The detection of colour-enhanced and synthetic gem diamonds by optical spectroscopy

Alan T. Collins*

Wheatstone Physics Laboratory, King’s College London, Strand, London WC2R 2LS, UK

Received 9 September 2002

Abstract

In this article, the spectroscopic methods used to assess gem-quality diamonds are reviewed. From such measurements it is possible to determine, in the majority of cases, whether the colour of a stone is natural, or has been changed by some form of treatment—either HPHT processing, radiation damage and annealing, or a combination of both methods. Methods used to identify synthetic diamonds are also covered briefly.

Keywords: Coloured diamonds; Colour enhancement; HPHT synthetic diamonds; Optical spectroscopy

1. Introduction

Spectroscopic measurements, carried out principally by gem-testing laboratories, can determine whether the colour of a diamond gemstone is natural, or has been changed by some form of ‘treatment.’ Increasing quantities of diamonds grown by high pressure, high temperature (HPHT) synthesis, are now finding their way into the gem market, and may be differentiated from natural diamonds. It will become evident that fundamental research on the optical properties of defects in diamond, carried out for more than half a century, underpins the work of laboratories assessing diamond gemstones.

The colour of a faceted diamond gemstone is one of four important parameters that determine its market value. The majority of mined diamonds are brown in colour [1] and most of these are unsuitable for use as gemstones. In near-colourless natural gem diamonds, the N3 defect is the most commonly occurring colour centre [2]. Fig. 1 shows the N3 absorption band which has a zero-phonon line (ZPL) at 415.2 nm; most of the vibronic band lies in the near-ultraviolet spectral region. The weak broad peak at 478 nm, labelled N2, and additional structure between 478 and 415 nm, are associated with additional transitions at the N3 centre and are primarily responsible for the colour observed. Diamonds having this characteristic absorption are often referred to as cape stones. As the concentration of N3 centres increases, the diamond initially acquires an insipid yellow tint and the market value drops considerably below that of an otherwise identical colourless diamond [3]. However, diamonds containing high concentrations of N3 centres can have a pronounced or ‘fancy’ yellow colour, which, because of their rarity, makes them more valuable than tinted yellow stones. As will be seen in Section 3.1, a tinted yellow diamond can be made more yellow (and potentially more valuable) by using radiation damage and annealing. By deepening the colour, this process can also make flaws, such as small inclusions, become less obvious. Provided the customer is informed, it is entirely legitimate to market diamonds that have been artificially coloured, but problems arise when attempts are made fraudulently to pass off, as naturally coloured, diamonds that have been treated.

Natural diamonds with other colours—red, orange, green, blue, violet—are also found occasionally and in recent years have been greatly prized by collectors [4,5]. Here, too, several of the colours can be simulated by suitable treatments.

Until approximately 4 years ago, it had generally been thought that permanent colour changes to natural diamonds (by, for example, radiation damage and

*Corresponding author. Tel.: +44-20-7848-2584; fax: +44-20-7848-2420.
E-mail address: Alan.Collins@kcl.ac.uk (A.T. Collins).
Overseas Ltd (existing colour annealing, see Section 3.1) can only add to the pre-existing colour [6]. However, in March 1999 Pegasus Overseas Ltd (POL) of Antwerp, Belgium, a subsidiary of Lazare Kaplan International, announced that they had begun marketing colour-enhanced diamonds [7]. The diamonds had been processed by General Electric (GE), and it was generally assumed, and subsequently confirmed [8] that the process involved treatment at high pressure and high temperature (HPHT). Information circulating in the trade [9,10] indicated that the starting material was brown type IIa diamond (diamond types will be discussed in Section 2) and that the GE process substantially reduced the brown colour. The processed diamonds are sometimes referred to as ‘GE POL’ stones.

Subsequently Novatek, which manufactures high-pressure presses used in diamond synthesis, announced that they had also successfully changed the colours of natural brown diamonds [11]. They did not pre-select the diamond type, and many of the stones they processed changed from brown to a more attractive yellow/green. Similar colour changes have been produced by research laboratories in Russia, and may have been for some time [12,13].

If an unattractive brown diamond is made almost colourless (in the case of type IaA material) or converted to a fancy yellow/green colour with type Ia specimens, the value of the stone can be substantially increased. Once again, it is important that gem testing laboratories are able to detect those diamonds that have been colour-enhanced by HPHT processing.

2. Defects in diamond

Diamonds that absorb in the visible region, and are, therefore, coloured, do so because they contain defects. These may be ‘point defects’ which have dimensions comparable with the distance between the carbon atoms in the diamond, or they may be ‘extended defects,’ some of which can be sufficiently large to see with an optical microscope. The scientific understanding of point defects is more advanced than that for extended defects, but, even so, is far from comprehensive. What is clear, however, is that nitrogen, which is a very common impurity in diamond, is involved in many of the point defects.

2.1. Nitrogen

Diamonds which contain sufficient nitrogen to produce easily measurable nitrogen-related absorption in the defect-induced one-phonon region are generically known as ‘type I.’ Other diamonds are generically known as ‘type II,’ and it is important to realise that a diamond classified as type II may, nevertheless, contain small concentrations of nitrogen.

The three major forms of nitrogen—isolated substitutional nitrogen (sometimes called the C form), the A aggregate and the B aggregate—giving rise to the diamond types Ib, IaA and IaB, respectively, have been discussed in previous publications [14,15]. Optical transitions at the C form of nitrogen produce absorption at the blue end of the visible spectrum, and this can result in an attractive yellow colour. Occasionally one finds natural diamonds with an absorption spectrum like this, and they are sometimes referred to as canary yellow diamonds. Vacancies can be produced in diamond by radiation damage. Absorption associated with the vacancy in its neutral charge state produces the GR absorption features, with a sharp zero-phonon line at 741 nm (the GR1 line) and a band to shorter wavelengths. This absorption gives the diamond a green or blue/green colour [14,15]. The vacancy becomes mobile on heating the diamond to approximately 800 °C. The trapping of vacancies to produce (N–V)− and (N–V)V in type Ib diamond, H3 [(N–V–N)V] and H2 [(N–V–N)V] in type IaA diamond and H4 in type IaB diamond has also been covered in the above publications [14,15]. Here we use that information to discuss the various natural and treated colours that may be seen in diamond.

2.2. Boron

Natural diamonds in which substitutional boron is the major impurity are extremely rare. These are the type IIb diamonds, and the presence of boron results in optical absorption, which starts at a wavelength of approximately 4 μm in the infrared region and extends into the red region of the visible spectrum. In favourable cases, this absorption gives the diamond an attractive blue colour [15]. Boron also produces some absorption in the defect-induced one-phonon region.

Fig. 1. Absorption spectrum in the visible region of a cape stone, containing the N3 absorption band, recorded with the specimen at 77 K. The spectrum has been offset from zero for clarity, and the long-wavelength region has been expanded by a factor of 10 to show the N2, and related, peaks more clearly.
Fig. 2. Schematic absorption spectra in the visible region of a brown type IIa diamond, (a) before and (b) after HPHT processing. (Redrawn from Ref. [16]).

2.3. Extended defects

An important family of extended defects in diamond is associated with plastic deformation; it appears that in certain stones an external shearing stress has caused some planes of carbon atoms to slip with respect to each other. Brown type IIa diamonds have a featureless absorption [16] which progressively increases from long wavelengths to short wavelengths (Fig. 2a). After HPHT processing, the intensity of this absorption is substantially reduced (Fig. 2b) and the diamond may then be almost colourless. At present it is not known why the plastic deformation produces a brown colour.

Many of the diamonds from the Argyle production in Western Australia show evidence of severe plastic deformation. Most of these (type Ia) specimens are brown, but a few are pink. There is only a subtle difference in the absorption spectra of the brown and pink diamonds, as illustrated in Fig. 3. Both spectra have an absorption, which progressively increases towards shorter wavelengths, a broad band at approximately 560 nm and a small amount of H3 absorption. The spectrum for the pink diamond has rather less of a slope from long to short wavelengths. When the crystals are examined under a microscope it is observed that the colour is not uniform, but is striated with the striations oriented in the direction of slip. These striations are referred to as ‘coloured graining’ in the gem trade [1,4]. Again, it is not known in detail why the plastic deformation in type Ia stones produces coloured diamonds, or why many are brown and some are pink. Indeed, an Argyle diamond has been observed which had three distinct regions—brown, pink and almost colourless [17]. One possibility is that a point defect is also involved, and this is trapped at, or ‘decorates’ the dislocation. An alternative explanation is that the pink colour is associated with small displacements of the planes of carbon atoms and that larger displacements result in a brown colour [18].

We shall not deal with ‘chameleon diamonds’ which change colour from green to yellow, either on heating or being left in the dark for extended periods. Nor shall we discuss the violet and grey colours, which appear to be connected with high concentrations of hydrogen in diamond [4]. There is, at present, no scientific understanding of the defects causing these colours, and there are no documented examples of their being produced artificially.

3. Changing the colour of diamond

Permanent changes in the colour of a diamond may be produced by radiation damage and annealing, or by HPHT processing. (‘Permanent’ should be interpreted as meaning that the colour is not altered by the temperatures used to fashion jewellery, or by illumination with daylight or bright artificial light.) Here we discuss characteristic features, which would enable a gem testing laboratory to differentiate between a naturally coloured and a treated diamond.

3.1. Radiation damage

As noted in Section 2, V0 is the dominant optical centre produced by radiation damage and gives rise to the GR1 absorption which gives the diamond a green or blue/green colour. Many uncut natural diamonds have a green ‘skin’ which has been produced by alpha particles, but this skin is only a few μm deep. Diamonds with a naturally produced absorption due to vacancies throughout their bulk are extremely rare. The Dresden Green is one example [19], but the intensity of the band is extremely low: at the peak of the band near 625 nm...
the absorption coefficient is no more than 0.2 cm$^{-1}$ above the background. The diamond only appears to have a green tint by virtue of its large size (40.7 carats). The shape of the absorption spectrum of the Dresden Green differs in no perceptible way from the absorption spectra of diamonds that have been artificially coloured using radiation damage by high-energy electrons. Consequently gem testing laboratories are reluctant to issue origin-of-colour certificates for green diamonds containing the GR1 absorption. However, if a diamond which exhibits a large GR1 absorption coefficient at 625 nm, compared with the Dresden Green, it is probably fairly safe to regard it as a 'treated green.'

Radiation damage is most frequently used with annealing (at approx. 800 °C) to increase the depth of yellow colour in a tinted yellow type Ia diamond. The major defect centres produced are H3, due to the trapping of a vacancy at the A aggregate of nitrogen, and H4 due to the trapping of a vacancy at the B aggregate. In diamonds containing both A and B nitrogen, the concentrations (indicated by square brackets) of the different centres follow the relationship [20].

$$[\text{H3}] / [\text{H4}] \propto [A] / [B]$$  \hspace{1cm} (1)

A typical spectrum for an irradiated and annealed type IaA diamond is shown in Fig. 4. We note particularly that, in addition to the H3 band, the diamond also has an absorption line at 594 nm. The defect responsible for this absorption line is not known, but it is produced by irradiation damage and annealing in all nitrogen-containing diamonds, and reaches a maximum intensity on annealing to approximately 800 °C [3].

Although the yellow colour of the diamond observed by eye may appear similar to that of a cape yellow diamond, the spectrum is clearly different to that in Fig. 1. However, natural diamonds in which the colour is principally caused by absorption in the H3 band are encountered occasionally [3], and further measurements may be required to be certain that the colour is artificial.

In the vast majority of naturally-coloured diamonds containing H3 absorption the 594 nm line is absent [3]. Furthermore, naturally coloured diamonds never show more than a trace of absorption in the H4 band, even when most of the nitrogen is present as B aggregates. This contrasts with the behaviour of artificially coloured diamonds summarised in Eq. (1). An understanding of this difference has been reached by high-temperature annealing measurements of artificially coloured diamonds [21,22]. When a diamond containing nitrogen exclusively in the B form is irradiated and annealed at 800 °C, the H4 band is the dominant absorption in the visible region. When the diamond is annealed at 1600 °C the H4 absorption is substantially reduced and some H3 absorption is produced, showing that the H4 centre (4 N atoms and two vacancies) is breaking up to produce some H3 centres (2 N atoms and one vacancy). The higher stability of the H3 centre over the H4 centre explains why the former dominates in natural diamonds, which have been annealed more gradually over millions of years.

Further important information comes from diamonds containing nitrogen exclusively in the A form. As the annealing temperature is increased from 800 to 1600 °C, initially the 594 nm line is annealed out, and as it is destroyed an absorption line at 2024 nm known as H1b is produced [3]. Then the H1b line anneals out, and, as it does so, a substantial amount of H2 absorption is produced [22]. High-temperature annealing measure-
ments are continuing in the author’s laboratory, and Fig. 5 shows the spectrum of an irradiated type IaA diamond after annealing at 1650 °C. The combined H2 and H3 absorption can give the diamond an attractive yellow/green colour.

When the 594 nm line is annealed out in a type IaB diamond an absorption line at 1934 nm known as H1c is produced [3]; it, too, anneals out by 1600 °C without apparently producing another colour centre [22].

There are no reports of natural diamonds containing H1b or H1c absorption, or substantial H2 absorption, and these investigations allow us to conclude that a yellow, or yellow/green diamond which exhibits significant absorption in the H4, H2, H1b, H1c or 594 nm bands has almost certainly been coloured artificially. (We shall see below that H2 absorption may also be produced by HPHT annealing of brown type Ia diamonds.)

When a diamond is heavily irradiated and then annealed at 800 °C, the absorption in the H3 and/or H4 bands may be so strong that the diamond is virtually opaque at wavelengths below approximately 500 nm [23]. The resultant colour can be similar to the very rare natural orange coloured diamonds in which the colour is produced by a broad absorption band peaking at approximately 480 nm [4,23]. Spectroscopically, however, the artificially and naturally coloured diamonds are easily distinguished.

Pink diamonds can be produced by radiation damage and annealing of type Ib specimens with relatively low nitrogen concentrations. The colour is similar to that of the natural pink diamonds, but the absorption spectrum of the (N–V)− centre, with a sharp ZPL at 637 nm, is quite unlike the spectrum of the natural pink diamonds, shown in Fig. 3b.

3.2. HPHT processing

Colour enhancement of diamond using HPHT processing has been extensively covered in the literature [7–10,14–16,24–28] and here we summarise some important issues.

3.2.1. Type Ia brown diamonds

When type Ia brown diamonds are subjected to HPHT processing, at approximately 1800 °C, luminescence spectroscopy shows that the emission system with a ZPL at 490.7 nm, that originates from the slip traces, is substantially reduced in intensity: in addition the N3 and H3 luminescence bands are considerably increased in intensity. Absorption spectroscopy shows that the brown component has been reduced, and that there is a considerable increase in the H3 absorption, and some increase in the N3 absorption.

The conclusion reached from these observations is that a partial healing of the plastic deformation is occurring (as evidenced from the reduction in the luminescence from the slip traces) and that this releases vacancies which are trapped by the nitrogen to form H3 centres and N3 centres. Although most of the nitrogen may be in the B form, no H4 centres are formed for the reasons noted in Section 3.1. The healing of the plastic deformation also reduces the brown colour, although the mechanism for this is not understood.

When higher annealing temperatures are used (2000–2300 °C), there is, in addition to the above changes, a further reduction in the brown component of the colour, substantial absorption is produced in the H2 band, and a small amount of absorption at 637 nm due to (N−V)− is evident, as shown in Fig. 6. Such diamonds can have a vivid yellow/green colour. In addition, because the concentration of A-nitrogen in type Ia brown diamonds is often low, the end product can exhibit strong green (H3) luminescence when excited with long-wave ultraviolet, or even in daylight. (Higher concentrations of nitrogen in the A form severely quench the H3 luminescence [29].) The interpretation of the annealing phenomena is that, at these higher temperatures, some dissociation of the aggregated nitrogen occurs, producing single nitrogen (which is a donor). Those (N−V−N)0 centres (i.e. H3) close to a nitrogen donor will be charge-compensated to form (N−V−N)− centres (i.e. H2) and some single nitrogen atoms capture a vacancy to produce (N−V)− centres.

Diamonds with intense H3 absorption are extremely rare in nature, and natural diamonds with spectra like that in Fig. 6 have never been observed. It is, therefore, straightforward for a gem testing laboratory to show that these intense fancy colours have been produced artificially.
It is interesting that the absorption spectra in Figs. 5 and 6 are very similar, but the H2 centres are believed to be produced by two quite different mechanisms.

### 3.2.2. Type Ia diamonds with negligible plastic deformation

When a diamond containing some nitrogen as A aggregates, but negligible plastic deformation, is annealed under conditions that some of the A-nitrogen dissociates, the absorption produced by the resultant single nitrogen will give the processed stone a yellow colour. When the processing conditions are optimised, a colour similar to the canary yellow colour of the rare natural type Ib diamonds can be achieved [14]. The appearance of the treated diamond can be much more attractive than the starting material if this had a poor colour grade or a low clarity grade.

A poor colour grade in the starting material could arise because of the presence of N3 absorption, as with the diamond studied by Collins et al. [14]. If the present understanding of the aggregation of nitrogen is correct, then it would not be expected that a natural diamond would exhibit absorption in the visible region characteristic of a type Ib diamond, but have an infrared spectrum showing that the nitrogen is predominantly present as A and B aggregates. Any such diamonds encountered in the gem trade should, therefore, be subjected to further examination to see if there is evidence that the specimens have been processed at HPHT.

### 3.2.3. Type IIa brown diamonds

Currently, the diamonds for which it is most difficult to establish the origin of the colour are the brown type IIa diamonds that have been converted to almost colourless stones by HPHT processing. However, many diamonds, classified as type IIa, contain a small concentration of nitrogen, often predominantly in the B-form. When such a diamond is subjected to HPHT annealing, some of the aggregated nitrogen decomposes to form single nitrogen. For diamonds that have a faint yellow colour after HPHT treatment it is often possible to detect the 1344 cm⁻¹ infrared absorption and the 270 nm broad peak, both characteristic of single nitrogen. (The absorption spectrum for a low-nitrogen synthetic diamond, recorded with the specimen at 77 K. The broad, nitrogen-related peak at 270 nm is clearly visible.

Fig. 7. Absorption spectrum in the visible and ultraviolet regions of a low-nitrogen synthetic diamond, recorded with the specimen at 77 K. The broad, nitrogen-related peak at 270 nm is clearly visible.

is much weaker than the 575 nm line. The HPHT processing increases the concentration of nitrogen donors, and in the majority of specimens [(N–V)⁻] > [(N–V)³⁺]; consequently the 637 nm line dominates. Using criteria like this, De Beers have produced an instrument, which refers for further checking virtually all HPHT-processed diamonds; however, it also refers approximately 25% of type IIa diamonds that have not been HPHT-processed, so additional visual inspection is required [30]. (Such an inspection would examine cracks and internal inclusions, which are more likely to be graphitised in HPHT-treated diamonds than in unprocessed specimens.) At the present state of knowledge, most HPHT-treated colourless and near-colourless type IIa diamonds can be detected, and occasionally a diamond that was colourless or near-colourless when mined will be wrongly classified as having been treated [30].

### 4. Synthetic diamonds

Type Ib diamonds are rare in nature because most specimens experience conditions of temperature, pressure and time, which causes the nitrogen to aggregate. However, nitrogen appears in the isolated substitutional form in the majority of diamonds produced by HPHT synthesis because of the relatively short growth time. Gem quality synthetic diamonds have recently been introduced to the market [2,31], and can have an attractive yellow colour with optical spectra very similar to those of natural type Ib diamonds.

The nitrogen concentration of synthetic diamonds can be reduced by adding nitrogen getters to the growth capsule. Such specimens can be almost colourless, but small concentrations (a few ppm) of single nitrogen give an unmistakable signature in the ultraviolet absorption spectrum with a maximum near 270 nm (Fig. 7).
Gem-quality diamonds, with a sufficiently low nitrogen concentration that they appear almost colourless, are, however, much more difficult to grow than those ungettered specimens containing typical concentrations (approx. 200 ppm) of nitrogen which produce the characteristic yellow colour [31].

An alternative method of creating a near-colourless synthetic diamond is to start with ungettered material, and convert most of the nitrogen to the A-aggregate form by prolonged HPHT annealing at approximately 1800 °C. This technique, however, does not produce any N3 absorption; as noted in Section 1, this absorption system is very common in natural diamonds. Test instruments designed to look for synthetic diamonds [2], therefore, refer all diamonds that have no N3 absorption, and this criterion will identify both low-nitrogen and HPHT-annealed high-nitrogen diamonds. Further tests on the diamonds with no N3 absorption are then required. A major difference between natural and HPHT synthetic diamonds is that the synthetic diamonds exhibit mixed growth sectors (in general {100}, {111} and {110} sectors are common, and {113} and {115} may also be present), whereas natural diamond exhibits almost exclusively octahedral growth. When excited with short-wave ultraviolet light the different growth sectors become visible because of their different luminescence characteristics [2]. In addition, low-nitrogen synthetic diamonds exhibit a very long-lived phosphorescence, which is not observed in natural diamonds [2]. Further evidence, if needed, can be provided by luminescence spectroscopy. Synthetic diamonds are frequently grown using nickel–iron or cobalt–iron alloys, and there are many luminescence systems associated with Ni and Co in diamond [32]. Ni-related luminescence is very rare in natural diamond, and there are no reports of luminescence associated with Co in natural specimens. With this wide range of techniques available it is not, in general, difficult to differentiate natural and synthetic diamonds.

Because of the difficulty in producing near-colourless gem-quality material, current production is concentrating on fancy colours [31]. Pink diamonds may be produced by irradiation and annealing of diamonds with a moderate nitrogen concentration, but as noted in Section 3.1, the absorption band of the (N–V−) centre is quite different to that of the natural pink diamonds. Boron is readily incorporated into synthetic diamond, and, if most of the nitrogen is removed by gettering, diamonds with an intense blue colour may be produced. There are no reports of the boron concentration in natural diamonds exceeding approximately 0.5 ppm, and significantly higher concentrations (which can be estimated optically) would immediately arouse suspicion. In addition, the boron concentration in synthetic diamond is strongly growth-sector-dependent, being highest in the {111} sectors and lowest in the {100} sectors. The resulting inhomogeneous distribution of the blue coloration is very clear on visual inspection [33].

5. Summary

This paper has reviewed the methods by which diamonds with a poor colour grade (or a low clarity grade) can have their colour enhanced. Tinted yellow type Ia diamonds can be given a deeper yellow colour by radiation damage and annealing which produces the H3 and H4 absorption bands. Such specimens can also be given a canary yellow colour by HPHT processing. In addition, making the colour more intense can disguise the fact that the starting material had a low clarity grade. Pink diamonds can be produced by subjecting pale yellow type Ib diamonds to radiation damage and annealing. HPHT processing of type Ia brown diamonds produces a more attractive yellow or yellow/green colour by generating H3 and H2 centres, whereas HPHT processing of type IIa brown diamonds can result in a colourless or near-colourless stone.

Fundamental research on the optical properties of defects in diamond, carried out for more than 50 years, has provided a background, which has enabled an understanding of the colour-enhancement processes to be reached (in greater depth for some mechanisms than others). This same research has enabled techniques to be developed which allow colour-enhanced diamonds, and HPHT synthetic diamonds, to be distinguished from natural diamonds having a natural colour. Ongoing research should lead to a better understanding and improvements in the detection methodologies.

References