

## A study on the HPHT-processed NOUV diamonds by means of their gemological and spectroscopic properties

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**Abstract** This study has been carried out with the eight HPHT processed NOUV diamonds - two yellow, two yellowish green, two green and two orangy yellow color stones. The gemological properties of these diamonds included a highly saturated body color, graphitized fractures around the girdles, tension cracks around crystalline inclusions, long-wave UV with medium yellowish green to a very strong yellowish green luminescence, and short-wave UV with faint yellowish green to a strong yellowish green luminescence. Distinctive features of spectroscopic properties include absorption peaks at 415 nm and 503 nm, a strong absorption band at 460~480 nm and a H2 center at 986 nm. Infrared spectra showed an absorption peak at 1344  $\text{cm}^{-1}$  (C center), which is the characteristics related to single substitutional nitrogen.

**Key words** HPHT processed NOUV diamond, H3 absorption, H2 absorption, C center

### 1. Introduction

Some companies in such as Russia, Sweden, China, India, and Korea as well as companies like General Electric (GE) company and Novatek are using brown colored diamonds to produce diamonds with colors ranging from yellow to green using the high pressure and high temperature (HPHT) process. Using the same types of apparatus as are used to synthesize single crystal diamonds, they place natural diamonds, they place natural diamonds under a high confining pressure of about 60 kilobars. While the stones are at high pressure, they expose them to high temperatures, up to 2100°C, for short periods (i.e., less than 30 minutes, in some cases much less). These conditions are similar to those used by GE to decolorize diamond, but the starting materials are nitrogen-bearing type Ia brown diamonds, rather than nominally nitrogen-free type IIa diamonds [1, 2]. Diamonds are classified scientifically into two types with subcategories for each. Type I diamonds - the most abundant in nature - contain nitrogen. Type I diamonds can be further subdivided into type Ia and Ib depending on the form that the nitrogen takes within the crystal structure of the individual stone. In type Ia diamonds, substitutional nitrogen atoms are aggregated. The most common diamond types are IaA (which have a

pair of nitrogen atoms, the A aggregate) and IaB (in which four nitrogen atoms surround a common vacancy, the B aggregate). In type Ib diamonds, a carbon atom is substituted by a single nitrogen atom. They usually vary from colorless to yellow or brown. Type II diamonds - which are rare in nature - lack all but tiny amounts of nitrogen. They are sometimes colorless, but more often brown; if they contain boron, they can be blue to gray. The brown coloration in diamonds of both types results when they have been subjected to plastic deformation (i.e., "strain") deep in the earth during long periods of geologic time. As a result of HPHT processing, type II brown diamonds can be transformed to colorless or near colorless. The same procedure can transform a limited number of brown-pink or brown-to-gray-blue type II diamonds to pink and blue, respectively. Type Ia brown diamonds become greenish yellow, yellowish green color after HPHT processing [3, 4].

In 2003, Iljin Diamond Co., Ltd. in South Korea introduced its HPHT processed diamond with a brand name of "NOUV diamond" at several major international jewelry trade fairs. NOUV diamonds [5, 6] have a wide range of vivid altered colors, such as intense green, yellow, greenish yellow, and yellowish green. These diamonds were made through the processing of natural brown-colored type Ia diamonds with Iljin's HPHT Reborn process technology. This technique has been developed by Iljin which has incorporated the method for manufacturing industrial synthetic diamonds.

While there have been several reports on the gemo-

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Table 1  
Illustrates properties of each of the diamonds

	S03-31	S03-32	S03-33	S03-34	S03-35	S03-36	S03-37	S03-38
Color	yellow	yellow	yellowish green	yellowish green	green	green	orangy yellow	orangy yellow
Weight (ct)	0.302	0.352	0.318	0.374	0.301	0.309	0.301	1.211
Clarity	SI <sub>2</sub>	SI <sub>2</sub>	SI <sub>2</sub>	SI <sub>1</sub>	SI <sub>2</sub>	SI <sub>2</sub>	Pique <sub>1</sub>	SI <sub>2</sub>
UV fluorescence								
Long-wave	medium yellowish green	strong blue	very strong yellowish green	strong yellowish green	very strong yellowish green	very strong yellowish green	medium greenish blue	partially faint blue /yellowish green
Short-wave	faint yellowish green	strong chalky blue	strong yellowish green	medium yellowish green	strong yellowish green	strong yellowish green	strong chalky greenish blue	partially medium blue /yellowish green
UV-Vis-NIR absorption spectra	weak peak at 415 nm, 503 nm and rising absorption toward shorter wavelength	weak peak at 415 nm, 503 nm and rising absorption toward shorter wavelength	415 nm, 503 nm, strong absorption band at about 460~480 nm, strong green H3 fluorescence at 530 nm, H2 peak	415 nm, 503 nm, strong absorption band at about 460~480 nm, strong green H3 fluorescence at 530 nm, H2 peak	415 nm, 503 nm, strong absorption band at about 460~480 nm, strong green H3 fluorescence at 530 nm, H2 peak	415 nm, 503 nm, strong absorption band at about 460~480 nm, strong green H3 fluorescence at 530 nm, H2 peak	weak peak at 503 nm and rising absorption toward shorter wavelength	rising absorption toward shorter wavelength
Infrared spectrum	moderate peak at 1365 cm <sup>-1</sup> , weak peak at 1405, 3107 cm <sup>-1</sup> and weak band at 1485 cm <sup>-1</sup>	weak peak 1344 (C center), 1405 and 1331 cm <sup>-1</sup> ; strong peak at 3107 cm <sup>-1</sup>	weak peak at 1405, 1430, 3107 cm <sup>-1</sup> ; strong peak at 1331, 1360 cm <sup>-1</sup>	weak peak at 1405, 3107 cm <sup>-1</sup> ; moderate peak at 1356, 1331 cm <sup>-1</sup>	weak peak at 1405, 1431 cm <sup>-1</sup> ; strong peak at 1360, 1331 and 3107 cm <sup>-1</sup>	weak peak at 1405, 1431 and 3107 cm <sup>-1</sup> ; very strong peak at 1331, 1360 cm <sup>-1</sup>	weak peak at 1344, 1405 cm <sup>-1</sup> ; strong peak at 3107 cm <sup>-1</sup>	weak peak at 1344, 1405 and 3107 cm <sup>-1</sup> ; moderate peak at 1365 cm <sup>-1</sup>
Diamond type	laA~B	laA<B	laA<B	laA~B	laA<B	laA<B	laA<B	laA>B

logical and spectroscopic properties of diamonds manufactured by GE and Novatek through literatures [7-11], it has been hard to get detailed information on properties of the HPHT processed diamonds produced by other manufacturers. Therefore, this study implemented a research on the gemological and spectroscopic properties of colored diamonds produced through the HPHT process by Iljin Diamond Co., Ltd. and intended to record relevant notable findings.

## 2. Methods

All samples were examined with a binocular gemological microscope and a long-wave (366 nm) and short-wave (254 nm) Ultraviolet products UV lamp unit. A spectrum of ultraviolet (UV), visible (Vis), and near-infrared (NIR) regions were measured by means of Kalnew's Gemcolor 2 spectrophotometer (360~800 nm) and Shimadzu's UV-3101PC spectrometer (200~1100 nm) equipped with the integrating sphere which was specially manufactured to measure a faceted jewel at liquid nitrogen temperature. Mid and near-infrared absorption spectra were measured in the range of 6000 to 450  $\text{cm}^{-1}$  at room temperature using Perkin-Elmer's Spectrum One Fourier transform infrared (resolution; 4.00  $\text{cm}^{-1}$ , beamsplitter; OptKBr) spectrometer.

## 3. Results and Discussion

### 3.1. Samples details

The eight HPHT processed diamonds studied have a color of yellow, yellowish green, green, orangy yellow ranging from 0.301 to 1.211 ct (60.2~242.2 mg) in weight and SI<sub>1</sub> (slightly included) to P<sub>1</sub> (pique) in clarity grades (see Table 1).

### 3.2. Gemological properties

#### 3.2.1. Features seen with magnification

Most of the diamonds under magnification showed microscopic evidence of heating. Some diamonds had black inclusions; the black inner area was surrounded by a brighter halo of outward radiating cracks; and graphitized fractures were observed around the girdle (Fig. 2). These eight diamonds had "NOUV" and the serial number laser-inscribed (Fig. 3), while "partially healed" cleavages with an unusual shape were observed in the S03-36

diamond (Fig. 4).

#### 3.2.2. Luminescence

We observed medium to strong, greenish yellow to yellowish green fluorescence to long-wave UV radiation in five samples. One sample (S03-37) showed a mixture of strong blue with weak green fluorescence to long-wave UV. And in S03-38 sample, blue appeared particularly faint at the culet. In general, the fluorescence was more intense to long-wave than to short-wave UV.



Fig. 1. The eight HPHT-treated diamonds studied.

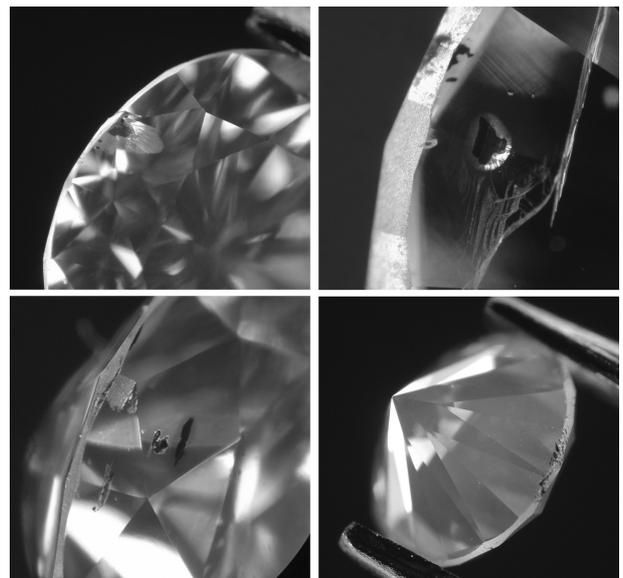


Fig. 2. In some of the diamonds that had solid inclusions surrounded by stress cracks, a black inner area (graphite) was surrounded by a brighter halo of outward radiating cracks (the first three photographs; magnified 28 $\times$ , 45 $\times$  and 33 $\times$ ) and also graphitized fractures around the girdles was observed (bottom right; magnified 15 $\times$ ).

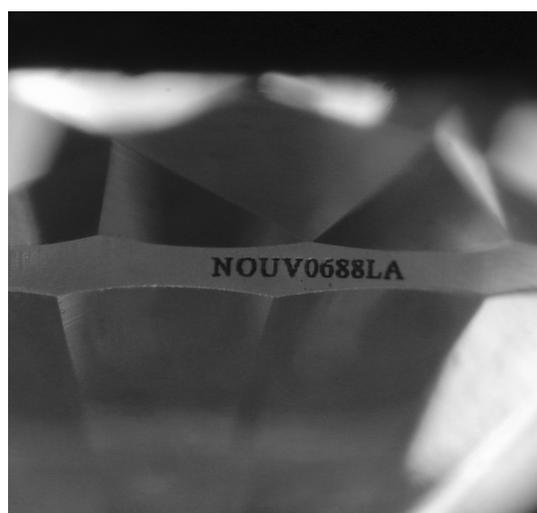


Fig. 3. The laser-inscribed “NOUV” is readily visible on the girdle surface of these diamonds (magnified 48 $\times$ ).

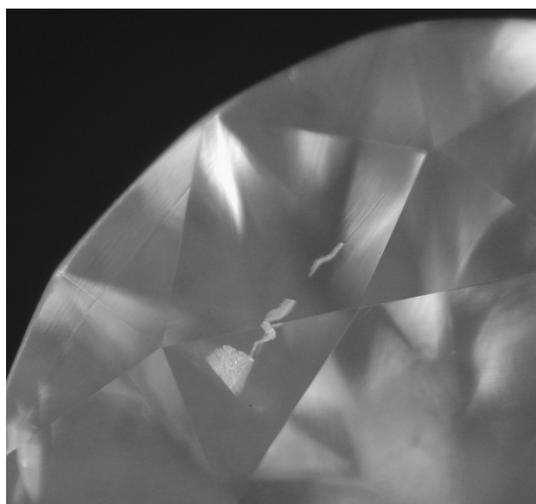


Fig. 4. “Partially healed” cleavages with an unusual shape were observed in the S03-36 diamond (magnified 31 $\times$ ).

### 3.3. Spectroscopic properties

The HPHT processed samples showed colors of yellow, yellowish green, green, and orangy yellow (Fig. 1), and in order to examine their spectroscopic properties the UV-Visible, UV-Vis-NIR, and FT-IR spectra were measured.

#### 3.3.1. UV-Vis-NIR absorption spectroscopy

The UV-Vis spectrum measured at liquid nitrogen temperature largely showed two patterns. HPHT processed diamonds with green or yellowish green color showed a weak transmittance band at 620 nm, a weak N3 band (primary line at 415 nm) and a strong H3 absorption (primary line at 503 nm) in Fig. 5a. HPHT processed diamonds with yellow or orangy yellow color showed

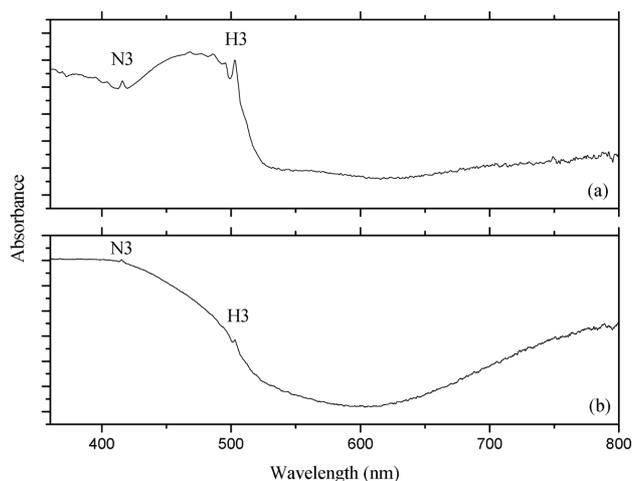


Fig. 5. Absorption spectra of in the ultra and visible regions of sample diamond which had a green, yellowish green (a) and yellow, orange yellow (b) color after HPHT processing at liquid nitrogen temperature.

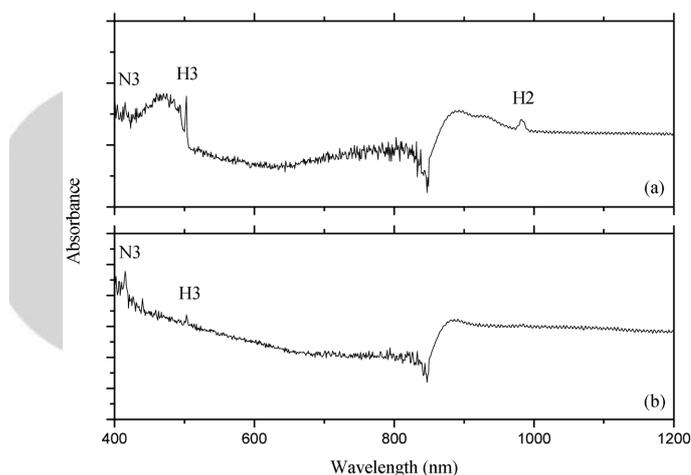


Fig. 6. Absorption spectra of in the visible and near infrared regions of sample diamond which had a green, yellowish green (a) and yellow, orange yellow (b) color after HPHT processing at liquid nitrogen temperature. The step in the range 840 to 880 nm is due to a detector change.

overlaid on a steep overall rise in absorbance from about 500 nm toward shorter wavelengths, as well as the N3 and H3 bands in Fig. 5b. In a type Ia diamond, vacancies are trapped by the nitrogen to increase the concentrations of H3 and N3 centers. In this case the original brown color is reduced, and the H3 absorption result in a yellow color. In the Vis-NIR spectrum, four (S03-33, S03-34, S03-35 and S03-36) among the eight diamonds have H2 absorption (Fig. 6a), but the rest of the samples have not H2 absorption (Fig. 6b). It probably is the result of a treatment process developed for changing brown color diamonds into increase yellowish green colored diamonds. H2 absorptions with a ZPL at

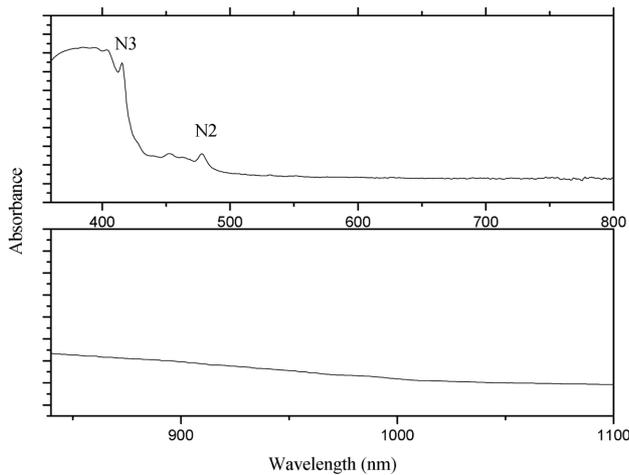


Fig. 7. Absorption spectrum of in the ultra, visible and near infrared regions of HPHT unprocessed natural diamond with greenish yellow color.

986.3 nm [12, 13] are produced at a temperature of at least 2,000°C, or preferably higher (~2,100-2,200°C). At the higher temperature, in addition to the increase in the N3 and H3 absorption, single substitutional nitrogen is produced by the break-up of some A aggregates. The presence of this form of nitrogen favor some (N-V-N) centers being in the negative charge state, thereby producing absorption in the H2 band, and giving a green component to the color. Accordingly, the samples in this study probably become yellow if annealed to 1,800°C (or below temperature of 2,000°C), and green if annealed at 2,000°C (or above temperature of 2,000°C).

HPHT unprocessed natural greenish yellow diamond show a distinct pair of lines at 450 and 475 nm (due to the N2 center) and typically show a weak to moderate absorption line at 415 nm (due to the N3 color center) as well in Fig. 7a. Also, the NIR spectrum of the HPHT unprocessed natural greenish yellow diamond does not show H2 absorption (Fig. 7b).

### 3.3.2. Infrared absorption spectroscopy

Typical properties of the type Ia diamond were observed at mid infrared spectra in every sample. There were diverse forms (A, B, and C center) of nitrogen aggregates; while most of the diamonds showed a more strongly absorbed B-aggregate than A-aggregate. Six among the eight HPHT processed diamonds have a platelet-related peak ( $\pm 10 \text{ cm}^{-1}$ ) at  $1360 \text{ cm}^{-1}$ . All diamonds have a peak related to vibrations of the vinylidene group ( $>\text{C}=\text{CH}_2$ ) at  $3107 \text{ cm}^{-1}$  and  $1405 \text{ cm}^{-1}$ . Three showed an absorption peak at  $1344 \text{ cm}^{-1}$  (C center), which is the property related to single substitutional nitrogen (Fig. 8a, 8b). It seems that this peak was formed when parts of nitrogen

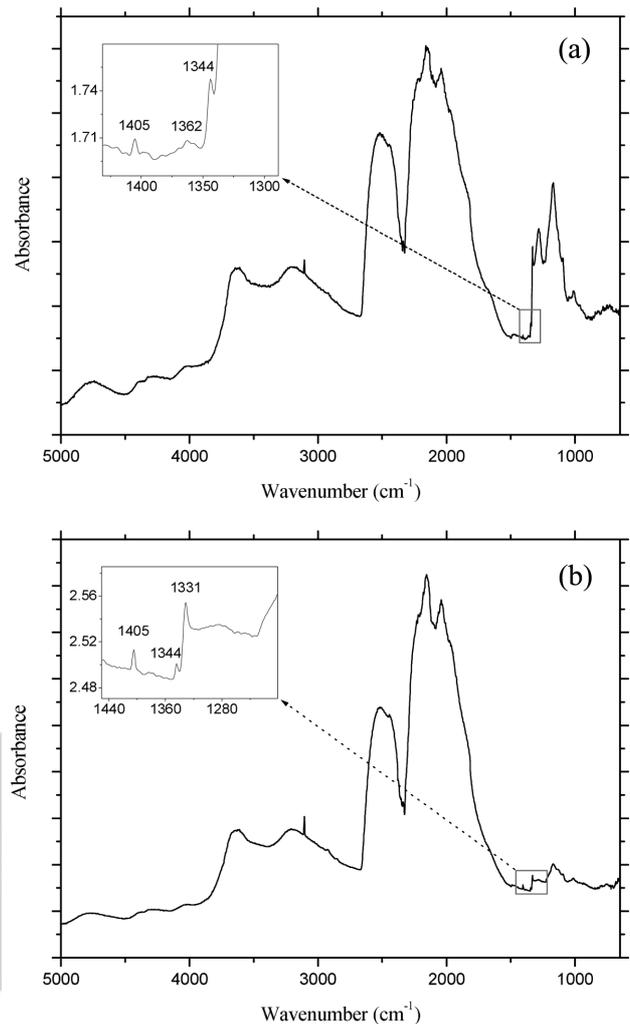


Fig. 8. FT-IR spectra for two of the HPHT processed diamonds at room temperature. The inset shows a small C center absorption peak at  $1344 \text{ cm}^{-1}$ .

separated while A-aggregate passed through the HPHT process. High resolution measurement (resolution  $4 \text{ cm}^{-1}$ ) show that some of the HPHT processed diamonds exhibit a small C center absorption peak at  $1344 \text{ cm}^{-1}$ . As a result of absorption spectra, all diamond samples clearly show a strong to weak H3 absorption and four among the all diamonds show a strong H2 absorption in UV-Vis-NIR spectrometer. Samples S03-32, S03-37 and S03-38 contain C centers detectable with high resolution FTIR measurements. This combination of A, B, C, H3 and H2 center is characteristic of HPHT processed in natural type Ia diamonds.

## 4. Conclusion

An analysis was carried out on eight HPHT processed

NOUV diamonds. The gemological properties typically included a highly saturated body color, while only some of the diamonds had solid inclusions surrounded by stress cracks, a black inner area surrounded by a brighter halo of outward radiating cracks and graphitized fractures around the girdle.

There was strong H3 absorption in HPHT processed natural diamonds with green, yellow or yellowish green color, which were analyzed by means of the UV-Vis-NIR spectrophotometer, while four of these eight samples showed H2 absorption. There was a weak C center as well as A and B centers in the infrared region. The presence of the H2 defect cannot be used as absolute proof of HPHT processed diamond. The strong H3 absorption and H2 absorption, however, is very strong indication of HPHT processed diamond. Therefore, existence of H3 absorption, H2 absorption and a C center is likely to characterize it as an HPHT processed NOUV diamond.

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