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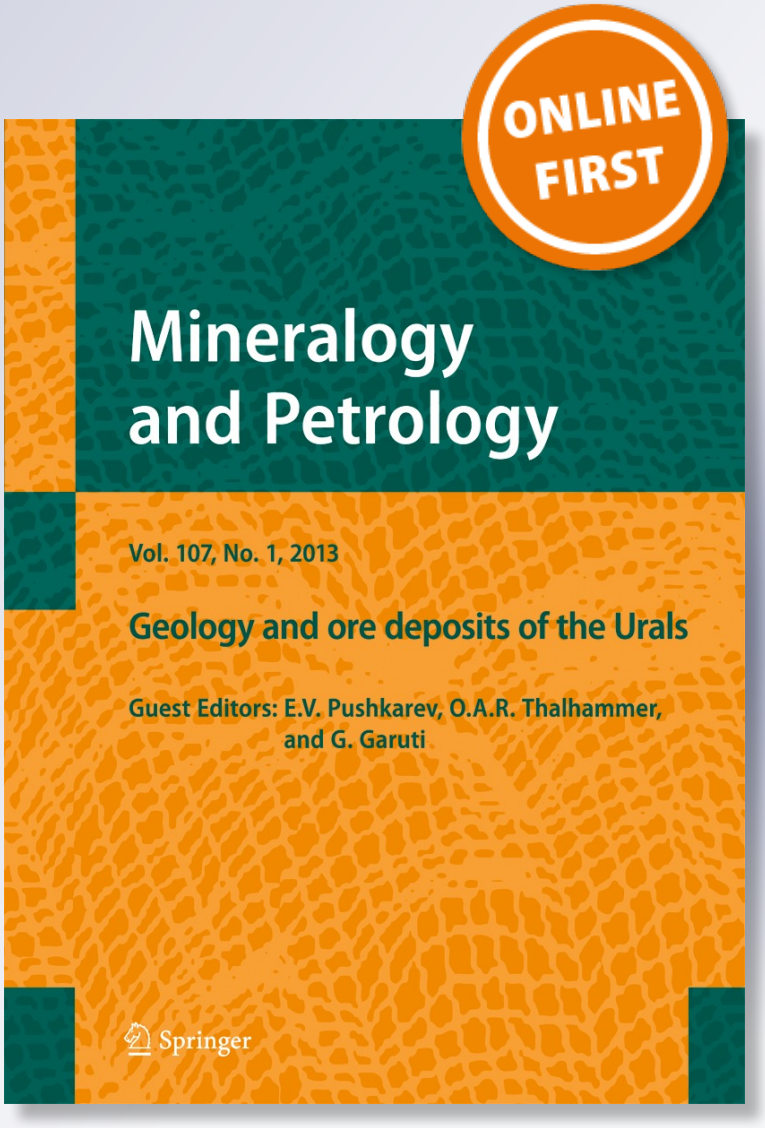
Mineralogy and Petrology

ISSN 0930-0708

Miner Petrol
DOI 10.1007/s00710-013-0273-7



Springer

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ORIGINAL PAPER

Luminescence spectroscopy and microscopy applied to study gem materials: a case study of C centre containing diamonds

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Received: 5 September 2012 / Accepted: 29 January 2013

Abstract The methods of luminescence spectroscopy and microscopy are widely used for the analysis of gem materials. This paper gives an overview of the most important applications of the analysis of laser and UV excited luminescence by spectroscopy and visually by microscopy with emphasis on diamond, and specifically natural type Ib diamond, little studied so far. Luminescence based techniques are paramount to the gemmological analysis of diamond, in order to determine whether it is natural, treated or synthetic. The great sensitivity of luminescence helps detect some emitting centres that are undetectable by any other analytical method. Hence, especially for diamond, luminescence is an enabling technology, as illustrated by its pioneering use of imagery for the separation of natural and synthetic diamond, and of spectroscopy for the detection of High Pressure–High Temperature treatment. For all other gemstones the applications are at the moment less numerous, but nevertheless they remain highly important. They provide quickly information on the identification of a gem material, and its treatment. Besides the study of broad band emissions caused by various colour centres, the typical PL-causing trace elements (amongst others) are chromium, manganese, uranium and rare earth elements. In pearls the study of broad band luminescence can be useful, and particularly the study of pink to red porphyrin luminescence in pearls from certain species such as Pinctada and Pteria and others can help identify the pearl-producing mollusc, or if a pearl has been dyed or not. Type Ib diamonds are representative of the importance and complexity of the analysis of luminescence by microscopy and spectroscopy. They show a wide range of sometimes very complex emissions that result in luminescence colours from green to yellow to orange or red. These emissions show generally very inhomogeneous distribution. They are caused by a range of defects, however only a few of them are well characterized.

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Introduction

The study of gem materials is mainly based on the analysis of their optical and chemical properties. In practical applications the use of destructive testing is not an option and since most gemstones are facetted in various shapes many methods such as EPR are only possible for research purposes. Besides absorption spectroscopy the study of the emission of light by imaging or spectroscopy is the preferred optical method for gem testing.

In gem testing the simple visual observation of luminescence excited by a properly filtered mercury lamp or its equivalent is still today an important method for characterization of many gem materials: for a review, see Fritsch and Waychunas 1993. The emissions observed under excitation at 365 nm (so called long wave UV [LWUV]) and at 254 nm (so called short wave UV [SWUV]) are being employed.

More sophisticated methods for the observation of luminescence by microscopic techniques and spectroscopy were

Published online: 13 February 2013

adapted for gem testing in the mid to late 1990's only, with the increasing need of gem testing laboratories to detect low defect concentrations. This is due to the great sensitivity of luminescence which helps detect some emitting centres that are undetectable by any other analytical method (Fritsch 2006). Hence, especially for diamond, luminescence is an enabling technology, as illustrated by its pioneering use of imagery for the separation of natural and synthetic diamond, and of spectroscopy for the detection of High Pressure–High Temperature treatment (Chalain et al. 1999).

As Raman spectrometers were already present in gem labs, they were put to use to measure the photoluminescence spectra. Home-made luminescence microscopes were paralellely developed for fluorescence imaging at higher magnification, in greater detail. One of the first fluorescence imaging system—with excitation at about 220 nm—was the DiamondView™ system (Welbourn et al. 1996) which was produced explicitly for diamond testing. It is now however used by many for other gems, for example corundum or pearls.

By luminescence microscopy and other luminescence imaging methods one can visually observe the defect distribution in gem materials. The observed emission colours can be indicative of the emitting defect. Luminescence spectroscopy, mostly through emission spectra, is used to better understand the nature of the defect responsible, since visually the emission colour of completely different defects may appear identical. By contrast with imaging, photoluminescence spectroscopy permits not only the analysis of the visual wavelength range, but (depending on the excitation source and detector available) also the UV and part of the NIR domain. Excitation spectra are still rarely published, as most spectra in gemmology are laser excited. The study of PL time-dependence spectra is still in its infancy for gemmological applications and thus there are only some academic studies, with no practical applications for gemmological expertise (Gaft et al. 2005; Fritsch et al. 2003b)

Initially these more complex methods of fluorescence analysis were mainly used for diamonds, but the past 15 years of research have led to many applications of these methods for other gem materials (see for ex. Gaillou et al. 2011). This contribution therefore is a witness to the recent development of luminescence as a diagnostic technique in gemmology through the use of spectroscopy and micro-imaging.

Background

Instrumentation

Photoluminescence spectroscopy

In photoluminescence spectroscopy the luminescence of a sample is excited by a light source and then analysed by a spectrograph. While a broadband light source can be employed either in combination with a monochromator or with suitable filtering it is generally preferable to use monochromatic light from a laser or near monochromatic light from a light emitting diode (LED). While with a broadband light source such as a xenon lamp that is coupled to a monochromator one can select any wavelength from about 200 nm to more than 1,000 nm, such light is often weak or not perfectly monochromatic; Often small artefacts are present when spectra of weakly luminescing samples are being recorded using such sources. LED's can be quite powerful, with a single LED having an output comparable to that of lasers, such as 50 mW or more. The problem with LEDs is that their emission is quite large, having FWHM (Full width at half maximum) from about 7 to 35 nm; additionally their line shape is often asymmetric and thus LED's emit not just at their indicated peak wavelength.

In consequence the best option for PL spectroscopy are lasers: they are truly monochromatic, have very narrow bandwidths (FWHM), can be very powerful and a wide variety of wavelengths are available. Additionally good quality lasers are the only choice for Raman spectroscopy in gemmology, which is usually performed with the same instrument that is used for PL spectroscopy.

The spectrometers in use can be either Czerny-Turner scanning spectrographs, CCD type Czerny-Turner spectrometers or Echelle spectrographs. Of these the first two spectrometer types are most commonly used, while only few Echelle spectrographs have enough throughput to be useful in Raman and photoluminescence applications. The Echelle instruments with high enough throughput have the great advantage of synchronous detection of wavelengths over a large range combined with extremely high resolution. In photoluminescence and Raman spectroscopy the excitation light source needs to be filtered by suitable notch or long-pass filters, so that the intense laser light does not blind the detector. Many systems used for photoluminescence spectroscopy are Raman spectrometers with an extended spectral range; for PL spectroscopy the detector used should cover as much as possible of the spectral range where radiative electronic transitions are found. Additionally the perfect system uses several lasers from the UV to the NIR and has an average resolution of at least 0.1 nm, in order to resolve the sharpest peaks that occur in PL spectroscopy, particularly of diamonds. Peaks with a FWHM of 0.05 nm were observed in CVD synthetic diamonds and on various occasions peaks with FWHM of 0.1 nm and below were observed in natural diamonds by the authors.

The modern research Raman systems are commonly using a microscope with confocal capacities, mostly for better selection of inclusions in gems, and mapping in X-Y and X-Y-Z directions with very high spatial resolution.

Luminescence microscopy

In luminescence microscopy the same conditions are used as in spectroscopy, but the spectrometer is replaced by a microscope or a camera. In contrast to the spectroscopic methods the imaging instruments take advantage of suitably filtered broadband light sources such as xenon arc lamps or mercury-vapour lamps. Some instruments such as confocal luminescence microscopes use lasers or LED's as excitation sources.

For gem testing the most versatile excitation is produced from UV xenon bulbs since these emit from about 200 nm all the way to about 2,000 nm. The desired excitation light is produced by filtering or even by the use of a monochromator; while monochromators allow the production of (near-) monochromatic light at the desired wavelength, the light output is often not sufficient for weakly luminescent samples. Suitable bandpass or shortpass filters, or dichroic mirrors help produce narrow band or broad band excitation in the desired spectral domain. Typically excitations range from 200 to 450 nm. Instruments that guide the light through the optics are limited to excitation wavelengths that are transmitted by the optics of the microscope; UV transmitting optics are very expensive, especially when very short wavelengths are involved. Therefore some instruments guide the excitation light outside the microscope toward the sample, and focalize the beam via fused silica optics. In order to protect the observer from the excitation light it has to be filtered before the microscope, using an appropriate longpass filter.

The observation of the luminescence is done either by microscope or by the use of a camera; while in biology highly sensitive monochrome CCD or sCMOS cameras are generally in use, for the analysis of gem materials a colour CCD or CMOS camera is usually preferred; they are more economic and the colour image is directly obtained

Applications

Photoluminescence spectroscopy and imaging of coloured gemstones and biogenic gem materials

Gemmological laboratories have only recently started applying photoluminescence spectroscopy on gemstones other than diamonds, also collectively known as "coloured stones". The cause of luminescence in most gems is still unknown; however, slow progress is under way. Today, chromium is the best known cause of luminescence in gems, with less-known but very common manganese, a small number of uranium-based, and some organic pigments of known nature (Fritsch et al. 2011, 2012). Most applications are restricted to coloured gems which contain chromium.

Spinel PL spectroscopy is useful for some top-quality pink-to-red spinels, virtually free of inclusions under microscope, and for which it is therefore impossible to determine if they are natural or synthetic. For spinels, Cr^{+3} emission bands are positioned around 685 nm, but their shape and exact position differ between natural and synthetic samples (Notari and Grobon 2003; Shen et al. 2004; Häger et al. 2010). In natural samples, the bands are sharp and the main band is centred around 685 nm, whereas in synthetics they are wider and the main band is centred at around 688 nm with a shoulder around 685 nm (Fig. 1a). The same bands are also useful to separate the natural unheated from the natural heated (to temperatures above 600 °C) pink-to-red spinels (Tijero and Ibarra 1993; Tuyen et al. 2003). The latter present similar bands to synthetic spinels (see again Fig. 1a). PL spectra acquired at liquid nitrogen temperature of the unheated material present splitted, finer bands compared to those at room temperature (Fig. 1, right). There is also a suppression of the emissions at the high energy side of the main emission line. On the other hand, the spectra of heat treated spinel are less dramatically modified by the low temperature with the exception of the suppression of the emissions at the higher energy side of the main emission line (see Fig. 1b). The broadening of the Cr^{3+} bands is likely due to cationic disordering caused by the heating of natural spinels or by high temperature synthesis (Tijero and Ibarra 1993; Cynn et al. 1992). However, to separate inclusion-free, natural heated samples from their synthetic counterparts, other methods are required such as chemical analysis (Kondo et al. 2010).

Corundum Rubies are also presenting strongly polarized Cr^{3+} emission bands at around 700 nm, with the two main lines at about 693 and 694 nm. It has been shown that the ratio of the intensity of two side bands at about 705 and at 714 nm is correlated with the Cr_2O_3 content of the ruby (Häger et al. 2010). The intensity of luminescence of rubies (even observed under a standard UV light) is affected by the presence of iron. The oxygen-Fe^{3+} charge-transfer absorbs the UV part of the excitation, quenching luminescence (see for ex. Fritsch and Waychunas 1993). This can give valuable clues for the origin of the ruby; e.g., rubies from Myanmar and Mozambique could look similar under magnification but most of rubies from Myanmar present intense red luminescence whereas most rubies from Mozambique present red luminescence of medium intensity due to relatively high iron content.

Another useful application of PL spectroscopy is the distinction of natural blue sapphire from its flame fusion equivalent. All flame fusion synthetic sapphires tested by the authors so far exhibit a broad band centred at approximately 765 nm underlying the Cr^{3+} emissions (Fig. 2a). This can be observed at room temperature and at 77 K, but the

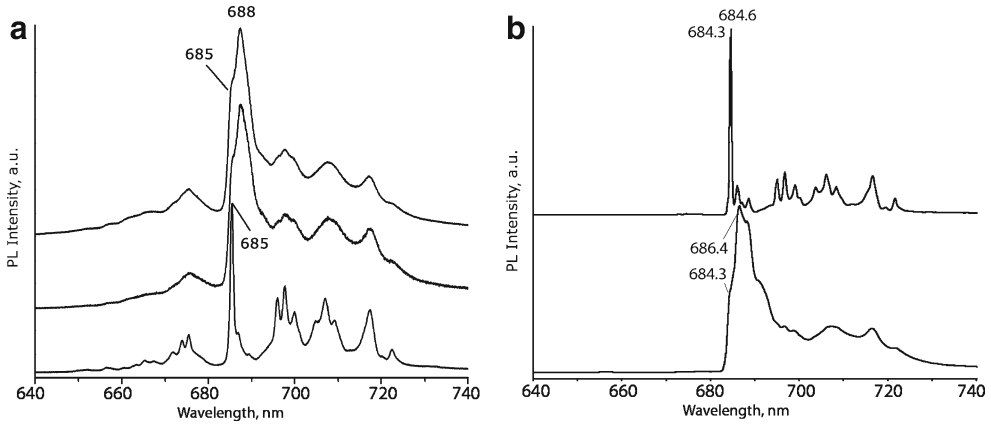

Fig. 1 **a** Photoluminescence spectra from 640 to 740 nm (excitation: 532 nm) recorded at room temperature of three pink-to-red spinels: natural unheated (*lower spectrum*), a natural heated (*middle spectrum*) and a synthetic (*upper spectrum*). The natural heated and synthetic samples present similar features with the main band situated at around 688 nm accompanied a shoulder at 685 nm. The natural sample present sharper bands with the main peak situated at 685 nm. Differences in the shapes and the exact positions of the PL bands are probably due to spinel's cationic disorder resulting from heating or by high temperature synthesis. **b** Besides a suppression of part of the emission the photoluminescence spectra (excitation: 532 nm) of the unheated and heat treated natural spinels recorded at 77 K show finer bands and band splitting for the unheated spinel. The spectra are shifted vertically for clarity

spectra at 77 K sharpen the Cr^{3+} emissions considerably: the synthetic sapphires tested so far by this method can have Cr^{3+} emissions with FWHM as low as 0.09 nm (692.0 nm) and 0.10 nm (693.4 nm), while all natural sapphires show somewhat larger peaks in their PL spectra (Fig. 2a).

The fact that chromium could be detected with PL spectroscopy even below ppm level concentrations gives a great potential for other applications as well. Our research team is currently looking for possible application of PL spectroscopy on the detection of heat treatment of other Cr-bearing gemstones such as tanzanite, demantoid and corundum. As it is cited above, less known causes of luminescence is manganese (Mn^{2+}) in spinel, carbonates and silicates, as well as some related to uranium for zircons and opals (uranyl molecule) (Tijero and Ibarra 1993; Fritsch et al. 2011, 2012). However, currently there is no application related to gemmological issues.

Luminescence imaging could sometimes reveal gemstones growth patterns and other characteristics which cannot be observed with optical microscopy (Devouard and Notari 2009). The dimension as well as the colour of these structures can give valuable clues for the geological environment of the stones as well as if they are submitted to a treatment (e.g.; blue sapphires). An example are sapphires that exhibit orange PL (Fig. 2b), a luminescence for which the cause is currently unknown; such stones are typically blue, yellow or orange to orangey pink (padparadscha sapphire) and most frequently this emission colour is found in stones from Sri Lanka and Madagascar. While this emission is believed to give clues on the country of origin of such a

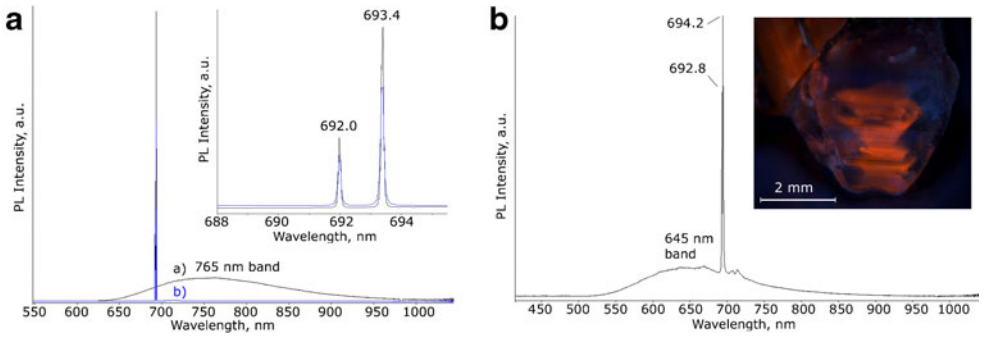

Fig. 2 **a** The PL spectrum under 532 nm excitation of a flame fusion synthetic blue sapphire (*upper trace*, a) compared to the spectrum of a heat treated natural blue sapphire from Sri Lanka (*bottom trace*, b), recorded with the stones cooled to 77 K. The spectrum of the synthetic sapphire shows a broad band centred at 765 nm on top of which Cr^{3+} emissions are visible, while the natural sapphire spectrum shows only Cr^{3+} emission. **b** The UV excited luminescence image and PL spectrum of a heat treated natural blue sapphire from Sri Lanka that shows very distinctly sectored orange PL; the luminescence image was captured under 300–410 nm broad band excitation of the fluorescence microscope and the PL spectrum was recorded using a 405 nm laser. Such orange PL can give clues on the country of origin of a sapphire, but does not help identifying heat treatment. The orange PL seen in heated and unheated sapphires is caused by an identical broad band, in both cases centred at approximately 645 nm

sapphire its presence or absence does not give any clues on heat treatment determination or even synthetic origin: this orange emission has been found in natural, but also heat treated (particularly Be-diffusion treated; Fritsch et al. 2003a; Notari et al. 2003) and synthetic gems (particularly purple or colourless flame-fusion crystals). Both heated and unheated sapphires can exhibit this type of PL, and spectroscopically they are identical for the heated and the unheated material; the orange PL is caused by a broad band emission centred at approximately 645 nm, underlying the Cr^{3+} emission (Fig. 2b). Some synthetics can also be quickly identified using luminescence microscopy. For example, the characteristics curved growth structures of flame-fusion (Verneuil) rubies (and other corundum varieties) are easily observable in deep UV luminescence imaging systems.

Beryl The colourless substances which are used to improve the clarity of emeralds can be easily identified by luminescence imaging, when present. Using this method, the nature of the filling material (e.g., oil, epoxy resin) is identified by the luminescence colours. Studying this luminescence under microscope is the only reliable way to identify the degree of clarity enhancement (Notari et al. 2002) (Fig. 3), while the nature of the substance is generally confirmed by infrared spectroscopy or more rarely Raman spectroscopy (Kiefert et al. 1999).

Biogenic gems—coral and pearls PL spectroscopy is also applied on some biogenic gems, mostly coral and pearls, in order to determine the pearl-producing mollusc, or whether the material colour is natural or results from treatment (dyeing for ex.). However, PL spectra should be acquired with care as these gems are more sensitive to heat and high power lasers risks to damage the samples (Fritsch et al. 2012). An application is the separation of natural colour pink-to-red *Corallium sp*. corals from its dyed counterparts (Smith et al. 2007). Using the green laser of a Raman spectrometer, natural colour *Corallium sp*. corals present a large band centred at about 630 nm with numerous Raman peaks due to natural pigments (i.e., "simple" polyenes). Treated-colour *Corallium sp*. corals present different PL peaks depending on the colour agent added. Similarly, PL spectroscopy can also help to identify treated-colour pearls from some molluscs. For example, natural colour freshwater cultured pearls from *Hyriopsis sp*. molluscs present different spectra compared to the treated colour counterparts (Karampelas 2008). Homogeneous sample colour with inhomogeneous luminescence distribution, excited by ultraviolet lamps, is an evidence of colour treatment.

PL spectroscopy can also help to identify the host mollusc of the natural colour saltwater cultured pearls (Miyoshi et al. 1987a). The most common bivalves used for cultivation of saltwater cultured pearls are Pinctada fucata (a.k.a. "Akoya"), Pinctada maxima (a.k.a. "South-Sea"), Pinctada margaritifera (a.k.a. "Tahitian" cultured pearls) and Pteria sterna (a.k.a. "Mexican"). Samples of the latter—even white ones—show a pronounced PL peaks at 620 nm, 650 and 680 nm. Similar bands in this region are present for some natural coloured samples from Pinctada margaritifera and some rare samples from Pinctada maxima (Karampelas et al. 2011; Karampelas 2012). Some of the bands above 600 nm were attributed to a kind of porphyrin, possibly one of the pigments of these cultured pearls (Miyoshi et al. 1987b; Iwahashi and Akamatsu 1994). However, when comparing similarly coloured pearls by PL spectroscopy the samples from Pteria sterna present stronger bands in the orange-red—i.e., above 600 nm—than in the blue-green—below 570 nm—(Fig. 4c). The samples from the other two mollusks present more intense bands in the blue-green than in the orange-red. Moreover, only samples from Pteria sp. luminesce red, either using longwave ultraviolet lamp (Kiefert et al. 2004), or visible laser excitations (Fig. 4a and b).

Photoluminescence spectroscopy and imaging of diamonds

Diamond is the principal gem material that is frequently analysed by PL spectroscopy. It exhibits an impressive

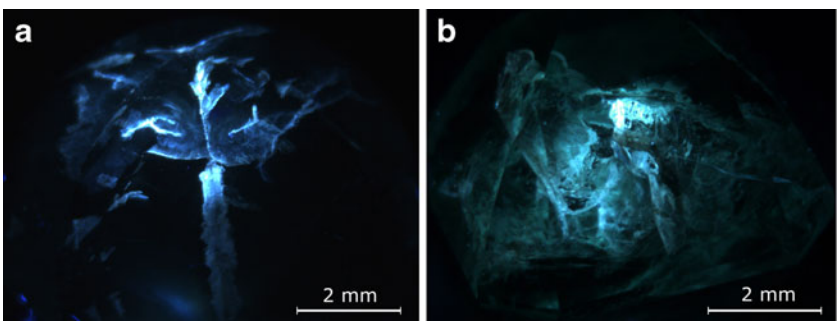

Fig. 3 Microscopic luminescence images captured using blue light excitation from a luminescence microscope of two clarity enhanced emeralds; in (**a**) an emerald enhanced using artificial resin is shown and in (**b**) an emerald clarity enhanced using oil. It is clearly visible that the resin fluoresces more bluish while the oil fluoresces more yellowish. This method is very useful for the determination of the degree of clarity enhancement

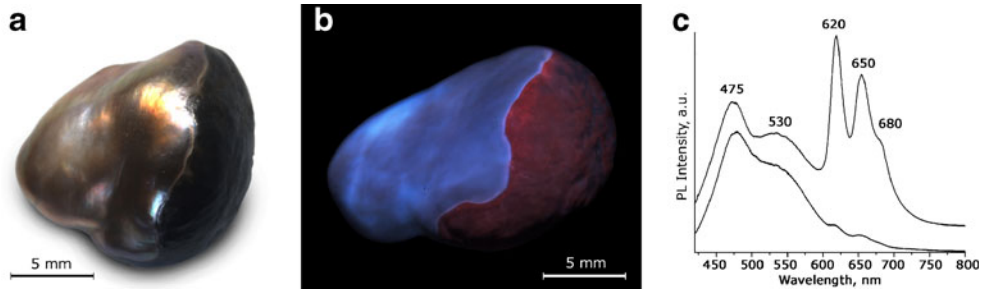

Fig. 4 A bicoloured "bronze"/black pearl of Pteria penguin (**a**) with red luminescence related to a type of porphyrin. The image was recorded under 300–410 nm broadband excitation of the fluorescence microscope. While the black non-nacreous calcitic portion luminesces strong red, the "bronze" nacreous portion shows red luminescence overlaid by more distinct blue-white luminescence (**b**). **c** shows the photoluminescence spectrum of this pearl (*upper trace*) compared to the spectrum of a dark coloured Pinctada margaritifera (*bottom trace*) from 420 to 800 nm (excitation: 405 nm laser) recorded at room temperature. Similar bands are observed in both spectra. To the sample from Pteria penguin the bands at the orange-red part of the electromagetic spectrum are more intense than those observed to the blue and green part, whereas the bands at the blue and green part spectrum are more intense than those observed to the orange-red to the sample from Pinctada margaritifera. The spectra are shifted vertically for clarity

variety of point or extended defects of which many are optically active only in PL spectroscopy. This is thanks to the large bandgap of 5.49 eV which is favourable for radiative electronic transitions, as such transitions are possible only if their ground and the excited states lie within the bandgap (Zaitsev 2001). Hundreds of emissions are known in diamond and of these many are summarized in the compilation by Alexander Zaitsev (2001).

As already stated above, PL spectroscopy can be sensitive to extremely low concentration of emitting centres, commonly down to ppm levels for many of those in diamond, sometimes much lower (ppb levels). Such sparse defects are undetectable by many other optical, non-destructive methods, such as optical absorption spectroscopy for example. Depending on the performance of a PL spectroscopy system the only limit to detection is imposed by a strong underlying band, with intensity close to detector limits. Arguably the most important diamond applications of PL spectroscopy in diamond gemmology is the detection of HPHT treatment, followed by the distinction of natural from synthetic diamond.

Identification of HPHT treatment of diamonds by photoluminescence spectroscopy In the late 1990's the first HPHT treated diamonds were officially detected and published (see e.g. Chalain et al. 1999; Smith et al. 2000; Collins et al. 2000). In this treatment usually essentially brown to "olive" diamonds are subjected to temperatures ranging from 1900 to about 2,500 °C (with experimental treatments up to 3,000 °C) and pressures of 5.5 to 8.5 GPa. Their colour is modified into a more desirable colour: colourless to near-colourless, blue, pink, or yellow-green for example. This process occurs at the limit of the diamond—graphite transition region. It causes mobility of some centres, resulting in the annealing of some defects (including clusters of vacancies responsible for the brown colour, and in the formation of new structures, inducing other colours).

The effects of this treatment must be divided according to the various diamond types and varieties:

- a) HPHT treatment of brown type II and low nitrogen type IaB diamonds
- b) HPHT and multi-step treatment of brown type I diamonds
- c) HPHT and multi-step treatment treatment of other coloured type I diamonds

a) In brown type IIa and low nitrogen type IaB diamonds the HPHT results in the decolouration of the diamonds; while IIa samples usually turn truly colourless the IaB samples are at best near-colourless after the treatment. Since IIa diamonds contain extremely low concentrations of nitrogen impurities the treatment basically anneals out the defects responsible for the brown colouration of the stones (Fujita et al. 2009). Some brown type IIa diamonds turn pink instead of colourless, and can be HPHT treated a second time to decolorize them completely.

The first published data indicated that PL should be used, and attention paid to the presence of NV^- centres in colourless type IIa diamonds, believed indicative for HPHT treatment (Chalain et al. 2000a). More extensive before and after treatment studies of type IIa diamonds have shown quickly that this criterion was not always valid; then it was shown that the ratio of the NV^0 to the NV^- centres—measured at liquid nitrogen temperature—are changed since generally the NV^- centres dominate the NV^0 centres after HPHT, while it is normally the opposite before (Fisher and Spits 2000); these authors have found that a 575/637 nm peak height ratio of <1 is indicative of HPHT treatment while a ratio of >1 points towards the absence of treatment. Another group (Chalain et al.

2000b) concluded that a peak height ratio 637/575 of >2.8 is indicative of HPHT treatment while a ratio of <1.6 is indicative of lack of treatment. While this NV centre ratio is a criterion which can help identifying a treated diamond in combination with other indications, used alone it was found be insufficient for HPHT treatment detection, and that other defects observed by PL at low temperature should be considered (Lim et al. 2010).

The FWHM of the NV^- centre has then been proposed as a probe for strain in diamond; it has been shown that the PL spectra of HPHT treated type IIa diamonds exhibit NV^- centre ZPL with a larger FWHM than the spectra of untreated type IIa diamonds (Hänni et al. 2000); in the PL spectra of untreated colourless type IIa diamonds the NV^- centre ZPL has a FWHM of 0.45 nm (11 cm^{-1}) or lower, and in the spectra of originally brownish to brown treated colourless type IIa damonds it has a larger FWHM of 0.53 nm [15 cm^{-1}] or higher. Since the treatment does not lower the strain in diamond the larger FWHM typical for strongly strained brown diamond persists also after treatment (Hänni et al. 2000).

The FWHM of the GR1 ZPL is equally used as a probe for strain in type IIa diamond and the FWHM measurement of the 741.1 nm GR1 line has been proposed as a tool for HPHT treatment detection (Fisher et al. 2006); HPHT treated type IIa diamonds re-treated by irradiation after HPHT exhibited a GR1 emission in their PL spectra with larger FWHM than untreated colourless type IIa diamonds. This is because of the strain around the defects that is present in the original brown diamonds; only very little or none of this strain is released by the HPHT treatment (Willems et al. 2006) and thus the GR1 of untreated IIa diamonds has usually significantly lower FWHM. These authors have found that the vast majority of natural colourless type IIa diamonds exhibit a 741.1 nm GR1 PL peak with FWHM from 0.3 nm to 0.75 nm (peaking at 0.44 nm), only rarely the band is larger (FWHM up to 1.2 nm and more). HPHT-treated colourless diamonds that are treated by irradiation in order to introduce GR1 show generally larger GR1 FWHM which is close to the FWHM of the original GR1 emission before HPHT treatment. The lowest FWHM was found between 0.65 and 0.75 nm and the largest FWHM was around 2.1 nm. For HPHT treated goods there is no main value for the FWHM since it depends on the depth of the brown colour of the diamonds before the treatment.

A Korean group (Lim et al. 2010) has published a method based on the presence or absence of the following minor PL features measured at 8 K in a helium cooled cryostat:(1) 633.9, 635.1 and 636.3, (2) the 580–625 nm broad bands, (3) 574.5 and 575.9 and (4) 494.3, 498.3 and 503.5 nm. Their conclusions are that based on this technique 99 % of HPHT treated diamonds can be detected. Curiously they do not at all take the published FWHM measurement techniques of NV and GR1 ZPL's into consideration.

The extremely rare brown to "olive" type IIb diamonds (thus containing traces of boron) can be treated by the HPHT process to eliminate the brown colour and consequently render the stones gray to blue, depending on the boron concentrations present. The only method to identify such treated diamonds is PL spectroscopy; natural colour blue diamonds can be identified by similar criteria as described for type IIa diamonds, plus the possible presence of emission bands at 517.6, 648.1 and 776.2 nm amongst others.

b) and c) For type I diamonds there are many ways of changing their colour by HPHT or irradiation and HPHT; stones that show deformation-related colouration (brown, "olive", pink) can be easily colour modified by short HPHT treatment at >1,900 °C under stabilizing pressure of >55 kbar (Collins et al. 2000). Typically greenish yellow colours are obtained at lower temperatures (approximately 1,900 to 2,100 °C). At higher temperatures (>2,200 °C) much more nitrogen dissociation and aggregation occurs and has an important influence on the colour: the single nitrogen produced induces a more intense yellow colouration (Collins et al. 2000).

Type Ia brown diamonds with deformation-related colour can be multi-step treated to produce pink, orange pink and red diamond; the treatment is a combination of HPHT annealing to create C centres, irradiation to create vacancies and annealing to create strong NV^- centres (Wang et al. 2005). Depending on the specific diamond type used the strong NV^- centre absorption results in the above mentioned colours. The treatment creates N3, H3, H4, NV^- and NV^0 plus H2 centres, of which all but H2 exhibit strong PL in the visible spectral domain. The inhomogeneous colour distribution of the brown starting material results in very inhomogeneous luminescence distribution after the multi-step treatment. In consequence such diamonds are easily identified by luminescence microscopy by their complex zoned luminescence (Fig. 5).

A phenomenon called "fluorescence cage"—apparent concentrations of fluorescence along facet edges—has been proposed as a criterion for distinction of HPHT treated and untreated type I diamonds (Dobrinets and Zaitsev 2009). This phenomenon has been described in irradiated diamonds as "facet edge luminescence" (Boillat et al. 2001), and is also known from certain untreated diamonds (Fritsch et al. 2009); we now interpret this phenomenon as an optical artefact that relates to the transparency of diamond to the

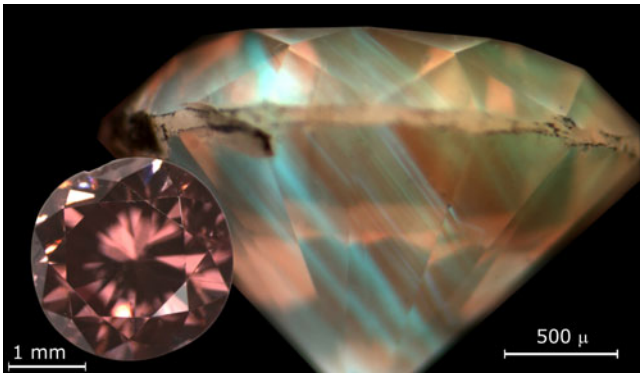

Fig. 5 The luminescence image of a multi-step treated type Ia diamond (inset) as seen under 300 to 410 nm broad band excitation of the fluorescence microscope; the originally brown stone turned vivid pink upon treatment and the fluorescence turned into a complex combination of blue N3, green H3 and H4, orange NV^0 and red NV^- emission

excitation light. Any diamond that is opaque to the wavelengths of the source used for luminescence excitation shows such "facet edge luminescence". Experiments by the authors showed that by faceting a large culet on a diamond with this phenomenon would create the same phenomenon along the newly created facet edges, and in consequence it relates to an optical artefact.

In order to use PL spectroscopy for HPHT treatment detection the high temperature behaviour of the various defect centres needs to be known. To cover this subject largely exceeds the scope of this paper, but a detailed study of PL spectroscopy, restricted to type Ib gems, with more details, is provided in the research section of this article.

Distinction of natural and synthetic diamond by photoluminescence spectroscopy and imaging Natural and synthetic diamond can be distinguished by a variety of spectroscopic and imaging methods, depending on the diamond growth method (HPHT or CVD; Field 1992) and the impurities that are present. Of these photoluminescence is the most versatile technique, especially when several lasers spanning the UV, visible and NIR range are available.

HPHT grown diamonds are usually produced using a nickel- or cobalt-containing molten metallic solvent. These elements form a large quantity of optically active defects, which are very efficiently detected by PL spectroscopy (Yelisseyev and Kanda 2007). In HPHT synthetic diamond analysis there are basically two scenarios, of which one includes diamonds which are luminescent with a standard UV lamp and thus rather rich in (optically active) defects, and the other includes diamonds which are practically inert and thus relatively poor in defects.

Both categories are rather easy to identify since some of the defects excited by PL spectroscopy are either unique to synthetic diamond, such as the 484 nm centre, or the defect density is too low to be possible in natural diamond. Examples of low defect-density synthetic diamonds can be often found in as-grown yellow melee HPHT synthetics (i.e. <0.17 ct). While natural deep, intense and vivid yellow diamonds are rich in PL-active centres, synthetic diamonds often contain very few such emitters; when e.g. NV^- centre emission less intense than the 2nd order Raman band is the only detectable defect in a strongly coloured type Ib or IaA diamond, then it is extremely likely that the sample is of synthetic origin. The 484 nm centre is one of the defects typically detected in as-grown (nickel) HPHT synthetic diamonds. Such stones may show practically no luminescence, except when the 484 nm centre is unusually strong; then this centre induces a weak green emission (Fig. 6). The 484 nm centre is believed to incorporate one nickel atom, possibly a substitutional Ni_s^- ion (Pereira et al. 1994).

Many of the nickel and cobalt-related defects that are detected by PL spectroscopy are formed after annealing at high temperature (Yelisseyev and Kanda 2007). One prominent defect frequently observed in the PL spectra of annealed HPHT grown diamonds is S3 which shows a ZPL at 496.6 and a associated structureless broad band at approximately 540 nm which results from the high Huang-Rhys factor S of ~5 to 10. This broad band is responsible for the intense green PL of some synthetic diamonds (Fig. 7). While nickel-related defects are also common in natural diamonds (see e.g. Iakoubovskii and Adriaenssens 2002) there is no confirmed report on the occurrence of cobalt-related defects in natural diamonds; fortunately the vast majority of nickel related PL emissions in synthetic diamonds do not coincide with those in natural diamonds. A notable exception is the 1.40 eV center which is a very common Ni-related centre in natural and synthetic diamond that manifests itself as a doublet at 884.85 and 883.15 nm (Nazaré et al. 1989).

Sectored luminescence is a characteristic feature of synthetic diamonds as can be seen in Figs. 7, 8 and 9 (see e.g. Fritsch and Shigley 1993) Cross-shaped PL as seen in Fig. 9 is very characteristic for HPHT grown synthetic diamond; the cross represents the defect enriched limits of individual octahedral and cubic growth sectors, the last ones present only in synthetics.

As-grown HPHT synthetic diamonds grown from a cobalt metal (usually cobalt–iron) often exhibit relatively weak PL from cobalt-related defects such as the 544.3/542.8/541.0 nm triplet emission (Lawson et al. 1996). After annealing at high temperature (HPHT or high temperature annealing under vacuum) this related defect strongly intensifies and a large number of sharp bands appear in the PL spectra (Fig. 9b and c). In consequence such stones exhibit bright orangey yellow PL after treatment (Fig. 9a). This treatment is of commercial importance since it transforms the colour of overly dark or

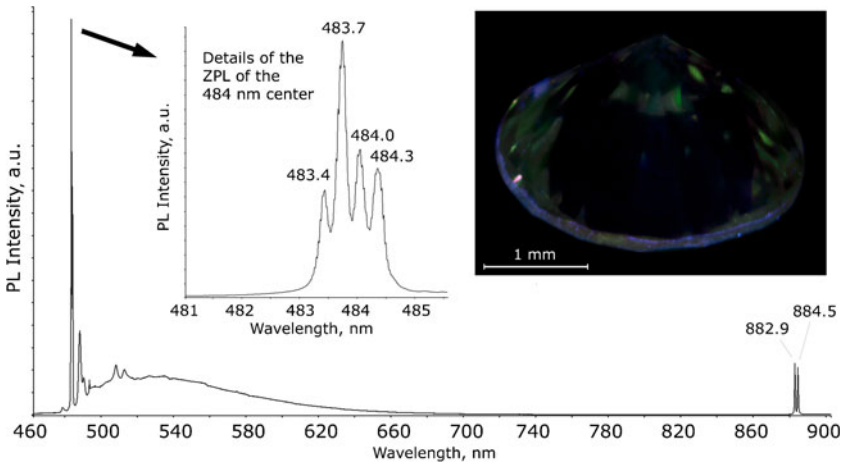

Fig. 6 The 405 nm laser photoluminescence spectrum and UV excited luminescence image (under 300 to 410 nm broadband UV excitation) of a HPHT grown synthetic diamond exhibiting unusually intense nickel-related 484 nm centre and in consequence faint green luminescence

brownish stones into bright yellow via aggregation of the C centres into A and B centres, even more efficiently so after irradiation to enhance the nitrogen aggregation (Collins 1980).

Such HIH (HPHT grown–Irradiated–High temperature treated) synthetic diamonds do not only exhibit stronger orangey yellow PL but also zones of intense blue N3 luminescence (Fig. 9a and d) since the enhanced nitrogen aggregation results in the formation of N3 centres at relatively modest treatment temperatures and times.

After the successful growth of single crystal Chemical Vapour Deposition CVD diamonds of sizes that permitted to produce facetted gems has been announced in 2001 by the company Apollo Diamonds USA, facetted single crystal synthetic diamonds grown by this method are commercially available since 2011 through the company Gemesis (Wang et al. 2012). Near inclusion-free, near colourless stones of about 0.25 to more than 1 ct can be purchased; the stones appear to be all HPHT treated since the as-grown goods are typically brownish.

The CVD diamonds are all type IIa and nitrogen doping results in very low nitrogen contents of around 1 ppm only (F. Silva, pers. comm 2012). In consequence CVD diamonds are either brownish or colourless; green or pink colours are possible via irradiation, or irradiation followed by annealing respectively.

The identification of CVD diamonds is based on the same type of testing as described above for HPHT grown diamonds. Photoluminescence spectroscopy and imaging are the primary methods for CVD diamond analysis.

As-grown CVD diamonds typically exhibit orange red UV excited PL from the NV centres (NV^0 and NV^-) (Fig. 10); while this PL can be strong in brownish CVD diamonds it tends to be very weak and barely visible to the eye in high quality single crystals. The luminescence may or may not show irregular distribution from dislocations, and this is best seen under deep UV excitation such as used by the DiamondView™ instrument.

Luminescence imaging helps recognize CVD diamonds through the growth striations resulting from so called "step flow" growth. The emission colour may vary from orange, when nitrogen impurities are present—to blue—very likely a dislocation related emission—and even to red (silicon related emission).

The PL spectra are thus generally dominated by NV^0 and NV^- centre emissions plus a large variety of sharp emissions.

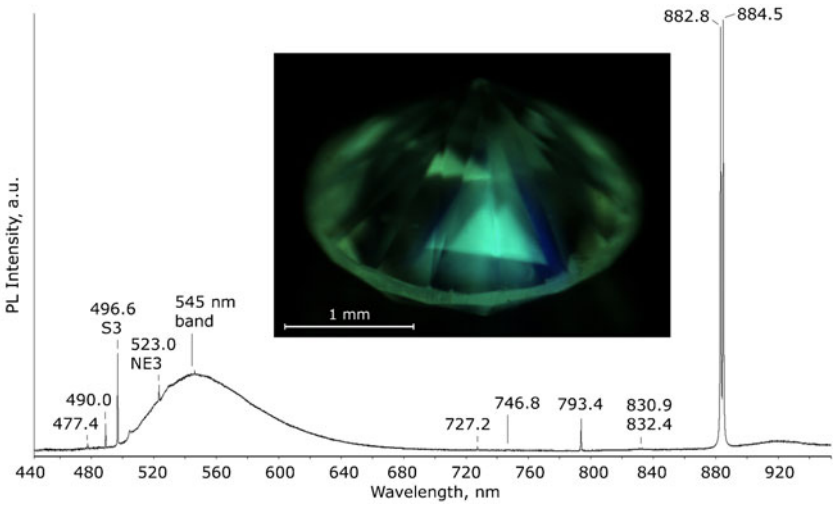

Fig. 7 The 405 nm laser photoluminescence spectrum and UV-excited (under 300 to 410 nm broadband UV) luminescence image of a high temperature annealed HPHT grown synthetic diamond exhibiting a very intense nickel-related 1.40 eV centre and intense green PL from the S3 centre with its ZPL at 496.6 nm and broad band emission at ~540 nm. Blue PL from the N3 centre can be seen on the luminescence image along the triangular green luminescent sector

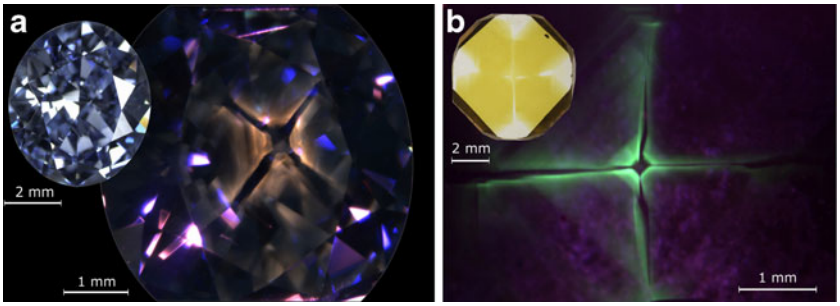

Fig. 8 The luminescence images under 300–410 nm broadband UV excitation of two HPHT grown synthetic diamonds (**a** type IIb blue, **b** type Ib yellow) show very distinct cross-shaped luminescence that clearly follow the diamond growth sectors, with inert cubic sectors forming the cross shape in this instance

In some high quality single crystal CVD diamonds large quantities of very sharp emissions can be found, especially in the 400 to 570 nm domain (Fig. 10); these exhibit mostly FWHM of <0.10 nm and some emissions as narrow as 0.045 nm were found in the spectra of samples from Element Six. In such high quality CVD diamonds the NV centre ZPL's also exhibit very low FWHM of typically 0.09 to 0.15 nm.

As for HPHT grown diamonds the identification of as grown CVD synthetic diamonds is often based on luminescence imaging combined with PL spectroscopy; orange UV excited PL is very uncommon in natural type IIa diamonds thus the observation of such luminescence alone is very suspicious. Additionally in certain as grown CVD's the dislocations typical of such diamonds can be seen directly in the PL images, especially when excitations of wavelength around 225 nm is used.

The PL spectra do generally identify CVD diamonds unambiguously since there is an array of emissions that are unknown in natural diamonds such as the lines at 467.6 nm, 563.2 nm, 596.3 nm and many others as seen in Fig. 10. A defect that can be prominent and that is usually detectable is the silicon centre with its doublet ZPL at 736.6 and 736.9 nm. This defect which is attributed to the negatively charged silicon split-vacancy center in diamond $[Si\text{-}V]^-$ (Goss et al. 1996) is also known in very rare cases in natural diamonds (Solin 1972; Breeding and Wang 2007); nevertheless its presence should caution an analyst that the tested diamond may be a CVD synthetic. Additionally the narrow FWHM of many of the PL emissions including the NV^0 and NV^- centres in high quality CVD synthetic diamond is very unlikely to occur in natural diamonds. In natural type IIa diamonds the NV^0 and NV^- centres typically exhibit FWHM of >0.2 nm, and only sometimes it can approach

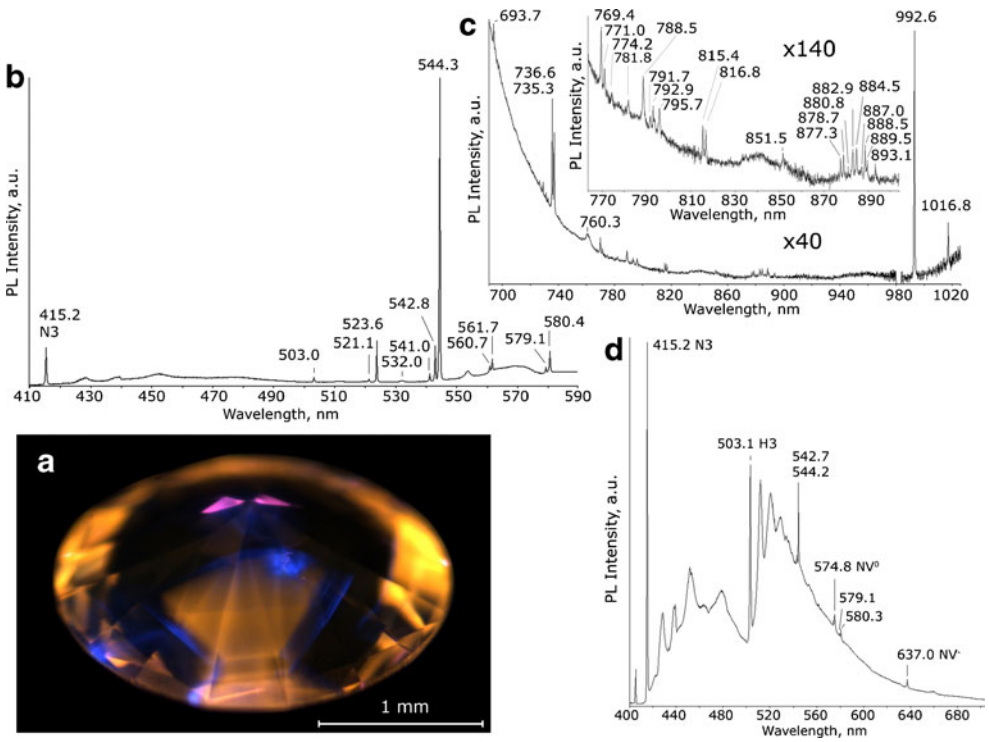

Fig. 9 A cobalt grown HIH (HPHT grown–Irradiated–High Temperature treated) synthetic diamond under strong UV excitation (broadband UV, 300 to 410 nm) (**a**) exhibiting blue/blue-green and orangey yellow luminescence. The purple reflections are from the excitation lamp. The corresponding photoluminescence spectra are shown for the blue/blue-green zones (**d**) and above for the orangey yellow sectors (**b** and **c**). The NIR spectra are strongly zoomed in order to visualize the weak sharp bands present in this domain

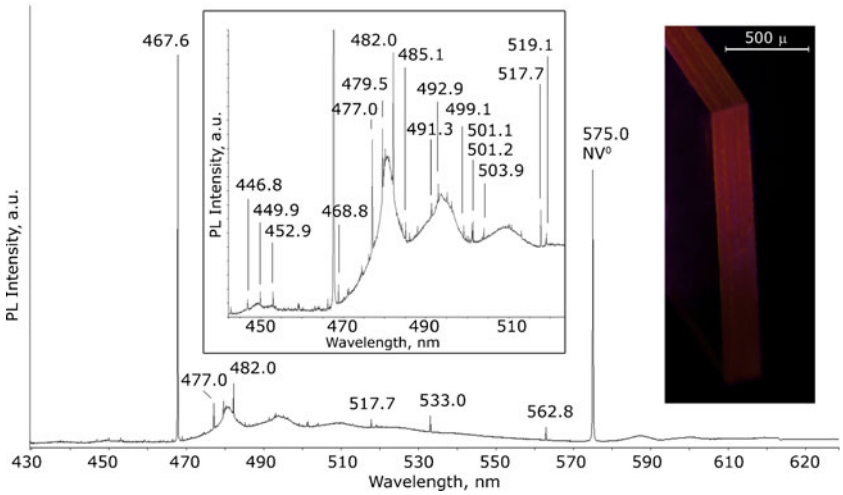

Fig. 10 An as-grown high quality CVD synthetic diamond from Element Six under strong broadband (300–410 nm) UV excitation (inset right) exhibiting faint orange NV centre luminescence. The low temperature (77 K) photoluminescence spectrum recorded using 405 nm laser excitation is characterized by very strong and narrow 467.6 nm emission (FWHM 0.076 nm), narrow NV^0 centre emission (FWHM 0.13 nm) and a large quantity of very narrow lines with FWHM from 0.045 to 0.11 nm

0.15 nm (Hänni et al. 2000). In natural diamond in general PL emissions with FWHM of close to 0.1 nm can be found only in rare cases.

In CVD diamonds that are HPHT treated after growth many of the identifying features known from as-grown CVD diamonds are not applicable. The PL colour under UV or violet light excitation changes from orange to either blue or bluish green and some of the PL spectra are dramatically different from the PL spectra of untreated CVD diamonds, especially when excitation at shorter wavelength are used.

The greenish blue PL is caused by broad band emission centred at 455 nm (Fig. 11a). Although H3 can be detected in HPHT treated CVD diamond the authors have not yet seen a stone where the luminescence was noticeably influenced by this defect; it was only a dominant feature under 473 nm excitation and only very weak under 405 nm excitation (see again Fig. 11a). The silicon centre is stable to temperatures above 2,200 °C (Zaitsev 2001) and in consequence present also in by far most HPHT treated samples observed so far (Wang et al. 2012). In the diamonds from Gemesis analysed by the authors the Si centre was frequently very strong under green laser excitation and the FWHM of the NV centres were significantly larger than in the CVD diamonds from ElementSix (> 0.3 nm). Likely the growth conditions to produce thick single crystals necessary to facet larger stones introduce a high dislocation density and in consequence the defects are influenced by strain; this strain is responsible for the larger bandwidth of certain defect emissions/absorptions in diamond (see e.g. Fisher et al. 2006).

The observation of UV excited PL by luminescence microscopy can reveal characteristic growth features from dislocations; these are typically near parallel slightly irregular linear striations (Fig. 11b). While the PL colour varied from green to blue under broad band UV excitation, under shorter wavelength UV the samples generally luminesce green and

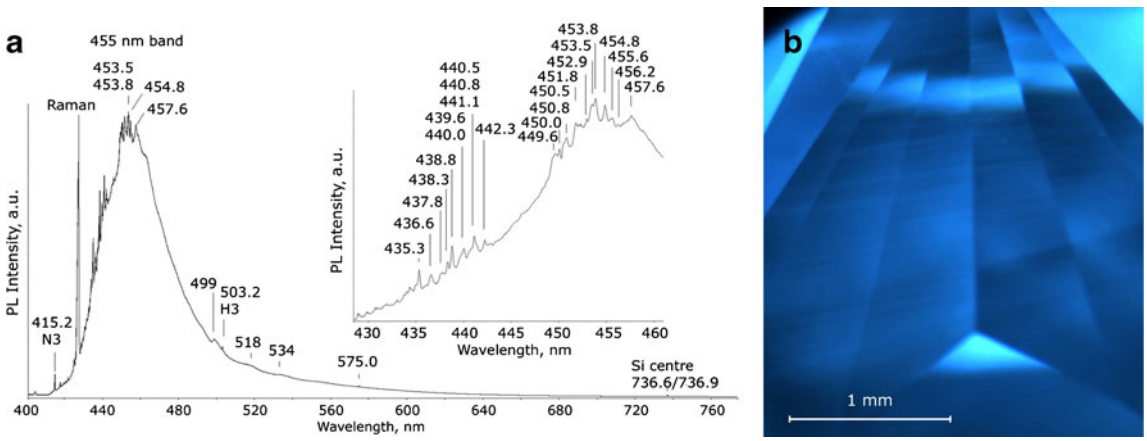

Fig. 11 An HPHT treated CVD synthetic diamond from Gemesis Corp. under strong 300–410 nm broadband UV excitation (**b**) exhibiting greenish blue luminescence, with slightly irregular linear striations from dislocations. The low temperature (77 K) photoluminescence spectrum recorded using 405 nm laser excitation is characterized by strong broad band emissions centred at 455 nm and many sharp lines overlaying the 455 nm band (**a**). Additionally weak N3, H3 and NV^0 and the Si centre are detectable. The spectrum clearly indicates that the greenish blue UV excited luminescence is caused by the 455 nm broad band emission

exhibit noticeable to strong green phosphorescence. This behaviour under UV combined with the PL spectroscopic properties clearly identify these HPHT treated CVD synthetic diamonds.

Other uses of photoluminescence spectroscopy and imaging for diamond Irradiated or irradiated-and-annealed diamonds can be identified be a variety of methods, among which the two techniques covered in this article play an important role. Many irradiated diamonds exhibit colour and luminescence distributions that are unique to treated stones; the fact that the relatively low energy electrons do not penetrate very deep into the stones results in inhomogeneous colour distribution. Colour is typically concentrated around the culet and often follows the diamond's outline.

Since the defect distribution is inhomogeneous the same is generally true for any related luminescence: such stones often show surface related luminescence due to the higher defect density in domains close to the surface.

In irradiated and annealed type I diamonds the high density in nitrogen-vacancy related defects causes strong PL. The most prominent irradiation-related defects causing PL in the visible domain are H4 (ZPL 495.7 nm), H3 (ZPL 503.2 nm), NV^0 (ZPL 574.9 nm), the 587.7 nm defect and NV^- (ZPL 637.0 nm).

In many cases irradiated and annealed diamonds exhibit UV excited luminescence which indicates treatment. The easiest to identify luminescence pattern is shown in Fig. 12; such strongly patterned H3 and/or H4 luminescence are unknown for untreated diamonds, even though these also commonly exhibit inhomogeneous PL.

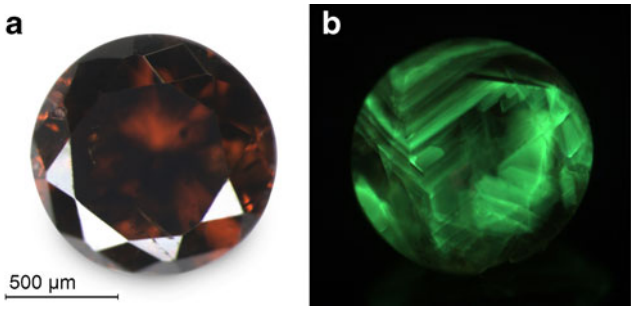

Fig. 12 A small (1.2 mm diameter) irradiated and annealed natural diamond (**a**) and its strongly patterned luminescence as observed under a fluorescence microscope using 300–410 nm broad band UV excitation (**b**). This type of pattern is strongly indicative for such treated diamonds and unknown in untreated stones

Case study: photoluminescence spectroscopy and imaging of C centre containing natural diamonds

Introduction

Nitrogen in diamond is by far the most prominent impurity and is responsible for many interesting properties of diamond. Many defects are nitrogen-related, such as the well-characterized N3, H4, H3, NV^-, NV^0 and H2 defects. Nitrogen occurs in diamond as A, B and C centres, also known as A aggregates (type IaA diamond), B aggregates (type IaB diamond), mixtures thereof (type IaA/B diamond) and single substitutional nitrogen (type Ib diamond) (Evans et al. 1981).

The nitrogen aggregates are formed in the sequence C centres ➔ A centres ➔ B centres via annealing either deep inside the earth's mantle or in a laboratory (Kiflawi and Bruley 2000).

Natural type Ib diamonds and even type Ia diamond containing single nitrogen are relatively rare and generally small. The C center defect causes absorption in the violet and blue portion of the visible spectrum due to its electron donor properties and the resulting energy level in the band gap at about 1.7 eV (Sobolev et al. 1968). This generates a featureless, fairly steep increase of the absorption from 560 nm towards lower wavelengths (higher energies). This pattern is called a continuum. Because it is fairly steep, it generates a rather saturated colour. While in theory the colour introduced by the C centre is yellow, natural Ib diamonds are not often yellow but their colour ranges from yellow to orange, "olive" (mixtures of yellow, brown, grey and green) to brown (Hainschwang et al. 2012). PL can unexpectedly be used as a tool to recognize and even categorize diamonds containing isolated nitrogen.

The group of C centre containing diamonds includes type Ib, type Ib > IaA, Ib> > IaA, IaA > Ib, IaA> > Ib and rarely stones that contain A, B and C centres ("ABC" diamonds [Hainschwang et al. 2006]). There are diamonds that exhibit properties similar to type Ib diamonds but with the isolated nitrogen undetectable by infrared spectroscopy; such stones are said to exhibit a Ib character. Spectroscopically type Ib diamonds appear at first to be simple however this is not the case: such diamonds, especially mixed type IaA/Ib samples, exhibit very complex spectral properties, particularly in photoluminescence spectroscopy.

This study of a large sampling of diamonds belonging to this group demonstrates that C centre diamonds can be categorized based on their PL, as observed by luminescence microscopy and PL spectroscopy. With the exceptions of some basic notions on the diamonds that exhibit only a type Ib character (i.e. diamonds with Ib-like properties, but with C centres undetectable by IR spectroscopy) only diamonds that have IR detectable C centres are covered here.

Materials and methods

Over 150 natural gem diamonds weighing 0.01 to 3.01 ct with C centres detectable with infrared absorption spectroscopy

were analysed in detail. Additionally several tens of thousands of intensely coloured yellow to orange diamonds were screened by luminescence microscopy following procedures described below to select those containing isolated nitrogen. For the sake of clarity the term "type Ib" is used in this study for all diamonds exhibiting at least some 1,344 cm^{-1} and/or 2,688 cm^{-1} absorption (that is the classic infrared absorption criterion). Nine of the stones were natural diamond crystals of mixed cuboid-octahedral growth (re-entrant cubes) and five were octahedral natural diamond crystals; all other natural diamonds were faceted into various shapes.

The luminescence of the diamonds was observed under 254 nm shortwave and 365 nm longwave radiation from a model UVP UVSL-26P, 6 W UV lamp and by broad band UV (240 to 400 nm) from a home-made luminescence microscope using a suitably filtered 300 W, full-spectrum Xenon lamp.

Infrared spectra of all the samples were recorded with a resolution 1 cm^{-1} and for some also 4 cm^{-1} on a Perkin Elmer Spectrum 100S FTIR spectrometer equipped with a thermoelectrically cooled DTGS detector, using a diffuse reflectance accessory as a beam condenser (for details see Hainschwang et al. 2006). The spectra of the crystals were recorded through a 5x beam condenser. The spectra were recorded over a range of 8,500 to 400 cm^{-1} with 100 to 1,000 scans for each diamond.

The nitrogen concentration was determined by progressive spectral decomposition via spectral calculations ("progressive decomposition" [Hainschwang et al. 2012]). The nitrogen concentration is calculated based on the known average absorbance of the intrinsic diamond infrared feature at 1,995 cm^{-1}, which has been defined by others as 12.3 absorbance units per cm of optical path (Field 1992). All diamond spectra must be normalized before any concentration calculation can be reliably conducted. This normalization is performed by spectral calculation, for which the absorbance value of the intrinsic diamond absorption at 1,995 cm^{-1} is noted and then the multiplying factor determined in order to obtain a value of 12.3 cm^{-1}. The spectrum is then multiplied by this factor. The method found to be the most satisfying and precise one was the progressive spectral decomposition in which the individual components (A, B, C and X centre) are subtracted from a given spectrum, using reference spectra of pure signals of the respective centres. The determination of type Ib diamonds and the C centre content was based on the presence and intensity of the 1,344 cm^{-1} and/or its overtone absorption at 2,688 cm^{-1}.

When using the terminology of low, moderate, high and very high for nitrogen concentrations then for simplicity this is commonly done based on the intensity of the nitrogen-related one-phonon infrared absorptions and not on calculated values. This method does not represent a precise quantitative approach since the different forms of nitrogen correspond to different concentrations per cm^{-1} of absorption coefficient; since several forms of nitrogen are often present at the same time a more precise simple system cannot be elaborated. The case for hydrogen quantification is similar, with the difference that for hydrogen no quantitative approach exists. In order to have an idea of the hydrogen content the sharp hydrogen-related absorptions in the 2,900–3,400 cm^{-1} domain are used and their intensity measured with reference points in the intrinsic diamond absorptions, such as it is done for nitrogen. Usually the H-related line at 3,107 cm^{-1} is used as a reference, but in some cases others are dominating such as the line at 3,235 cm^{-1} or even the one at 2,973 cm^{-1} for certain type Ib diamonds. Figure 13 shows this simplified system used by the authors that uses maxima and minima of the intrinsic diamond absorption to define this simplified terminology for the hydrogen (Fig. 13a) and nitrogen (Fig. 13b) content.

Photoluminescence spectra were recorded on a home-made system using 405, 473, 532, 635 and 785 nm laser excitations, and a high resolution Echelle spectrograph by Catalina Scientific equipped with a thermoelectrically cooled (to −70 °C) Andor EMCCD camera. The system was set up to record spectra in the range of 350 to 1,150 nm with an average resolution of 0.05 nm; the resolution of the installed Echelle spectrograph can be selected by changing channel slits, aperture stops and the dispersion cassette, and the average resolution ranges from 0.02 nm to 0.15 nm depending on the setup. All photoluminescence spectra were recorded with the diamonds cooled to 77 K by direct immersion in liquid nitrogen. Of the PL spectra recorded with the various laser excitations only the ones recorded using the 405 nm laser are discussed since the observed spectra correspond well to the observed emission colour under the UV excitation of the luminescence microscope, and since a lengthy discussion on the data obtained on the four other lasers would largely exceed the scope of this paper. The data obtained by the other lasers was used to verify that the defined groups indeed were similar defect-wise and that no unexpected differences could be observed.

Results and discussion

General UV luminescence observations

In untreated natural yellow to yellowish orange type Ib diamonds, green is by far the most common UV-excited emission colour, followed by gems with yellow PL. Orange PL is uncommon and finally blue PL is only detected in some rare cases. In "olive" type Ib diamonds orange PL and sectored orange red/green luminescence are seen on occasion, but dominantly green PL is still most common. In brown type Ib diamonds, which are rare, all stones exhibit orange red PL or sectored PL consisting of orange red and green luminescing zones.

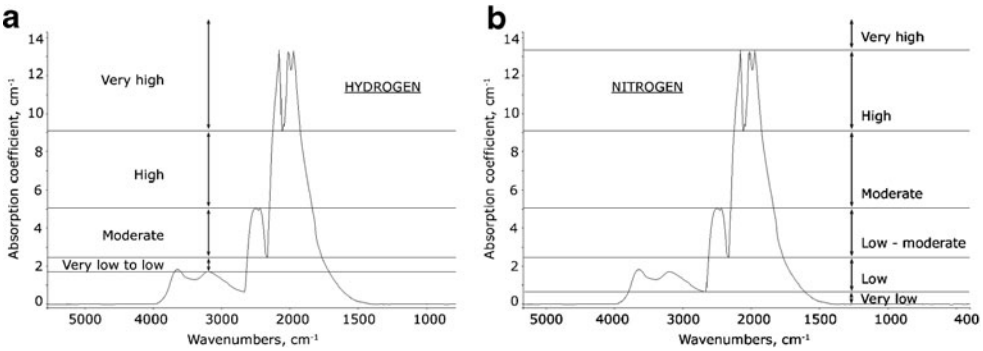

Fig. 13 The simplified system used for hydrogen (**a**) and nitrogen (**b**) content terminology based on the intensity of the nitrogen-related one phonon infrared absorptions and the intensity of the hydrogen-related peaks in the domain around 3,000 and 3,300 cm^{-1}

In contrast to diamonds with FTIR detectable C centre content most stones that only have a Ib character exhibit yellow PL. Such stones can also commonly show some blue PL, usually distributed as distinct blue luminescent zoning.

Correlating FTIR, 405 nm PL spectra and luminescence imaging of type Ib diamonds

Green PL All yellow to yellowish/brownish orange diamonds that had a low to moderate nitrogen content (22 to 130 ppm total nitrogen [A + C + X centre] with 17 to 72 ppm of C centres) and that were dominantly type Ib with minor A and minor Y centre content (Fig. 14a) exhibited extremely faint to medium green luminescence under the intense broadband UV excitation. This luminescence was always present as green, sharp bands following {111} planes (Fig. 14b). This green PL is caused by the H3 defect, as can be seen from the PL spectrum in Fig. 14b. The H3 defect distributed within this so-called "graining" along {111} planes is associated with post-growth plastic deformation. Vacancies created when lattice bonds rupture via dislocations introduced by plastic deformation are thought to form roughly spherical aggregates consisting of a large quantity of vacancies, the so-called vacancy clusters (Fujita et al. 2009). During this process part of the vacancies are captured by A centres to form H3 centres and, as a consequence, green PL. The "strain" (anomalous double refringence) along the green PL bands is clearly seen between crossed polarizing filters. Only very few dominantly type Ib diamonds were found to be of a pure and bright yellow colour, the vast majority of such diamonds exhibits a yellow body colour that is more or less modified by brown and/or orange. The PL features observed in these diamonds clearly follow a regular octahedral growth pattern.

The most saturated and pure yellow diamonds—so-called "canary yellow diamonds"—were found to be dominantly type IaA with minor C centre content instead of truly type Ib as it is claimed so frequently in the literature (see e.g. Breeding and Shigley 2011). These diamonds exhibit all very similar spectral and optical properties: they all have a very high nitrogen, and a moderate to very high hydrogen content (Fig. 15a). The total nitrogen content was determined to range from 870 to 1,902 ppm with a C centre content between 6.6 and 64 ppm. Such stones all exhibit faint to strong yellowish

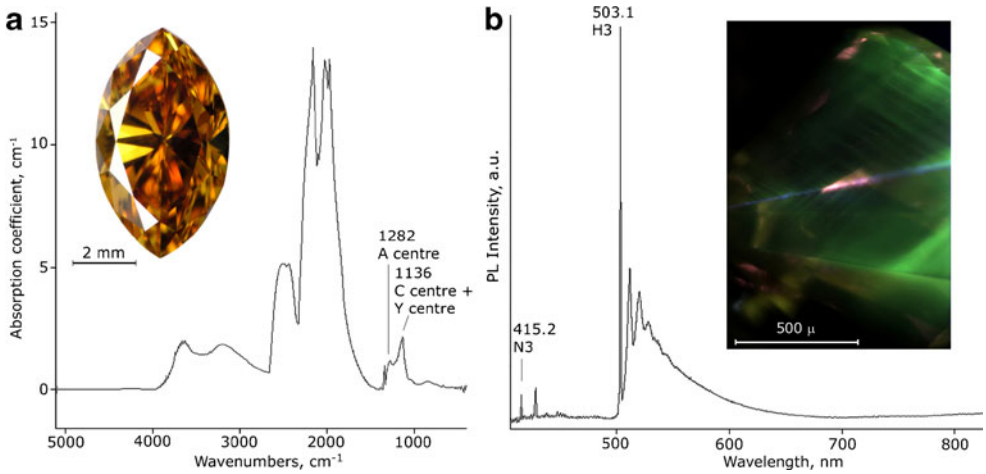

Fig. 14 The infrared spectrum, PL spectrum (405 nm laser excitation) and broadband UV excited luminescence image of a 0.63 ct natural deep yellow orange type Ib diamond (Sample GOD26; **a**). Such diamonds generally show weak to very weak H3 PL, distributed as parallel bands along octahedral slip planes (so-called "graining") which originates from post-growth plastic deformation (**b**). In dominantly type Ib diamonds of yellow to orange colour this "simple" green H3 emission is the most commonly observed PL

green PL that shows distinctly different distribution from the previously described graining: they often show undulating lines arranged to form geometric patterns such as "Mercedes star" and more rarely "snow flake" patterns (Fig. 15b).

Photoluminescence spectroscopy has shown that this specific yellowish green PL is caused by the broad band associated with the S1, S2 and S3 centres (ZPL at 503.5, 510.7 [S1 α and S1 β], 488.9 and 496.6 nm respectively) which is centred at approximately 545 nm (see again Fig. 15b). The S3 centre is believed to be a nickel-nitrogen based defect. (Nadolinny and Yelisseyev 1994).

From analyses of rough diamonds included in this study it was found that only re-entrant cube diamonds exhibit the properties shown by the facetted bright yellow diamonds like the one shown in Fig. 15a. The uncommon geometrical luminescence distribution seen in the nine rough samples that can also be seen in practically all facetted yellowish green luminescing samples included in this study is a strong indicator that such properties are restricted to re-entrant cube diamonds; these are diamonds of mixed, simultaneous, octahedral and cuboid growth (Welbourn et al. 1989). In large parcels of vivid yellow diamonds analysed during this study it was found that more than 70 % of the diamonds were of this specific type. The mixed habit growth these diamonds have experienced has been associated with unusually high nickel and hydrogen contents in diamond (Lang et al. 2004).

Orange red PL Only very few samples of natural type Ib diamonds with orange red PL were found in the large quantities of diamonds tested by luminescence microscopy. Such luminescence was restricted to the very rare brown type Ib diamonds (Fig. 16a). These diamonds are of a medium brown colour, with low saturation, in contrast to the deep brown yellow type Ib stones that occur more frequently, which are dark and saturated.

Infrared spectroscopic analysis of such stones has shown that they are generally pure or nearly pure type Ib diamonds with very low nitrogen concentrations, lacking the Y centre and hydrogen absorptions. (Fig. 16a); the samples studied contained from about 5 to 10 ppm of nitrogen only. The infrared spectra of all of them exhibited strong type Ib related amber centre absorption at 4,110 cm^{-1} (Hainschwang 2003; Massi et al. 2005). These diamonds, together with the "olive" type Ib diamonds are—with exception of type II diamonds—the only natural diamonds we know of in which hydrogen is undetectable by infrared spectroscopy. The orange red PL, which must be covered separately from the more common orange PL, was shown to be caused by the NV^0 centre only (Fig. 16b), since the NV^- centre is very inefficiently excited by UV and blue light (Iakoubovskii et al. 2000).

Together with "olive" type Ib diamonds the brown coloured type Ib diamonds have by far the highest NV centre defect density of all type Ib diamonds. The presence of brown graining, strong strain under crossed polarizing filters, and strong amber centre absorption in the infrared spectrum together with the intense nitrogen vacancy centres points towards events of strong post-growth plastic deformation for the group of type Ib brown diamonds.

There appears to be a link between the nitrogen content and the presence or absence of the Y centre with the NV centre and vacancy cluster defect density. The diamonds with the lowest nitrogen content and lacking the Y centre exhibit spectra with the most intense NV^0 and NV^- emissions and in consequence distinct orange red PL. Hence it seems that very low nitrogen-containing, pure type Ib diamonds are most efficiently affected by deformation and that

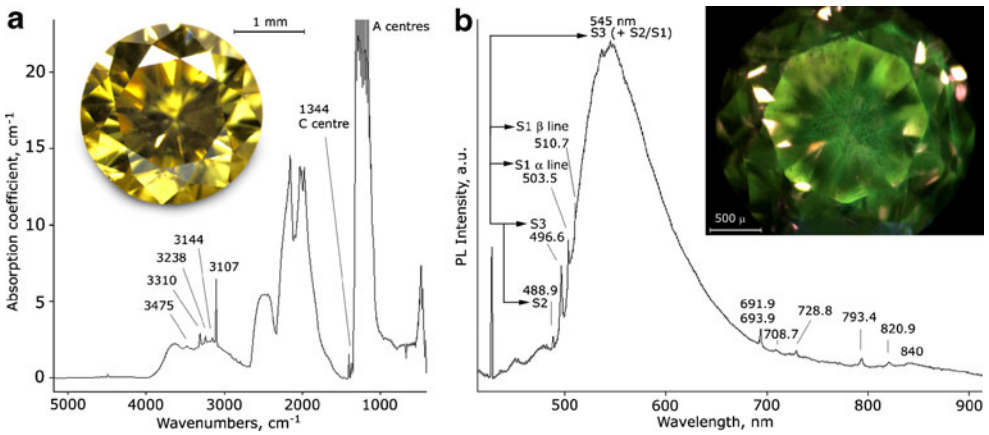

Fig. 15 The infrared spectrum, PL spectrum (405 nm laser excitation) and broadband UV excited luminescence image of a 0.15 ct natural vivid yellow diamond featured in **a**. This stone represents an example of re-entrant cube diamonds, which are always high nitrogen- and hydrogen-containing type IaA> > Ib (**a**). This very specific type of diamond generally exhibits the most saturated and pure yellow colours of all C-centre containing diamonds. They always exhibit an apple green PL that is caused by the S1, S2 and S3 centres (**b**); the broad and intense vibronic band of these centres is found at approximately 545 nm, thus in the green spectral domain. Sometimes the PL can have a beautiful geometrical pattern as in this case, where it takes the shape of a snowflake, hence an apparent 6 fold symmetry

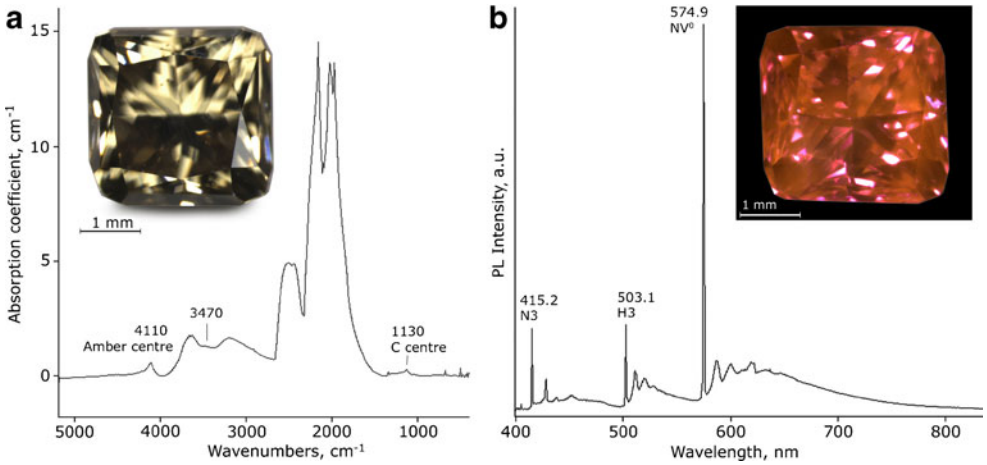

Fig. 16 The infrared spectrum, PL spectrum (405 nm laser excitation) and broadband-UV excited luminescence image of a 0.15 ct natural fancy light brown type Ib diamond (Sample TH 2.210; featured top left). This very rare colour variety of type Ib diamond is often a nearly pure type Ib, with generally very low nitrogen (**a**). The strong amber centre absorption is characteristic for these stones and also the distinct orange red PL that results from the NV^0 defect (**b**)

the defect production is distinctly higher than for mixed C centre/Y centre diamonds.

Mixed green–orange red PL The PL of type Ib diamonds can be very inhomogeneously distributed and sectored luminescence is a relatively common phenomenon. The most characteristic examples are represented by "olive" and some brown diamonds. The "olive" diamonds commonly exhibit sectored green and orange red PL. The sectors can be alternating parallel green and orange-red luminescing lamellae or distinct irregularly shaped sectors that may be distributed symmetrically according to growth sectors (Fig. 17b).

The two emissions were shown to be H3 and the NV^0 centre by PL spectroscopy (see again Fig. 17b). Most olive type Ib diamonds have very similar spectroscopic and optical properties to type Ib brown diamonds; their infrared spectra always show distinct type Ib related amber centre absorption, lack hydrogen absorptions and generally demonstrate low to very low nitrogen content; such diamonds are often nearly pure type Ib diamonds lacking the Y centre, and more rarely type IaA > Ib lacking the Y centre (Fig. 17a). As for the brown type Ib diamonds their properties point towards events of strong post-growth plastic deformation and in consequence they are generally as rich in defects as type Ib brown diamonds.

Orange PL Some type Ib diamonds show orange PL with a noticeably different hue than the orange red NV^0 centre related PL. This luminescence can be seen in type Ib diamonds that contain significant concentrations of Y centres or diamonds that exhibit infrared spectra with very dominant Y centre absorption (Fig. 18a).

Typically such stones range from bright yellow to brown yellow and their PL spectra demonstrate that the orange luminescence is caused by a very broad, composite and asymetric emission band with a large quantity of sharp PL peaks overlaying it (Fig. 18b). While the spectrum in Fig. 18b with the two broad band maxima at approximately 555 nm and 650 nm is the most frequently observed type of PL, we have seen several differently shaped broad band emissions that also result in orange PL. The broad band at approximately 555 nm is caused by the S1 and S3 centres. From the sharp emissions not very many have been understood so far, with the notable exceptions of the N3, H3 and NV^0 centres and the

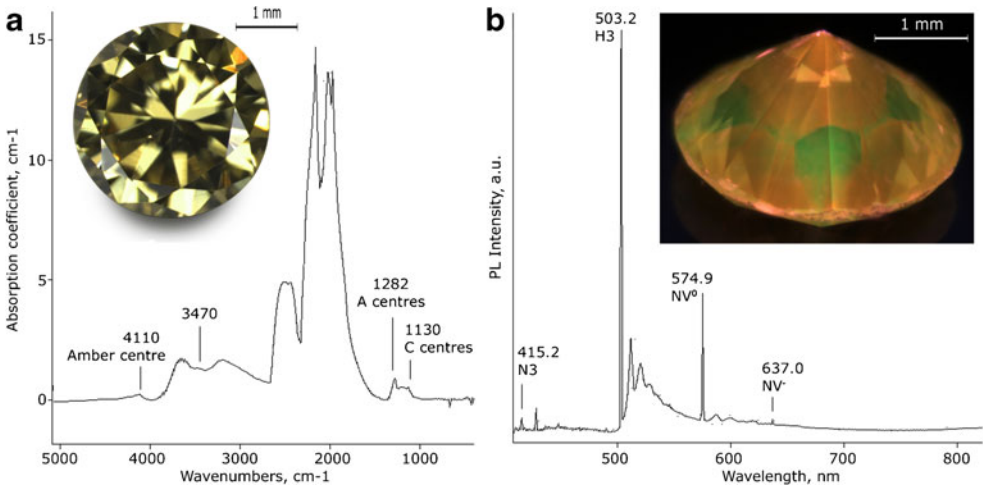

Fig. 17 The infrared spectrum, PL spectrum (405 nm laser excitation) and broadband-UV excited luminescence image of a 0.10 ct natural olive low nitrogen type IaA > Ib diamond (Sample TH 2.187, **a**). Many of the olive coloured type Ib diamonds show a strong amber centre infrared absorption and exhibit mixed PL from H3 and NV^0 defects. In consequence their PL is mixed green–orange red, generally strongly zones such as in this case (**b**)

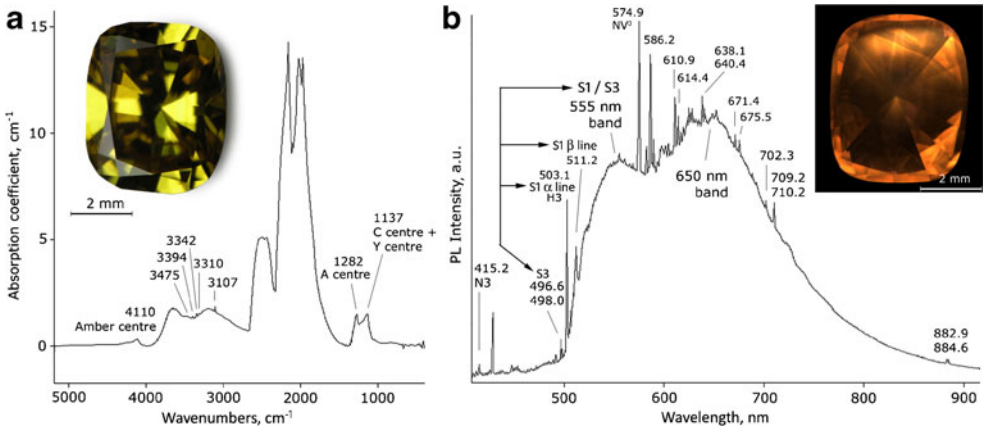

Fig. 18 The infrared spectrum, PL spectrum (405 nm laser) and broadband-UV excited luminescence image of a 0.45 ct natural deep greenish brownish yellow type Ib diamond (sample oliveint006, **a**). This stone represents a group that ranges from yellow to olive in colour and that always exhibits orange PL from 2 very broad bands centred around 555 nm and at 645 to 650 nm of which the 555 nm band is caused by the S1 and S3 centres. Overlaid on these broad bands are usually distinct H3 (ZPL partially hidden by the S1 α line) and NV^0 centre emissions and a large quantity of sharp emissions, of which a few are known to be nickel related (e.g. the 882.9/884.6 nm doublet) (**b**)

882.9/884.6 nm doublet which is known to be nickel-related (Nazaré et al. 1989);

Yellow PL Yellow luminescence is relatively common in C centre containing diamonds but has not yet been seen in any dominantly Ib diamond. This PL occurs most commonly in diamonds that exhibit dominant Y centre absorption in their infrared spectrum (Fig. 19a) and in relatively low nitrogen type IaA>>Ib diamonds of mixed cuboid/octahedral growth that often have a somewhat elevated hydrogen content (Fig. 20a). Additionally the yellow emission was found to be the most frequent PL in diamonds that exhibit a type Ib character such as chameleon diamonds and diamonds coloured by the 480 nm absorption. Yellow PL in type Ib diamonds was spectroscopically defined as complex, asymmetric broad band emission with an apparent maximum peaking at approximately 560 to 580 nm, and many sharp lines overlaid (Figs. 19b and 20b). For some diamonds additional broad bands were found in their spectra, such as the weaker band centred at approximately 690 nm seen in Fig. 19b. Strong 692.0 nm emission in the spectra of some diamonds causes an additional band centred at around 720 nm (see again Fig. 19b). The main band at 560 to 580 nm is caused by the S1 and/or the S3 centre.

The broad band observed in the spectra of the yellow luminescent mixed growth diamonds is caused by the S1 centre, which consists of two zero phonon lines at 503.3 and 510.6 nm and a broad asymmetric band centred at approximately 570 nm

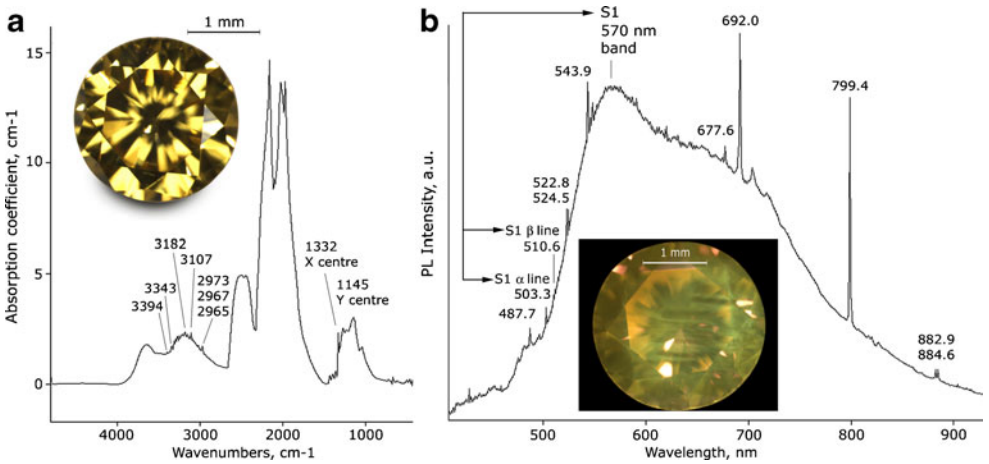

Fig. 19 The infrared spectrum, PL spectrum (405 nm laser excitation) and broadband-UV excited luminescence image of a 0.08 ct natural vivid yellow "Y centre" diamond (sample TH 2.239, **a**). The PL originates from a complex broad band emission that consists of several components, with an apparent maximum centred at 570 nm (**b**); the strongest band at 570 nm is caused by the S1 centre. Overlaid on these broad bands are a large quantity of sharp emissions of which some are known to be nickel-related (e.g. the 882.9/884.6 nm doublet); in contrast to other diamonds with spectra exhibiting broad band emission the spectra of near-pure Y centre diamonds practically lack the nitrogen vacancy defects such as H3 and NV^0

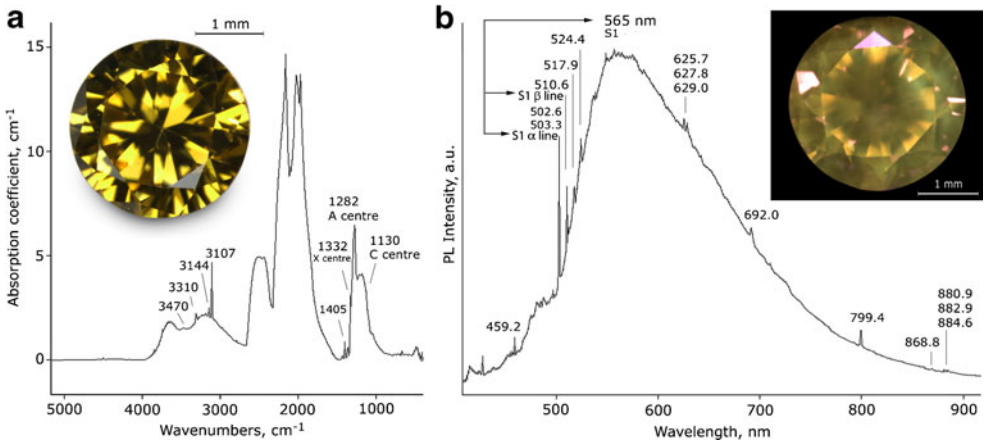

Fig. 20 The infrared spectrum, PL spectrum (405 nm laser excitation) and broadband-UV excited luminescence image of a 0.07 ct natural vivid yellow type IaA> > Ib diamond (sample TH 2.178-2, **a**). The PL originates from a broad band emission with an apparent maximum at approximately 570 nm caused by the S1 centre with ZPL's at 503.3 and 510.6 (**b**). Overlaid on these broad bands are a large quantity of sharp emission of which some are known to be nickel-related (e.g. the 882.9/884.6 nm doublet)

(Pereira et al. 1984) (Fig. 20b). Of the sharp emissions seen in all diamonds with yellow PL, many have not been attributed, but some lines have been assigned to nickel-related defects, such as the bands at 799.4 nm and the doublet at 882.9/884.6 nm.

Conclusions

Luminescence imaging and spectroscopy are very useful tools to characterize type Ib diamonds. Using intense UV excitation the luminescence colour and distribution observed via a luminescence microscope can give important clues on the characteristics of C centre containing diamonds. The nature of the observed PL can then be verified by photoluminescence spectroscopy. Using a laser wavelength close to the excitation used for imaging, a good match of the PL spectrum and the UV excited PL image is gained. The main emissions observed in such a PL spectrum correspond well to the colours seen through the luminescence microscope.

For natural type Ib diamonds, the combination of these two analytical methods, together with infrared spectroscopy, helps classifying this inhomogeneous group of diamonds into distinct categories. Six classes are proposed in Table 1. This classification does not include diamonds with just a type Ib character.

Looking at the data of this group of diamonds one can see that the type Ib diamonds with the lowest C centre nitrogen content exhibited the highest defect density and the most intense N3, H3 and NV^0 PL. By contrast, type Ib diamonds with much higher C centre content have much weaker PL and clearly a lower N3, H3 and NV^0 defect density. As a consequence the stones with low to very low C centre content are not yellow or yellowish orange but olive to brown due to their numerous deformation-related defects. Interestingly, within the group of dominant type Ib diamonds, these strongly deformed low nitrogen Ib diamonds are the only ones that show no Y centre component in their infrared spectrum.

This study shows that a very complex group of diamonds can be categorized into sub-groups based on relatively few criteria; for practical uses this classification of type Ib diamonds helps selecting specific sub-types of diamonds from large parcels rapidly, and furthermore is a good tool to efficiently distinguish treated and synthetic diamonds in such parcels.

Final remarks

Luminescence studies of gem materials have considerably increased since the mid-1990s due to a number of factors. First, a number of luminescence imaging devices have appeared, starting in 1996 with the DTC DiamondView, confronted to the necessity of separating quickly natural from synthetic diamond. They take advantage of the intrinsic great sensitivity of photoluminescence, provided that an adequate excitation source is found. Imaging provides a view of the internal morphology of the gem, that is its growth history. Thus it is instrumental in separating natural from synthetics, as often their growth sectors are different, and this is particularly true for diamond. Furthermore, even relatively simple luminescence imagery visualizes emissions that are treatment-related. Several procedures have been developed for emerald and corundum, which are very helpful to quantify the importance of impregnation in a transparent material.

Secondly, starting in 1999, gem labs need to have a luminescence set-up to identify HPHT-treated diamonds. Generally Raman system with several lasers are used, at liquid nitrogen temperature. Once the system works effectively, it is tempting to develop other applications. Gemmologically useful tests

Table 1 The proposed classification of the group of C centre containing diamonds, excluding diamonds with a type Ib character

No	Class	Colour(s)	Type N content	Y centre content	H content	Dominant PL defect(s) (405 nm excitation)	Typical luminescence, intensity[a]
1	Typical Ib	Orangey yellow to yellowish orange, often brownish	Ib to IaA > Ib Low to moderate N	Very low to low	Very low to low	H3	Green, in fine graining bands along [111], very weak to weak
2	Deformed Ib	"Olive" to brown	Ib to IaA > Ib, very low to low N	None	None	N3, H3, NV^0	Orange-red, green or green with orange red sectors. Green usually in fine graining bands along [111], medium to strong
3	Low nitrogen IaA> > Ib	Yellow to orange	IaA> > Ib Low to moderate N	N.d. to moderate	Very low to moderate	S1 centre (570 nm band)	Yellow, very weak to medium
4	Re-entrant cube	Yellow to orangey yellow	IaA> > Ib Very high N	N.d.	Moderate to very high	S1, S2, S3, (545 nm band), 793.4 nm	Yellowish green, often exhibiting geometric growth pattern. Very weak to medium
5	Y centre	Yellow to brownish yellow to orange yellow	Y centres > or > > Ib Low to very low N	High to very high	Low to moderate	Broad band PL in part caused by S1 and/or S3, often 692.0, 799.4 nm, 905 nm	Yellow to orange, medium to very strong
6	High C center concentration	Dark brown yellow to dark brown orange	Various with high to very high C centre content	N.d.	Low to moderate	Broad band PL, H3	White to yellow, green, inhomogeneous, very weak.

[a] observed using 300–410 nm broadband excitation using a xenon based luminescence microscope

N.d. non determinable because of restraints from overlaying absorption bands

have appeared for corundum and spinel in particular. The example of type Ib diamonds, which represent a very small subsection of the lucrative coloured diamonds industry, illustrates the great usefulness of combined imaging and spectroscopy to quickly classify and identify gem materials.

Even if luminescence spectroscopy has proven a very fertile ground for gemmological applications, the use of predominantly laser excitation has limited its reach to strictly emission spectra. Excitation spectra, fundamental to draw information on the cause of emission, would provide a true understanding of the physics behind the pretty colours, and a comprehension of what happens at the atomic scale in treatment processes for example. Time-resolved spectroscopy, otherwise booming in other fields of physics, has so far provided little clues of gemmological significance, but should nevertheless be kept in mind for the most subtle gem identification challenges. Therefore, there is likely a very bright future for a larger variety of luminescence-based techniques applied to gems, as long as they remain non-destructive and do not alter the visual appearance of the gem under study.

Acknowledgments The authors would like to thank Wendy and Burt Beardsley of Catalina Scientific for all their assistance with the implementation of the echelle spectrograph into our photoluminscence system and the two anonymous reviewers for the constructive comments to make the publication of this paper possible.

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