

Spectroscopic study of a yellowish green HPHT synthetic diamond

Jean-Pierre Chalain

SSEF Swiss Gemmological Institute

Basel, Switzerland

Introduction and background

For research purposes, the SSEF Swiss Gemmological Institute has recently studied a series of nine polished coloured synthetic diamonds. Their weights range between 0.31 ct and 1.74 ct. Their colours are brown, yellow, yellow orange, yellowish green, brownish green, green and dark reddish (figure 1). The two last colours were obviously obtained by irradiation and annealing was only applied to the last one.

They were presented to us as being part of the latest production of the Siberian Branch of the Diamond Growth Laboratory Design and Technological Institute of Monocrystal in Novosibirsk, Russia.

In this article, we focus on the study of the yellowish green synthetic diamond (0.46 ct) because its colour is similar to that of most HPHT type Ia treated diamonds of natural origin. In fact, it is more than five years now, since the HPHT treatment of type Ia natural diamonds was first described to gemmologists (Van Bockstael, 1997). When applied to brown natural diamonds of type Ia, this treatment produces yellowish-green diamonds but also many other fancy treated colours: orange, greenish-brown, yellow, etc. Complementary information about the gemmological properties of the HPHT treated diamonds of

type Ia may be found in Collins, 2001; De Weerd and Van Royen, 2000 ; Reinitz et al., 2000.

The spectroscopic properties of this round brilliant synthetic diamond (figure 2) are presented here because they are totally different from those of HPHT treated diamonds of the same colour but of natural origin. The major spectroscopic features of HPHT treated diamonds of type Ia are extensively documented in Collins et al., 2000.

It is important for the diamond trade to be able to distinguish synthetic diamonds from natural diamonds and certain gemmological properties make it possible to distinguish immediately between the two.

Additionally, in the case of a synthetic diamond, a complete spectrometric study enables us to plot the history of its growth conditions, providing a greater insight into some of the properties of the stone. It is proposed, here, to plot this history.

Methods

Instruments

The Infra-red spectrum presented here was recorded at room temperature on a Fourier Transformer Infra-red (FTIR) Nicolet Nexus spectrometer. The beam was focused by a x5

beam condenser through the sample. The scan range is 6000 cm^{-1} to 400 cm^{-1} and the resolution is 4 cm^{-1} .

The UV Visible spectrum was recorded at low temperature (ca -140°C) on a Varian Cary 500. The beam was directly focused on the centre of the samples. The scan range is 800 nm to 200 nm. The parameters of the instruments are set up with a data interval of 0.1 nm, a scan rate of 60 nm per minute and a spectral band width of 0.5 nm.

The Photoluminescence spectrum was induced by a Renishaw Raman system 1000. The 514.5 nm Laser beam was focused onto the table of the sample maintained at low temperature (ca -160°C). The power Laser was set to 30 mW.

The growth pattern images were screened on a DeBeers - DTC DiamondView™ viewer using a very short wavelength UV lamp.

Results

Infra-red spectrometry

The infra-red (IR) spectrum presented in figure 3 is normalised to the sample thickness, so it is quantitatively comparable to the IR spectrum of other diamonds.

The two-phonon and the three-phonon regions of the IR absorption spectrum show no other noticeable features than that of the diamond's lattice.

The defect-induced one-phonon region of the spectrum ($\sim 500 - 1500\text{ cm}^{-1}$) shows a major absorption at 1282 cm^{-1} which indicates the presence of A aggregates (two neighboured nitrogen atoms in the diamond lattice). Although the absorption feature at 480 cm^{-1}

is also known to be due to A aggregates, a slight shift of 4 cm^{-1} is noticed.

Although it is badly resolved because of a 4 cm^{-1} resolution, an absorption peak is noticed at 1344 cm^{-1} and is attributed to single substitutional nitrogen atoms in their neutral charge.

Two other slight absorptions at 1046 cm^{-1} and 950 cm^{-1} together with the 1332 cm^{-1} absorption peak indicate the presence of N^+ centres (Lawson et al., 1998).

After decomposition of the defect-induced one-phonon region, the concentrations of the different defects is calculated. The results of this quantitative analysis are presented in figure 4.

UV visible spectrometry

The spectrum presented in figure 5 is normalised to the thickness of the sample.

Two bands dominate the spectrum. The first one is centred around 680 nm and the second one around 440 nm.

Six major sharp peaks are easily visible. They are located at 793.5 nm, 546.7 nm, 478.8 nm, 477.3 nm, 473.1 nm and 467.8 nm.

Photoluminescence spectroscopy

Apart from the diamond Raman peak, 18 photoluminescence peaks are visible (figure 6). They are located at 523 nm, 536 nm, 561 nm, 698 nm, 700 nm, 705 nm, 709 nm, 719 nm, 721 nm, 729 nm, 738 nm, 750 nm, 753 nm, 766 nm, 774 nm, 792 nm, 793 nm and 808 nm. Several weaker peaks are also detectable.

Discussion

The **infra-red** spectrum shows that the sample is a diamond. This is clearly shown by the typical intrinsic absorption of the diamond lattice in the two and three-phonon regions (figure 3).

The presence of the A aggregates does not indicate directly whether the diamond is of a natural or synthetic origin. The concentrations of the different defects, calculated by decomposition of the one-phonon region, shows the presence of N⁺ centres and C centres. So far, the first centre only occurs in synthetic diamonds and although its concentration is weak (4 ± 1 atomic ppm), it is a first indication that this diamond is synthetic.

During the growth of a synthetic diamond, nitrogen is incorporated inside the diamond lattice in the form of single nitrogen atoms in their neutral charge and they form the so called C centre. Here the weak concentration of this centre, namely 16 ± 2 atomic ppm, compared to that of the A centres (74 ± 5 atomic ppm) indicates that the nitrogen atoms are now in an aggregated form instead of being isolated. This aggregation is possible when an as-grown synthetic diamond - originally of type Ib containing only single nitrogen atoms - is treated at high temperature under high pressure (HPHT treatment).

Therefore, based on the infra-red spectrum of this stone we can give the following conclusions: It is a synthetic diamond. It is HPHT treated. It now contains about 95 atomic ppm of nitrogen mainly in the A aggregated form and the C to A centre conversion induced by the HPHT treatment reaches 79%.

It is well known that C centres (single substitutional nitrogen atoms in their neutral charge) have a strong influence on the colour of diamonds. A few ppm of single nitrogen atoms gives a yellow to brown colour to diamond. Therefore, in view of its current total nitrogen concentration, it is reasonable to suppose that before HPHT treatment the original colour of this synthetic diamond was yellowish brown to brown. Unlike C centres, A centres are not active colour centres. Therefore, by inducing this aggregation process, the HPHT treatment has lightened the colour of this synthetic diamond.

The UV visible spectrum, the photoluminescence spectrum and the DiamondView™ image bring further indications that the diamond is synthetic as well as other complementary information.

The following peaks noticeable on the **UV visible** spectrum of our sample (figure 5) are related to the presence of Nickel (Ni) in HPHT synthetic diamond: 467.7 nm, 473.1 nm, 478.8 nm and 793.5 nm (Prelas et al., 1998). These are shown in green on figure 5. This confirms the interpretation of the infra-red spectrum from which it is deduced that the diamond is synthetic.

Ni is usually mixed with iron (Fe) to catalyse the synthesis of diamond. Note that only Ni is incorporated inside the diamond lattice to create an active colour-centre in this synthetic diamond.

The very wide band centred around 670 nm absorbs the red part of the spectrum and the three major peaks (467.7, 473.1 and 477.3 nm) together with the band centred at 440 nm absorb the blue part of the spectrum. As a

result of the absorption of the red and the blue parts of the spectrum, the sample looks yellowish green.

The peak at 477.2 nm will be discussed in the photoluminescence paragraph.

The 523 nm peak observed on the **photoluminescence** spectrum of the sample is reported as being present in synthetic Ni containing catalyst diamonds after HPHT treatment and as being observable either in PL or in absorption. A fine structure containing a 477.2 nm absorption peak and related to this centre is also reported as being present in as-grown synthetic diamonds (Prelas et al., 1998).

Although on this sample we observed the 523 nm peak in PL, we could not observe it in absorption (figure 5). Interestingly we note here that although this synthetic diamond is not an as-grown synthetic diamond, an absorption peak at 477.2 nm is present (figure 5).

The 793.5 nm PL peak is observed on the PL spectrum of the sample. It is reported as being present in synthetic diamonds heated above 1700°C and also as being stable above 2200°C (Prelas et al., 1998). We also observed this peak in absorption on the UV visible spectrum. It is related to the presence of Ni. We could not assign the 16 other PL peaks observed in this sample.

Figure 7 shows the **DiamondView™** image of the sample.

The overall stone shows a yellowish green luminescence. Growth sectors are distinct. Cubic sectors do not show any luminescence, therefore they appear black on the image as

does the seed trace at the centre of the image and the four patches at the corners of the square drawn underneath the table. Pointing at the centre of the stone, four green triangular sectors alternate with four other lighter sectors.

These cube-octahedron features are typical for synthetic diamonds. They reflect both fast and homogeneous growth of the stone compared to that of natural diamonds and temperature growth conditions below 1900°C. This last temperature is not in contradiction with the temperature applied during the later HPHT treatment (between 1700°C and more than 2200°C).

When observed with a gemmological binocular microscope this synthetic diamond does not exhibit any metallic inclusions. This indicates that a small gradient temperature was probably applied during the growth of the crystal (Kanda, 1999).

Conclusion

Although in many instances, synthetic diamonds can be readily distinguished from natural diamonds by gemmological means, only their spectrometric properties can trace their growth conditions and detect a possible post treatment.

By studying the spectrometric properties of this yellowish green diamond, we have highlighted its particular properties. Infra-red spectrometry enabled both a qualitative and quantitative evaluation of its nitrogen concentration. Indirectly, it was deduced that the synthetic diamond was HPHT treated. From its UV visible and PL spectra we observed that the diamond was grown in the presence of an Ni containing alloy.

Although its colour is similar to that of a yellowish green HPHT treated diamond of natural growth, each of its spectrometric features is very different.

Acknowledgments

The author thanks Dr. Paul Spear, Dr. S. Lawson and Dr. David Fisher of the De Beers DTC Research Centre, U.K. for their help and support.

References

- Collins A.T., Kanda H., Kitawaki H., 2000. Colour Changes Produced In Natural Brown Diamonds By High-Pressure, High-Temperature Treatment. *Diamond And Related Materials*. N°9. pp. 113-122.
- Collins A.T., 2001. The Colour Of Diamond And How It May Be Changed. *Journal Of Gemmology*. Vol. 27, N°6, pp.341-359.
- Kanda H. Growth Of High Pressure Synthetic Diamonds, 1999. *Journ. Gemmol. Soc., Japan*, Vol.20 pp. 37-44.
- Lawson S.C., Fisher D., Hunt D.C., Newton M.E., 1998. On The Existence Of Positively Charged Single-Substitutional Nitrogen In Diamond. *J. Phys.: Condens. Matter* 10, 6171-6180.
- Prelas M.A., Popovici G., Bigelow L.K., 1998. *Handbook Of Industrial Diamonds And Diamond Films*. Marcel Dekker, Inc., New York.
- Van Bockstael M., A New Treatment. HRD's Gemmological Conference, Antwerp, 9-10 November 1997.

De Weerd F., Van Royen J., 2000. Investigation Of Seven Diamonds HPHT Treated By Novadiamond. *Journal Of Gemmology*. Vol. 27, N°4, pp. 201-208.

Reinitz I.M., Buerki P.R., Shigley J.E., McClure S.F., Moses T.M., 2000. Identification Of HPHT Treated Yellow To Green Diamonds. *Gems And Gemology*. N°2, pp.128-137.

The author can be contacted on:
(gemplab@ssef.ch)



Figure 1: A series of nine coloured synthetic diamonds recently grown in Novosibirsk, Russia

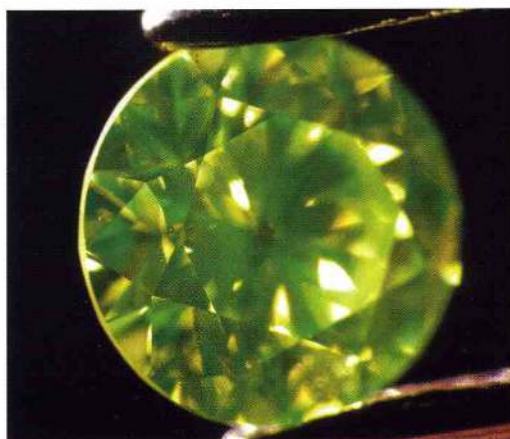


Figure 2: This round brilliant cut yellowish green synthetic diamond weights 0.46 ct.

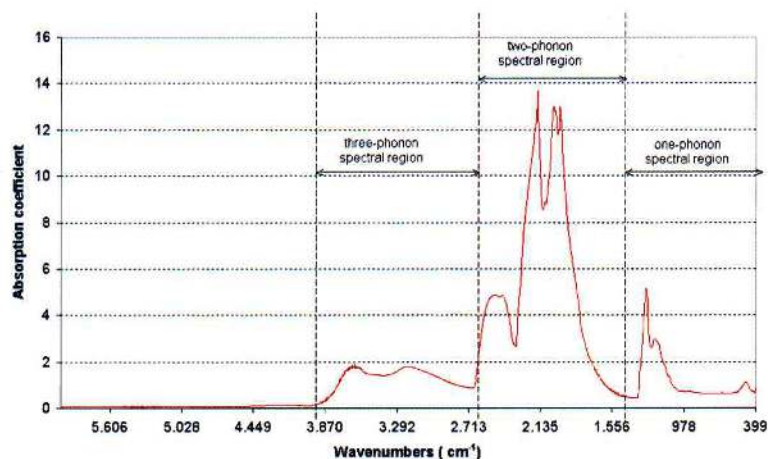


Figure 3: Infra-red spectrum of an HPHT treated synthetic diamond

Centre	C	A	N ⁺
Absorption coefficient (cm ⁻¹)	at 1130 cm ⁻¹ : 0.64	at 1282 cm ⁻¹ : 4.50	at 13.32 cm ⁻¹ : 0.69
Nitrogen concentration	16 ± 2 atomic ppm	74 ± 5 atomic ppm	4 ± 1 atomic ppm

Figure 4:

Nitrogen concentrations of three different optical centres in an HPHT treated synthetic diamond.

C centres are formed with single substitutional nitrogen atoms in their neutral charge (N⁰).

A centres are formed with two neighboured nitrogen atoms (A aggregates).

N⁺ centres are formed with positively charged single substitutional nitrogen atoms.

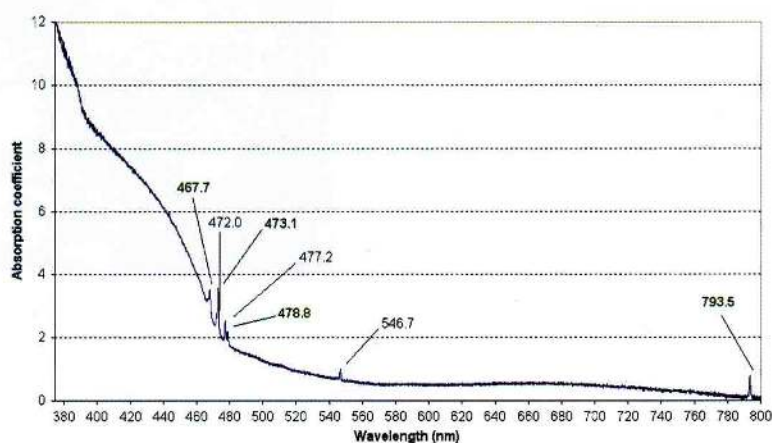


Figure 5: Low temperature UV visible spectrum of a yellowish-green HPHT treated synthetic diamond.

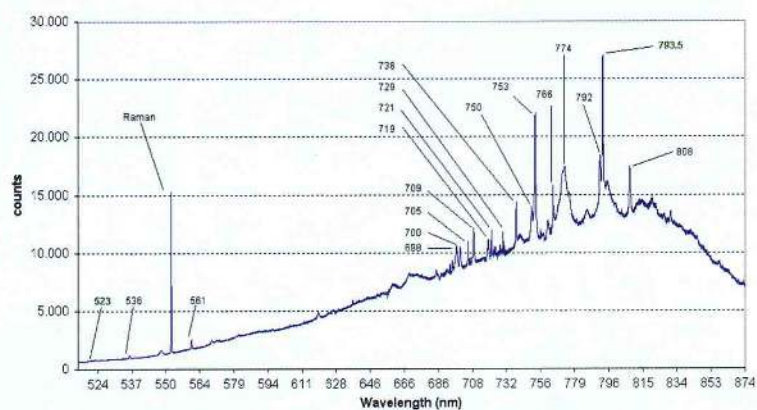


Figure 6: Low temperature photoluminescence spectrum of a yellowish-green HPHT treated synthetic diamond.

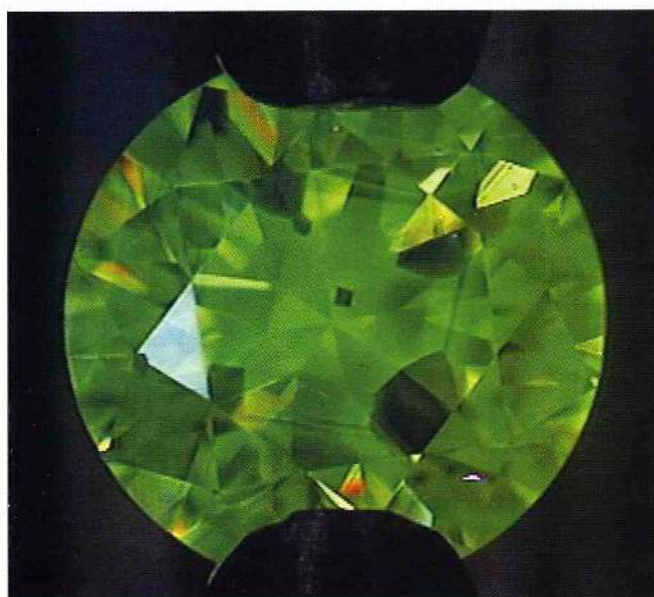


Figure 7: DiamondView™ image of a yellowish green HPHT treated synthetic diamond.