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A comparison of diamonds irradiated by high fluence neutrons or electrons, before and after annealing

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ABSTRACT

Neutron- and electron-irradiated type Ia "black" diamonds were analyzed: three near colorless type Ia diamonds were treated in a nuclear reactor with a dose of 1.8×10^{17} neutrons/cm^2 and three equivalent samples were irradiated in an electron accelerator with a dose of approximately 0.5 GGy 10 MeV electrons. The diamonds were then annealed and analyzed after the different steps of the treatment. The samples turned from near colorless to very dark green to opaque black upon irradiation and deep greenish yellow to deep orangy brown upon annealing (Fig. 1). The amount of brown color developed during the treatment was found to relate to the type of irradiation used and likely to the total dose of irradiation. The absorption and photoluminescence features as well as the color changes that were observed were found to be unusual and characteristic for diamonds treated with such high irradiation doses. Certain spectral features such as the 644/649 nm, the 724/734/738 nm, the 920 nm and the 967 nm absorptions were only detected in the neutron-irradiated diamonds while others such as the 6165 cm^{-1} and the 805 nm absorptions were only found in the spectra of the electron-irradiated stones.

In addition to these treatment experiments some neutron-irradiated very dark green (appearing black) diamonds were heated from 300 to 1100 °C in increments of 50 °C to get a precise idea of the temperature at which color changes occur and the various absorption peaks form. All diamonds turned yellowish to orangy brown after annealing above 700 °C and most of them exhibited unusually strong H1b and/or H1c absorptions after annealing at >900 °C.

1. Introduction

The earliest method of irradiating diamonds by highly energetic particles is known since the late 19th and early 20th centuries, when Antoine-Henri Becquerel and after him Sir William Crookes experimented on the effect of radium on diamond. They rendered the diamonds green by subjecting them to the alpha particles emitted by the radium; however, this process also induces long-lived radioactivity.

Later, irradiation with gamma rays by exposure to cobalt-60, with protons and deuterons via a cyclotron [1], with neutrons in a nuclear reactor and with electrons by electron accelerators replaced the dangerous radium treatment; of these, electrons and neutrons are the most common particles used today for diamond treatment. These irradiations do not generally create any lasting residual radioactivity in inclusion-free diamond, as long as they are properly applied. If not properly performed or if too high an energy is involved, radionuclides can be created in diamonds (and other materials), rendering them radioactive; neutrons especially are known to strongly "activate" materials if not used with caution [2].

Irradiation with fast neutrons, or gamma rays from Co-60, induces homogeneous coloration; however the 1.17 and 1.33 MeV gamma rays from Co-60 have an extremely low efficiency in defect production. Depending on the energy of electrons this type of irradiation can either create relatively shallow "skin" coloration or penetrate several mm of diamond and thus induce homogeneous "body" coloration [3]. Nowadays, the preferred treatment methods are primarily electron irradiation with still some neutron irradiation; gamma irradiation is practically never used since it takes months or even years until a diamond acquires some color, while it is of the order of a few hours to a maximum of a few days for electrons and neutrons, depending on the size of the samples and the desired depth of color.

The defects and color changes induced in diamond by irradiation and by irradiation and subsequent annealing at $T > 500$ °C have long been the subject of many publications and extensive research [4]. The effects of high doses of neutron irradiation (followed by annealing) on diamonds have been studied, but the published data appear to be incomplete. The goal of this study is to gain a more detailed insight into the effects of heavy bombardment by neutrons and electrons and annealing on natural diamonds. There are some published indications of neutron-irradiated and annealed diamonds based on Vis–NIR and/or photoluminescence spectra [5–7]. These "exotic" spectral features

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published for neutron-irradiated diamonds include bands at 604, 644, 649, 651, 655, 681, 724, 733, 738, 774 and 813 nm [8].

2. Materials and methods

3 round brilliant cut colorless to near colorless diamonds (E to I color on the GIA color scale) of high clarity (VVS to VS) of 0.10–0.11 ct were irradiated in a nuclear reactor in Poland with a dose of 1.8×10^{17} neutrons/cm^2; the diamonds did not heat significantly as a consequence of this irradiation. They were then annealed at 1000 °C (protected by borax) for 3 h after irradiation.

3 round brilliant cut colorless to near colorless diamonds (F to G color on the GIA color scale) of high clarity (VS) of 0.07–0.09 ct were irradiated in a 10 MeV electron accelerator in Switzerland with a dose of approximately 0.5 GGy. The stones were placed on a steel plate which was found to be sufficient to keep the diamonds at a temperature below 200 °C — such that it does not affect any of the more important spectral features. They were then annealed under vacuum in three steps at 500 °C, 600 °C and 800 °C, each time for 3 h.

To obtain additional and complete data on the formation and annealing temperature of all absorption features three transparent enough, very dark green diamonds were chosen from those previously described in Ref. [9]. The samples were three “as-irradiated” very dark green (appearing black) small polished diamonds of 0.01 (sample AR-031), 0.07 (sample AR-016) and 0.09 ct (sample AR-015) and were used for an annealing experiment and detailed spectral analysis. 17 further polished diamonds (also from the diploma work of AR) were included in this study in order to confirm the repeatability of the annealing temperatures of the individual infrared absorptions. These twenty “black” diamonds were purchased in India around 1995 and were irradiated in one of the local nuclear reactors, but no details are known about the irradiation conditions.

Selected samples were analyzed by standard gemological and spectroscopic methods. Observations with magnification were made in three sets of conditions: in immersion in diiodomethane ($n = 1.74$) in order to reduce reflection effects, combined with diffuse lighting geometry to observe color distribution and with a dark field in order to observe the inclusions. Luminescence of the samples was observed using a standard longwave and shortwave ultraviolet radiation lamp (365 and 254 nm respectively, 4 W).

In addition, a 425 nm excitation was used with the U-Visio luminescence microscope system, equipped with an Osram 300W Xenon source. Luminescence pictures were recorded with an Olympus Camedia 5050 digital camera. Examination with the U-Visio system was performed using the wavelength range 460–700 nm (the filter transmits to 1000 nm) for the observation.

Infrared spectra of all samples were recorded in the range of 7500–400 cm^{-1} at 4 and 2 cm^{-1} resolutions with a Nicolet Nexus FTIR spectrometer at room temperature. The instrument was equipped with a DTGS detector and a KBr and XKBr beam splitter respectively. A Spectra Tech diffuse reflectance accessory was used as a beam concentrator to facilitate the absorption measurements in transmission for the small samples [10]. The spectra were recorded with 1000–12,000 scans.

The nitrogen concentration was determined by two methods: the nitrogen concentration was determined by peak fitting methods using the peak fitting spread sheet developed and supplied to us by David Fisher of the DTC (Diamond Trading Company). The nitrogen concentration is calculated based on the known average intensity of the intrinsic absorption of diamond at 2000 cm^{-1}, which has been defined as 12.3 cm^{-1} [11], to which all diamond spectra must be normalized for this calculation; this normalization is performed by spectral calculation, for which the arbitrary absorbance value of the intrinsic diamond absorption on the *y* axis at 2000 cm^{-1} is noted and then the multiplying factor is determined in order to obtain a value of 12.3 cm^{-1}. The spectrum is then multiplied by this factor. When the principal nitrogen one-phonon absorption was too strong to be resolved the approximate nitrogen content was determined based on the intensity of the 482 cm^{-1} and 1010 cm^{-1} absorptions of which the 482 cm^{-1} peak correlates with the intensity of the 1282 cm^{-1} A-aggregate absorption and the 1010 cm^{-1} absorption with the intensity of the 1174 cm^{-1} B-aggregate absorption.

The hydrogen was quantified as none, low and medium based on the intensity of the 3107 cm^{-1} line in the NIR spectrum; no line corresponds to “none”, a line lower in intensity than half of the height of the intrinsic diamond absorption at 2450 cm^{-1} corresponds to “low” and a line higher than half the height but lower than the 2450 cm^{-1} peak is defined as “medium”. A 3107 cm^{-1} absorption higher than the 2450 cm^{-1} band but lower than the 2155 cm^{-1} intrinsic diamond absorption would correspond to a high hydrogen content [12], and as soon as the 3107 cm^{-1} lines exceed the height of the 2155 cm^{-1} band the hydrogen content is quantified as “very high”.

Visible–near infrared absorption spectra in the 400–1000 nm range were recorded for 9 samples with a modified SAS2000 custom-built system, equipped with an Ocean Optics SD2000 dual channel spectrometer with a resolution of 1.5 nm. A 2048-element linear silicon CCD detector was employed; the samples were analyzed in an integrating sphere.

Photoluminescence spectra of 4 diamonds were recorded using a 532 nm DPSS laser, with the same Ocean Optics SD2000 spectrometer and CCD detector as described above, at a resolution of 1.5 nm; for the PL measurements the diamonds were placed in front of laser filters on a suitable low temperature holder blocking all laser light which was not hitting the stones. The samples were cooled at 77 K in liquid nitrogen for both the Vis–NIR and PL spectra.

The heat treatment experiment was performed with a Nabertherm Model L3 oven with a S27 program controller, up to a maximum temperature of 1100 °C. The 20 samples including the 3 diamonds AR-015, AR-016 and AR-031 were annealed from 300 °C to 1100 °C in increments of 50 °C; each step consisted of 30 min heating up and 3 h at *T* max, and then removal of the samples from the oven. The three samples FN-7772, FN-7783 and FN-7795 were heated only once at 1000 °C for 3 h, with an additional hour to increase the temperature from ambient to 1000 °C.

Above 700 °C the diamonds were protected by borax in order to avoid burning of the samples. The three electron-irradiated diamonds were annealed at 500 °C, 600 °C and 800 °C for 3 h each time under vacuum in a high temperature oven.

3. Results

3.1. Neutron irradiation/annealing experiment

3.1.1. Background and standard gemological properties of the samples

The 29 samples that were neutron irradiated were chosen based on their IR spectra and luminescence; some of their properties are shown

Table 1
Details of the three samples analyzed before neutron irradiation, after neutron irradiation and then after annealing at 1000 °C for 3 h.

Sample	Color untreated	Color after neutron irradiation	Color after neutron irradiation + annealing	Type	Hydrogen content estimated from IR absorption	N concentration	LWUV emission untreated
FN-7772	E	Black	Deep yellowish orangy brown	IaA pure	Moderate	170 ppm (±20)	Inert
FN-7783	H	Black	Deep reddish orangy brown	IaA$\gg$B	None	850 ppm (±60)	Weak yellow
FN-7795	I	Black	Deep yellowish orangy brown	IaB>A	Low	350 ppm (±40)	Medium blue

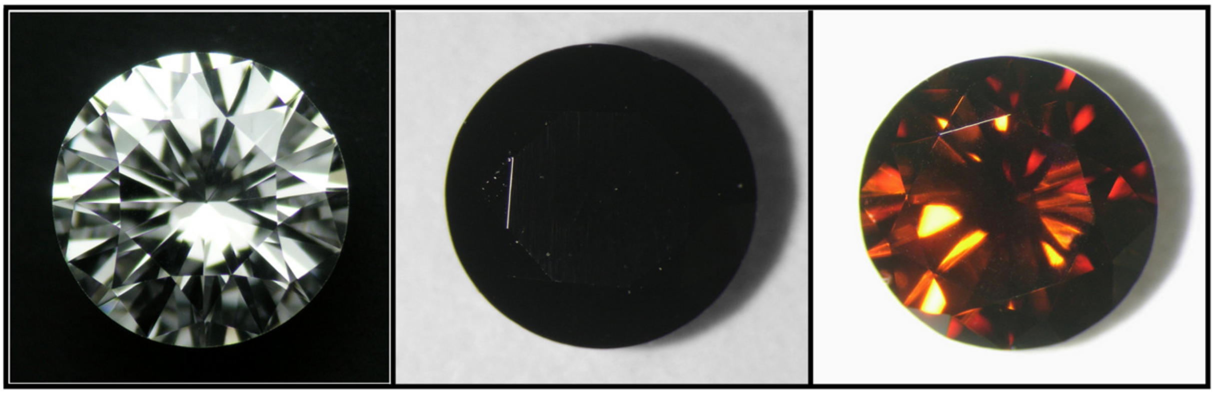

Fig. 1. The appearance of sample FN-7795 before treatment (near colorless, left), after neutron irradiation (opaque black, center) and after annealing at 1000 °C for 3 h (orangy brown, right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Table 1. The diamonds showed three responses to LWUV before the treatment: no luminescence (inert), blue luminescence (Fig. 2) and yellow luminescence prior to irradiation. The stones were truly optically opaque and even with the strongest fiber optic light source not a glimmer of green could be detected (Fig. 1, center). After irradiation all samples were inert to UV and 425 nm excitation.

After annealing the samples were of brown color with yellow or orange modifiers, optically transparent and much lighter (Fig. 1, right). The samples exhibited varying degrees of green luminescence, which appeared turbid and opaque (in contrast to the transparent luminescence appearance before the treatment) when either excited with UV or the 425 nm light of the U-Visio luminescence microscope (Fig. 2, right).

3.1.2. Vis–NIR spectroscopy

The spectra of the diamonds before treatment were characterized by either a total lack of absorption features or typical N3 and N2 related absorptions at 415 and 478 nm respectively (Fig. 3). After neutron irradiation the samples were so dark that spectral analysis was impossible, since the light could not pass the diamonds. After 1000 °C annealing the samples were light and transparent enough for spectral analysis. The main characteristic was absorption continuum with total absorption below 490 nm and overall rising transmission toward higher wavelengths. The total absorption explains why the luminescence of the stones appeared turbid and opaque after the treatment. The observed spectra were characteristic for neutron-irradiated and annealed diamonds having some classic absorption peaks (such as H3 and H2) and unusual absorptions such as the 644–649 nm doublet (Fig. 3). Interestingly, in the spectrum of sample FN-7795 the 594 nm absorption survived 1000 °C annealing while in the other samples an absorption at 592 nm had formed instead at this temperature (Fig. 3, red and purple traces). The doublet at 644 and 649 nm and/or a triplet at 724, 733 and 738 nm were found to be predominant peaks overlaid on the absorption continuum in all three of the spectra, together with strong relatively broad bands at 967 and/or 920 nm. The two broad bands at 871 and 822 nm appear to be a component of the 920 nm band (with some influence of the weak local vibrational mode of the H2 center at 871 nm), and the broad band at 861 nm as part of the 967 nm band; this was established based on the fact that the intensities of these bands clearly correlate. In sample FN-7795 a distinct absorption at 699 nm was detected, that exhibited a shoulder at 703 nm.

3.1.3. FTIR spectroscopy

Before irradiation the diamonds did not exhibit any unusual infrared absorptions. In addition to intrinsic diamond absorptions, the regular one-phonon absorption features due to nitrogen are found, and in samples FN-7783 (type IaA$\gg$B) and FN-7795 (type IaB$\gg$A) some common hydrogen-related absorptions (Fig. 4). Sample FN-7772 is a pure type IaA diamond without infrared-active hydrogen. Post irradiation FTIR absorption measurements were not possible due to the opacity of the diamonds to infrared radiation. After 1000 °C annealing the stones were transparent enough for spectral analysis and the spectra of the samples (Fig. 4) exhibited H1a, H1b and/or H1c absorptions, sometimes very intense. In sample FN-7783 the H1b absorption was extremely intense and had an absorption coefficient of 18 cm^{-1}; a structure associated with H1b could be seen in the two samples with an intense H1b absorption, with peaks at 5401, 5498, 5724, 5887, 6026 and 6910 (Figs. 4 and 8). In the sample FN-7783 H1a

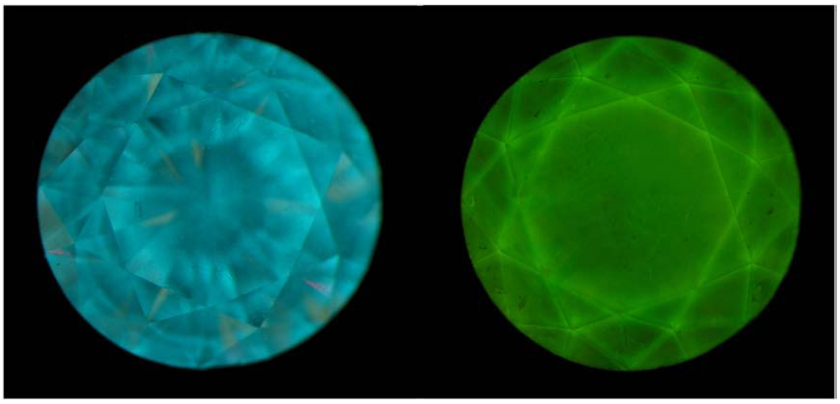

Fig. 2. The blue luminescence under 425 nm U-Visio excitation of sample FN-7795 before treatment (left), and its green luminescence after neutron irradiation and 1000 °C annealing (right); after irradiation only, the sample was inert (not shown). After annealing the luminescence appears turbid or opaque (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

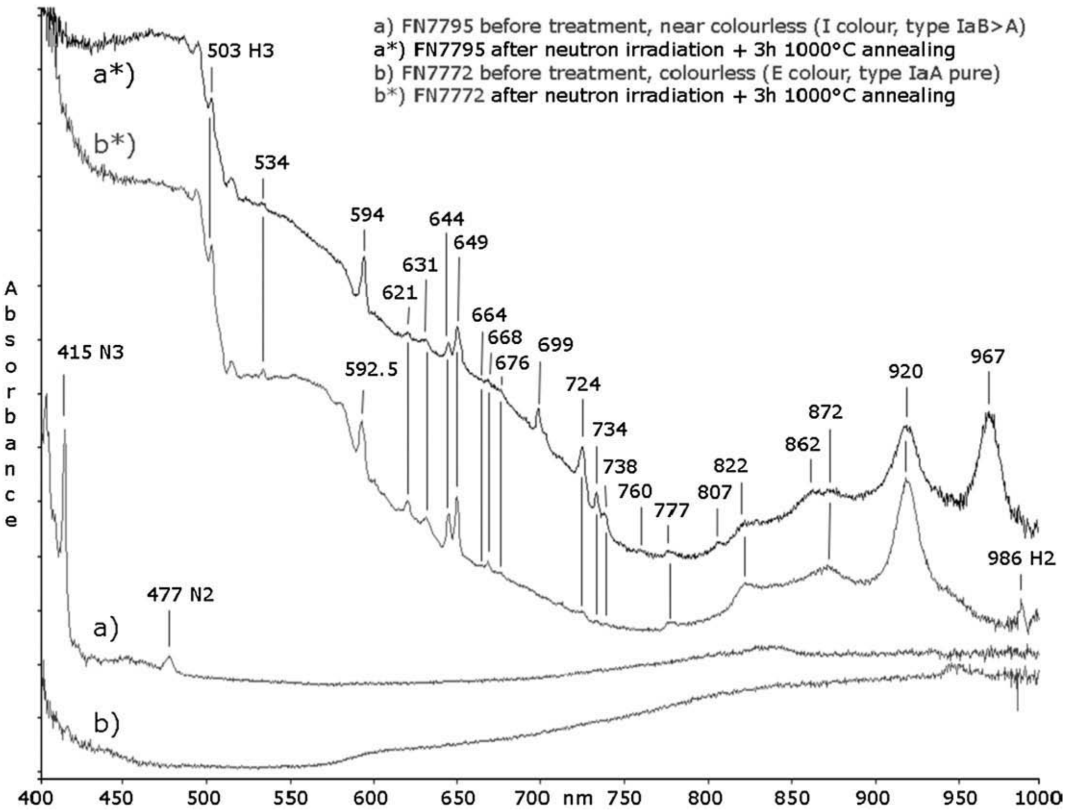

Fig. 3. The Vis–NIR spectra of sample FN-7772 and 7795 before irradiation and annealing (a and b) and after heavy bombardment with neutrons and 3 h annealing at 1000 °C (a* and b*). After the treatment the spectral region at wavelengths below 490 nm showed total absorption. The spectra are shifted vertically for clarity.

had an absorption coefficient of 10 cm^{-1}. Also features at 6139, 6070, 6021, 4446, 4432, 1856 and 1573 cm^{-1} were detected (Fig. 4). Samples FN-7772 and FN-7795 exhibited a fairly broad band with an apparent maximum at 714 cm^{-1}. In the spectrum of the diamond FN-7795 a very broad band ranging from about 1600 to 800 cm^{-1} underlying the one-phonon nitrogen absorption peaks was apparent. This sample's spectrum which had dominating H1c absorption exhibited additional weak absorptions at 5769, 5724 and 5672 cm^{-1} (Fig. 4, FN-7795 after).

3.1.4. PL spectroscopy

Before treatment, the only distinct PL emissions – besides some very broad luminescence bands – were the 701 nm center with its associated vibronic bands at 716 and 725 nm, and in some cases the typical bands for diamonds with the 701 nm center, like emissions at 604, 641 and 655 nm [13] (Fig. 5, trace a). After neutron irradiation, the diamonds were inert. After 1000 °C annealing PL spectra could be recorded and characteristic spectra for such treated diamonds were found (Fig. 5, trace b). The emissions included features typical and characteristic of all the irradiated and annealed diamonds, such as the NV^- and the NV^0 centers with ZPL's at 637 and 575 nm respectively, as well as the 588 nm center [14]; beside these, peaks at 649, 676, 681, 699 and 730 nm were detected, which are in the authors' experience rare or possibly never present in electron-irradiated and heat treated diamonds, but typical for reactor treated samples after annealing.

3.2. Step-by-step annealing of neutron-irradiated diamonds

3.2.1. Background and standard gemological properties of the samples

A separate experiment was carried out on 20 highly included neutron-irradiated diamonds. Upon annealing, the 20 practically black (extremely dark green) stones – previously bombarded by an unknown but apparently high dose of neutrons – reacted very much like the above mentioned samples. During the experiment, all stones changed color from very dark green via brown to orange or yellowish brown. One sample became brownish yellow and distinctly lighter. Three of the diamonds that were sufficiently transparent (samples AR-015, AR-016 and AR-031; see Table 2) were used for a detailed and complete analysis including Vis–NIR spectroscopy, for which all other samples were too dark.

The data obtained must be regarded with care since it is not known whether the stones were efficiently cooled during the irradiation; some lines that may be seen in "as-irradiated" samples, are only detected in others after some annealing; this kind of observation may be due to elevated temperatures during neutron irradiation.

As-irradiated diamonds were generally inert. Upon annealing, they all emitted various intensities of green when excited with LW and SWUV or 425 nm light.

3.2.2. Vis–NIR spectroscopy

The spectrum of the "as-irradiated" diamonds was characterized by the GR1 system with a rather broad ZPL at 741 nm (Fig. 6) with a FWHM of 5.33 nm for sample AR-015; upon annealing the absorptions of the GR1 system became sharper and more intense up to 600 °C, where in the case of sample AR-015 the FWHM was 3.32 nm; at 650°°C the absorption decreased in intensity by a factor of 3 and annealed out completely at 700 °C. With the annealing-out of the GR1 system, a triplet at 724, 733 and 738 appeared and increased in intensity with higher temperatures. The 594 nm center absorption was detected in one "as-irradiated" diamond and appeared at 600 °C in the two other diamonds; the absorption of this center increased strongly in intensity in all stones from 600 °C upwards; the line attained its maximum intensity at 800 to 850 °C. The 594 nm center absorption was very intense at these temperatures. From 900 to 950 °C the 594 nm absorption annealed out and a new center at 592.5 nm was formed, which showed a sufficiently different vibronic structure in order to be

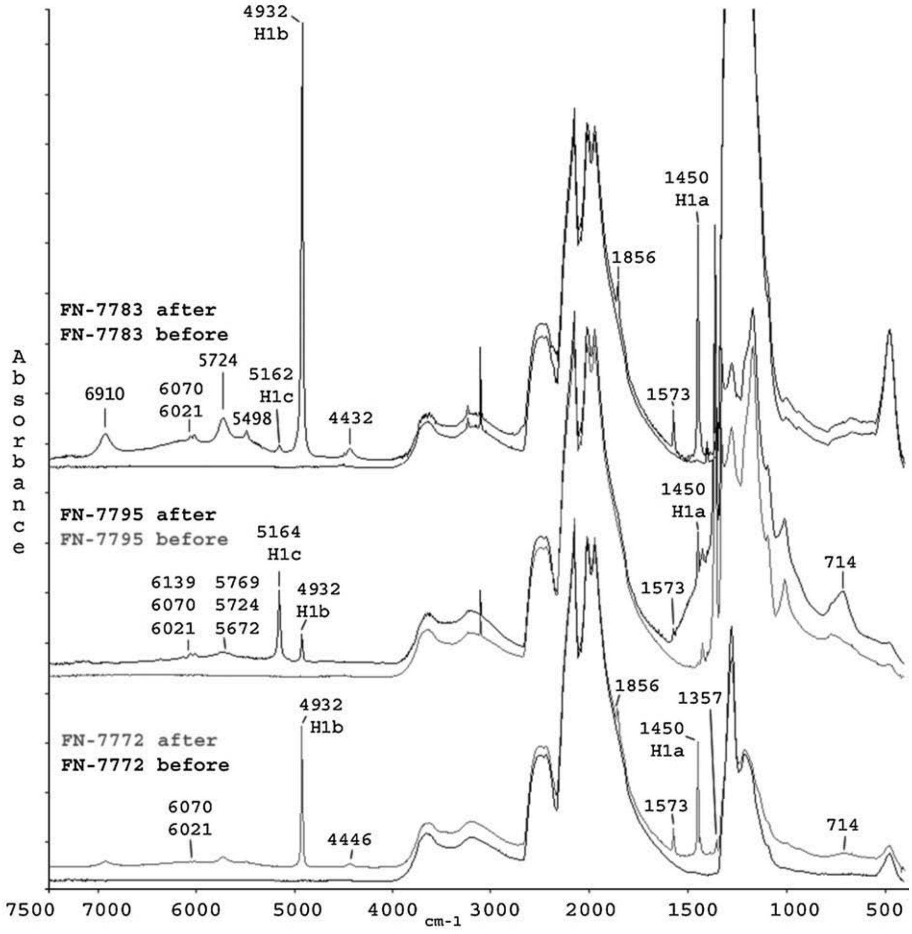

Fig. 4. The FTIR spectra of samples FN-7772, FN-7783 and 7795 before irradiation and after heavy bombardment with neutrons and 3 h annealing at 1000 °C. The spectra are normalized to the intrinsic diamond bands and shifted vertically for clarity.

differentiated from the 594 nm center; this absorption intensified slightly to 1100 °C.

Another known defect, the H3 center, became visible between 600 and 650 °C and its absorption strengthened in intensity with higher temperatures. The H2 center absorption was detected in two samples at 800 and 950 °C respectively and increased its intensity at higher temperatures. A peak at 604 nm was formed at 550 to 600 °C and disappeared at 750 to 800 °C. An absorption at 681 nm, was detected after 700 °C annealing and strengthened in intensity with higher temperatures. The slightly broad band at 655 nm was formed at 650 °C and disappeared around 950 °C. A weak absorption at 774 nm appeared at 800 °C and annealed out at 950 °C. A doublet at 644/

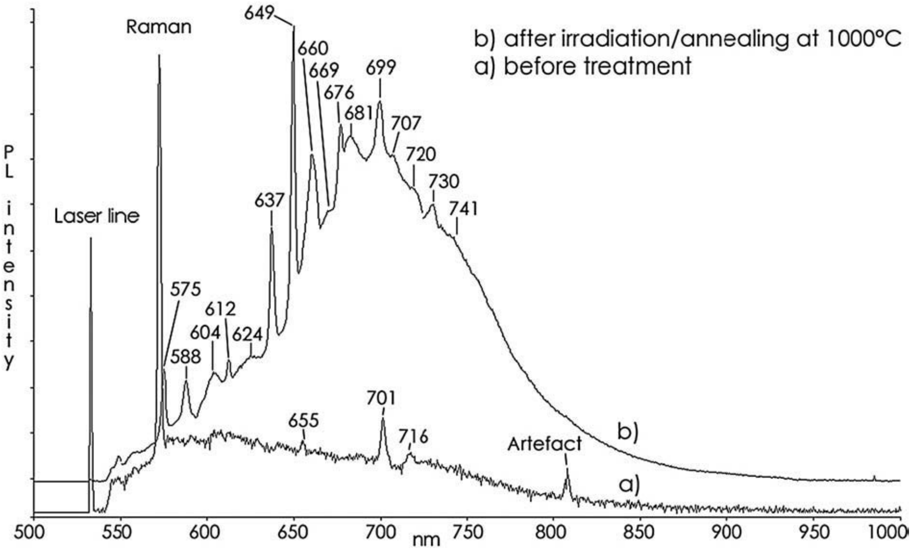

Fig. 5. The 532 nm laser PL spectra of sample FN-7795 before irradiation and annealing (brown trace) and after heavy bombardment by neutrons and 3 h annealing at 1000 °C (purple trace). The spectra are shifted vertically for clarity.

Table 2
Details of the three samples analyzed before neutron irradiation, after neutron irradiation and then after annealing to 1100 °C.

Sample	Color after neutron irradiation	Color after neutron irradiation + annealing	Type	Hydrogen	Nitrogen concentration
AR-015	Very dark green	Dark yellowish brown	IaA>B	Very low	670 ppm (±50)
AR-016	Very dark green	Deep brownish yellow	IaA>B	Very low	630 ppm (±50)
AR-031	Very dark green	Dark yellowish brown	IaA	High	1700 ppm (±100)

649 nm was created between 750 and 800 °C and strengthened to 1100 °C. Most notable was the formation of some broad bands in the NIR, of which the 920 nm band and the 967 nm band are the most intense ones; both features formed at rather elevated temperatures, being 800–850 °C and 900–950 °C respectively. The 920 nm band was very intense at 1100 °C in the type IaA sample (AR-015). The Vis–NIR spectra after annealing of other samples were essentially similar to the spectra of the above diamonds.

A detailed list of all absorptions found during this annealing experiment and their annealing behaviour is presented in Table 3.

3.2.3. FTIR spectroscopy

In the spectra (Fig. 7) of the "as-irradiated" very dark green diamonds continuous increasing absorptions towards the NIR including a weak very broad band centered at ~5670 cm^{-1} (extending from >7500 to 4000 cm^{-1}), a weak broad band at 4650 cm^{-1} and sharp bands at 1570, 1544, 1521 and 1450 cm^{-1} (H1a) were detected. In the spectra of two samples the H1a line was very intense with heights of about 6 cm^{-1} (~half the intensity of the diamond intrinsic bands at 1995 cm^{-1}). In one "as-irradiated" stone a very weak triplet at 6021, 6070 and 6139 cm^{-1} was visible.

It seems that the absorbance of as-irradiated samples increased from 1500 cm^{-1} towards the NIR; this appears to be the reason why many of the diamonds were opaque to IR radiation prior to annealing.

Upon annealing (Figs. 7 and 8) the H1a band remained stable up to 1100 °C. The other sharp band at 1570 cm^{-1} attained its maximum at 550 °C, and then annealed out at 750 to 800 °C. At 800 °C simultaneously with the disappearance of the 1570 cm^{-1} absorption a weak sharp feature at 1573 cm^{-1} was formed, which remained stable to 1100 °C. The well known H1b absorption at 4932 cm^{-1} was detected in one sample at a temperature as low as 500 °C and H1c (5160 cm^{-1}) at 700 °C. In the other two samples H1b was detected at 700 °C and H1c at 750 °C. In sample AR-031, this band attained a high intensity of ~19.6 cm^{-1} at 1100 °C, which is 60% higher than the diamond intrinsic bands at 1995 cm^{-1} (Fig. 7).

The broad bands at ~5670 cm^{-1} and at 4650 cm^{-1} in the NIR intensified steadily with rising temperature. The triplet at 6021, 6070 and 6139 cm^{-1} was enhanced by annealing above 600 °C. The spectral features and annealing behaviour of these were confirmed by comparison of the spectra of all other 17 diamonds included in the study of AR.

Perhaps not surprisingly the absorptions formed in the FTIR spectra after annealing at >900 °C were practically identical to the

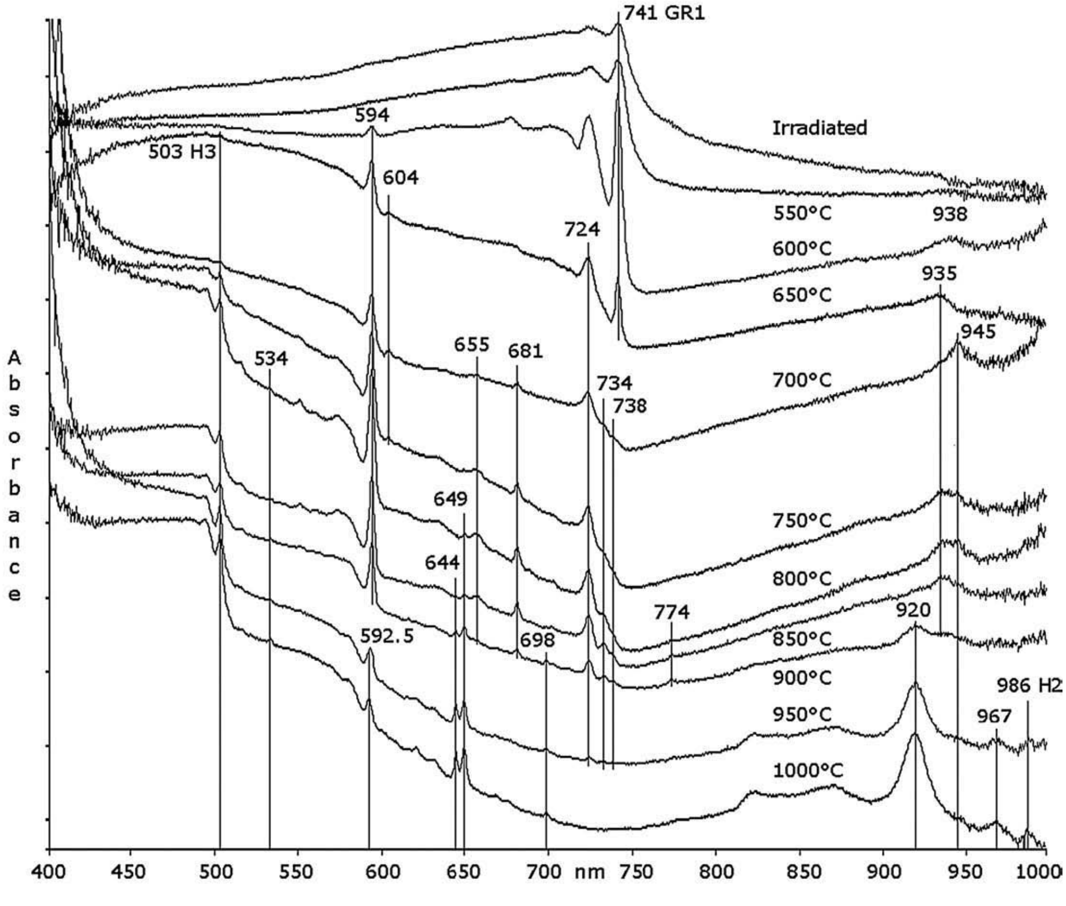

Fig. 6. The Vis–NIR spectrum of sample AR-015 recorded at 77 K after each annealing step is typical of diamonds irradiated by fast neutrons and annealed post irradiation. The peaks at 604, 655, 681, 724, 733, 738 and 774 nm have been related to this kind of radiation. At temperatures above 700 °C the spectral region at wavelengths below 490 nm shows total absorption. The spectra are shifted vertically for clarity.

Table 3
The spectral peculiarities and annealing behaviour of features observed in the Vis–NIR spectra of the three analyzed neutron-irradiated diamonds (based on the three samples AR-015, AR-016 and AR-031).

Position (nm)	Name	Temperature of apparition (°C)	*T* at which apparent maximum intensity is reached	*T* at which it anneals out (°C)	Comments
503	H3	600–650 °C	n/a	n/a	Intensifies to 1100 °C
534		800 °C	n/a	n/a	Intensifies to 1100 °C
592.5		950 °C	n/a	n/a	Vibronic structure differs strongly from the 594 nm center. Intensifies to 1100 °C
594		As irradiated, up to 600 °C	800–850 °C	950 °C	Vibronic structure corresponds to the “594 center” in all cases
604		550–600 °C	700 °C	750–800 °C	
637	NV−	600 °C	n/a	n/a	Intensifies to 1100 °C
644/649		750–800 °C	n/a	n/a	Doublet, intensifies to 1100 °C
655		650 °C	800 °C	900–950 °C	
681		650–700 °C	800 °C	950 °C	
698		800 °C	n/a	n/a	Intensifies to 1100 °C
724		650 °C	800 °C	950–1000 °C	
734		650 °C	850 °C	950–1000 °C	
738		650 °C	850 °C	950–1000 °C	
741	GR1	As irradiated	600 °C	700 °C	
774		800 °C	900 °C	950 °C	
920		800–850 °C	n/a	n/a	Intensifies to 1100 °C, relatively broad band; associated bands at 871 and 822 nm
935–938		~600 °C	750–800 °C	900 °C	Relatively broad band
945		As irradiated to ~600 °C ?	750–800 °C	n/a	Relatively broad band
967		900–950 °C	n/a	n/a	Intensifies to 1100 °C, associated band at 861 nm
986	H2	800–950 °C	n/a	n/a	Intensifies to 1100 °C

features found in the spectra of the three neutron-irradiated and annealed diamonds FN-7727, FN-7783 and FN-7795.

In Table 4 a listing of all infrared absorptions is presented, with a detailed annealing behaviour of the various infrared absorptions (based on the data for all 20 samples).

3.3. Electron irradiation/annealing experiment

3.3.1. Background and standard gemological properties of the samples

To compare the Vis–NIR and FTIR spectroscopy results obtained from the neutron-irradiated and annealed diamonds three near colorless (E, F and J on the GIA color scale) samples of 0.07–0.09 ct were selected as typical on the basis of their diamond type and UV luminescence: a type IaA hydrogen containing diamond with yellow luminescence, a type IaA diamond lacking luminescence and a type IaB diamond with blue luminescence. The three samples were irradiated for several days by a dose of approximately 0.5 GGy 10 MeV electrons in a Rhodotron electron accelerator and turned very dark green to extremely dark green, but none of them turned opaque black.

Annealing at 500 °C, 600 °C and 800 °C changed the colors of the samples to brownish orange up to deep greenish yellow; the modification of color started at 600 °C and was distinct at 800 °C (Table 5). The luminescence behaviour was similar to the one of the neutron-irradiated samples, with all samples being inert after electron

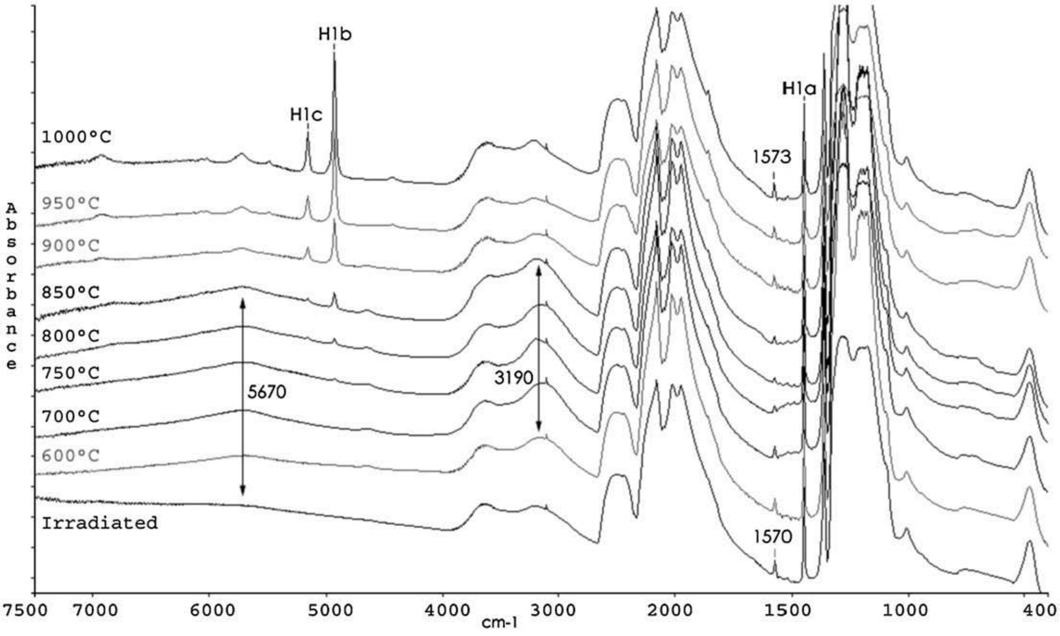

Fig. 7. The evolution of the FTIR spectra of sample AR-015 from the as-irradiated state to 1000 °C. No distinct changes were observed from 300 to 550 °C, except of the strengthening of the 5670 and the 4560 cm^{-1} bands. The spectra are normalized to the structural diamond bands and shifted vertically for clarity.

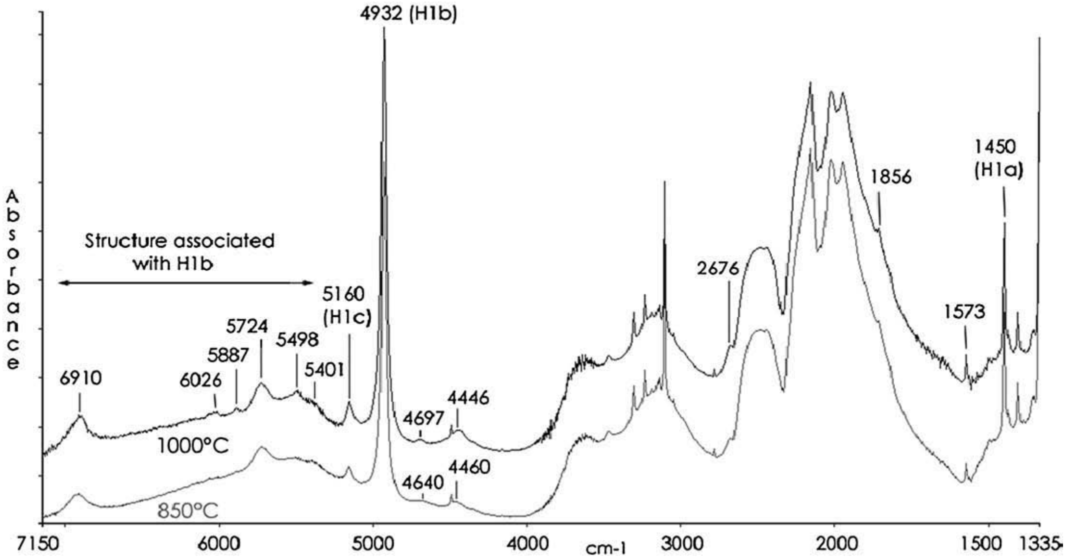

Fig. 8. The FTIR spectrum of sample AR-031 after annealing at 1000 °C exhibits a strong H1b absorption with an intensity of 17.3 cm^{-1}. The broader bands at 5401, 5498, 5724, 5887, 6026 and 6910 cm^{-1} are features associated with H1b. The naturally occurring absorptions such as the many hydrogen-related peaks in the 3300 to 2700 cm^{-1} domain are not labelled since they are not relevant to this paper. The spectra are normalized to the structural diamond bands and shifted vertically for clarity.

irradiation and exhibiting green luminescence due to the formation of H3 or H4 centers during annealing.

3.3.2. Vis–NIR spectroscopy

The spectra of the diamonds before treatment were characterized by either a total lack of absorption features or typical N3 and N2 related absorptions with zero phonon lines at 415 and 478 nm respectively (Figs. 9 and 10). After electron irradiation the samples were very dark but still transparent enough that spectral analysis was possible. In the two type IaA diamonds (TH-001 and TH-002) the broad band GR1 spectrum (FWHM of 5.3 nm of the 741 nm ZPL) after irradiation had a typical evolution upon annealing: GR1 absorption sharpened to 600 °C (FWHM of 741 nm ZPL was 3.9 nm) and was completely annealed out at 800 °C and during the annealing of GR1 the H3 (503 nm), NV^- (637 nm), strong H2 (986 nm) and the 594 nm center absorptions developed; additionally peaks at 527, 604, 681 and 805 nm were created, of which the 527 and 604 nm peaks were only detected at 600 °C, but annealed out at 800 °C.

The spectrum of the type IaB sample TH-003 reacted slightly differently to annealing: the GR1 bands did not sharpen at 500 °C as in the spectra of the type IaA diamonds, but only at 600 °C; at 800 °C it was not detected anymore, but instead a weak peak at 724 nm was found. As expected the H4 center absorption (496 nm) formed instead of the H3 center absorption, the H2 and NV^- center absorptions were

Table 4
The spectral peculiarities and annealing behaviour of features observed in the FTIR spectra of the analyzed neutron-irradiated (and annealed) diamonds (based on all 20 diamonds).

Position (cm^{-1})	Name	Created at *T* (°C)	Maximum intensity reached at *T* (°C)	Anneals out at *T* (°C)	Comment
6763		700 °C	850 °C	900 °C	Broad band
6021/6070/6139		“As irradiated”, up to 400 °C	1000 °C	n/a	Triplet, correlates to B aggregates
5712		“As irradiated”	850 °C	Around 1000 °C	Very large band (from ~8000 to ~4000 cm^{-1}); diminishes strongly or anneals out at 1000 °C
5162–5165	H1c	700–900 °C	Between 950 °C and 1050 °C, some samples >1100 °C	n/a	No detection below 700 °C; diminished strongly in one sample at 1000 °C
4932–4933; bands at 5401, 5498, 5724, 5887, 6026 and 6910 are associated with H1b	H1b	500 °C, up to 750 °C	n/a	n/a	The lowest temperature of detection is independent from the intensity of H1b. Intensifies to 1100 °C
4697		650 °C	n/a	n/a	Intensifies to 1100 °C
4650		“As irradiated”	850 °C	950–1000 °C	Broad band
4460		650–700 °C	n/a	n/a	Shifts to 4446 cm^{-1} at 900–950 °C, intensifies to 1100 °C
4432		850–900 °C	1000 °C (1 sample)	n/a	
3620		Intensifies at 1000 °C	n/a	n/a	Broad band underlying the intrinsic diamond bands
3470		950 °C	n/a	n/a	Broad band
3348		950 °C	n/a	1000 °C	Broad band
3190		Intensifies at 600 °C	750–800 °C	900–950 °C	Broad band underlying the intrinsic diamond bands. In one stone it shifts to 3210 at 800 °C, and to 3240 at 950 °C
2676		750 °C	n/a	n/a	Intensifies to 1100 °C
1856		“As irradiated”	n/a	n/a	Intensifies to 1100 °C
1573		750–800 °C	n/a	n/a	Intensifies to 1100 °C
1570		“As irradiated”	550 °C	750–800 °C	Peak “transforms” gradually into the 1573 cm^{-1} absorption
1450	H1a	“As irradiated”	n/a	n/a	Remained stable or intensified to 1100 °C
1436–1438		“As irradiated”	n/a	n/a	Starts as shoulder of H1a and develops into a distinct peak, intensifies to 1100 °C

Table 5
Optical properties of the three samples analyzed before electron irradiation, after electron irradiation and then after annealing to 800 °C.

Sample	Color untreated	Color after electrons	Color after electrons + annealing	Type	Hydrogen
TH-001	Colorless (E)	Very dark green	Deep greenish yellow	IaA≫B	None
TH-002	Near colorless (F)	Very dark green	Deep brownish yellow	IaA	Medium
TH-003	Near colorless (J)	Very dark green	Deep brownish orange	IaB	Low

weak and the 594 nm center absorption was very intense. More uncommon absorptions such as small features at 628, 670, 681, 703, 805, 813, 890 and 940 nm developed in the spectrum after 800 °C annealing (Fig. 10).

3.3.2.1. FTIR spectroscopy. The FTIR spectra of the electron-irradiated diamonds corresponded closely to what one may call “standard” infrared spectra of irradiated/annealed stones: after 800 °C they exhibited weak to distinct H1a (present after irradiation in all samples), distinct H1b (samples TH-001 and TH-002) and H1c (weak in sample TH-001, distinct in sample TH-003), plus an additional sharp feature at 6165 cm^{-1} (weak in sample TH-001 and distinct in sample TH-003) (Fig. 11). The structure associated with H1b was not detected due to the low intensity of the absorption, most likely because the annealing temperature of the samples was lower and H1b and H1c have their highest intensities at about 1000 °C.

4. Discussion

The experiments conducted have led to some interesting results concerning the comparison of the two most common types of irradiation used for diamond treatments. First of all it was very easy to make the small diamonds opaque black with neutrons, but it was – while theoretically possible – not possible in our case using 10 MeV electrons: even after the highest dose of electrons the diamonds were still visibly (extremely dark) green under very strong illumination. This difference indicated that the defect density in the neutron-irradiated diamonds was much higher than that in the electron-

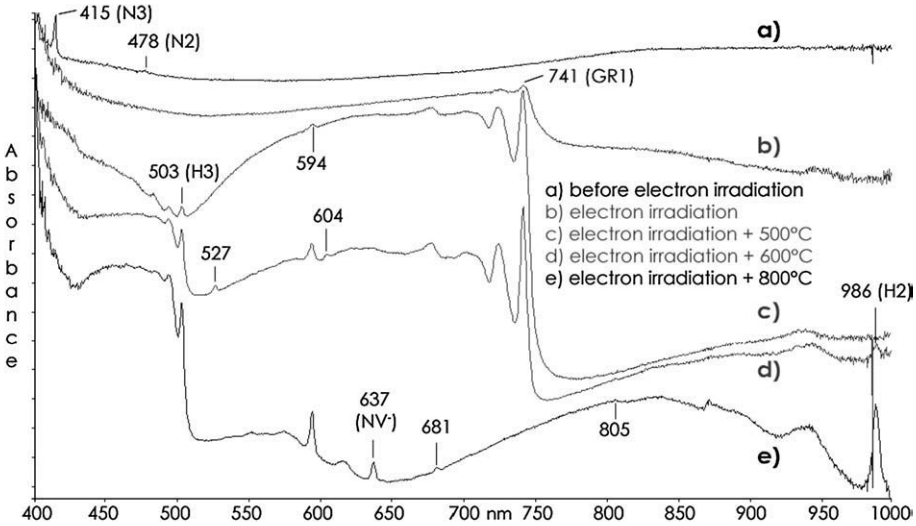

Fig. 9. The evolution of the Vis–NIR spectra of sample TH-001, a type IaA≫B diamond, from untreated to irradiated and annealed up to 800 °C.

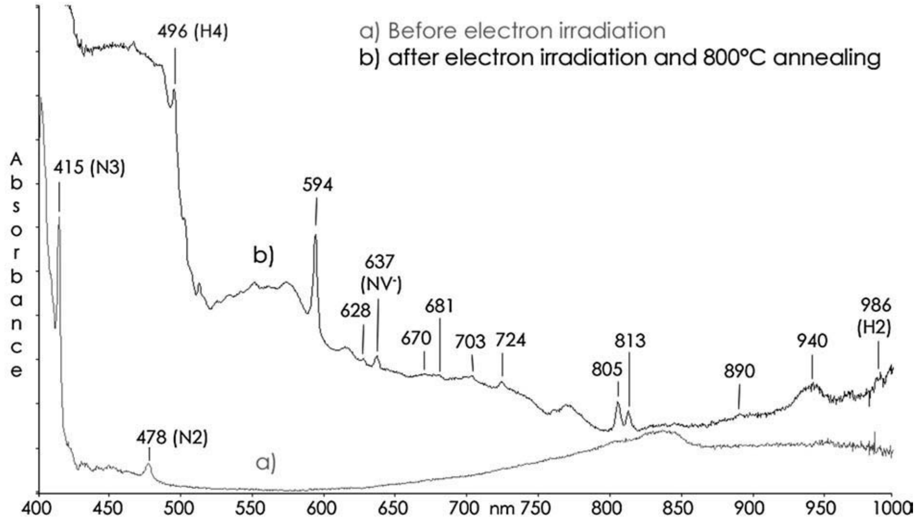

Fig. 10. The Vis–NIR spectra of sample TH-003, a type IaB diamond before and after treatment by electron irradiation and 800 °C annealing. There is some tentative evidence that the 805 nm absorption is correlated with the 6165 cm^{-1} NIR absorption (see Fig. 11).

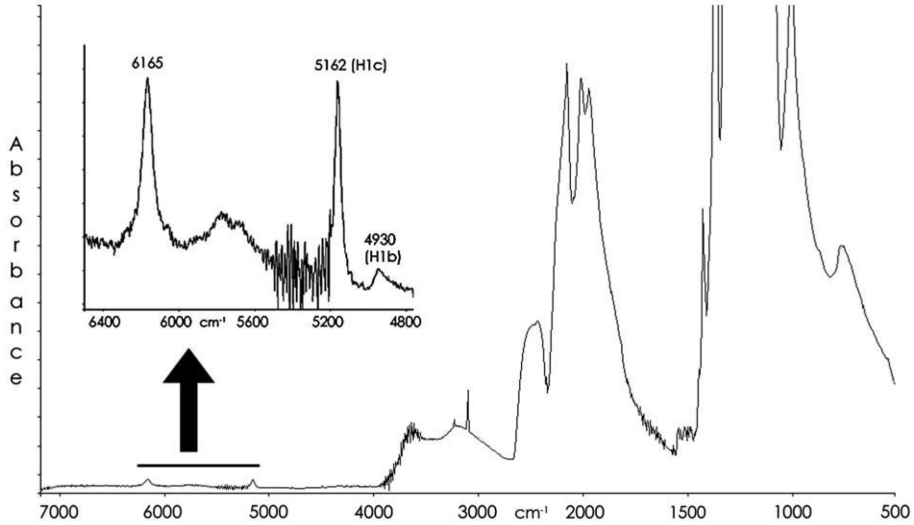

Fig. 11. The FTIR spectrum of the nearly pure type IaB diamond TH-003 after annealing at 800 °C. The spectrum is typical for irradiated and annealed diamond with H1b, H1c and a peak at 6165 cm^{-1} that has not been seen to this date in neutron treated stones.

irradiated samples. After annealing simple visual examination did not show clear differences color-wise between the two irradiation techniques even though all neutron treated stones were brownish orange to orangy brown in color while the electron-irradiated samples exhibited a wider variety of hues from yellow to brownish orange. The apparent difference is thus the brownishness which was more distinct in the neutron-irradiated and annealed stones.

Diamonds exhibiting blue luminescence before the treatment were inert after irradiation, and their blue luminescence was not reactivated by annealing; this suppression of the N3 emission can be explained by the very intense absorption from the UV to about 480 nm that is developed by irradiation and that even increases in intensity after annealing [15].

The relatively homogeneous distribution of luminescence in both neutron- and electron-irradiated diamonds is important for identification purposes. In natural diamonds green luminescence is following growth or deformation-related features, such as slip in the crystal lattice resulting in dislocations. H3 centers are typically concentrated within these dislocations and thus can typically be seen in the slip-related brown color bands of diamond [16]. Very rarely green luminescence in natural untreated diamond can be found relatively homogeneous in the body of the sample, due to natural irradiation and annealing.

In comparable orangy brown diamonds of natural color, the fluorescence can be very distinct and is then always found associated with the brown color banding; in such stones the H3 center responsible for this emission is in general directly caused by the deformation and resulting defects.

Spectroscopically the samples differed distinctly, particularly in their Vis–NIR absorption spectra. The Vis–NIR spectra of the electron-irradiated diamonds only exhibited the well known irradiation/annealing related absorptions [17], except for the type IaB diamond that had a somewhat exotic spectrum. In contrast to this all the neutron-irradiated and annealed diamonds showed a number of remarkable features, of which some have been published in the 1990s [5,6]. A summary of the absorption and photoluminescence bands as observed in neutron-irradiated and annealed diamonds can be found in the compilation by Zaitsev [8]. Electron-irradiated and annealed diamonds exhibit usually the rather “classical” features expected in treated diamonds such as H3, H4, NV^0, NV^- and H2 centers. In contrast the spectra of neutron-irradiated and annealed diamonds are known to be characterized by additional absorptions such as 644, 649.5, 655, 663, 676, 681, 724.4, 731.7, 734 and 774 nm [8]. The experiments performed for this study confirm that these and further, formerly unpublished bands can be created in diamond by heavy irradiation by neutrons plus annealing. Heavy irradiation by electrons apparently does not create the majority of these absorptions, with the exception of the 681 nm feature, at least after irradiation doses which are used to create electron-irradiated black diamond.

The continuum of absorption giving rise to the brown color after irradiation and annealing, absent before treatment, is particularly difficult to interpret as it is featureless: it is found in the most common brown diamonds [18], those with graining [19], where it is now interpreted as being due to vacancy clusters [20,21]. It is also found in a class of H-rich diamonds without graining [22]. Neither class of brown diamonds has experienced irradiation or annealing. It is not unreasonable to speculate that the category of continuum documented in this work might be related to vacancies [15], as those are the main product of irradiation; it appears that a very stable vacancy defect, possibly consisting of similar vacancy clusters as described in natural brown diamonds, is being produced during the annealing of the diamonds having a very high vacancy-density. There are several indications which point towards this conclusion:

1) There is an apparent correlation between the irradiation dose and the brownishness of the stones; the higher the dose the browner a diamond after annealing.
2) The brown hue is not eliminated or reduced by annealing at 1100 °C; after its appearance at about 650 °C it intensifies to 750 °C and remains stable to the maximum temperature used for this study (1100 °C).
3) The continuum responsible for the brown hue appears together with the decreasing GR1 band, thus vacancies could be involved.
4) The same effect has been observed at the time of writing of this paper in an originally colorless type IIa diamond that was irradiated by a dose of 12.4×10^{17} neutrons/cm^2 and then annealed to 1000 °C: this stone turned black after irradiation and extremely dark orangy brown after 650 °C annealing; the brown color remained stable even after 1000 °C annealing. Since the type IIa diamond contained (by definition) negligible nitrogen but nevertheless the brown color was very distinct after the treatment, it appears reasonable to state that the defect responsible for brown color after irradiation and annealing is caused by a very stable defect consisting of vacancies only.

The evolution of the various bands with temperature has been demonstrated by the step-wise annealing experiment. The large width of the GR1 absorption system after heavy irradiation by neutrons and electrons has been attributed by Collins [23] to peak-broadening by strain and by regions of complete disorder in the lattice induced by the neutrons (and electrons) ("strain broadening"). Reduction of strain by annealing at above 550 °C strongly sharpens and apparently intensifies the GR1 absorption [8]. The weakening at 650 °C and complete annealing of GR1 at 700 °C is rather surprising since it is known to survive temperatures up to 1000 °C [8]; in all samples of neutron-irradiated diamonds and in the type IaB electron-irradiated diamond (TH-003) we had a gradual increase of the the 724, 733 and 738 nm triplet as the GR1 band decreased. This triplet could not be correlated to any form of nitrogen since first of all it was present in both type IaA and IaB diamonds and second of all because it has been seen by the authors in a greenish yellow type IIa diamond. The doublet at 644/649 nm was detected in all neutron-irradiated samples, and, although stronger in type IaA diamonds than in IaB$\gg$A samples, cannot be restricted with certainty to a specific type of diamond; this is even more so the case since the lines have been described in neutron-irradiated natural IaB and synthetic Ib diamonds by other authors [7].

The 594 nm absorption was found to be intense in all samples after 800 °C annealing; in all but one sample of the neutron-irradiated diamonds a gradual increase of a feature at 592 nm was noted from 900 °C on while the 594 nm center absorption diminished. The 592 nm absorption appears to be a new center and not just a shifted 594 nm band; this is supported by the fact that the 592 nm absorption intensified slightly from 950 to 1100 °C, while the 594 nm feature started to reduce drastically at 850 °C in the same stone. Additionally the strongest phonon sidebands of the 594 nm center are found at 574.5 and 561 nm while for the 592 nm center they are found at 581 and 570 nm. Two notable features can be seen in the NIR region of the spectra of the neutron treated diamond, forming between 800 and 950 °C and intensifying to 1100 °C: the relatively broad band at 920 nm with associated features at 871 nm plus 822 nm and the band at 967 nm with the associated feature at 861 nm. Comparison with the infrared spectra has shown, that the 920 nm band correlates clearly with the A aggregates, while the 967 nm band relates to the B aggregates of nitrogen (see e.g. Fig. 3).

The infrared spectra indicate that the absorption at 6165 cm^{-1} is typical for electron-irradiated diamonds while it was never detected in the spectra of the neutron-irradiated diamonds. This feature is known to the authors from many known electron-irradiated diamonds and has recently been detected in the spectra of multi-step-treated type Ia pink diamonds that were HPHT treated, electron irradiated and then annealed [14]. By contrast the unusual absorptions in the IR spectra of the neutron treated diamonds were not detected in any of the electron-irradiated samples, which always showed the "standard" irradiation-annealing absorptions (H1a, H1b and/or H1c).

The unusual infrared spectra of the neutron-irradiated diamonds were characterized by very intense H1a, H1b and H1c absorptions and many weaker complex bands. The observation of these uncommon, unusually intense and numerous absorption features must be related to the high defect density and disorder induced in the diamond lattice by neutron bombardment. The high intensity of H1b (with a maximum absorption coefficient of almost 20 cm^{-1}) has made it possible to observe an associated broad band structure with apparent maxima at 5401, 5498, 5724, 5887, 6026 and 6910. This association is indicated by the observation of all these bands only in diamonds with a strong H1b absorption, with an absorption coefficient of ≥ 3.5 cm^{-1} (at room temperature), and by the synchronous appearance and strengthening of this structure with the growth of H1b. Whether this feature is the vibronic structure of the H1b defect is not clear, since intensities and spacing of the individual bands that appear together with H1b are rather irregular.

Another noteworthy feature is the broad band from 1600–800 cm^{-1} and the 714 cm^{-1} band that is most probably associated with it, that have been induced in the one-phonon region of the spectrum of two neutron-irradiated/annealed samples. This band is an indication for high defect density and disorder in the lattice, since such one-phonon absorptions are only induced by defects that disturb the perfect diamond lattice and therefore produce a weak dipole moment [23].

The extremely broad and strong infrared absorption that prohibits the recording of infrared spectra after heavy irradiation of diamond is one more band that lacks publication and even more so interpretation; what appears like a distorted baseline that is present in all diamonds of this study after high doses of irradiation is the increasing absorption from the mid-infrared to the near-infrared.

5. Conclusions

The neutron irradiation and annealing behaviour of type Ia diamonds have been presented in detail and compared to similar but heavily electron-irradiated type Ia diamonds. The high efficiency of neutrons to induce defects in the lattice of diamond was demonstrated by spectroscopic methods; extremely intense absorptions and some new absorption features were described: in the visible–near infrared peaks at 592.5, 699 + 703, 920 + 871/822 and 967 + 861 nm and in the near- to mid-infrared peaks at 6139, 6070, 6021, 5712 (very broad), 4460–4446, 4432, 3620 (broad), 3470 (broad), 3348 (broad), 3190–3210–3240, 2676, 1573 and 1438–1436 cm^{-1}. Additionally the features associated with H1b and H1c were – likely for the first time – described in detail: 5401, 5498, 5724, 5887, 6026 and 6910 cm^{-1} (associated with H1b); 5672, 5724 and 5769 cm^{-1} (associated with H1c). A neutron is uncharged, and is almost 2000 times heavier than an electron; fast neutrons therefore produce a highly defective and disordered diamond; it is well known that neutron irradiation can create dislocations, and even swelling in materials [24]. Based on spectral evidence, neutron-irradiated and annealed diamonds can apparently be separated from electron-irradiated and annealed diamonds. While the spectra of neutron-irradiated and annealed diamonds are very complex with many uninterpreted absorption features, the spectra of electron treated samples generally just exhibit the more common radiation and radiation/annealing related absorptions such as GR1, H2, H3, H4, NV^-, NV^0, H1a, H1b, and the H1c features.

Maybe it would be possible to create these more complex defects by irradiating diamonds by more energetic electrons above 10 MeV and/or by extremely long periods of irradiation of the order of weeks.

While brown color in natural brown diamonds is in most cases distributed within color bands along octahedral planes, it has apparently a homogeneous distribution in the irradiated/annealed diamonds; the fact that the natural color is related to vacancies due to plastic deformation of diamond while the vacancies are more evenly distributed by irradiation could explain why these types of brown color are differently distributed while they may be caused by a similar and very stable defect consisting of multiple vacancies (vacancy cluster).

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