

“FLUORESCENCE CAGE”: VISUAL IDENTIFICATION OF HPHT-TREATED TYPE I DIAMONDS

Inga A. Dobrinets and Alexander M. Zaitsev

HPHT-treated type I diamonds of various colors may exhibit unusually intense fluorescence at the facet edges and junctions. This effect, here named the “fluorescence cage,” is observed with a fluorescence microscope as a luminous network on the diamond’s surface. It was not observed in untreated diamonds or colorless type IIa HPHT-treated diamonds. This fluorescence pattern is believed to result from a high concentration of HPHT-induced optical centers, which remain on facet edges after repolishing.

The identification of high-pressure, high-temperature (HPHT) treatment of diamond poses a great challenge to gemologists (Collins, 2006). Since this enhancement was officially introduced to the diamond market in 1999, its gemological and economic implications have been discussed at length (e.g., Shigley, 2005). HPHT treatment, originally announced as undetectable, actually can be recognized in most cases by a combination of characteristic microscopic and spectroscopic features. However, most advanced spectroscopic methods are expensive and time consuming, so they cannot be used effi-

ciently for routine characterization of every diamond. Moreover, some HPHT-treated diamonds may lack the standard identifying features. Therefore, further studies of HPHT-treated diamonds and the development of practical detection methods remain important activities at gemological laboratories.

In this article, we report on a new characteristic of faceted HPHT-treated type I diamonds: intense fluorescence on facet edges and junctions (e.g., figure 1). This feature is easily observed with a fluorescence microscope and can be used to identify HPHT enhancement.

MATERIALS AND METHODS

Fluorescence images of 60 HPHT-treated and more than 100 untreated cut diamonds of various colors and clarity grades were studied. Of the HPHT-treated stones, 50 ranged from brown to yellow to green to orange, and the other 10 were colorless and near-colorless. To our knowledge, all the stones were faceted prior to HPHT annealing and repolished after treatment. The untreated diamonds, selected from those submitted to EGL USA for grading, were colorless, near-colorless, and brown to yellow (over 30 stones in each of these three color groups).

The HPHT-treated diamonds were loaned by Nice Diamonds. They were confirmed as HPHT treated by our testing with polarized-light microscopy, Fourier-transfer infrared absorption spectroscopy (Nicolet 800 Nexus 670 FTIR spectrometer), visible-transmission spectroscopy (SAS2000 spectrometer), and photoluminescence spectroscopy (SAS2000 with PL excitation at 532 and 658 nm). The visible absorption and

See end of article for About the Authors and Acknowledgments.
GEMS & GEMOLOGY, Vol. 45, No. 3, pp. 186–190.
© 2009 Gemological Institute of America

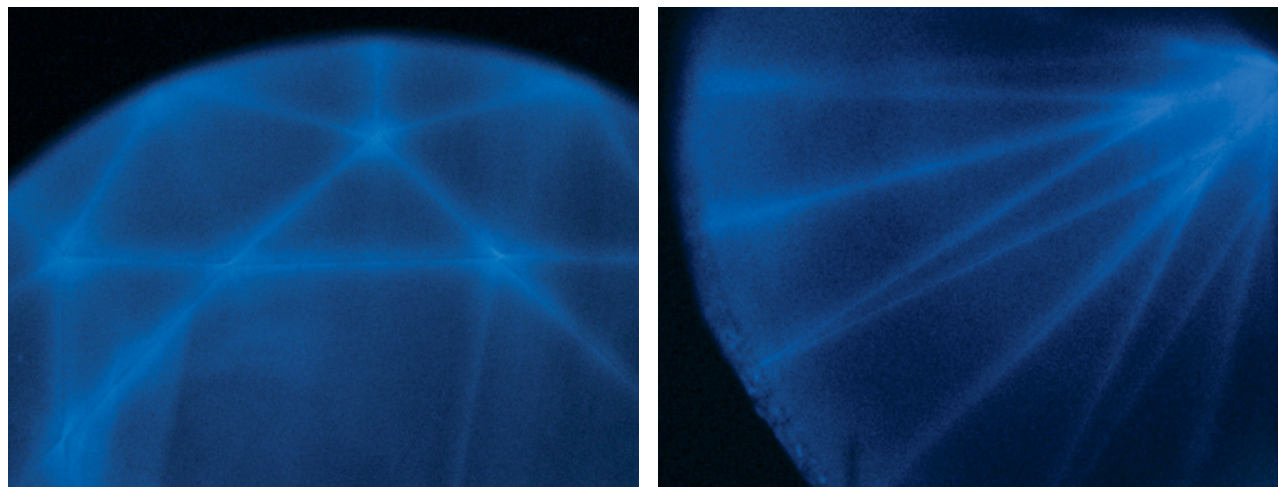


Figure 1. These face-up and table-down views of a Fancy Vivid yellow HPHT-treated type I diamond show intense fluorescence on facet edges and junctions, which is here called a “fluorescence cage.” Photomicrographs by I. Dobrinets; magnified 40 \times .

PL spectra were measured at room and liquid-nitrogen temperatures. The same techniques were used to ascertain the untreated nature of the other diamonds.

Fluorescence images of all the diamonds were taken with a Nikon Eclipse Ti inverted fluorescence microscope equipped with a 100 W high-pressure mercury lamp and optical edge filters (Hoecht UV-2A Ex355/50 Dm400 Bar420), enabling UV excitation with Hg lines at wavelengths of 365 nm (i.e., long-wave UV; ~70% of the total excitation intensity) and 334 nm (~30% of the total excitation intensity), as well as imaging at wavelengths >400 nm (across the entire visible spectrum). Prior to the measurements, the diamonds were ultrasonically cleaned in acetone and alcohol to remove any surface contaminants that might affect the fluorescence imaging.

RESULTS AND DISCUSSION

Gemological Observations. This research stemmed from the characterization of a 0.76 ct diamond submitted to EGL USA for grading and origin-of-color determination (figure 2). The diamond received a color grade of Fancy brownish-orangy yellow and an I1 clarity grade. It was inert to long-wave UV excitation and fluoresced a faint greenish yellow with some green patterns to short-wave UV. The diamond contained a few cracks with obvious graphitization, an indication of possible HPHT treatment.

Examination with 100 \times magnification revealed several features characteristic of HPHT-treated diamonds in addition to the graphitized cracks: cleavages with etched surfaces, fingerprint-like inclusions, and small frosted facets (Moses et al., 1999; Smith et

al., 2000; Hall and Moses, 2001). The stone exhibited a strain interference pattern typical of natural type Ia diamond. No chips or delaminations were detected on the facets or edges, which led us to believe that this colored diamond was not coated by any films such as those documented by Shen et al. (2007).

The FTIR absorption spectra showed that the stone was a mixed type IaA/B+Ib with about 1 ppm of C defects, 25 ppm of A defects, and 45 ppm of B defects. The presence of nitrogen in both dispersed and aggregated forms—a rare occurrence in natural diamonds (Hainschwang et al., 2006)—offered further evidence of HPHT treatment. The visible

Figure 2. The fluorescence cage was first discovered during the examination of this 0.76 ct HPHT-treated diamond. Photo by Fernando Paredes.



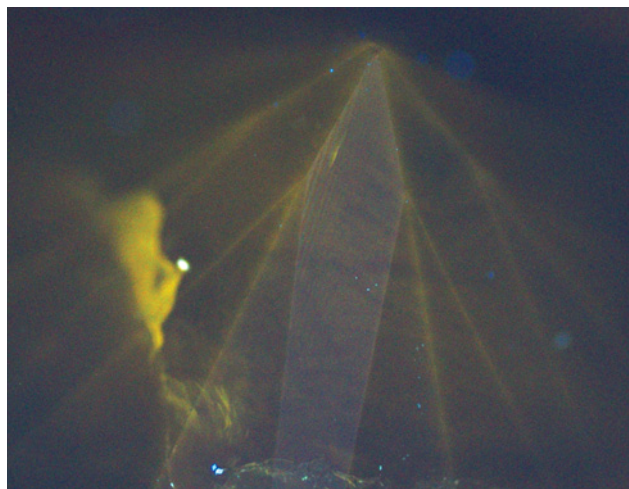
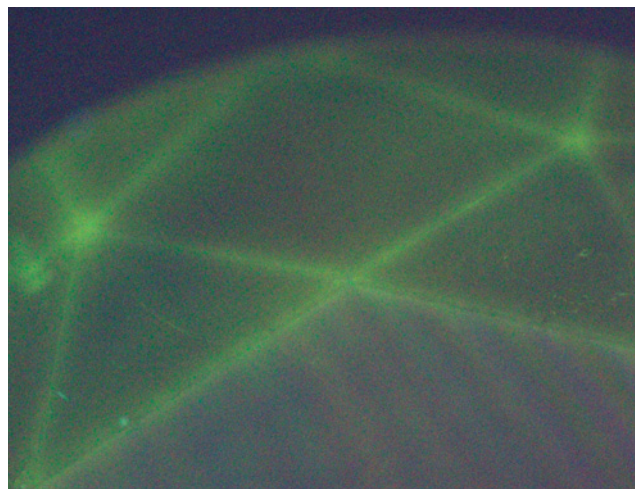


Figure 3. These images, taken with a fluorescence microscope, show the fluorescence cage on both the table (left) and pavilion (right) of the 0.76 ct HPHT-treated diamond in figure 2. The different fluorescence colors are due to the different relative intensities of nitrogen-related centers: yellowish green (dominated by H3) on the crown, and yellow (dominated by NV⁻) on the pavilion. Photomicrographs by I. Dobrinets; magnified 40 \times .

transmission spectrum was dominated by an absorption continuum with a threshold at 650 nm (absorption of C defects), and revealed a rather weak signal for the H3 center, which was observed in the absorption and luminescence regimes (the “green transmission” effect). Both the C-defect absorption continuum and “green transmission” are common features of mixed-type HPHT-treated diamonds. The photoluminescence spectra revealed a dominant nitrogen-related NV⁻ center with a zero-phonon line (ZPL) at 638 nm and three more centers with ZPLs at 542, 564, and 574 nm, which are believed to originate from nickel impurities. These centers are common for HPHT-treated natural diamonds with brown-to-yellow-to-orange coloration, and the latter two are also found in HPHT-treated synthetic diamonds (Yelissev and Kanda, 2007).

Fluorescence microscopy revealed a weak, predominantly yellowish green fluorescence, which could be a superposition of the H3 and NV⁻ center emissions. None of the cross-like patterns characteristic of synthetic diamonds were detected. The most intense fluorescence was concentrated in some cracks and—surprisingly—along the facet edges and at the table and pavilion junctions (figure 3). Because of these bright edges, the diamond looked as though it had been placed in a “fluorescence cage.”

To investigate whether this fluorescence pattern was the product of HPHT treatment, we conducted a comparative study of the numerous HPHT-treated and untreated faceted diamonds described above. Spectroscopic measurements of several HPHT-treated colored, near-colorless, and colorless diamonds

revealed that the colored diamonds were type Ia with total nitrogen contents over 100 ppm and the near-colorless and colorless ones were type IIa with total nitrogen contents below a few ppm. The untreated diamonds did not show such a straightforward dependence of color on type, and those that were colorless revealed a broad range of nitrogen content.

All of the intensely colored type Ia (20 stones) and some light-colored type Ia (8 of 20 samples) HPHT-treated diamonds exhibited the fluorescence cage, whereas none of the untreated diamonds revealed any traces of it (see, e.g., figure 4). The pattern was especially distinct in those HPHT-treated diamonds that had high nitrogen concentrations and were more deeply colored (e.g., figure 5), especially those with low overall fluorescence. In contrast, the fluorescence cage was very faint in low-nitrogen near-colorless type Ia HPHT-treated diamonds, and it was not observed at all in the colorless type IIa HPHT-treated diamonds. This is consistent with our belief that the fluorescence cage is formed by nitrogen-related optical centers.

Origin of the Fluorescence Cage. Our study of the spectral content of the fluorescence cage showed that the main contributors to the luminescence were the optical centers generated during HPHT treatment: H3, NV, and some nickel-related centers. On the basis of these results, we believe that the fluorescence network is caused by HPHT-induced modification (plastic deformation) of the diamond lattice in a layer close to the surface. This modified layer contains optical centers generated by high

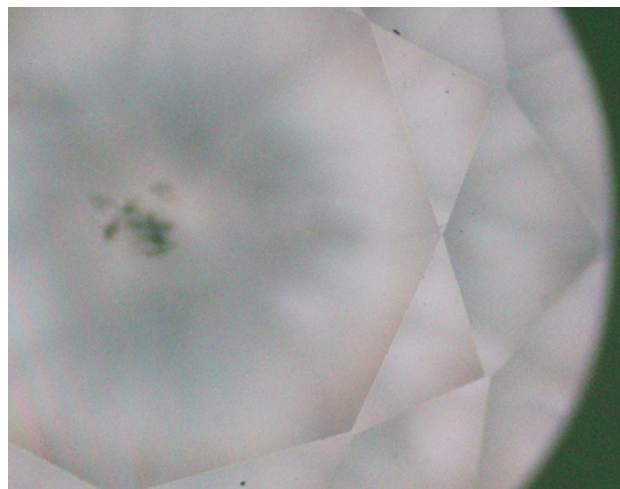


Figure 4. This untreated brownish yellow diamond exhibits whitish pink overall fluorescence and no fluorescence cage. Photomicrograph by I. Dobrinets; magnified 40 \times .

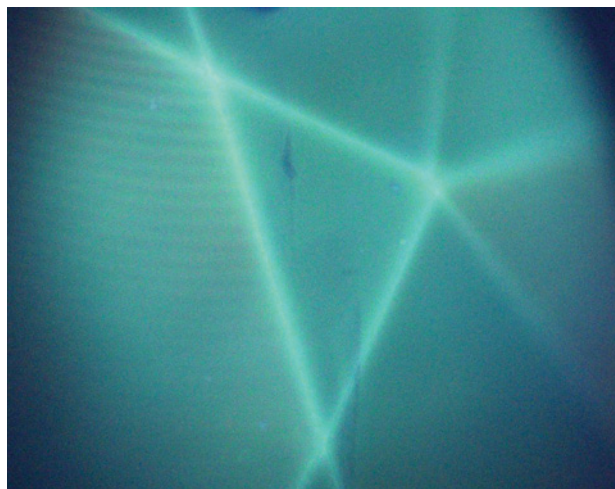


Figure 5. This deeply colored greenish yellow HPHT-treated diamond shows a strong fluorescence cage along with bluish luminescence. Photomicrograph by I. Dobrinets; magnified 40 \times .

mechanical stress and high temperatures. One would expect the modified layer to be thicker on protrusions such as facet edges and junctions, where the mechanical strain during HPHT compression reaches a maximum. After repolishing, the modified layer is largely removed from the flat facets, but there are remnants on the facet edges.

To support this explanation, we studied several surface-reaching cracks in one of the HPHT-treated diamonds with the fluorescence microscope. Although the area around those cracks was damaged by repolishing, it did not show strong fluorescence (figure 6). This observation confirmed that mechanical damage and plastic deformation alone did not produce strong luminescence centers: Simultaneous application of high mechanical stress and high temperature was required to generate them, as seen in the cracks of the 0.76 ct diamond, which were generated during HPHT processing.

So far, we have observed the fluorescence cage only in HPHT-treated type I diamonds. It has not been detected in any diamonds treated with irradiation alone, or with irradiation and low-pressure annealing. Indeed, it is difficult to imagine a mechanism other than HPHT annealing and repolishing that could result in the precise concentration of optical centers along facet edges. For instance, electron irradiation with energy below 1 MeV may generate optical centers of varying intensity (Fritsch and Shigley, 1989). This nonuniformity, however, is very different from that of the fluorescence cage. Neutron irradiation is very uniform and cannot

selectively produce defects at facet edges.

Important questions about the fluorescence cage are whether it can be removed from a diamond and whether it is generated by HPHT treatment of both rough and faceted type Ia diamonds. If we correctly understand the nature of this effect, the concentration of optical centers at facet edges can be enhanced by HPHT annealing of faceted diamonds only. It will not be observed on diamonds that were treated in rough form and faceted after treatment. If the cage is indeed located close to the surface, then it can be removed by a deeper repolishing. However, deep repolishing may reduce the diamond's weight to the point of being commercially impractical. Nor will it appear on type II HPHT-treated pink or blue diamonds, because their nitrogen content is too low.

Detecting the Fluorescence Cage. Fluorescence microscopes such as the one used in this study are uncommon in gem labs. As an alternative, the DiamondView instrument should be suitable to observe fluorescence images. Although the DiamondView is not an exact analogue of a conventional fluorescence microscope due to its very short excitation wavelength (<225 nm compared to 365 nm for fluorescence microscopes), we expect the fluorescence cage to be observable with the DiamondView in many stones. It must be noted, however, that the shorter excitation wavelength of the DiamondView will not excite certain HPHT-induced optical centers (e.g., the 638 nm NV⁻ center); thus, in some cases a cage pattern that might be revealed with

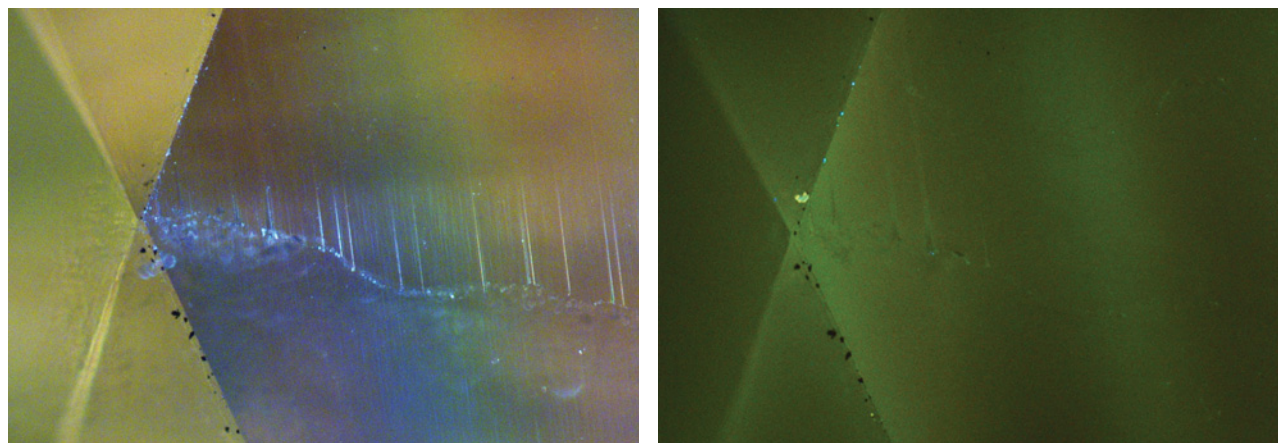


Figure 6. The conventional microscopic image of a brownish-greenish yellow HPHT-treated type I diamond on the left shows a crack surrounded by polish lines. The fluorescence image of the same area (right) shows enhanced luminescence on the facet edges and junction, but no strong luminescence around the crack and polish lines. Photomicrographs by A. Zaitsev; magnified 100 \times .

a fluorescence microscope will not be seen with the DiamondView.

If the fluorescence cage is strong, then it may also be seen using a standard gemological microscope while the diamond is exposed to long-wave UV radiation from a standard gemological lamp. The excitation wavelengths for such lamps are the same as those of the mercury lamps used in fluorescence microscopes. We observed the fluorescence cage in several stones using this method. However, since gemological microscopes are not designed to completely filter out UV radiation, for safety reasons we do not recommend implementing such a testing method unless the observer's eyes are properly shielded.

CONCLUSIONS

We report a new observational feature of some HPHT-treated diamonds—enhanced fluorescence on facet edges and junctions—which we term a *fluorescence cage*. On the basis of our study of numerous HPHT-treated diamonds (both colored and colorless) and their untreated counterparts, we conclude that the fluorescence cage can be readily observed on most deeply colored HPHT-treated type I diamonds with the use of a fluorescence microscope. Recognizing this feature considerably simplifies identification of HPHT treatment. We believe that the fluorescence cage cannot be generated by mechanical polishing or by other treatments such as irradiation and annealing at low pressure.

ABOUT THE AUTHORS

Dr. Dobrinets is a research gemologist at EGL USA in New York.
Dr. Zaitsev is a professor of physics at the College of Staten Island, City University of New York.

ACKNOWLEDGMENTS

The authors are very grateful to Nilesh Sheth, president of Nice Diamonds (New York), for providing samples for this research. Mitchell Jakubovic, director of EGL USA, graciously provided research support.

REFERENCES

- Collins A.T. (2006) Identification technologies for diamond treatments. *G&G*, Vol. 42, No. 3, pp. 33–34.
- Fritsch E., Shigley J.E. (1989) Contribution to the identification of treated colored diamonds: Diamonds with peculiar color-zoned pavilions. *G&G*, Vol. 25, No. 2, pp. 95–101.
- Hainschwang T., Notari F., Fritsch E., Massi L. (2006) Natural, untreated diamonds showing the A, B and C infrared absorptions ("ABC diamonds"), and the H2 absorption. *Diamond and Related Materials*, Vol. 15, No. 10, pp. 1555–1564.
- Hall M., Moses T.M. (2001) Lab Notes: Update on blue and pink HPHT-annealed diamonds. *G&G*, Vol. 37, No. 3, pp. 215–217.
- Moses T.M., Shigley J.E., McClure S.F., Koivula J.I., Van Daele M. (1999) Observations on GE-processed diamonds: A photographic record. *G&G*, Vol. 35, No. 3, pp. 14–22.
- Shen A.H., Wang W., Hall M.S., Novak S., McClure S.F., Shigley J.E., Moses T.M. (2007) Serenity coated colored diamonds: Detection and durability. *G&G*, Vol. 43, No. 1, pp. 16–33.
- Shigley J.E. (2005) High-pressure and high-temperature treatment of gem diamonds. *Elements*, Vol. 1, No. 2, pp. 101–104.
- Smith C.P., Bosshart G., Ponahlo J., Hammer V.M.F., Klapper H., Schmetzer K. (2000) GE POL diamonds: Before and after. *G&G*, Vol. 36, No. 3, pp. 192–215.
- Yelisseyev A.P., Kanda H. (2007) Optical centers related to 3d transition metals in diamond. *New Diamond and Frontier Carbon Technology*, Vol. 17, No. 3, pp. 127–178.