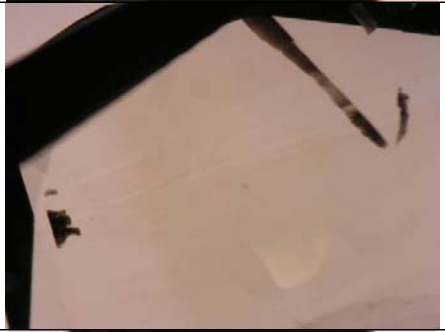
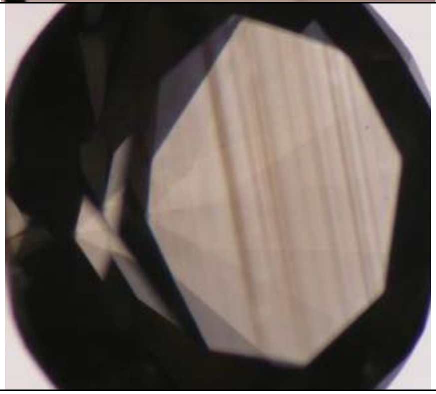
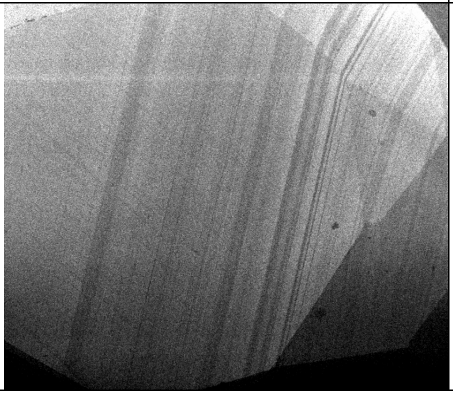
#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
4	Type IaA Solid CO_2				
51	Type IaA/B? Solid CO_2				
52	Type IaA/B? Solid CO_2				

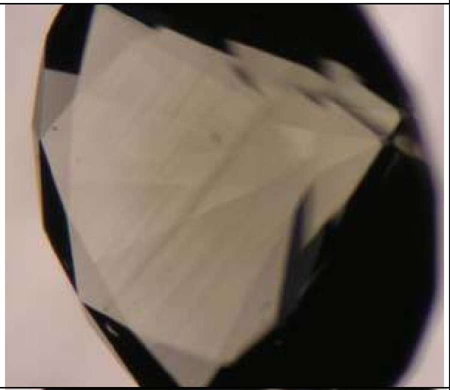
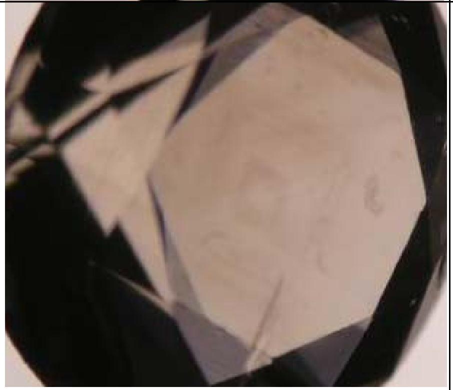
#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
62	Type IaA Solid CO_2				
5	Type IaA/B? "Pseudo-CO_2"				
8	Type IaA/B? "Pseudo-CO_2"				

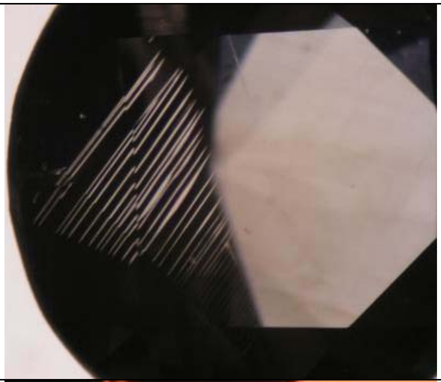
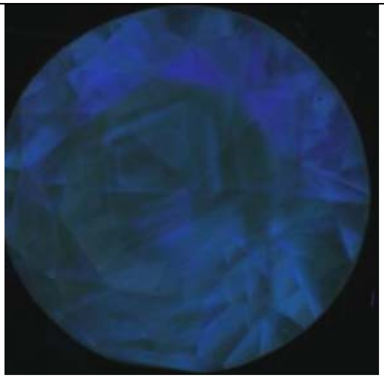
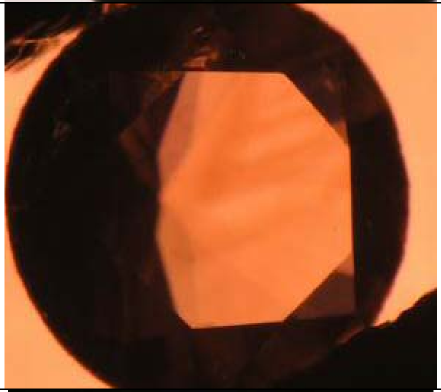
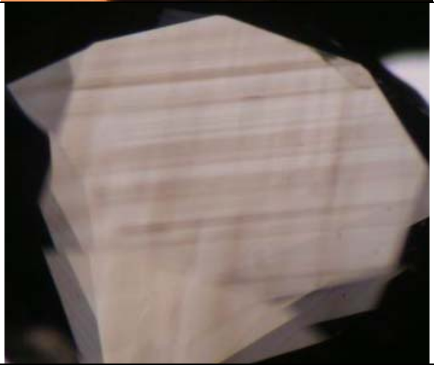
#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
9	Type IaA/B? "Pseudo-CO_2"				
30	Type IaA/B? "Pseudo-CO_2"				
6	Type Ib Very strong 4114 cm^{-1} peak				

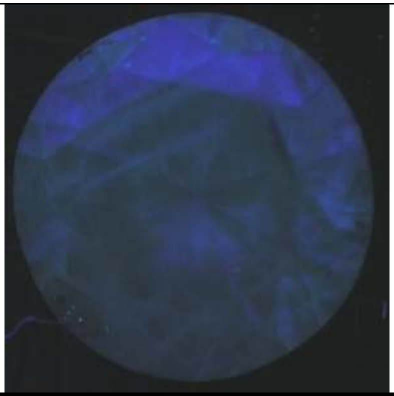
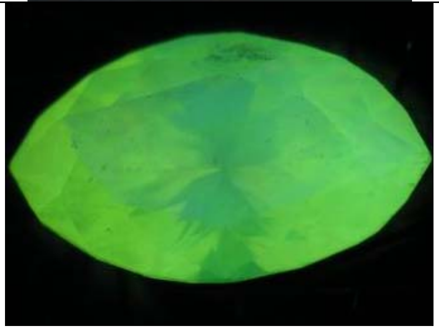
#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
7	Type Ib Very strong 4114 cm^{-1} peak				
50	Type Ib/aA Very strong 3456 cm^{-1} peak, 4934 cm^{-1} (H1b) 4238/4065 cm^{-1} peaks				
54	Type Ib Very strong 4114 cm^{-1} peak				

#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
61	Type Ib MONSTER				
26	Type IIa				
27	Type IIa				

#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
28	Type IIa				
63	Type IIa				
12	Type IaA/B “Double amber center”				

#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
53	Type Ib, near pure 4065 cm^{-1} peak				
25	Type IaB				
36	Type IaA/B, A>>B				

#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
42	Type IaA/B, A<<B				
45	Type IaA				
47	Type IaA				

#	FTIR	Picture of color distribution	Picture of LW luminescence	Picture of cathodoluminescence	Picture of internal features
48	Type IaA/B, A<B				
11	Type IaA				

Sample # 62=CO2 30="Pseudo-CO2" 6=type Ib 22=type IaB 12=double amber center (4165/4065 cm^{-1}) 28=type IIa 17=very strong platelets 49="regular brown" diamonds 56=others

5. Suggested classification of brown diamonds

The above results and correlations between the determined data lead us to suggest the following classification for the group of brown diamonds.

N°	**Class** (and type)	**Characterized by**	**Approx. % of the 900 diamonds**
		EXHIBITING AN AMBER CENTER	
1	Typical brown (type Ia)	Defined amber center peak at 4165 cm^{-1} in IR, color distributed as brown "graining", no or blue to yellow-blue fluorescence to LWUV. Most stones highly strained, some strain always present.	95 %
2	Double amber center (type Ia+Ib)	Apparent double peak at 4065 cm^{-1}/4165 cm^{-1} in IR, color distributed as olive and brown "graining". Most stones highly strained, some strain always present.	2 %
3	Regular type Ib	Peak at 4115 cm^{-1} in the IR, "normal" brown color, practically homogeneous color distribution. Some strain present.	0.3 %
		EXHIBITING NO AMBER CENTER	
4	"Orange-brown group" Type Ia / Ib	Lack of the 4165cm^{-1} amber center, brown color modified by orange, color usually distributed quite homogeneously possibly with little graining. Some strain present.	not represen-tative in this study
5	Typical brown Type IaB pure	Lack of the 4165cm^{-1} amber center, color usually distributed as graining, most stones highly strained	0.1 %
6	Extreme type Ib	Lack of the 4115cm^{-1} IR feature, instead a 4234 cm^{-1} peak may be present. Unusually strong C-center absorption at 1135 cm^{-1}. Color distributed around phantom ("color bands"). Sometimes strained, sometimes no strain observed.	0.2 %
7	Type IIa	No 4165cm^{-1} amber center, no clearly visible nitrogen absorptions in IR, color usually not predominantly due to "graining". Most stones highly strained, some strain always present.	0.5 %
8	Solid CO$_2$ diamonds (type Ia)	No amber center, frequently unusual nitrogen absorptions in the IR, 2390 cm^{-1} and 645 cm^{-1} absorptions; in about 60% of the CO2 diamonds, several PL peaks between 750 and 880 nm can be found; mostly irregularly distributed yellow UV fluorescence with lasting phosphorescence; homogeneous or patchy color distribution. No strain observed.	0.8 %
9	"Pseudo-CO$_2$" diamonds (type Ia)	No amber center, unusual nitrogen absorptions in the IR but no 2390 cm^{-1} and 645 cm^{-1} peak; mostly irregularly distributed yellow UV fluorescence with lasting phosphorescence; homogeneous or patchy color distribution. No strain observed.	0.5 %

6. Discussion

The first part of this work has shown, that the origin of the brown coloration in diamonds might have various causes. Most certainly, the color origin of the "CO_2" and "Pseudo-CO_2" diamonds is not even similar to the color origin of all other diamonds; the absence of strain-patterns under crossed polarizers and the generally patchy brown color distribution is unique to these stones. In the other diamonds, the strained lattice (and/or defects caused by the dislocations which appear in a strained lattice) appears to be at least partly responsible for the color. In this discussion, we will try to get some ideas about the color origin of the brown diamonds; thus this section will include a close look at the amber center and some results of an HPHT experiment performed on samples analyzed in this study.

6.1. Comparison of the results with the theories regarding the origin of brown color in diamonds

There are several theories on the brown coloration of diamonds. These were discussed in the introduction and include:

1) Absorption only due to lattice dislocations
2) Absorption due to sp^2 carbon in the form of graphite at dislocation loops
3) Absorption due to sp^2 carbon in the form of amorphous carbon at micro domains

Simple absorption due to dislocations and thus a general distortion of the lattice cannot be the only reason for the brown coloration; dislocations/lattice distortion can be observed in diamonds of any color, including colorless. We find some strain in nearly all colorless diamonds of any type, but type IIa colorless diamonds are typically highly strained by such distortions. This can be observed between crossed polarizers- interference colors are very clearly visible in such stones. Type IIa and by far most type Ia brown diamonds do show some interference colors under crossed polarizers; these interference patterns do not change considerably after HPHT treatment of brown diamonds (Smith et al., 2000)- e.g. all HPHT treated greenish yellow diamonds we have observed did always show strong interference colors when viewed between crossed polarizers (Fig. 56).

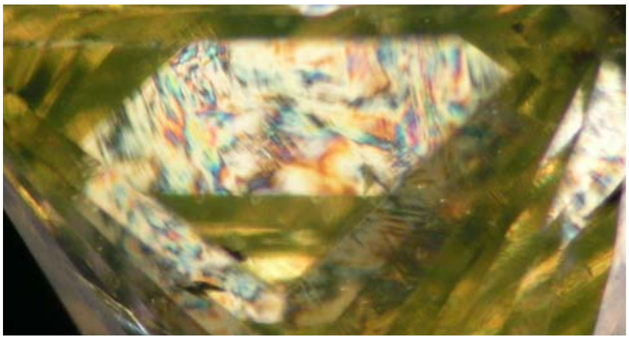


Figure 56. Intense interference colors due to strain in a formerly brown diamond after HPHT treatment

The only stones without noticeable strain were all type Ia diamonds which contained solid carbon dioxide, the "Pseudo-CO_2" diamonds and the extreme type Ib deep red-orange-brown diamond (sample 61); these stones did not show any interference color under crossed polarizers, sample 61 exhibits an unusual cross-like extinction

pattern following the phantom. The origin of the brown coloration of these stones is very apparently different from all other brown diamonds.
The amber center absorptions appear to play an important role in the coloration of by far most diamonds. It has been shown in this study, that this defect is closely related to the A aggregates of nitrogen and rarely to neutral single nitrogen (N^0); it has also been shown, that it is not present when only B aggregates of nitrogen are present or when a stone is practically nitrogen-free.

6.2. The amber center: a closer look at the NIR region

To see, whether the NIR region from 4400 to 7200 cm^{-1} did differ in the various types and if the features observed in stones from the same type matched each other, spectra of selected stones were recorded with 1000 sample scans, mainly from "culet" prepared samples. This enhances the signal to noise ratio. The strongly enlarged NIR region of the seven types can be seen in the following graphs (Fig. 57 to 65):

Regular brown (type Ia) ("culet" prepared sample)

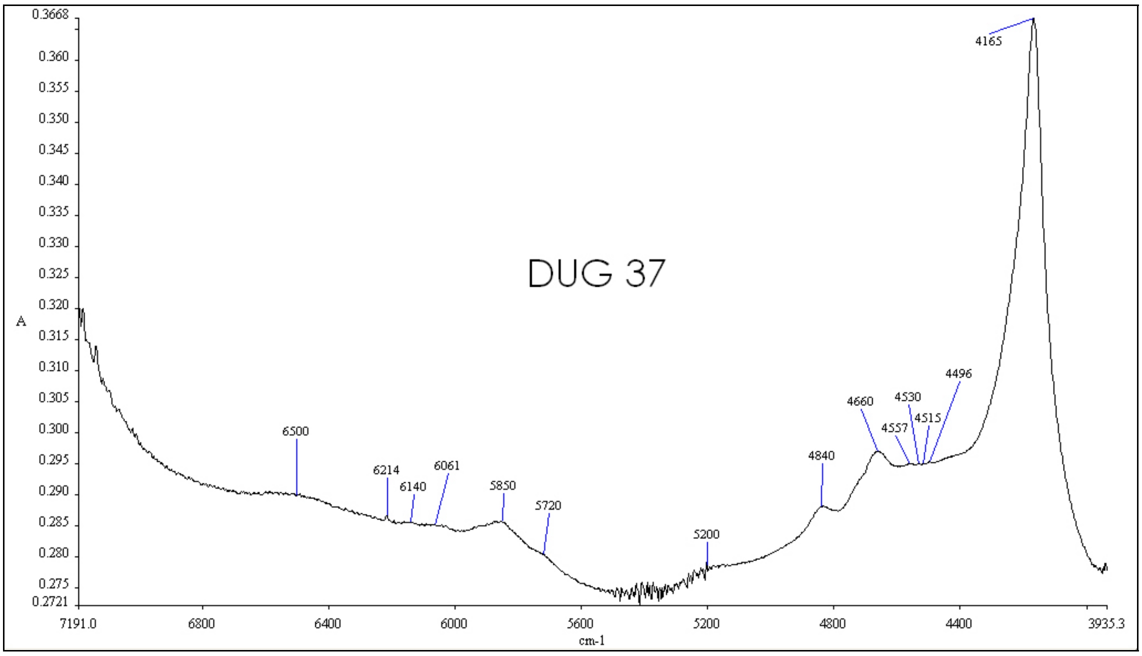


Figure 57. Close-up of the NIR region of a brown diamond of type Ia showing a very strong 4165 cm^{-1} absorption

Double amber center (type Ia+Ib) (“culet” prepared samples)

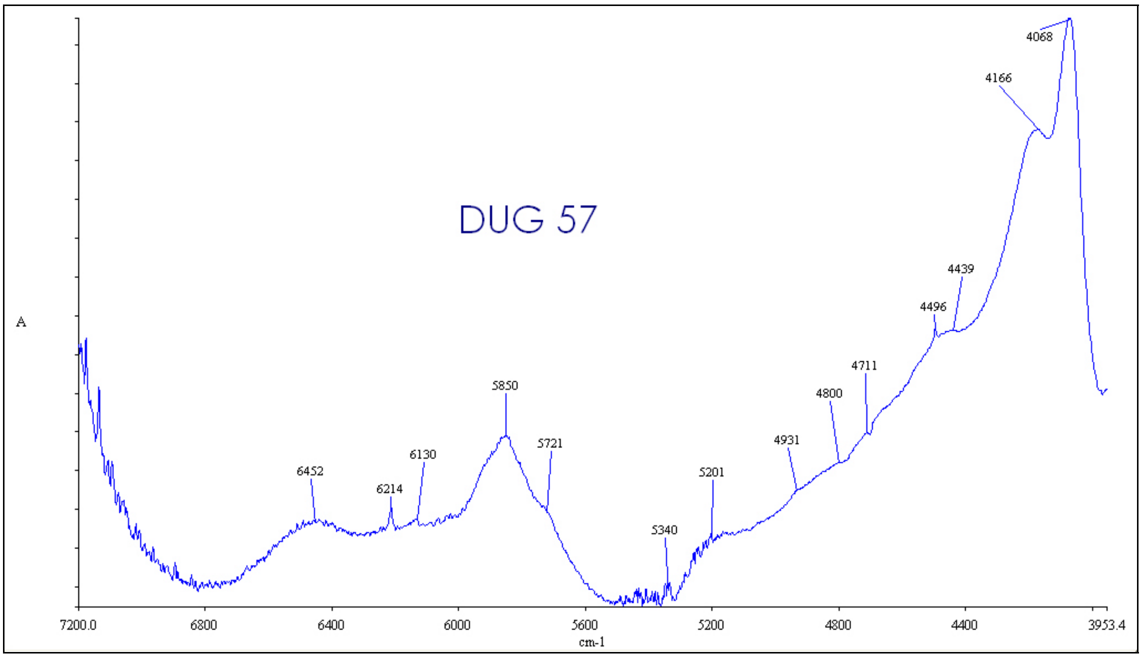


Figure 58. Close-up of the NIR region of an olive-brown diamond of type Ia exhibiting the double amber center

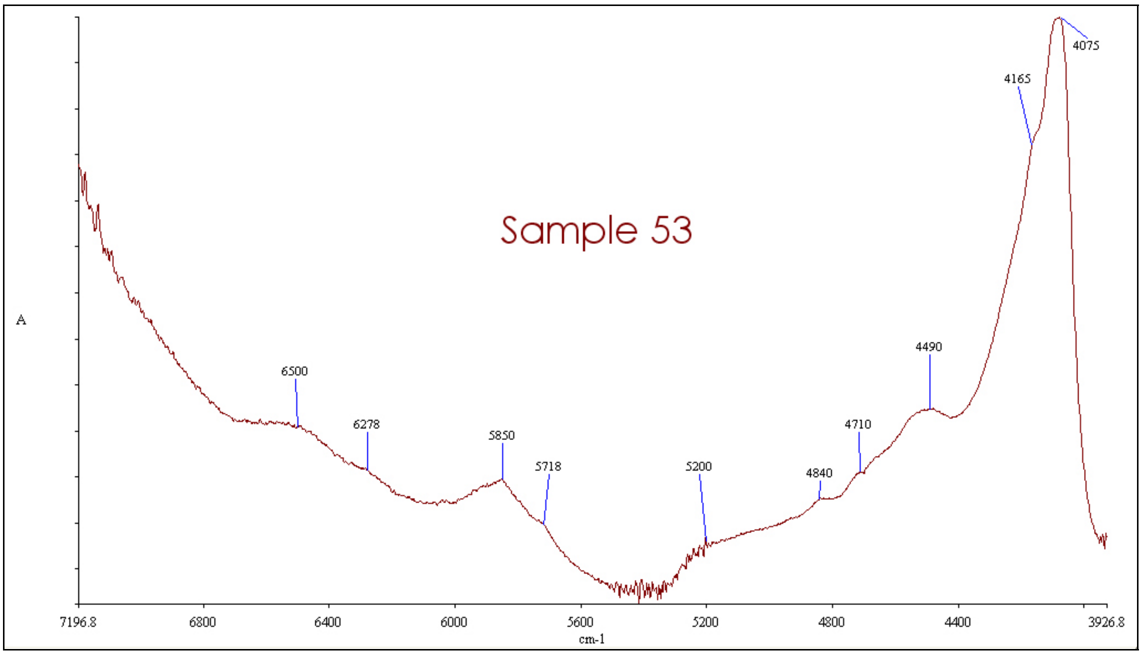


Figure 59. Close-up of the NIR region of an olive diamond of type Ib with a faint A-aggregate component, also exhibiting the double amber center

Regular type Ib (“culet” prepared sample)

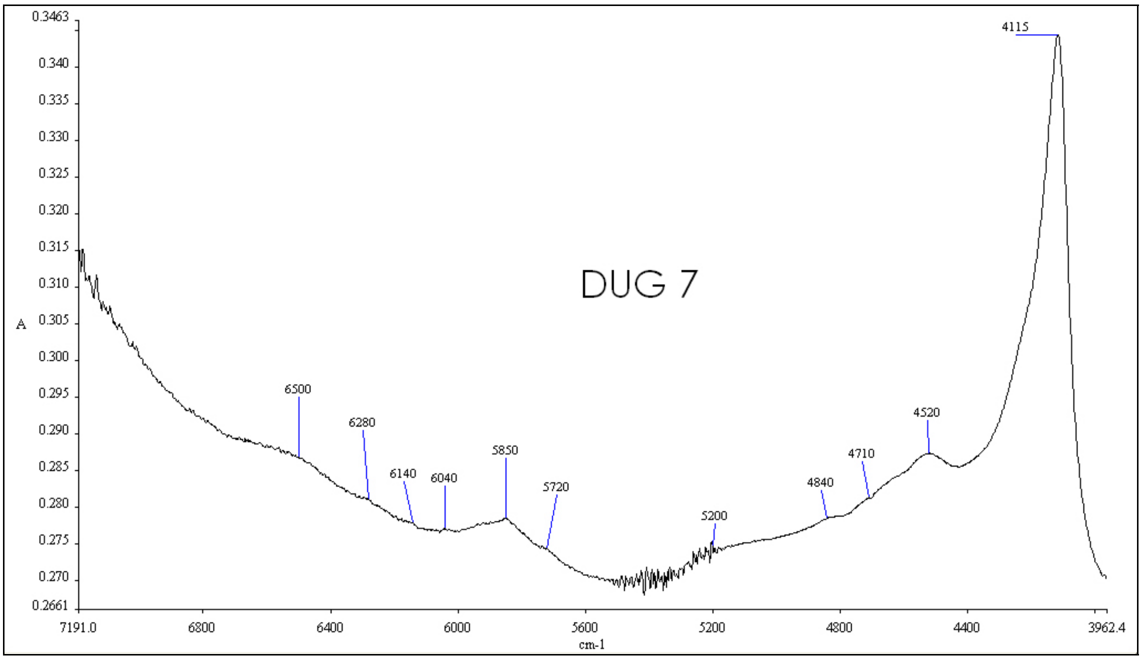


Figure 60. Close-up of the NIR region of a “regular” brown diamond of type Ib with its very strong 4115 cm^{-1} peak

Extreme type Ib

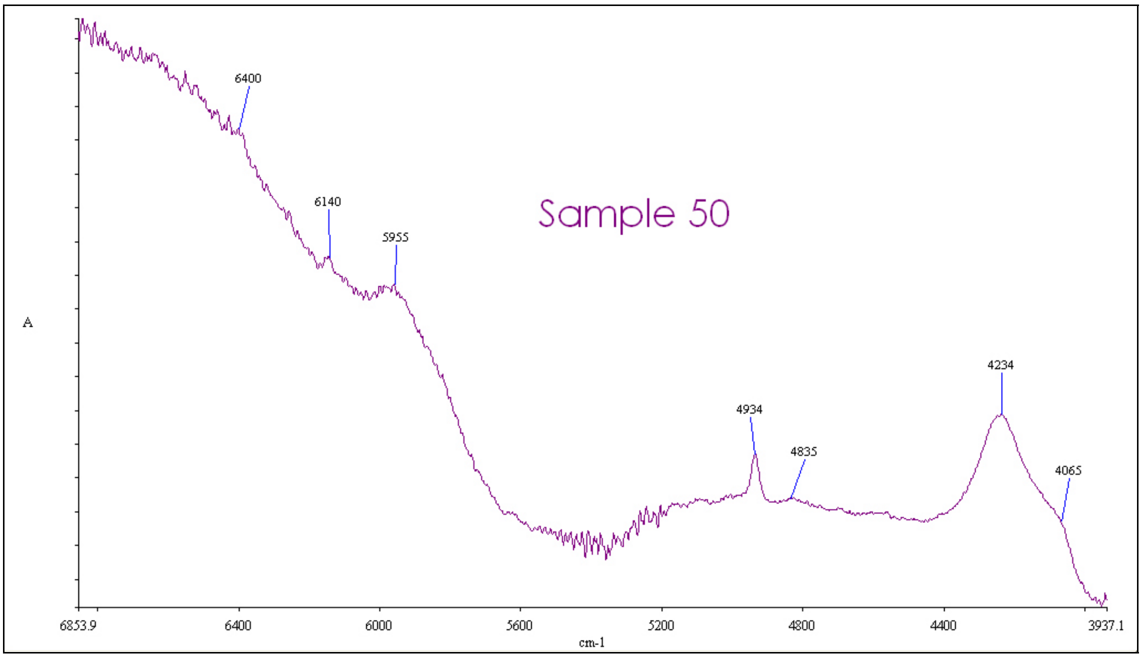


Figure 61. Close-up of the NIR region of an extreme brown diamond of type Ib/aA

Extreme type Ib

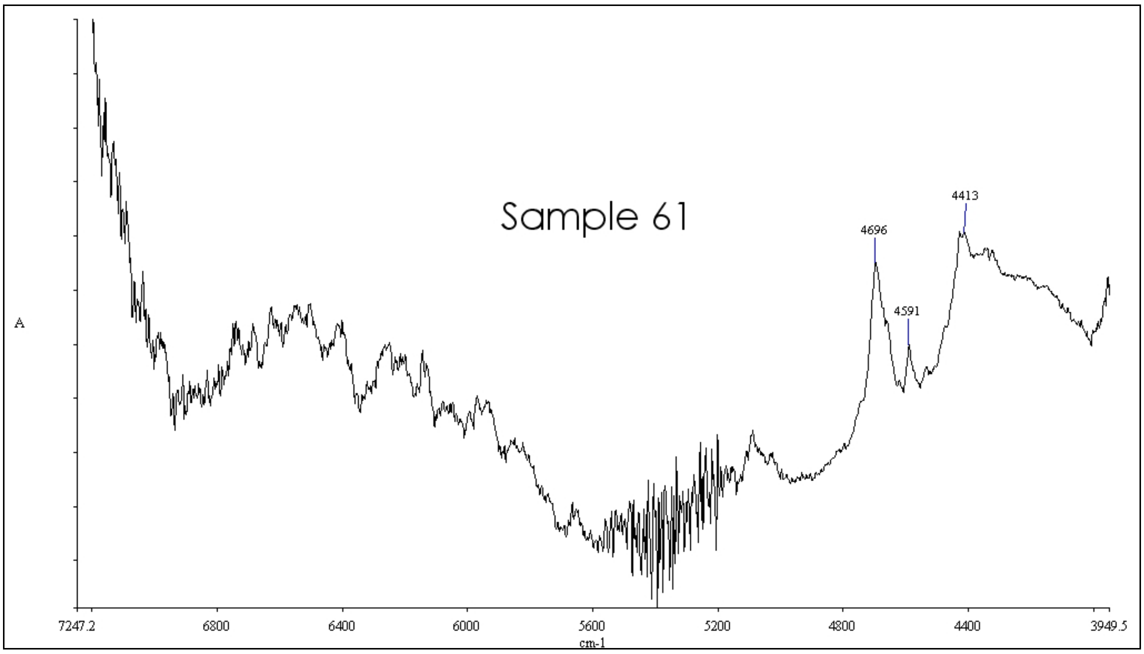


Figure 62. Close-up of the NIR region of the red orange brown type Ib/aA diamond; the absorptions above 5200 cm^{-1} are not indicated because some of them may be caused by interference and artefacts since the stone was not prepared by a large culet

Solid CO_2 containing (type Ia) ("culet" prepared sample)

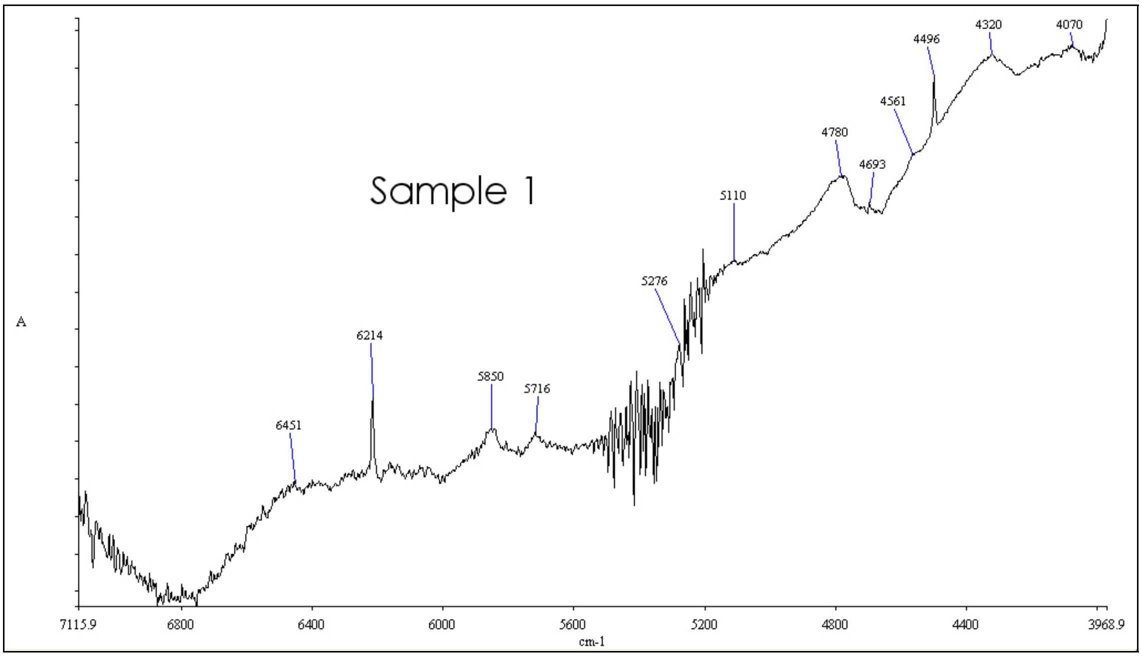


Figure 63. Close-up of the NIR region of a brown (regular) CO_2 diamond of type Ia

“Pseudo-CO_2” (type Ia) (“culet” prepared sample)

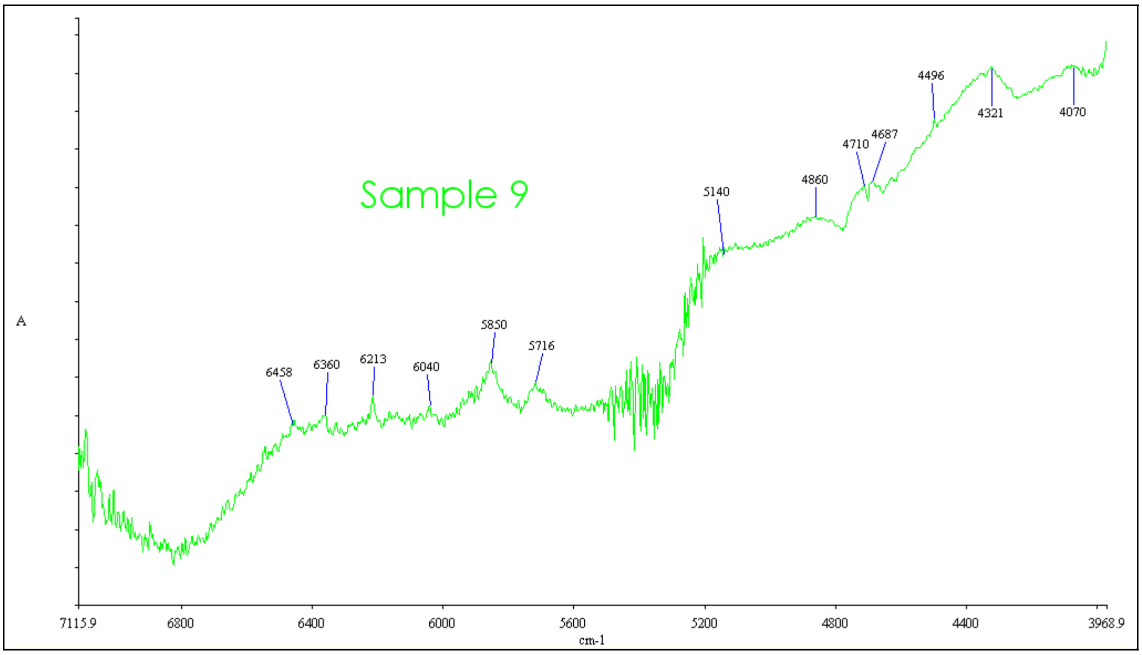


Figure 64. Close-up of the NIR region of a brown “Pseudo-CO_2” diamond of type Ia

Comparison of the “types” (all “culet” prepared stones)

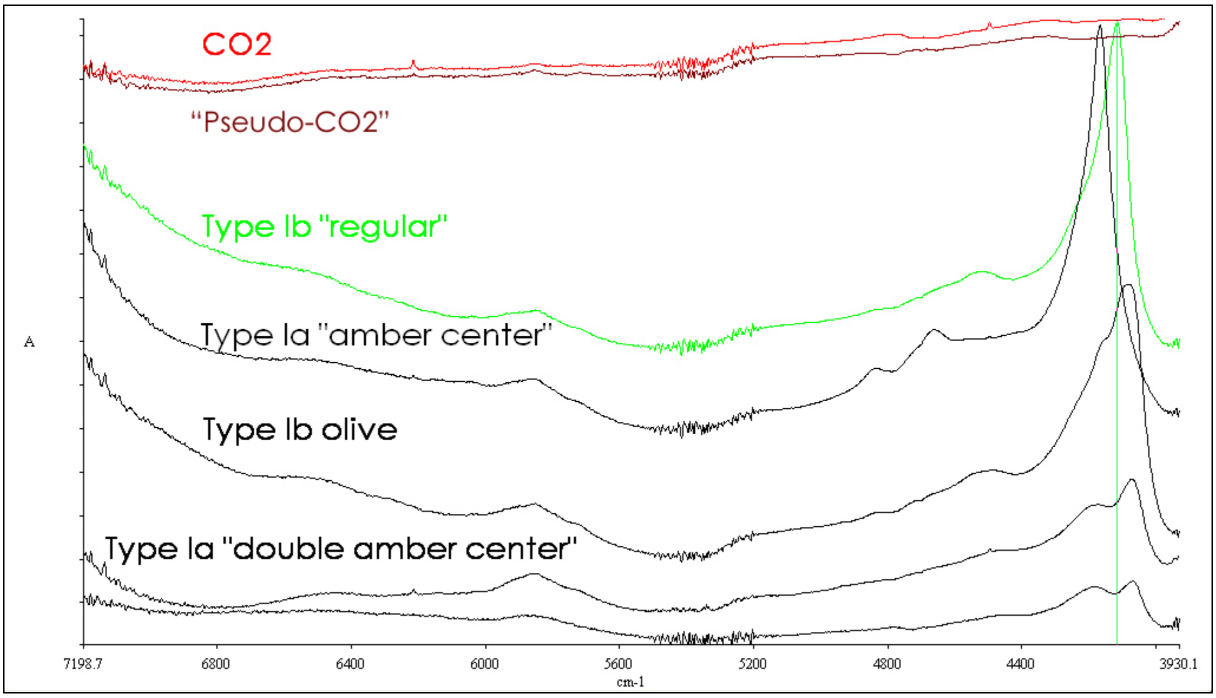


Figure 65. The NIR region of all culet prepared diamonds compared with each other

The above spectra clearly show, that the region between 7200 and 4000 cm^{-1} does not only differ by the dominant peak present between 4320 cm^{-1} and 4065 cm^{-1}, but that some of the described classes differ distinctly over the range of 4800-4065 cm^{-1}. Except the NIR region of the CO_2 diamonds, which showed clearly different features, the area between 7200 and 4800 cm^{-1} appeared very similar in all stones. Several stones of all classes were scanned this way to demonstrate the repeatability of the results; and it became apparent, that stones of the same class had equal or very similar NIR regions. The noise apparent in spectra recorded on stones without large culets prohibits precise assignments of peaks observed; nevertheless, approximate peak positions were determined. The absorptions visible in the highly enlarged IR spectra are very complex, and, although most stones of the same class show nearly equal spectra, there are minor differences visible in many stones. It is difficult to say, whether some of the observed peaks and bands are artefacts due to interference, noise etc, and not "real" absorptions; this is especially true for the "non-culet" diamonds. Since we did not have a "culet" prepared type IIa diamond, the NIR region was rather noisy; it appears though, that the region is a match to the NIR region of regular nitrogen containing diamonds but with strongly reduced bands and peaks; thus, a very weak feature between 4115 and 4065 cm^{-1} was observed, sometimes forming a broad band between 4115 and 4065 cm^{-1}.

Peak positions observed at 4000 to 4400 cm^{-1}

The positions observed were related to type and sometimes to the color.

position	**observed in**
4065 cm^{-1} to 4070 cm^{-1}	olivish brown colors of all type Ia and Ib
4115 cm^{-1}	type Ib
4165 cm^{-1}	type Ia
4234 cm^{-1}	type Ib
4320 cm^{-1}	solid CO_2

The absence of a significant absorption in this region in type IIa diamonds and pure IaB diamonds indicate, that certain forms of nitrogen are involved in the formation of these absorptions, as has been proposed above by the correlation of the amber center peaks with the A center (4165cm^{-1}) and the C center (4115 cm^{-1}).
To get some insight into the formation of the brown coloration, we decided to select one stone of each class and subject it to a half hour HPHT anneal. Below see a preliminary look at the results

7. HPHT annealing of brown diamonds of the different suggested classes

7.1. Background

It has been shown in the past few years, that exposing a brown diamond to conditions close to those of the diamond stability field will cause a reduction of the brown coloration in type IIa brown diamonds (Smith et al., 2000) and a reduction of the brown coloration with a formation of yellow to yellow-green color, often accompanied by green fluorescence, in type Ia brown diamonds (Collins et al., 2000). Furthermore, some stones turned orange, pink or blue. Intermediate colors such as brownish-yellow can also be encountered. The reduction of the brown color has been attributed to a reconfiguration of the lattice by HPHT. The formation of the yellow to yellow green color with green fluorescence was explained by the release of vacancies by the realignment of the lattice, thus giving rise to the H3 center (Collins et al., 2000). Using the more recent theories concerning the brown color in diamonds, the reduction of the brown coloration would be explained by the formation of sp3 carbon out of the sp2 carbon either by graphite to diamond transformation or by recrystallisation of amorphous carbon to diamond by HPHT.

7.2. Experiment

We exposed 5 diamonds, representing the three classes, which contain an amber center (see above), plus one CO_2 and one "Pseudo-CO_2" diamond, to very high temperature and pressure to see, whether all would change their brown coloration. We did not treat a type IIa stone since all stones which were analysed represented a rather high value and had attractive colors or to many fractures for this treatment. All stones were heated at a temperature of ~2000°C and 6.5 GPa pressure for ~10 minutes; the complete heating cycle lasted 30 minutes, and during ten minutes the stone was kept at the highest temperature.
The following diamonds were treated by the HPHT process:
Sample 3 (CO_2)
Sample 30 ("Pseudo-CO_2")
Sample 7 (type Ib "regular")
Sample 10 (type IaA with "double amber center")
Sample 18 (type IaA/B with strong platelets)
Sample 22 (type IaB)
Sample 46 (type IaA)
For these diamonds, all "before" data were compared to the "after" data; here, we just present a preliminary look at the results, which includes visual and standard gemological results as well as the comparison of the IR spectra.

7.3. Results

7.3.1. Visual observation

All stones except the two CO_2 and the "Pseudo-CO_2" diamonds lost their brown coloration; the color after the treatment varied from light yellow to intense greenish yellow (Fig. 66). Interestingly, none of the stones developed strong green fluorescence.
The CO_2 diamonds did not change their color considerably, except that the brown color was somewhat reduced, which resulted in a brownish yellow color. It was quite interesting to see, that the color distribution of the irregular 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 by the treatment.

Figure 66. Sample 46 before (left) and after the HPHT treatment at 2000°C and 6.5 GPa (right, not repolished)

7.3.2. Luminescence to LW and SW UV excitation

Despite the high annealing temperature of 2000°C, we did not observe the formation of strong green luminescence in any of the treated samples; this is rather surprising since under the same conditions, most samples form such luminescence caused by the H3 defect (A. Katrusha, pers. comm. 2003). More often, a mixed luminescence due to N3 and H3 was observed, giving a chalky greenish blue to chalky yellow (yellow-blue) appearance to the emission when excited by UV radiation.
In the below table, the before and after data is presented:

	Before HPHT		**After HPHT**	
	LW UV	**SW UV**	**LW UV**	**SW UV**
3	medium yellow	weaker yellow with weak lasting phosph.	same as before	same as before
7	faint reddish orange	weak reddish orange	med. greenish blue	strong chalky yellow
10	none	none	faint greenish yellow	inert
18	weak blue	faint yellowish blue	medium chalky blue	medium chalky yellow
22	weak chalky blue	faint chalky blue	strong chalky blue, lasting phosphorescence	very strong chalky greenish yellow, lasting phosph.
30	medium yellow	weak yellow	same as before	same as before
46	faint yellow	none	medium chalky blue	medium chalky greenish yellow

7.3.3. IR spectroscopy

The IR spectra of the seven stones all showed more or less pronounced changes; reported before was the reduction of the platelet peak and the 4165 cm^{-1} amber center peak; these reductions were observed in all our samples. Besides a strong reduction of the platelet peak at ~1360 cm^{-1}, the amber center peak at 4165 cm^{-1} was not present anymore after the HPHT anneal (Fig 67); it was extremely interesting to see, whether this change occured also with the shifted peaks seen in type Ib diamonds as well as olivish brown diamonds: indeed the 4115 cm^{-1} peak and the 3460 and 3360 cm^{-1} features of the Ib diamond as well as the 4070 cm^{-1} peak of the olive-brown diamond were eliminated by this treatment.
Besides this, aggregation and dissociation of nitrogen was observed: the type Ib diamond formed A-aggregates and possibly minor B-aggregates while the C-center

absorption was reduced. The type IaA diamond formed more B aggregates, as did the platelet-rich type IaA/B and the type IaB (with very little A) diamonds. The type IaA olivish brown diamond showed only minute changes in the one-phonon region. In the CO_2 diamond, only minute differences of the spectra were found; most interestingly, the CO_2 related absorption at 2390 cm^{-1} appeared unaltered and the feature at 645 cm^{-1} appeared to be reduced. Besides this, the distorted one-phonon nitrogen absorption appeared to be slightly altered and this whole structure seemed to be clearly reduced.

The "Pseudo CO_2" diamond showed more severe changes though: after the HPHT anneal, the 2390 cm^{-1} peak appeared, which was absent before the treatment; also, the peak in the region around 600-650 cm^{-1} was strengthened considerably, while it was not found to shift position; it was still found at ~615 cm^{-1}.

A look at the minor features present in the treated diamonds revealed that the peaks assigned to hydrogen were considerably reduced or eliminated by the HPHT treatment; thus the hydrogen-related absorptions at 4496, 3106 and 1405 cm^{-1} were all reduced or even eliminated. Besides, the peaks at 4667, 3235, 1430 cm^{-1} showed the same reaction as the hydrogen peaks to the HPHT treatment.

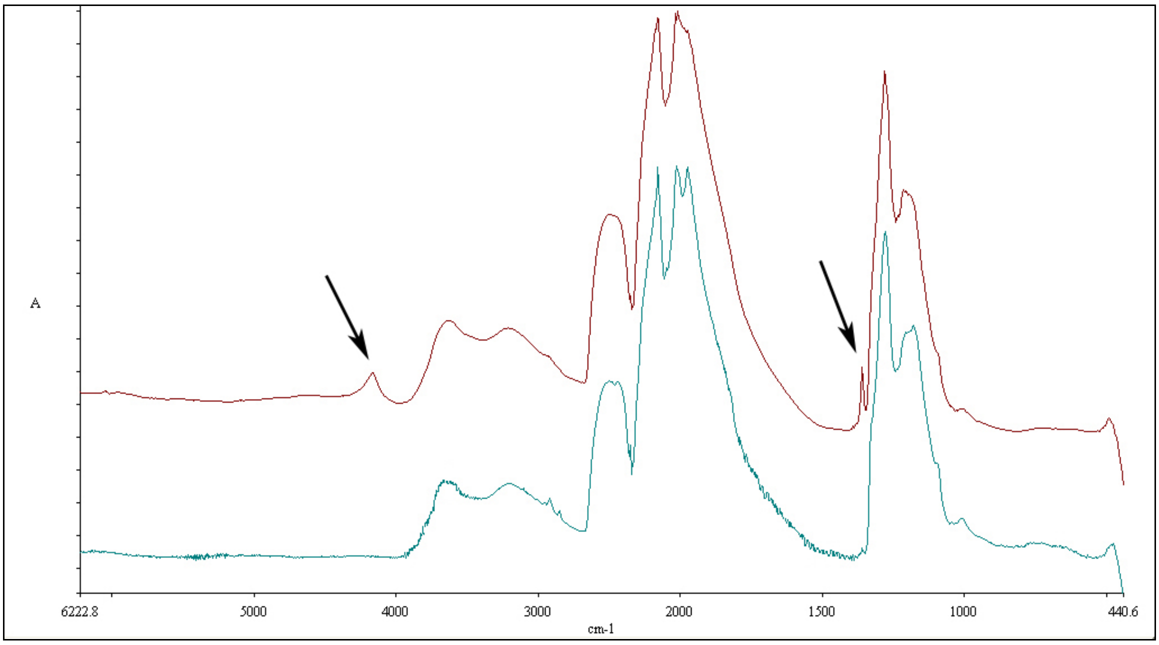


Figure 67. Comparison of the IR spectra of sample 46 (a type IaA diamond) before treatment (purple trace) and after HPHT treatment (blue trace)

7.4. Discussion

Besides the reduction of the above described peaks, changes in nitrogen aggregation can be observed after HPHT annealing. Surprising is the reduction of the hydrogen absorptions, which were believed to be very stable.

Another surprise was that HPHT treatment did not affect the "solid CO_2" absorptions at 2390 and 645 cm^{-1}; to the contrary, in the "Pseudo CO_2" diamond the 2390 cm^{-1} peak missing before was formed and the feature at ~615 cm^{-1} was strengthened by annealing at 2000°C and 6.5 GPa. This is very surprising, since it has been suggested by Schrauder and Navon (1993) that the CO_2 is present as sub microscopic inclusions; following this annealing experiment, it may be doubted, that CO_2 is present in its solid state at high pressure of 5 GPa in the "Pseudo-CO_2" diamonds; the temperature of ~2000°C would most certainly cause a change of phase of the CO_2. It appears that indeed a change of state has taken place in the "Pseudo-CO_2" diamond and that

CO_2 may be present in these stones in another phase or form than in the CO_2 diamonds; it has been shown by HPHT experiments on liquid CO_2, that various solid phases can be produced, some of which fairly stable at ambient conditions (see- http://www.llnl.gov/str/Yoo.html).
Our temperature/pressure of 2000°C and 6.5 GPa (65 kilobar) would suggest the formation of liquid CO_2 during the treatment, which does not explain the findings of the formation of the 2390 cm^{-1} peak by HPHT annealing of the "Pseudo-CO_2" diamond.

8. Conclusions

The results of this classification and characterization of brown diamonds were unexpected looking back before our analysis; the variety of brown diamonds is highly complex and the color formation not easy to understand. The HPHT annealing experiment was helpful to clear up some points, but others still remain mysterious; a good example is the main "amber center" peak, which can be found at different positions, depending on type and/or color; the HPHT experiment has shown that all these absorptions are not very temperature stable. They were eliminated in all cases by annealing at 2000°C at 6.5 GPa stabilizing pressure; this was always accompanied by a strong reduction of the platelet peak and some hydrogen features. The amber center peak at 4165 cm^{-1} has been found to be related to the presence of A-aggregates and the ratio of A vs. B aggregates; besides this, a shifted amber center absorption in "regular" Ib brown diamonds has been found at 4115 cm^{-1} which appears to be correlated to the single nitrogen content; and a side peak at 4070 cm^{-1} was found to be related to olive coloration and to the presence of nitrogen, but not to the nitrogen aggregation state; this peak has been found in all type I diamonds with an olivish brown to olive color; it may be related to the C-centers since most of these diamonds, despite having type Ia IR spectra, show a Ib character; this can be seen in their PL spectra, where strong NV^- related emissions (e.g. at 637 nm) can often be detected.
Looking at these facts, it can be postulated, that the amber center is a defect directly related to the A-aggregates and to the defect, which causes the brown coloration in diamonds. If indeed amorphous carbon is responsible for the brown color, this defect may well be due to an "aggregate" consisting of the A-aggregates and amorphous carbon; the shifted peak at 4115 cm^{-1} seen in "regular" type Ib browns appears thus to be related to N^0, and, if the amorphous carbon theory is correct, may be an "aggregate" consisting of single nitrogen and amorphous carbon. Since no defect in this region has been found in type IIa brown diamonds, this nitrogen-dependence must be assumed. No amber center was present in the few pure type IaB brown diamonds thus it can also be proposed that the B-aggregates do not form an IR active defect with the defect responsible for the brown coloration.
The observed decrease of the 4165 cm^{-1} peak in all near-pure type IaB diamonds supports this idea. Thus the amber center defect at 4165 cm^{-1} appears to be dependent on the presence of A-aggregates and no strongly dominating B-aggregates while the C-centers in regular brown diamonds and some olive stones of type Ib appear to cause a shifted amber center at 4115 cm^{-1}.
The lack of an "amber center" in some brown diamonds exhibiting regular colored graining can be explained as follows:
Type IIa ➔ no or nearly no nitrogen present.
Type IaB pure➔ B-aggregates are not involved in the formation of the amber center.

Type Ia, type Ib/aA ➔ only brown diamonds with strong orange color modifier were found which did not contain an amber center; apparently many these "orange" colors have a different formation from "regular" brown diamonds.
We have not seen a single type IaA or IaA/B diamond (not being of the type CO_2 and "Pseudo- CO_2") of "normal" brown color without a distinct amber center peak yet and it may be postulated, that all of these brown diamonds do exhibit such a defect. It has to be kept in mind though, that a sampling problem may be responsible for this; as mentioned before, most probably all 900 diamonds may have originated from the Argyle Mine in Australia.

As a general conclusion, it can be stated, that some of the above proposed different classes of brown diamonds owe their brown coloration to a very similar defect, while some appear to have a clearly different color origin; this applies especially to the CO_2 and the "Pseudo- CO_2" diamonds. This conclusion is supported by the fact, that all except the CO_2 and "Pseudo- CO_2" diamonds lost their brown coloration after the HPHT annealing experiment. Thus, although 9 apparently different groups were proposed in this work, a truly different formation process appears only to be responsible for the brown color of the CO_2 diamonds, the "orange-brown" group and the "extreme" type Ib diamonds. Also, the close correlation not only between pink and brown, but actually between pink, brown and olive has been shown: all three colors are closely related to colored graining and grain bands of all three colors can coexist in one and the same stone; also, brown and olive diamonds show related amber center and/or modified amber center absorptions at 4165 cm^{-1}, 4115 cm^{-1} and 4070 cm^{-1} respectively. Concerning the pink coloration, it has been shown by the HPHT treatment of brown diamonds, that some type IIa and some very rare low nitrogen IaB stones may turn pink after the treatment; some type IIa brown diamonds can be turned pink by a first HPHT anneal and then colorless by a second run (A. Katrusha, pers. comm. 2003).
Also, one of these rare type IaB brown diamonds has been treated HPHT twice at equal conditions and turned pink after the first run and light yellow with green fluorescence after the second run (A. Katrusha, pers. comm. 2003). In this case after the first run, the brown color was changed into pink and in the second run vacancies were released producing yellow color and green fluorescence by forming H3 and other defects out of the combination of vacancies with the small amount of nitrogen in the stone. Thus it seems that the pink coloration is an intermediate color when the brown color is reduced by the HPHT process.
The relation between the "CO_2" diamonds and the "Pseudo- CO_2" diamonds has been suggested and is strongly supported by the following features seen in the two groups:
-Unusual 1 phonon region
-Very similar PL spectra with peaks between 750 and 880 nm (not seen in any other diamonds)
-Same inclusions (highly reflective particles and extremely fine needles), seen only in these two groups
-Same totally featureless VIS/NIR spectrum
-Same patchy coloration
-Same response to UV excitation (incl. phosphorescence)
The lack of the CO_2 absorptions in the IR spectra of the "Pseudo- CO_2" diamonds cannot be explained at present; it is very interesting though, that the HPHT treatment caused the formation of the 2390 cm^{-1} peak in the "Pseudo- CO_2" diamond.
This work has given some insight into the world of the brown diamonds and their color origin; some of the ideas presented are merely speculative but may be helpful to finally find conclusive evidence for the defect(s) which cause(s) the color "brown" in diamonds.

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