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EXPERIMENTAL REPORT

ASTERIATED DIAMONDS

By
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Acknowledgments

First I would like to thank Pr. Emmanuel Fritsch and Dr. Benjamin Rondeau for their time, advice and guidance to succeed with this project. Also thank you for allowing me to use a sample of the University’s collection for this study.

Special thanks to Brenda, Alan and Kaylan from EGL South Africa for sending me samples to complete this study while in Nantes and to allow me to use the equipment available at the laboratory to complete this work.

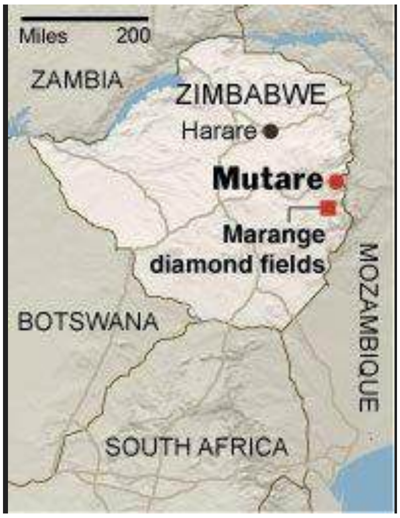
Warm thanks to Fulvia for finding me the two stones of Zimbabwean origin and to Candice and Aron from Ernest Blom to allow me use the samples for testing.

Finally, thank you to my husband Koos for his help and encouragements.

Introduction

Asteriated diamonds have always fascinated researchers, scientists and collectors. These diamonds have specific characteristics and exhibit particular zoning which are of great interest : they sometimes display petal or lobe – like zones which can be visible to the naked eye.

Living in Johannesburg, South Africa I had the opportunity to see and work with such diamonds. These stones usually have an unattractive colour often being a mixture of grey, yellow or brown. The diamonds found in South Africa are mainly coming from Zimbabwe where enormous diamond deposits have been found in 2006 in Marange (Map 1).



Map 1 : Zimbabwe and the Marange diamond fields. (Source : The New York Times)

I have been very interested in asteriated diamonds since working in Africa and decided to choose this subject for my experimental report. Few questions come to my mind thinking of these diamonds. Are Zimbabwean diamonds any different from other asteriated diamonds ? Is the colour of asteriated diamond related to a certain level of hydrogen ? What about growth structures ?

For this report five diamond samples have been analysed. Samples one to three are asteriated diamonds from an unknown source whereas the last two samples are asteriated diamonds from Zimbabwe.

I- Background

A- Diamond type

Diamonds have been classified by type. This classification is built on the analysis of the infrared absorption spectrum of the diamond. It is based on the presence or absence of nitrogen (N) impurities within the diamond lattice. In that regard, diamonds are divided in two categories : type I and type II. The infrared spectrum shows the diamond spectral signature in the two phonon and three phonon regions whereas the type is observed in the one phonon region of the spectrum (Fig. 1). The only exception is for type IIb diamonds where boron absorptions are also observed in the two and three phonon regions.

Type I diamonds contain nitrogen and are further subdivided in two depending on the arrangement of the nitrogen atoms in the crystal lattice: type Ia with aggregated nitrogen and type Ib with isolated or single nitrogen. Type Ia is further divided into A aggregate made of a pair of nitrogen atoms (N-N) and B aggregate made of four nitrogen atoms and a vacancy (V) noted (4N-V) (Fig.2).

Type II diamonds are divided into type IIa which doesn’t contain any measurable nitrogen or boron impurities and type IIb which contains boron (Fig.2) (C. M. Breeding et al, 2009).

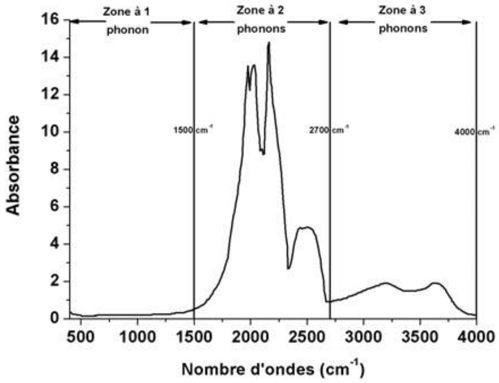


Fig. 1: Infrared Spectrum of a type IIa diamond showing the different phonon regions (S. Karempelas, 2007).

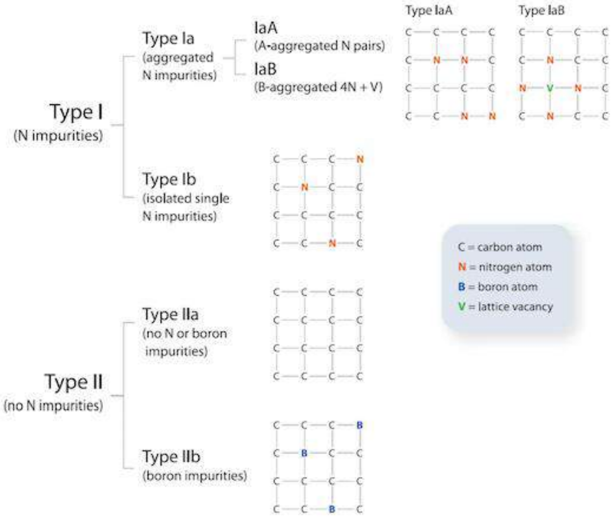


Fig. 2: Diamond type classification (C. M. Breeding et al, 2009)

B- Hydrogen

The infrared spectrum gives the diamond spectral signature and type. It is also used to determine the following:

- presence of treatment
- presence of other impurities such as hydrogen (H)

Hydrogen's discovery dates back from the 1950's. It was discovered simultaneously by two different laboratories. At the time, a group of sharp lines of unknown origin was identified in infrared spectroscopy and named the « 1405 cm^{-1} group » by Charette in 1959 and the same year hydrogen was discovered by mass spectroscopy (E. Fritsch et al, 2007). Later on, many other absorptions observed in the infrared spectrum of natural diamond where associated to the presence of hydrogen in the crystal lattice. Several groups of peaks have been identified and named « system ». The most common and important hydrogen related system in the diamond's infrared spectrum is called the « 3107 cm^{-1} system ». This system is of great importance because the intensity of the peak located at 3107 cm^{-1} will determine whether the diamond is considered hydrogen rich (H – rich) or not. This is established by looking at the absorption's height of the 3107 cm^{-1}. If this peak is greater than the intrinsic value of the diamond positioned at approximately 2450 cm^{-1} the diamond will be called H – rich (E. Fritsch et al, 2007).

It must be noted that the presence of hydrogen as an impurity in the diamond lattice has very important consequences regarding for example colour, luminescence and growth. These types of diamonds have specific properties. Furthermore, hydrogen is also present in almost all diamonds of type Ia, even though it can be observed in very small concentrations. The presence of nitrogen is of upmost importance for the incorporation of hydrogen into the diamond lattice.

C- Growth morphology

Diamond crystallises in the cubic system and most of the time, asteriated diamonds are associated with either cuboid growth or a mix of cuboid and octahedral growths (mixed growth). Cuboid diamonds are uneven with non-plannar faces and wavy edges. In the case of a mixed growth diamond, cuboid and octahedral growth sectors are observed growing most of the time simultaneously.

As noted previously, the presence of hydrogen has a direct influence in the diamond's growth. It has been mentioned that hydrogen related defects are associated with cuboid growth (E. Fritsch et al, 2007). In addition, when mixed growth is observed colour zoning is often present. In general the cuboid growth sectors are the richest in hydrogen therefore showing a typical colour.

II- Materials and methods

A- Samples

Several samples are included in this study: three were studied at the University of Nantes and two were studied in Johannesburg.

The samples studied in Nantes were composed of a thin diamond slice that was faceted on one side and two polished round brilliant diamonds. The slice is part of the collection of the University of Nantes whereas the two polished diamonds belong to European Gemmological Laboratory (EGL) South Africa. The two sampled studied in Johannesburg are also polished round brilliant diamonds of known Zimbabwean origin.

Each of the samples have been described in details in the table below (Table 1).

Sample name	1288	A1	A2	A3	A4
Photo					
Description/cut	Thin slice with a faceted side: table and crown, brilliant cut.	Round brilliant	Round brilliant	Round brilliant	Round brilliant
Weight in carat (ct)	0.680	0.234	0.230	3.640	2.350
Colour	Greyish brown	I	J	Greyish yellowish Brown	Greyish Yellow
Clarity	N/A	SI2	VS2	I2	I1
10X loupe observations	- Growth structure observed with the unaided eye: cuboid and octahedral creating colour zoning. - With the 10x loupe fine cloud of tiny inclusions observed.	- Cloud of fine inclusions scattering light therefore looking whitish. - Some black inclusions observed.	- Cloud of fine inclusions scattering light therefore looking whitish.	- Cloud of fine inclusions with a light yellowish cross shape observed under the table. - Scattering of light observed due to the cloud.	- Cloud of fine inclusions scattering light. - Some reflective inclusions observed on the pavilion on the side.

Table 1: Description of the samples.

B- Methods

1- Classic gemmology

Gemmological properties have been obtained by classic means including:

- Long wave and shortwave ultraviolet
- Cross polarized filters
- Microscopic observations

The fluorescence has been checked with a Vilber Lourmat ultraviolet lamp, model VL-215.LC with shortwave and long wave radiations, respectively 254nm and 365nm light tubes of 15W each. A Macbeth Judge II has also been used in Johannesburg for the filtered near ultraviolet as well as a portable shortwave ultraviolet lamp.

The Vilber Lourmat lamp has been used in a dark room and the samples have been tested on a black background. The fluorescence with the Macbeth Judge II has been done on a grey background whereas with the portable shortwave ultraviolet lamp the background is black. The fluorescence, phosphorescence and evaluation of the colour have been done with the unaided eye without the use of master samples, especially for the fluorescence.

The microscopes used were a Leica MZ6 with a Canon camera attachment, Euromex fibre optic light source EK1 and a Zeiss CL 1500 ECO cold light or a Leica MZ12 equipped with a Volpi Intralux 5000-1 cold light (EGL South Africa). Very high magnification photographs were taken with a VHX 2000 digital microscope in transmission mode which was operated by Dr Benjamin Rondeau.

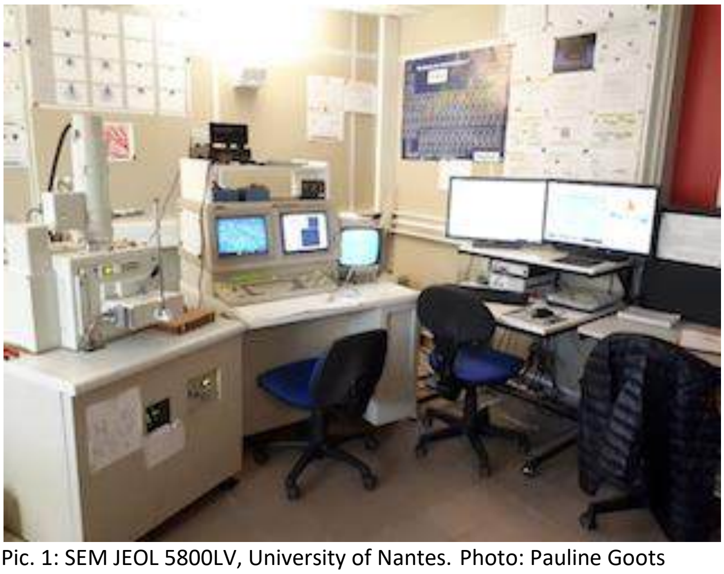
Diamond being over the limit (OTL) the refractometer has not been used. It would have been possible to use a Gemeter but the one available at the university of Nantes was missing its power cord therefore the tests have not been conducted.

2- Scanning Electron Microscope and DTC DiamonView

a- Cathodoluminescence

Cathodoluminescence has been observed only on three of the samples using a Jeol-5800LV Scanning Electron Microscope (SEM) equipped with a black and white camera (Pic. 1). The SEM has been used with the following acquisition parameters:

- beam accelerating potential : 15kV
- current : 5nA

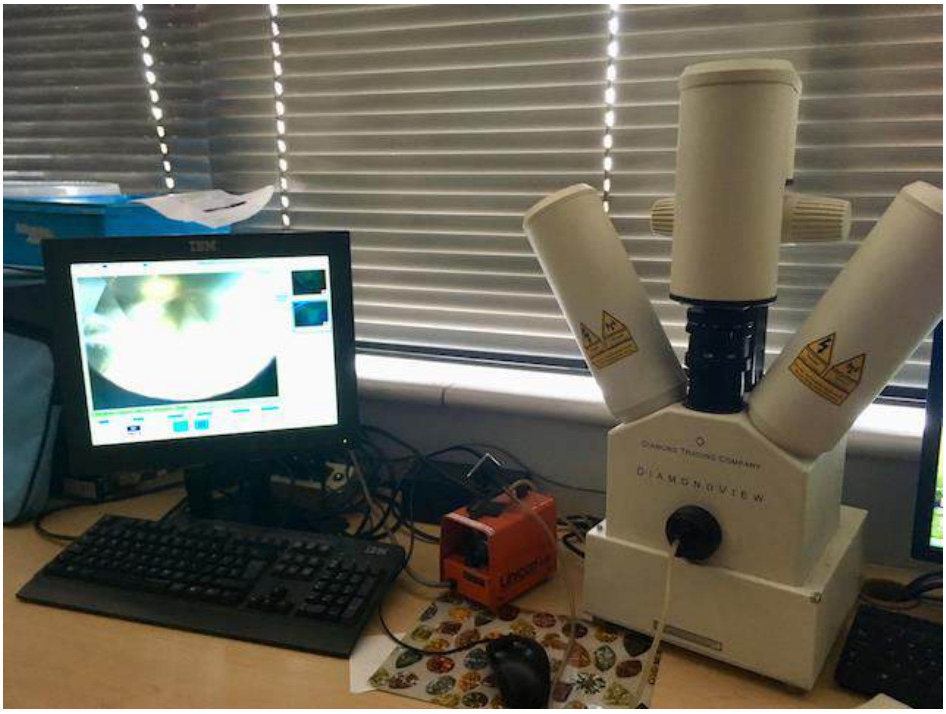


Pic. 1: SEM JEOL 5800LV, University of Nantes. Photo: Pauline Goots

The diamond slice as well as the samples A1 and A2 have been metallized with carbon in order to be used in the SEM for the cathodoluminescence.

b- DTC DiamondView

The Diamond Trading Company's DiamondView ultraviolet imaging system (Pic. 2) has been used on all samples except the diamond slice which was not available at the time of testing. The DiamondView used for this report, model number 3616, is composed of very powerful shortwave ultraviolet lights with a voltage of +24V. In addition, the current is of 4A and the instrument is equipped with a suction cup to hold the sample that is connected to a Linicon LV-125 Medo Vacuum Pump. For this test samples do not need any kind of specific preparation except thorough cleaning to avoid any dust or particles to remain on the sample.



Pic. 2: DTC DiamondView model number 3616, EGL South Africa. Photo: Alix van der Wat

3- Spectroscopy

a- Fourier Transform Infrared

A Bruker Vertex 70 Fourier Transform Infrared (FTIR) has been used with a Hyperion microscope attachment (Pic. 3) or a Bruker Alpha Fourier Transform Infrared equipped with a diffuse reflectance attachment (Pic. 4 and 5). The tests have been conducted in the range of 7000 cm^{-1} to 400 cm^{-1} for the Vertex 70 and the Bruker Alpha and from 4000 cm^{-1} to 400 cm^{-1} for the microscope. The measurements have been done in absorption mode with a resolution of 4 cm^{-1} with an accumulation of either 100 or 1000 scans. The accumulation of 1000 scans has been specifically used with the Hyperion microscope attachment. In addition, the Vertex 70 is equipped with a pump.

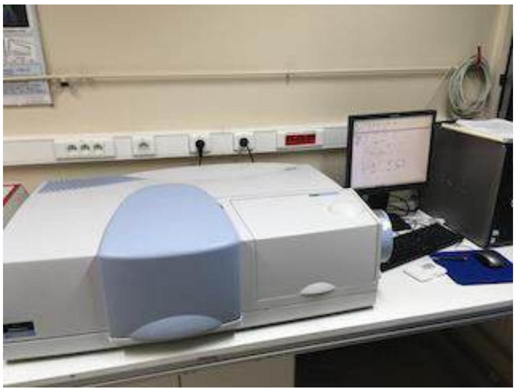
Pic. 3: Bruker Vertex 70 with Hyperion microscope attachment, University of Nantes. Photo: Alix van der Wat

Pic. 4 and 5: Bruker Alpha FTIR with diffuse reflectance attachment. EGL South Africa. Photo: Alix van der Wat

b- UV-VIS-NIR

The visible light spectrum of one of the sample has been collected with a PerkinElmer Lambda 1050 (Pic. 6) at room temperature with respectively the following acquisition parameters:

- Spectral range from 300 nm to 800 nm.
- Data interval 1 nm.
- Scanning speed 266,75 nm/min.
- Absorption mode.
- Photomultiplier Tube (PMT) detector set with a 1nm slit, a response of 0,20s and an auto gain.
- Indium Gallium Arsenide (InGaAs) detector set with a 2nm slit, a response of 0,32s and a gain of 12.



Pic. 6 : PerkinElmer Lambda 1050. Photo : Alix van der Wat

It is important to note that the two diamonds of Zimbabwean origin have not been tested with a visible light spectrophotometer as I was not granted access to use such equipment for research purposes. I must admit this was very disappointing.

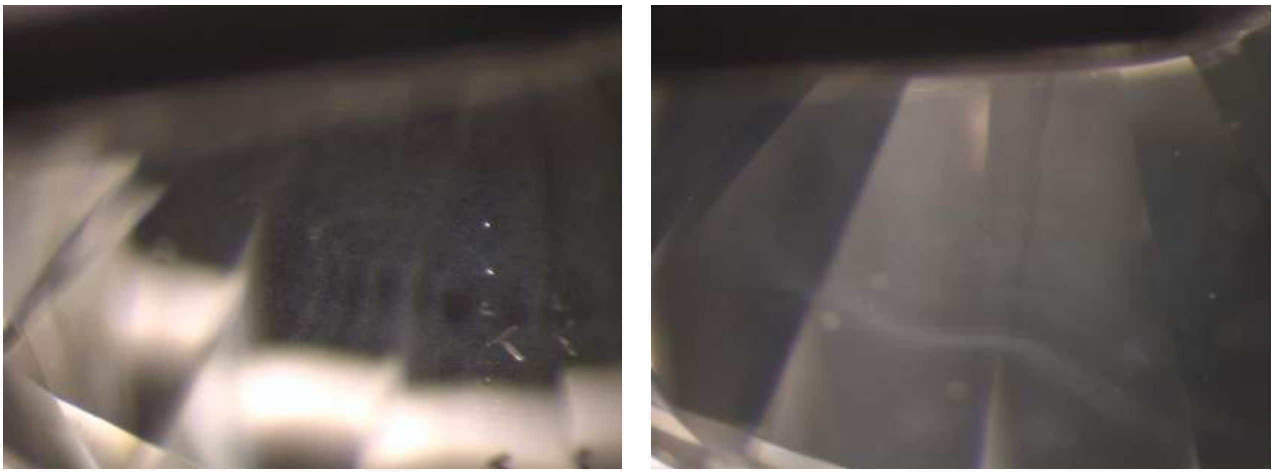
III- Results

A- Classic gemmology

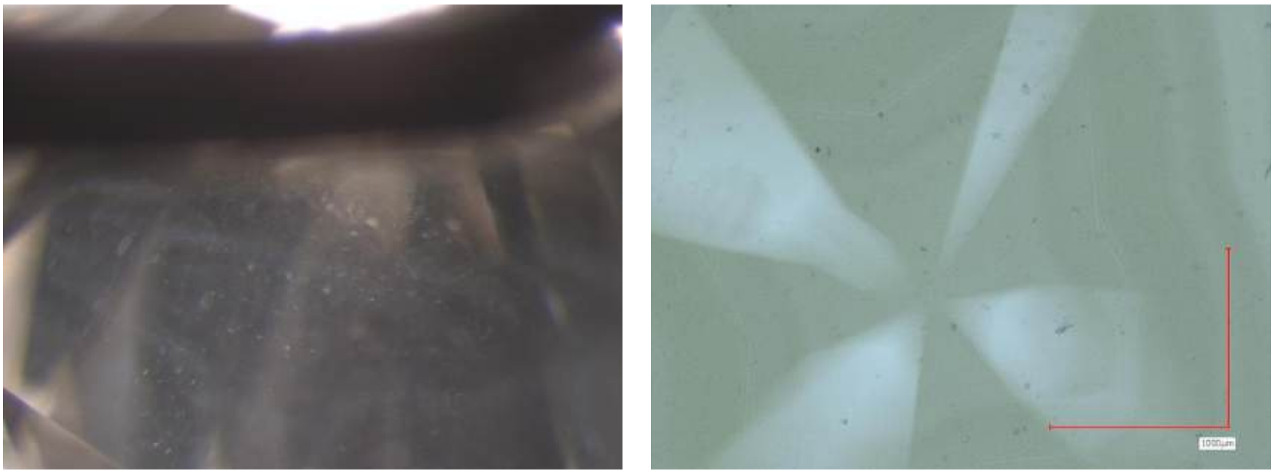
Classic gemmology tests were conducted on all the samples and the results have been summarised on the table below.

Sample name	1288	A1	A2	A3	A4
Microscopic observation	- Colour zoning. - The colour is concentrated on the cuboid sectors. - The brown areas are made of tiny dot like inclusions.	- Small cloud observed below the table made of small dot like inclusions ; light scattering. - Some black reflective inclusions observed, most probably sulphide or graphite.	- Small cloud of tiny dot like inclusions located below the table ; light scattering. - The shape of the cloud is following the crystal growth.	- Cloud of fine dot like inclusions throughout the stone ; light scattering. - Cross shape observed made of tiny yellowish dot like inclusions. - Small feathers on the side.	- Cloud of fine dot like inclusions ; light scattering. -The cloud has a very random shape, curvy. - Reflective inclusions observed on the pavilion.
Cross polarized filters (CPF)	Not performed on the sample	-Localised low order blue interference colours. - Strain.	-Localised low order blue interference colours. - Strain.	-Localised low order blue interference colours. - Strain.	- Yellowish brown colour observed. - Transparent curvy «lines».
Shortwave ultraviolet (SWUV)	- Faint yellowish green, no phosphorescence observed.	- Faint yellowish green, no phosphorescence observed.	- Faint yellowish green, no phosphorescence observed.	- Faint yellowish green, no phosphorescence observed.	- Faint yellowish green, no phosphorescence observed.
Long wave ultraviolet (LWUV)	- Strong yellowish green. The cross seems inert, no phosphorescence observed.	- Strong yellowish green, no phosphorescence observed.	- Strong yellowish green, no phosphorescence observed.	- Moderate greenish yellow, no phosphorescence observed.	- Moderate greenish yellow, no phosphorescence observed.

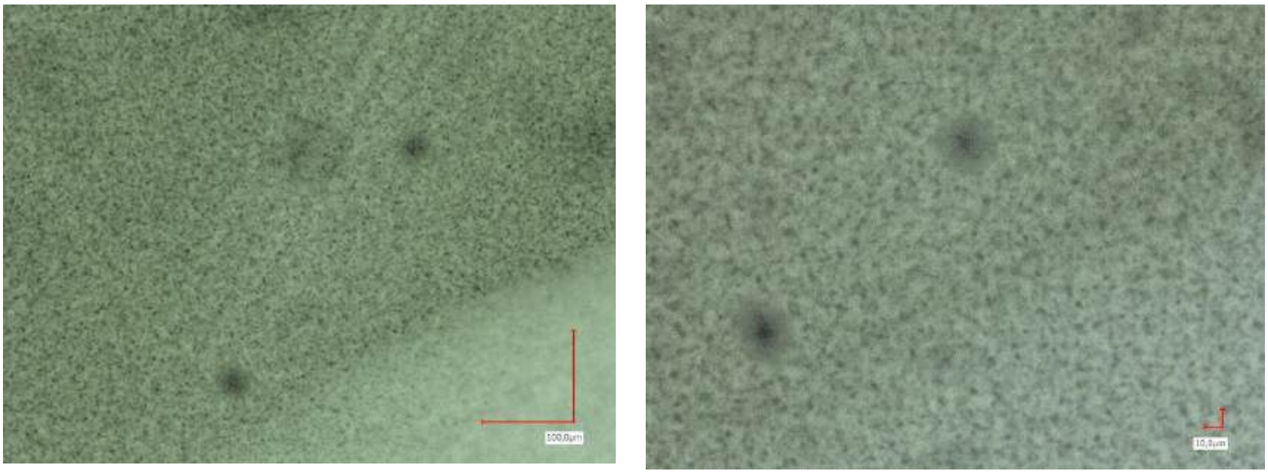
Several pictures of the samples have been taken during the microscopic observations. You will find below a selection of the best photographs.



Pic. 7 and 8 : **LEFT**, sample A1, cloud and reflective inclusions. Leica MZ6, camera attachment, zoom x4. **RIGHT** : sample A2, cloud. Leica MZ6, camera attachment, zoom x2,2.



Pic. 9 and 10 : **LEFT**, sample A2, cloud. Leica MZ6, camera attachment, zoom x2,2. **RIGHT**, sample 1288, octahedral and cuboid growth sectors. Digital microscope, magnification x100.



Pic 11 and 12 : **LEFT**, sample 1288, cloud on cuboid sector. Digital microscope, High Dynamic Range (HDR), magnification x500. **RIGHT**, sample 1288, cloud. Digital microscope, HDR, magnification x1000.

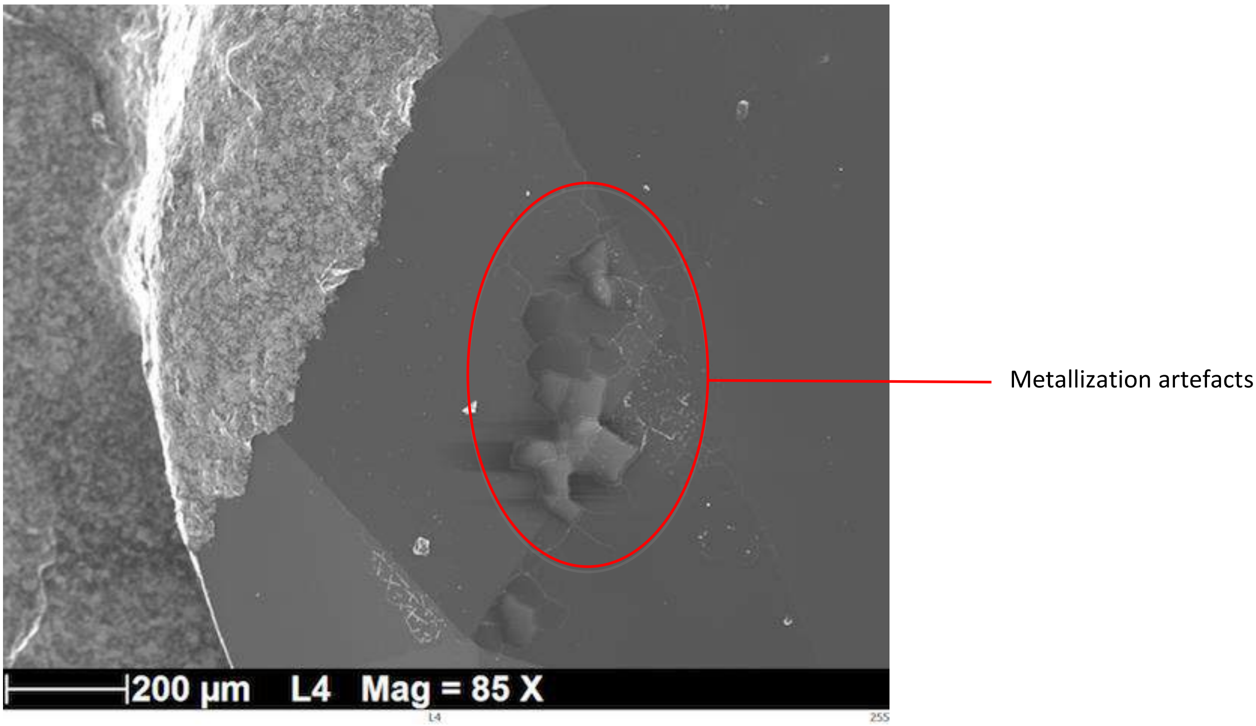
The pictures acquired with the digital microscope do show several artefacts such as two black spots (Pic. 11 and 12) and some dusts (Pic. 10).

B- Scanning Electron Microscope and DTC DiamondView

1- Cathodoluminescence

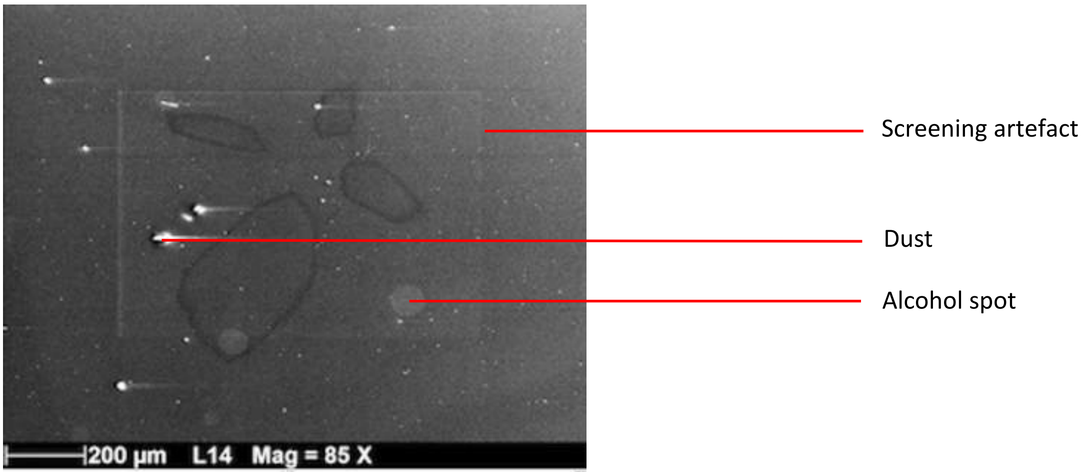
First of all the cathodoluminescence images collected do show several artefacts related to either metallization, screening or cleaning.

The metallization artefacts consists of several cracks observed on several pictures as well as some kind of « growth » looking feature (Pic. 13)



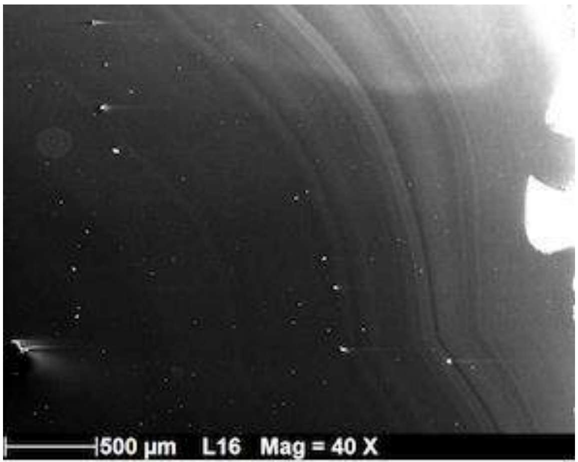
Pic 13 : Artefacts of metallization : cracks and « growth » looking feature. Photo taken with scattering electron (SE) mode.

Screening artefacts can be observed on several pictures (Pic. 14 and 18). It corresponds to a rectangular zone of slightly different colour. Also some dust particles can be observed as well as roundish spots which are probably traces of the alcohol that evaporated. Indeed alcohol was used to clean the samples prior to the metallization process.



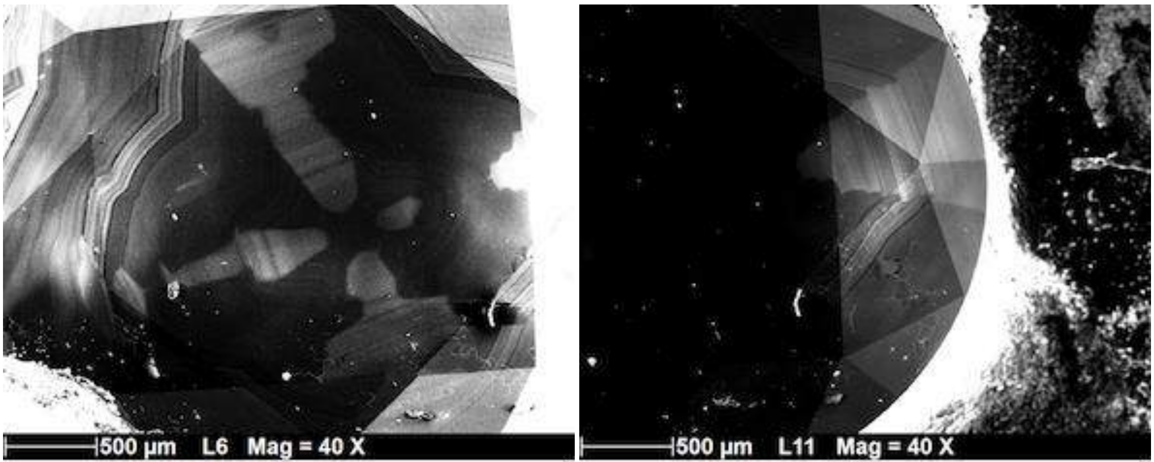
Pic. 14 : sample 1288 (Slice) showing a four – lobe pattern as well as screening, dust and cleaning artefacts.

The slice is showing a four – lobe or petal pattern corresponding to octahedral growth sectors (Pic. 14). In addition one lobe is more developed than the other ones. The same sample also shows parallel lines or banding corresponding to cuboid growth sectors, especially located towards the sides of the sample (Pic. 15).



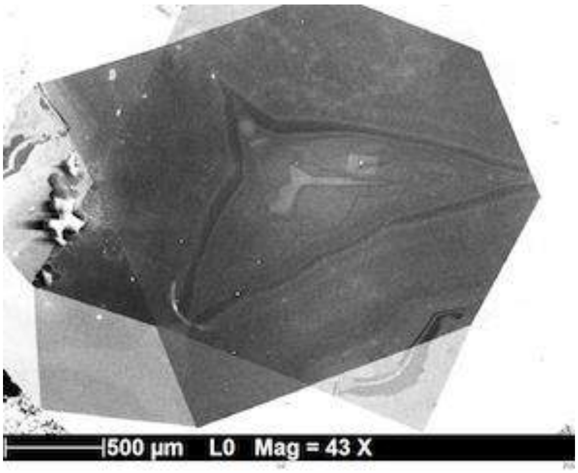
Pic. 15 : sample 1288, structural lines observed corresponding to cuboid growth.

The second sample (A1) like for the previous sample (1288) is showing four elongated lobes corresponding to octahedral growth sectors as well as banding or lines corresponding to cuboid growth sectors (Pic. 16 and 17).

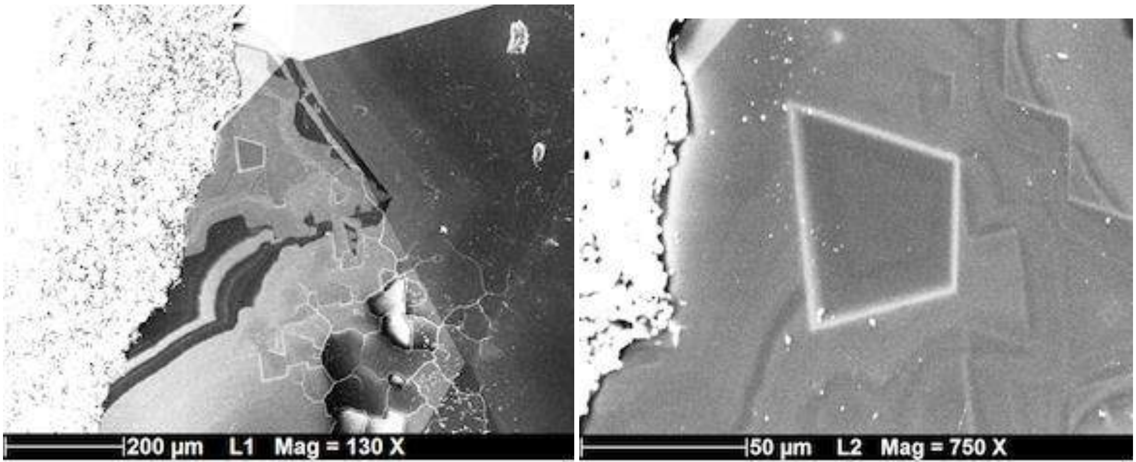


Pic. 16 and 17 : sample A1, octahedral and cuboid growth structures observed.

Sample A2 is quite different from the two previous ones studied as the stone shows a triangular shape with small uneven lobes located inside (Pic. 18). There is a very small and short lobe and two other ones which are longer. In addition the growth structures on the side of the sample are quite different and show geometrical features such as step like lines and trapezoid like pattern which seems to follow a slight different direction than the main growth patterns (Pic. 19 and 20).



Pic. 18: sample A2, triangular pattern with uneven lobes.



Pic. 19 and 20 : sample A2, growth structures on the side of the sample.

2- DTC DiamondView

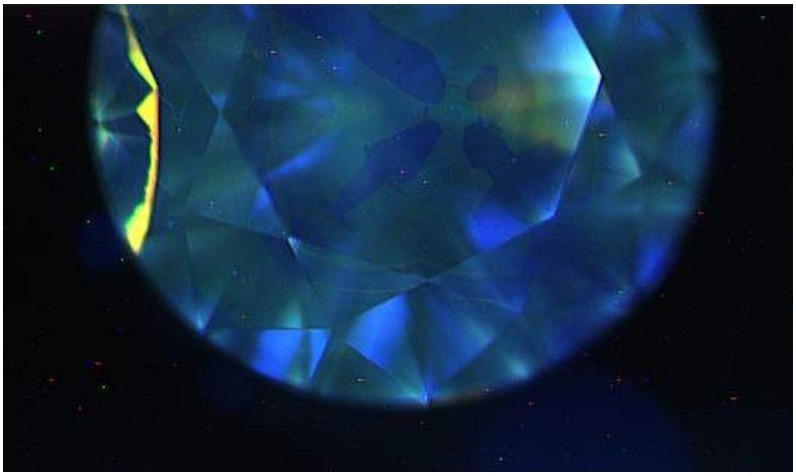
This instrument exposes polished stones to shortwave UV radiations and translates it into a digital image of the surface luminescence. The diamond reacting to the ultraviolet radiations is going to luminesce with different colours showing different patterns. Cathodoluminescence and DiamondView imaging both show surface structures of the diamond but the two instruments use very different technics (electron beam vs. shortwave ultraviolet radiations) to get these images.

The images obtained are all showing blue and yellowish green fluorescence with one stone (sample A1) showing localised bright yellowish areas with some brownish or greenish tints. The pictures of sample A1 and A2 are similar to the pictures acquired using cathodoluminescence. The only difference being the luminescence colours and the fact you can observe the luminescence patterns on the pavilion (Pic. 21 and 22). Sample A1's pictures show a bright yellowish line with localised angular patterns on the side which is not observed on the cathodoluminescence pictures. This could be due to fact that the area is confined to side of the sample and could have been hidden by the silver paint used for the metallization. This yellowish area is also observed on the pavilion. There is also a yellowish « ring » around the culet. We can easily identify cuboid and octahedral growth patterns which are also visible on the cathodoluminescence pictures. Sample A2’s DiamondView images do show the same type of growth patterns than the one observed on the cathodoluminescence pictures. A picture of the pavilion shows an elongated lobe (octahedral growth) fluorescencing blue and surrounded by curved, rounded growth patterns fluorescing yellowish green which are probably corresponding to cuboid growth (Pic. 23 and 24).

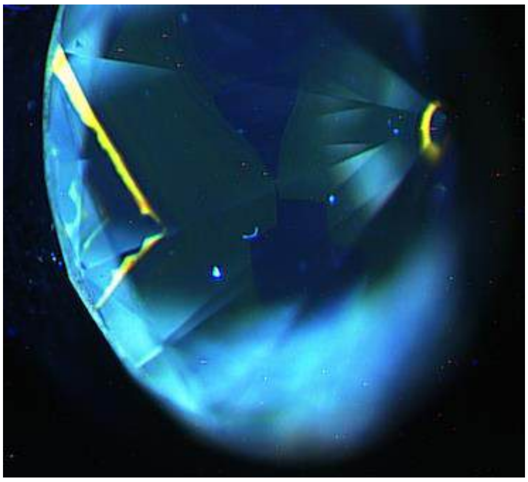
Sample A3’s images (Pic. 25) do show the typical mixed octahedral and cuboid growth usually observed on diamonds of Zimbabwean origin. One lobe is very prominent in comparison to the other ones.

On the other hand, sample A4’s images (Pic. 26 and 27) are very different from all the other ones. I must admit that it is the first time I see a diamond of Zimbabwean origin with this type of growth patterns, especially knowing that this diamond has a noticeable cloud, a typical greyish yellow colour and a very high hydrogen and nitrogen content. The fluorescence patterns look more random and cuboid or octahedral growth sectors don’t appear as clearly as the previous images. The blue « swirls » do somehow follow the shape of the cloud while observed under the microscope.

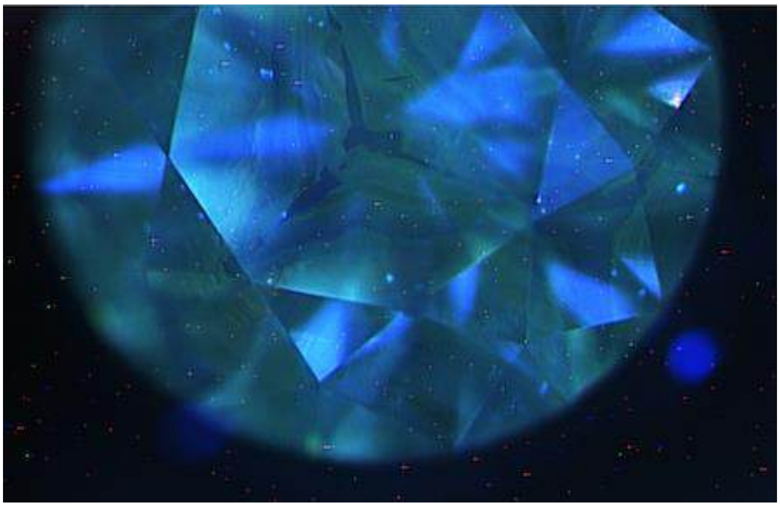
Please find below a selection of DiamondView images.



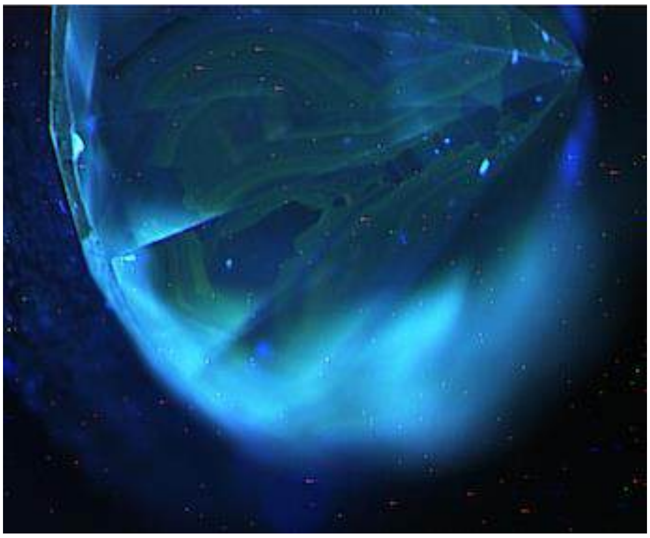
Pic. 21: sample A1, face up, medium magnification. Measured at medium aperture, exposure 2.0s.



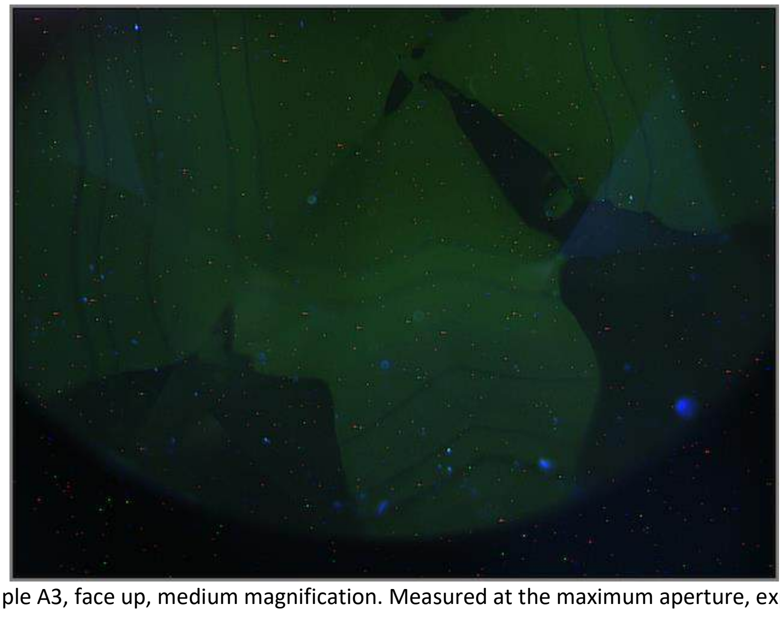
Pic. 22: sample A1, pavilion view, medium magnification. Measured at medium aperture, exposure 2.0s.



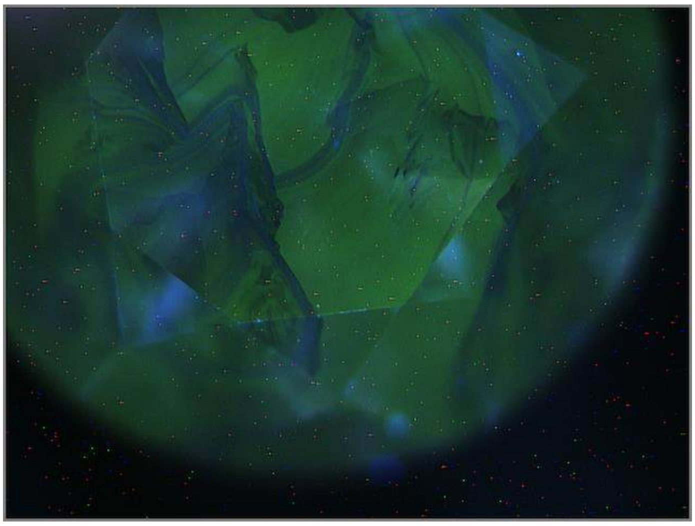
Pic. 23: sample A2, face up, medium magnification. Measured at medium aperture, exposure 2.0s.



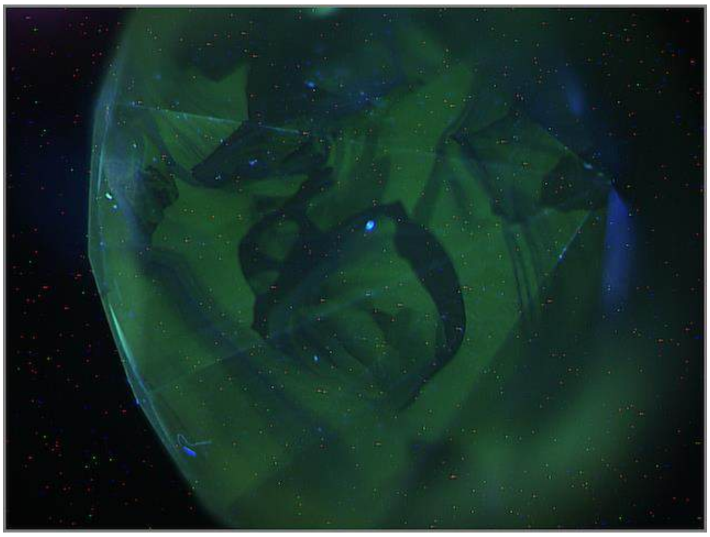
Pic. 24: sample A2, pavilion view, medium magnification. Measured at medium aperture, exposure 2.0s.



Pic. 25: sample A3, face up, medium magnification. Measured at the maximum aperture, exposure 4.0s.



Pic. 26: sample A4, face up, medium magnification. Measured at the maximum aperture, exposure 4.0s.



Pic. 27: sample A4, pavilion vie, medium magnification. Measured at the maximum aperture, exposure 4.0s.

3- Spectroscopy

a- Fourier Transform Infrared (FTIR)

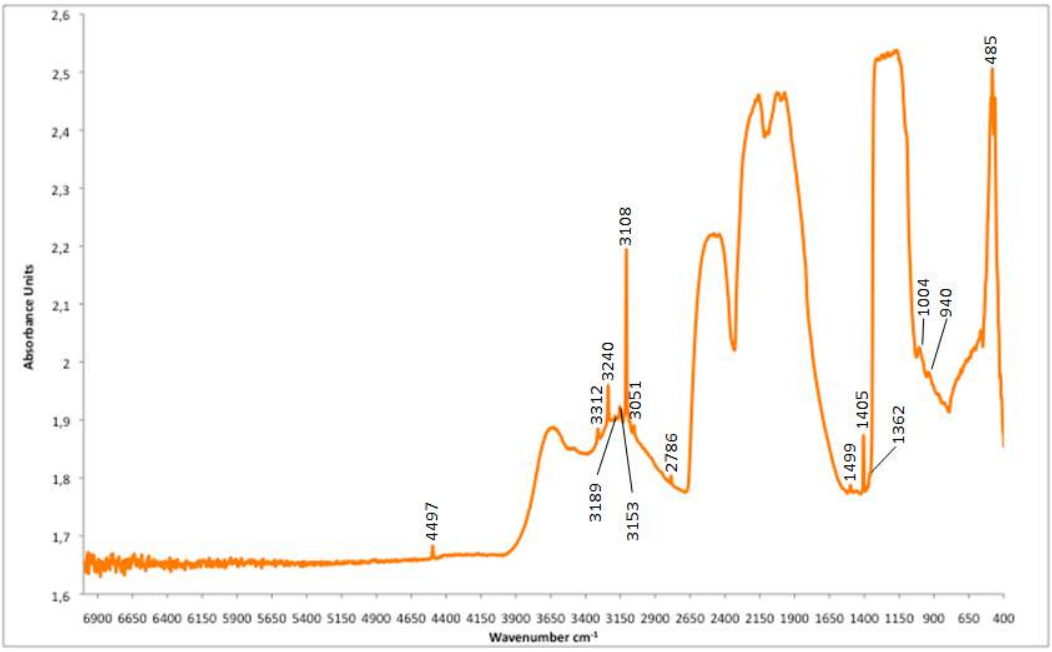
All samples have been tested on the FTIR and they all show nitrogen and hydrogen impurities.

Samples A1 and A2 are quite similar in term of their classical gemmology features therefore their infrared spectra are going to be compared.

Sample A1 infrared spectrum (Graph. 1) shows a very high amount of nitrogen in the one phonon region. It is higher than the peaks located in the 2000 cm^{-1} region (diamond spectral signature) and can be considered nitrogen rich. The main absorptions in the one phonon area are at approximately 1405 cm^{-1} (hydrogen peak), 1004 cm^{-1}, 940 cm^{-1} and 485 cm^{-1}. The peak at 485 cm^{-1} is indicative of the presence of A aggregates. In general the very high level of nitrogen observed in the one phonon region (in our case the peak is wide and noisy) and the peak at 485 cm^{-1} are correlated as a function of the amount of A aggregates present. The main nitrogen peak is very noticeable and prominent so is the peak at 485cm^{-1}. Furthermore the peak at around 1004 cm^{-1} can indicate that some B aggregates are present as well.

A very small platelet peak is observed at around 1362 cm^{-1}. Platelets represent a complex association between nitrogen and carbon atoms. They are elongated planar defects in diamonds very rich in nitrogen. Platelets are usually observed in association with B aggregates (L. Massi, 2006). They can be referred as B' in the literature. The presence of the small platelet peak is therefore related to the presence of the peak at 1004cm^{-1} indicating the presence of some B aggregates.

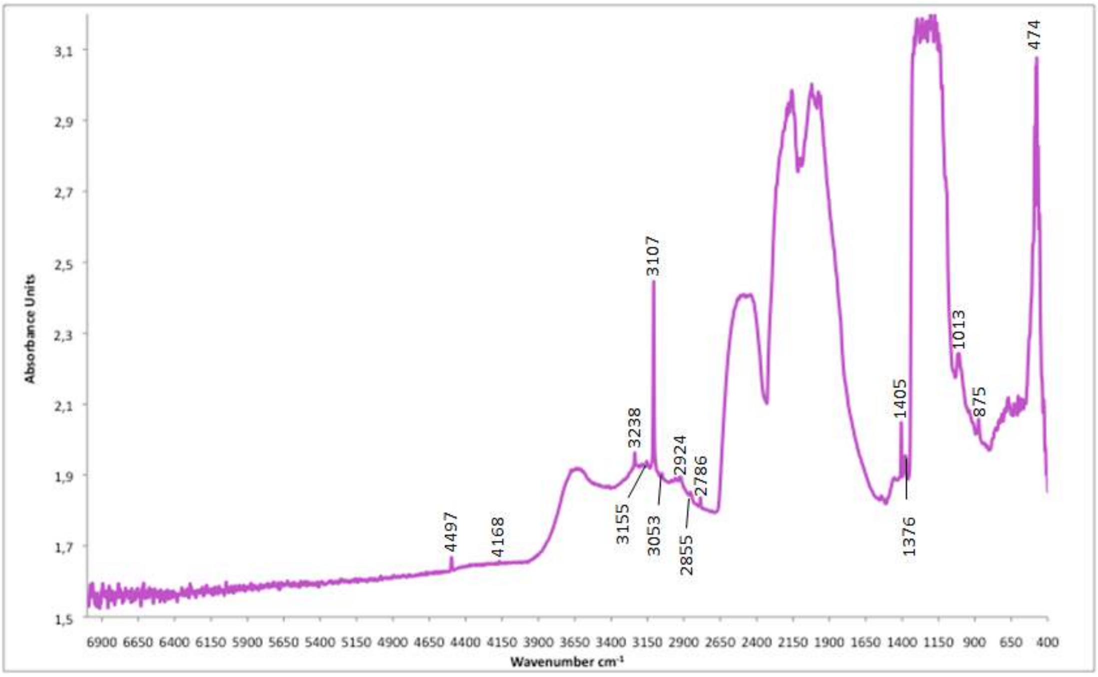
In addition, sample A1 does show noticeable peaks in the three phonon region which are related to hydrogen impurities. The main peaks observed are at around 2786 cm^{-1}, 3108 cm^{-1}, 3240 cm^{-1}, 3312 cm^{-1} and 4497 cm^{-1}. The 3108 cm^{-1} peak is very high but slightly lower than the intrinsic value of the diamond at around 2450 cm^{-1}. This stone is almost hydrogen – rich.



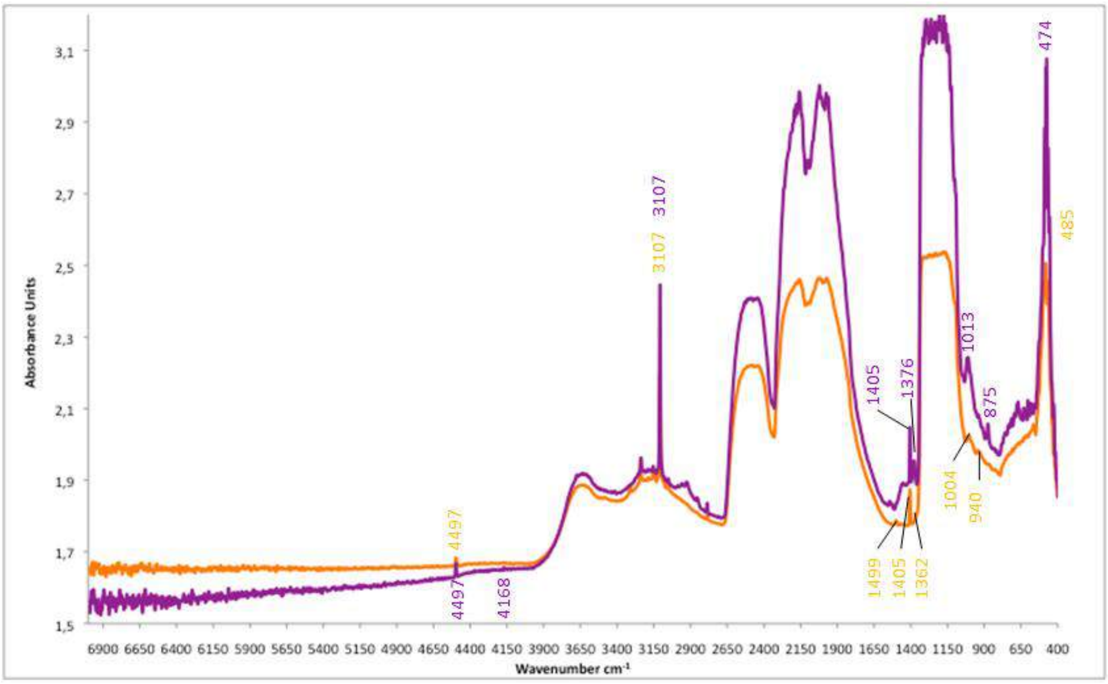
Graph 1 : FTIR spectrum of sample A1.

Sample A2 (Graph 2) like sample A1 does show a very high amount of nitrogen. It can be considered nitrogen rich since the nitrogen absorption in the one phonon region is higher than the diamond signature observed in the two phonon region. In addition the peak at around 474 cm^{-1} is very high too and indicates that A aggregates are present. Also a peak at approximately 1013 cm^{-1} is observed and is related to B aggregates. In comparison this peak is higher than the one observed in sample A1 which indicates that sample A2 contains more B aggregates. This is also confirmed by the presence of a platelet peak at around 1376 cm^{-1}: it is higher than the one observed in sample A1. Also the amount of nitrogen presents in sample A2 is much higher than the one observed in sample A1 (Graph 3). Furthermore, the spectrum shows noticeable hydrogen related absorptions and in this case the peak at 3107 cm^{-1} is slightly higher than the diamond's intrinsic value therefore sample A2 is considered hydrogen – rich. It must be noted that sample A2 has a few hydrogen absorptions that are not present in sample A1 such as 2855 cm^{-1}, 2924 cm^{-1} and an amber centre at around 4168

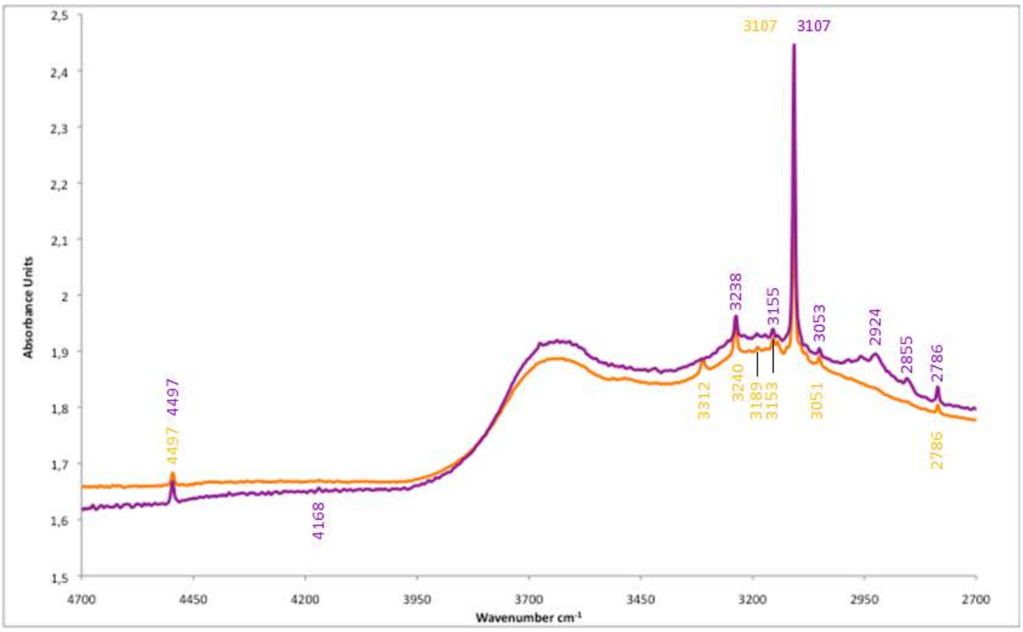
cm^{-1} and sample A1 has an absorption at around 3312 cm^{-1} that is not observed on sample A2 (Graph 4).



Graph 2: FTIR spectrum of sample A2.



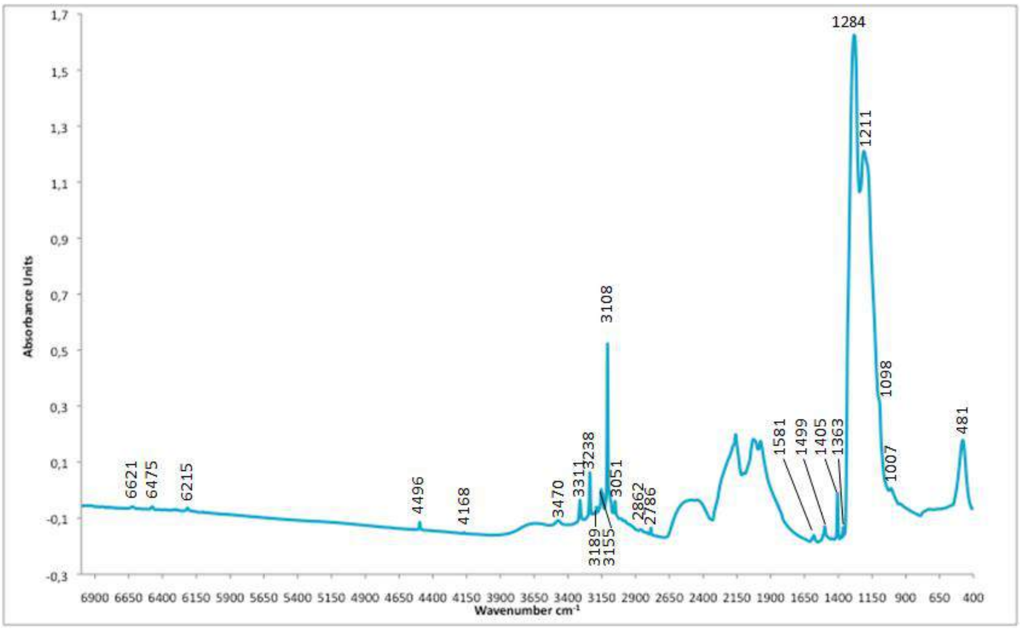
Graph 3: Comparison of FTIR spectra of sample A1 (orange) and sample A2 (purple).



Graph 4: Zoom of the hydrogen related absorptions in sample A1 (orange) and sample A2 (purple).

The diamond slice (sample 1288) has been studied using either the Vertex 70 or the microscope attachment. The idea was to get infrared spectra of the different areas of the slice meaning the colourless one and the brown one and compare them accordingly. The acquisition has been done using 100 scans for the classic set up and a 1000 scans for the microscope in order to see if we could get better results on more localised areas.

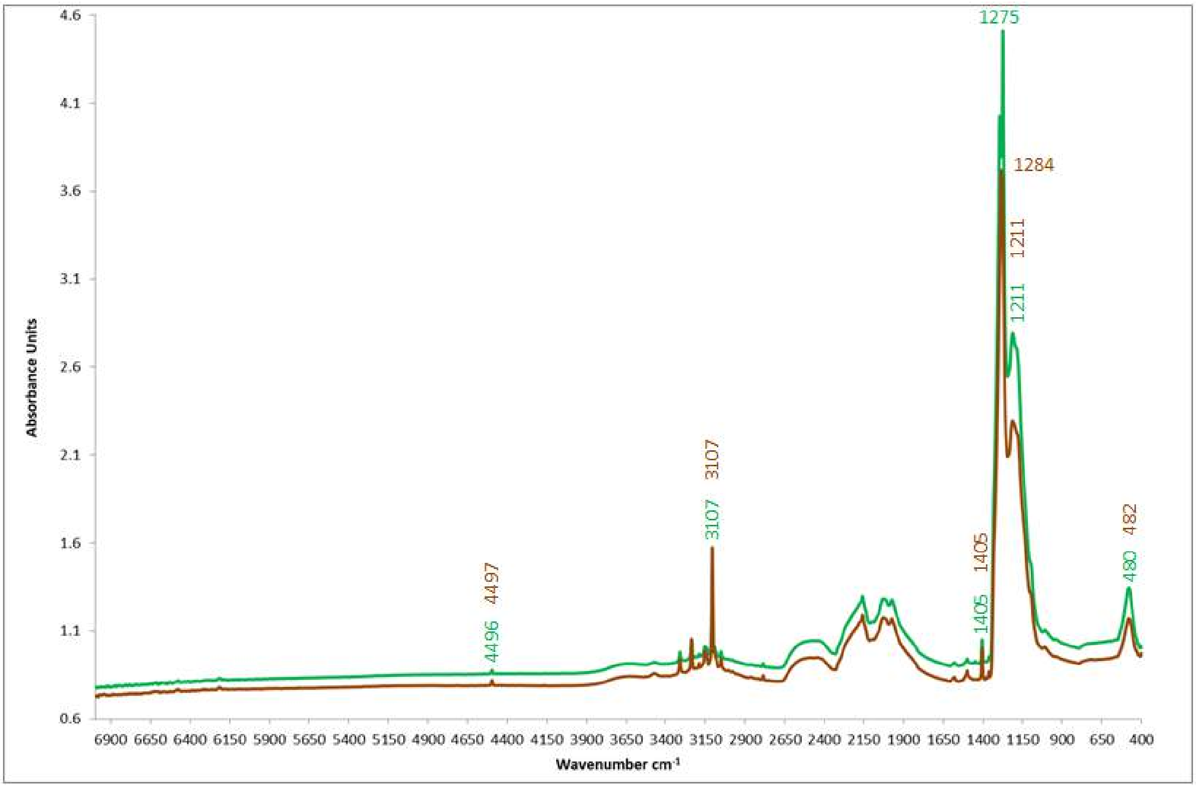
First of all the spectrum of the full slice at 100 scans (Graph 5) indicates that it is a type IaA diamond with the presence of a very small amount of B aggregates. Indeed, the nitrogen peaks observed are as follows : 481 cm^{-1}, 1007 cm^{-1}, 1098 cm^{-1}, 1211 cm^{-1} and 1284 cm^{-1} with 481 cm^{-1}, 1211 cm^{-1} and 1284 cm^{-1} corresponding to A aggregates and 1007 cm^{-1} and 1098 cm^{-1} corresponding to B aggregates. There is also a small platelet peak observed at around 1363 cm^{-1}.



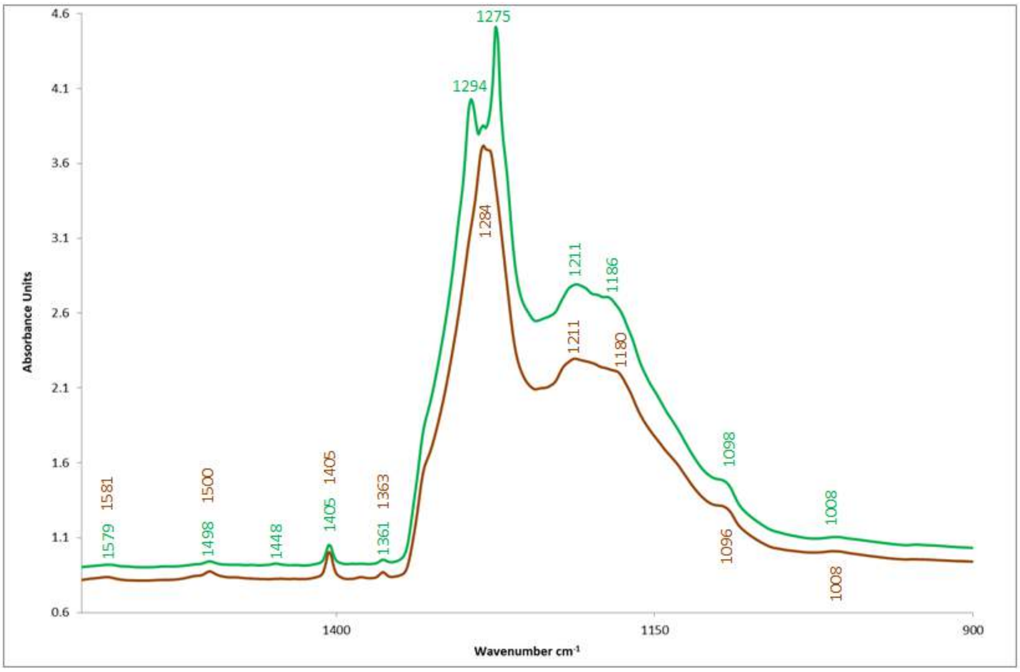
Graph 5 : FTIR spectrum of the full slice, 100 scans.

Moreover there is a noticeable level of hydrogen which is higher than the diamond intrinsic value meaning that the sample is hydrogen – rich. The classic hydrogen absorptions are observed such as peaks at 1405 cm^{-1}, 3051 cm^{-1}, 3238 cm^{-1}, 3311 cm^{-1} and 4496 cm^{-1} with the main absorption peak at around 3107 cm^{-1} (Graph 5). There is also an amber centre at around 4168 cm^{-1} and three small absorptions at around 6215 cm^{-1}, 6475 cm^{-1} and 6621 cm^{-1}.

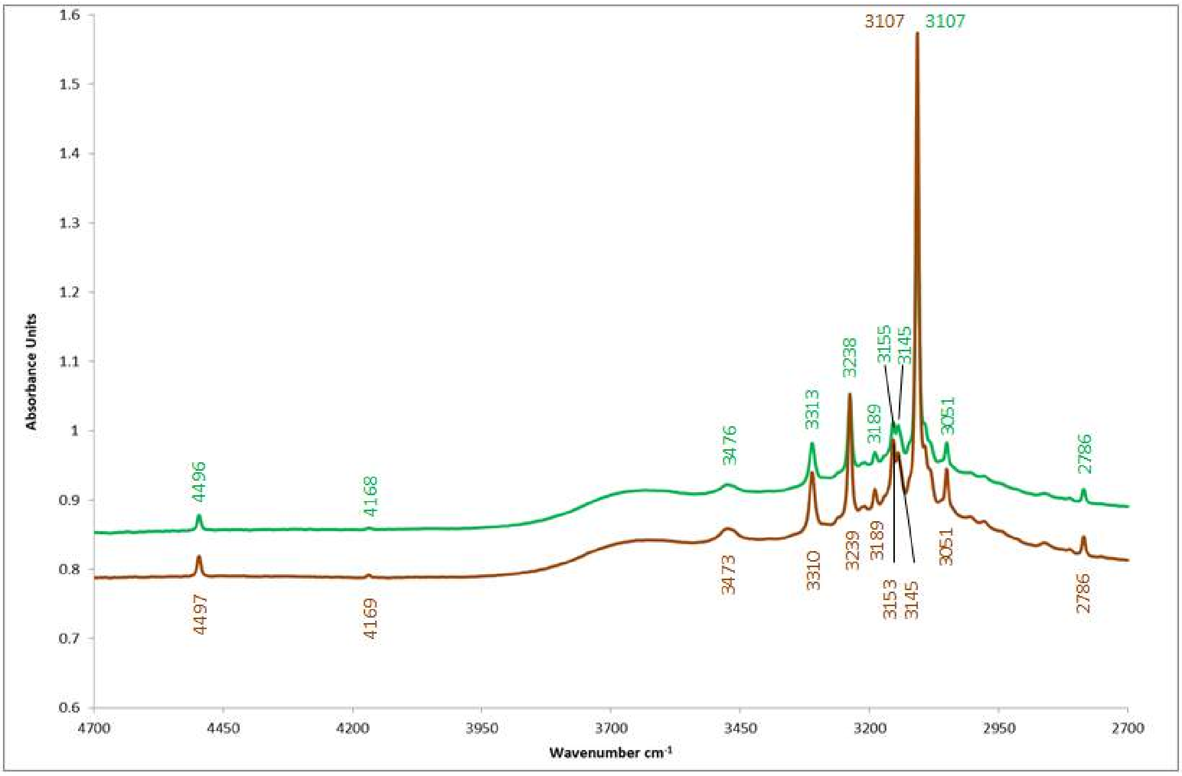
A spectrum of each sector (colourless and brown) has also been done in order to see if a certain sector shows more hydrogen or nitrogen impurities (Graph 6). Zooms of the nitrogen and hydrogen areas have been included to get better peak details (Graph 7 and 8). For easier reading, the colourless sector's spectrum is in green and the brown one is in brown.



Graph 6: Spectra of the colourless (green) and brown (brown) sectors, 100 scans.



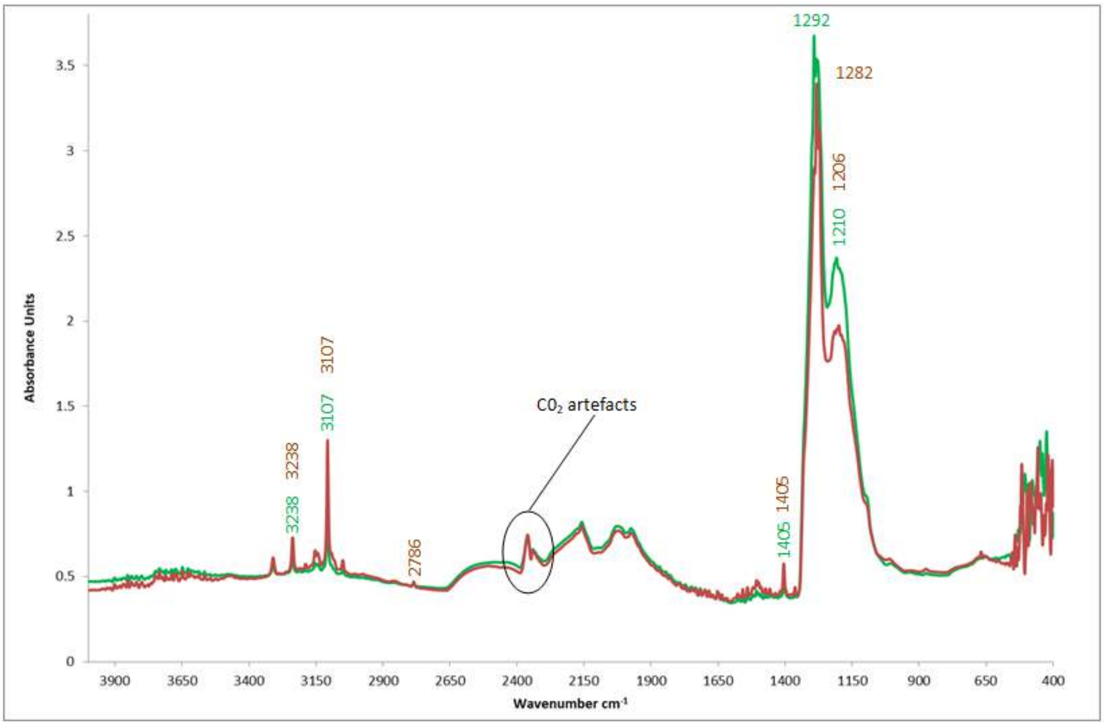
Graph 7: Zoom in the one phonon area showing the nitrogen related absorptions in the colourless and brown sectors, 100 scans.



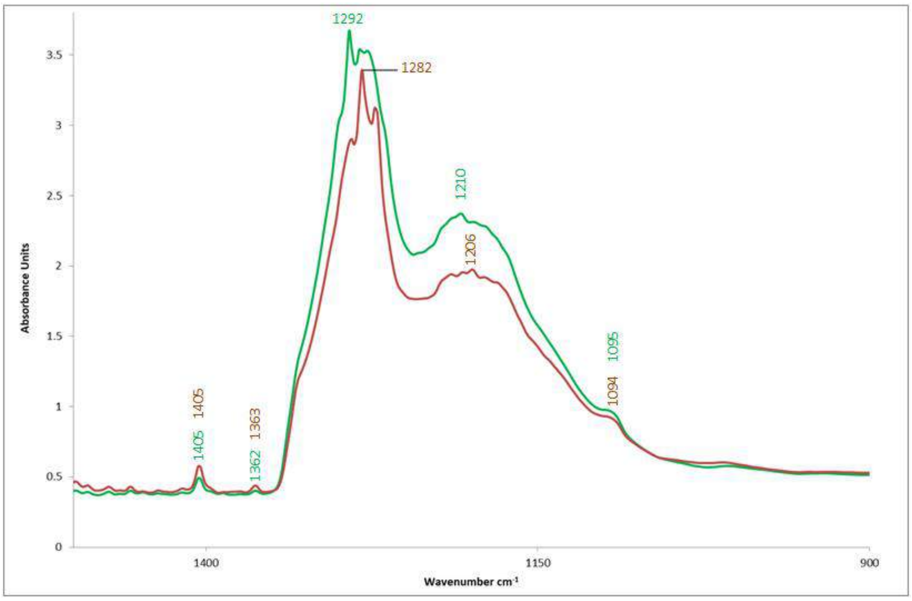
Graph 8: Zoom in the three phonon area showing the nitrogen related absorptions in the colourless and brown sectors, 100 scans.

The first thing that we notice by comparing the spectra of the two sectors is that the amount of nitrogen observed in the colourless sector (green spectrum) is more important than the one from the brown sector. In addition there is a very small peak in the green spectrum at approximately 1448 cm^{-1} which is not observed in the brown one. Furthermore, the amount of hydrogen is more important in the brown spectra compared to the green one. The peaks are also sharper and higher.

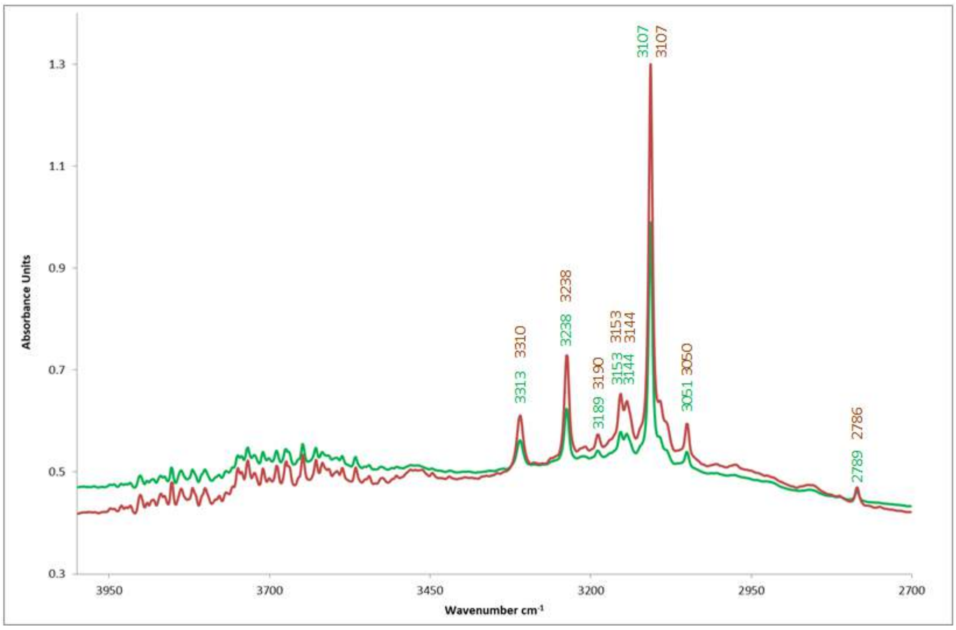
Looking into the spectra obtained with the 1000 scans we notice noise and several artefacts related to the presence of CO_2. Also as seen on the previous spectra (100 scans), the level of nitrogen in the colourless sector (green spectrum) is more important than the brown one whereas it is the reverse regarding the level of hydrogen. It is more important in the brown sector than the colourless one. On the overall, the measurements done at 100 or 1000 are very similar but do show some slight differences : noise, height of nitrogen peaks, height of hydrogen peaks, CO_2 artefacts and a slight shift of the peaks in some cases (Graphs 9, 10 and 11).



Graph 9: colourless (green) and brown (brown) sectors spectra, microscope attachment, 1000 scans.

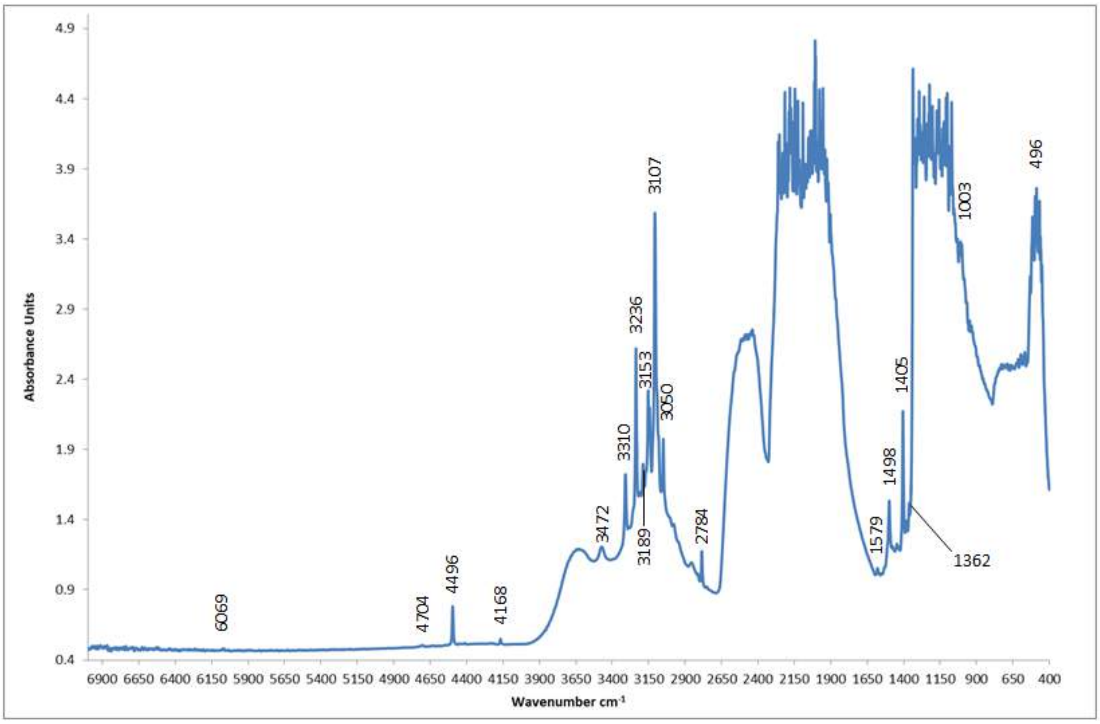


Graph 10: zoom of the one phonon region of the colourless and brown sector, microscope attachment, 1000 scans.

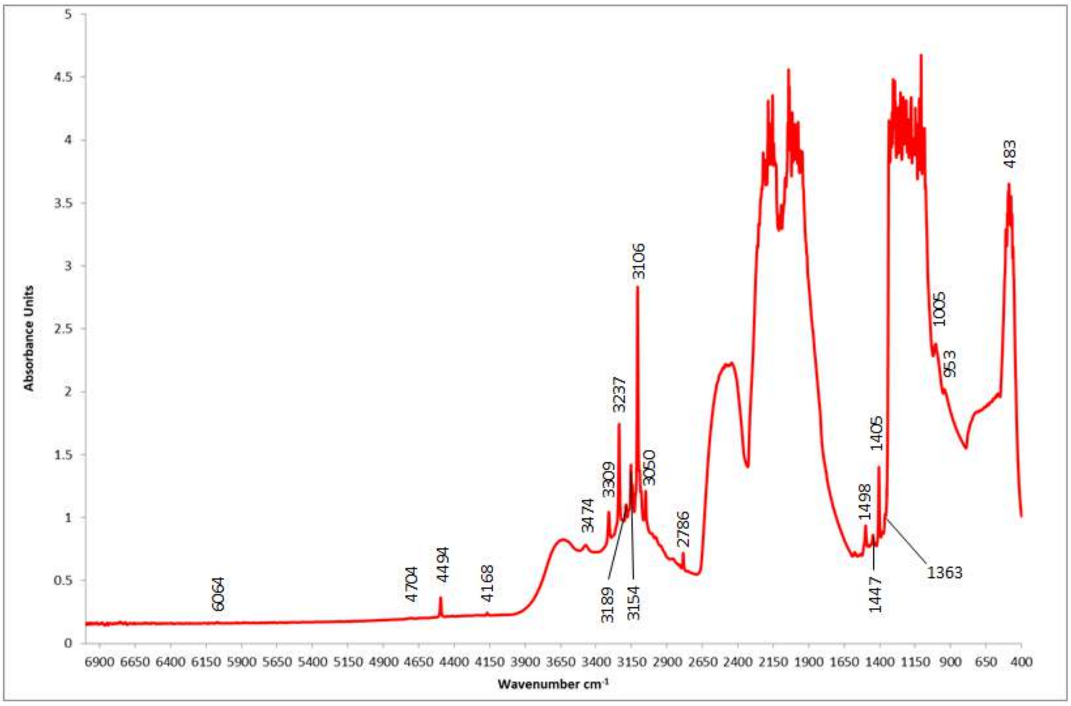


Graph 11: zoom of the three phonon region of the colourless and brown sectors, microscope attachment, 1000 scans.

Regarding the two diamonds of Zimbabwean origin, their infrared spectra are typical (Graph 12 and 13) : very high amount of hydrogen (H – rich) and nitrogen. Both stones show absorptions related to the presence of A aggregates : peaks at 483 cm^{-1} for sample A4 and peaks at 496 cm^{-1} for sample A3. Some B aggregates are also observed : 1003 cm^{-1} for sample A3 and 1005 cm^{-1} for sample A4. The only sharp but small peak which is related to the B aggregates is the platelet peak observed at 1362 cm^{-1} for sample A3 and 1363 cm^{-1} for sample A4.

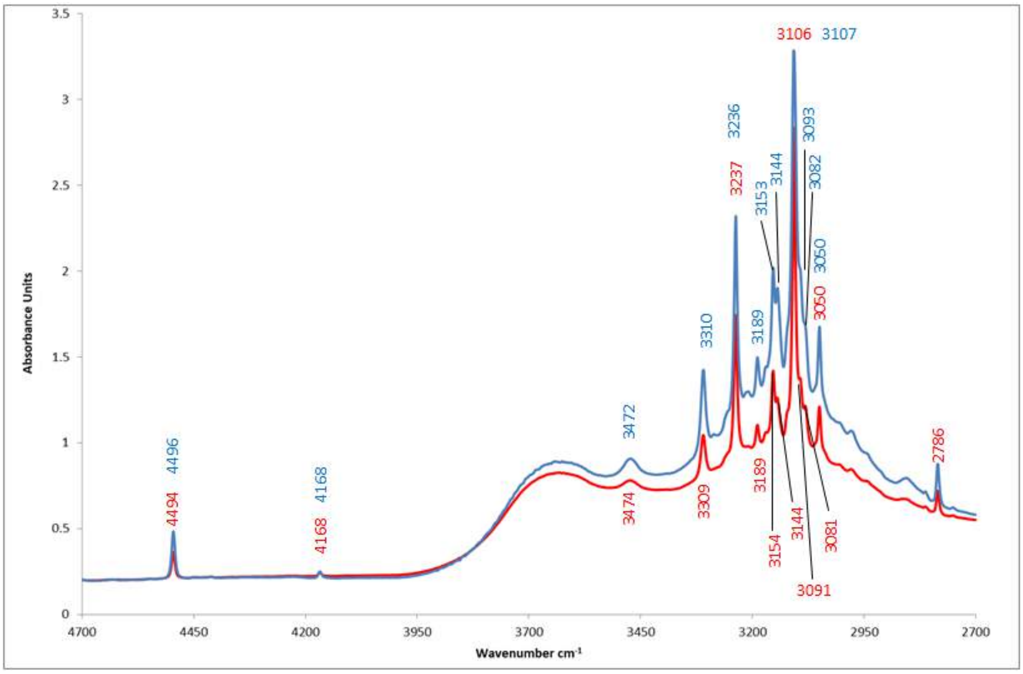


Graph 12: FTIR spectrum of sample A3, 100 scans.



Graph 13: FTIR spectrum of sample A4, 100 scans.

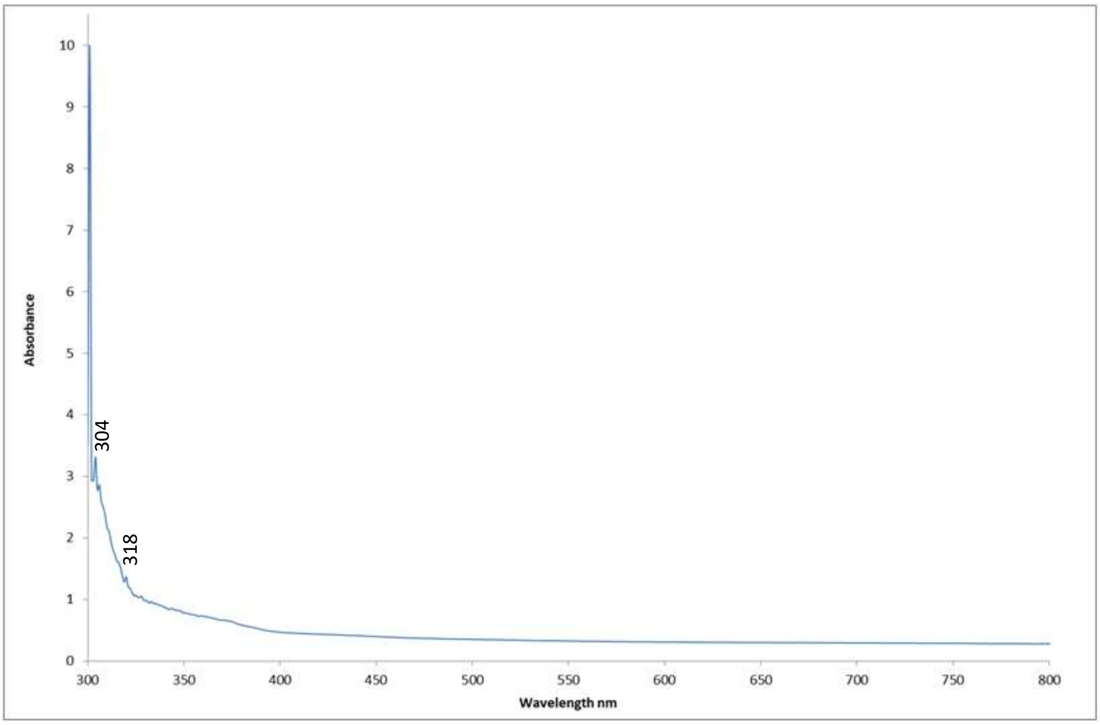
Moreover sample A3 has a higher content of hydrogen than sample A4. For both spectra the main peaks are at approximately 2786 cm^{-1}, 3050 cm^{-1}, 3106 /3107 cm^{-1}, 3154/3153 cm^{-1}, 3189 cm^{-1}, 3237/3236 cm^{-1}, 3309/3310 cm^{-1}, 3472 cm^{-1}/3474 cm^{-1} and 4494/4496 cm^{-1}. Both stones show an amber centre located at around 4168 cm^{-1}. Furthermore sample A4 like sample A3 has a small peak at approximately 1447 cm^{-1}. It is important to note that sample A3 is darker in colour than sample A4 which could explain the higher hydrogen amount measured for the sample. Graph 14 shows a comparison of the three phonon region of A3 and A4 and especially the hydrogen content of both stones.



Graph : comparison of the hydrogen content of sample A3 (blue) and sample A4 (red), 100 scans.

b- UV-VIS-NIR

The visible light spectrum (Graph 15) has been performed only on one of the sample (slice 1288). Due to samples' A1 and A2 colour (near colourless), the visible light spectrum has not been conducted. Indeed, the spectra would have been featureless. Furthermore, as mentioned earlier, A3 and A4 (Zimbabwean diamonds) have not been tested due to logistic issue : I was not allowed access to the instrument.



Graph 15: UV-VIS-NIR of sample 1288, room temperature.

The visible light spectrum of the slice shows two main features. First, the spectrum is very flat from around 350nm to 800nm indicating a grey colour and second we observe an absorption increase from 300nm to 800nm related to the brown colour. The cut-off in the ultraviolet range is very sharp and steep and there is two small peaks at around 304 and 318 nm.

IV- Discussion.

First of all, these five samples, even though having very different colours (from near colourless to greyish yellowish brown) do share several characteristics. They all have a high content of nitrogen, hydrogen and they also all have a cloud. The cloud is of different size and colour and is either localised (samples A1 and A2) or spread throughout the stone (slice 1288, sample A3 and A4).

All the samples, except sample A4 are a combination of cuboid and octahedral growth. The octahedral growth is usually represented in our samples by a cross and the cuboid sectors are looking like « wavy squares ». Both growth happen simultaneously. In sample 1288 (slice) and most probably sample A1 the cuboid growth prevails which is quite unusual. Indeed, most of the case the octahedral growth wins over the cuboid one. In sample A3 on the other hand, the octahedral growth seems to take over when looking at the edge of the stone near the girdle.

Samples 1288, A1 and A3 do show a four lobe or petal pattern which indicates that the stones are observed along the four fold symmetry axis. Sample A2 is quite different as the centre growth structure shows a three lobe pattern. This means that the stone is observed along the three fold symmetry axis. In addition there is some sort of short wavy structure next to the three lobe pattern on the left (Pic. 23) which is observed mainly on the DiamondView image. This could indicate that the stone grew as a re – entrant cube. Indeed, the three lobe pattern look like an uneven and skew « Mercedes star ».

Sample A4 is quite puzzling because it doesn't show any clear cuboid or octahedral growth patterns as seen in the previous samples. There is some curvy lines which could indicate some cuboid growth but it is not straight forward. It can be possible that the stone underwent episodes of dissolution which impacted the initial growth structure. This would explain the peculiar growth features of this stone.

Moreover, all the sample show a characteristic yellowish green fluorescence which is due to the presence of nickel (E. Fritsch et al, 2007) as an impurity in the diamond. This greenish fluorescence is usually confined in the cuboid sector which explain why the octahedral sector look rather dark or inert. This can also mean that the cuboid sector incorporates nickel impurities in comparison to the octahedral one.

In addition, all the samples studied are of type Ia with IaA>>B. Several hydrogen absorptions and especially the ones at around 3145 cm^{-1}, 3181 cm^{-1}, 3310 cm^{-1} and 3372 cm^{-1} have been observed on several of our samples. These absorptions have been attributed to a type Ib character (E. Fritsch et al, 2007 and T. Hainschwang, 2014). Samples 1288 (slice), A4 and A3 do show some or all these characteristic absorptions even though C centre (isolated nitrogen) related absorptions such as 1344 cm^{-1}, 1130 cm^{-1} and 2688 cm^{-1} are not observed in their infrared spectra. Therefore they can be considered to have some Ib character. This is especially true for sample A3 and A4 that do show prominent hydrogen peaks.

The 3107 cm^{-1} system characterized by the following absorption peaks at approximately 1405 cm^{-1}, 2786 cm^{-1}, 3107 cm^{-1}, 4167 cm^{-1} (if present) and 4496 cm^{-1} are observed on all the samples but with varying peak heights. The highest peaks observed being for samples A3 and A4 (Zimbabwe) which are the darkest in colour and the weakest peaks for the near colourless samples. The peak at 5555 cm^{-1} which is the weakest of the 3107 cm^{-1} system (E. Fritsch et al, 2007) has not been observed on any of the samples even though for some samples the 3107 cm^{-1} is quite strong (samples A3 and A4). Samples A3 and A4 show quite a high peak at around 3236 cm^{-1} which is frequently observed in H – rich diamonds of the grey to blue to violet family (B. Rondeau et al, 2004 and E. Fritsch et al, 2007). This is very interesting knowing that both samples are grey with a yellow or brown component to their colour and no blue or violet. The yellow to brown to green family can also show a peak at around 3236 cm^{-1} which is often quite small. In our case, the peaks are quite noticeable. Those stones can be a mix of the two families : grey and brown or yellow. We can established a link between the intensity of the colour and the amount of hydrogen present in the stone but this need to be further researched to positively confirm if there is an actual correlation between hydrogen and colour.

In addition a peak a 3236 cm^{-1} has also been noticed in the slice on both sectors (cuboid and octahedral) but the peak in the cuboid sector is higher. The presence of this peak is most probably related to the grey colour component. This is also confirmed by the visible light spectrum which shows the typical absorption continuum related to the brown colour and the flat tendency of the spectra which is linked to a grey colour.

Furthermore, peaks at around 3050 cm^{-1} and 3155 cm^{-1} have been observed on sample 1288 (slice). Both peaks are observed in the spectrum of the colourless (octahedral sector) and brown sector (cuboid) which raises some questions. Indeed, these peaks were detected in the cuboid growth sector and not the adjacent octahedral growth sectors (E. Fritsch et al, 2007). This needs to be investigated in order to determine if those peaks can be found on both sector or if the preparation of the sample for the testing in the infrared has not been done properly : maybe some of the cuboid sector was not hidden properly to perform the reading. This would imply an overlap of the results between the two sectors. In addition a peak has been observed on sample 1288 at around 6621 cm^{-1} which has not been reported before in the literature used for this study.

Moreover the infrared spectra of the slice show that the cuboid sector is the one with the highest hydrogen content which confirms that cuboid sectors incorporate a higher amount of hydrogen than octahedral ones (B. Rondeau et al, 2004). It could be possible that hydrogen acts as an inhibitor to nitrogen which would explain why cuboid sectors have less nitrogen than octahedral ones which have a smaller level of hydrogen. Furthermore, platelets have been observed on both sectors of the slice but the peaks are both very small and we notice that it is slightly higher in the brown sector (cuboid growth). This result is in contradiction with previous findings (B. Rondeau et al, 2004) where platelets are present in octahedral sectors and not in cuboid ones. Unfortunately, the UV-VIS-NIR spectrum has not been done on the different sectors and therefore it is not possible to confirm the presence or not of N3 in the spectrum of the octahedral or the cuboid sectors. Platelets and the presence of N3 in octahedral sector indicates that aggregation of nitrogen is limited in the cuboid sector compared to octahedral ones (B. Rondeau et al, 2004). In addition N3 is present in the spectrum of the octahedral sector and not the cuboid one (B. Rondeau et al, 2004). On the other hand the presence of the platelets on both sectors can be the result of an overlap of the data due to an inadequate preparation of the sample for testing. Nevertheless, this needs to be further studied to determine if either platelets can also be observed on cuboid sectors or if it is due to an inadequate sample preparation and set up of the sample.

The two Zimbabwean diamonds show a small peak at around 1448 cm^{-1} which most probably corresponds to H1a and indicates that the stones experienced some radiations. Due to the size of the peaks being very small these radiations are believed to be of natural causes. The H1a peak has also been observed on the slice but only on the colourless sector and the peak is extremely small. It is especially interesting as the peak doesn’t really appear on the full slice spectrum, it is looking like a very flat « bump » and is difficult to see. In the spectrum obtained in the microscope the peak is in the noise. We can wonder if this is an actual H1a peak. If it is, this could indicate that some radiations have been incorporated in the diamond in the cuboid sector and not the octahedral one which raises some questions. Indeed, cuboid and octahedral growth happen simultaneously and both sectors are subjected to the same growth environment (temperature, impurities present, etc.,…). It would be quite uncertain to have one sector incorporating radiations and not the other one. It could also be possible that the peak is so small in the spectrum of the octahedral sector that it doesn't properly appear at a resolution of 4 cm^{-1}. It could be therefore interesting to perform the tests at a higher resolution and see if the peak is present or not on both sector as well as on the full slice spectrum.

V- Conclusion

This study has allowed us to confirm several facts regarding asteriated diamonds. Indeed, they all have a very high nitrogen and hydrogen content and do show a typical cloud. They are usually a mix of octahedral and cuboid growth which happen simultaneously. Hydrogen is usually higher in cuboid growth sector than in octahedral ones but it is the reverse for the nitrogen content. Also, it is often observed that one of the growth mode prevails. Moreover the typical yellowish green fluorescence is attributed to the presence of nickel and is usually observed in the cuboid growth structures. Several asteriated diamonds observed do show some Ib character which is determine by looking at characteristic hydrogen peaks in the three phonon region. In addition a peak at around 6621 cm^{-1} has been identified but not found in the scientific articles used as references for this project.

Moreover, the two samples of Zimbabwean origin share the same characteristics than the other samples observed for this study : high level of hydrogen, high level of nitrogen, yellowish green fluorescence, presence of the cloud and mixed growth (sample A3). Sample A4's growth pattern is very different from the other asteriated diamonds examined. It could be interesting to find more diamonds showing this type of structure. In this case, it would be better to work on rough rather than polished to precisely determine their growth history. In addition, the two Zimbabwean diamonds were the darkest in colour compared to the other ones and they both have a very high level of hydrogen. Sample A3 has a higher level of hydrogen than A4 and it is darker in colour. Extra research must be done to determine whether there is an actual correlation between colour and hydrogen content.

Furthermore, several questions have been raised which need to be investigated regarding the following :

- presence of platelets
- peaks at 3050 cm^{-1} and 3155 cm^{-1}
- H1a

Finally, on a personal point of view this study has raised an even higher interest on this type of diamonds. It encourages me to, if possible, study in more details Zimbabwean diamonds which have been briefly addressed in this report.

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