DETECTION OF TREATMENT IN TWO UNUSUAL GREEN DIAMONDS

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A pair of sharp absorption bands in the near-infrared region, referred to as H1b and H1c, have been detected in one (and the H1b band in the other) of two green diamonds known to have been treated. Until now, these bands have been associated with the annealing of yellow to brown laboratory-irradiated diamonds. This is the first reported observation of these bands in green treated diamonds. Although these two diamonds may represent a special case, in that they are believed to have been irradiated, annealed, and then re-irradiated, the presence of one or both of these bands in a green diamond is one of the few reliable characteristics that identify that the stone has been treated in a laboratory.

Distinguishing diamonds of natural color from those colored by treatment is one of the greatest challenges facing the gemologist today (see, e.g., Collins, 1982; Nassau, 1984), and green diamonds present some of the most serious difficulties. This arises from the fact that the green color in diamond is usually the result of irradiation only (whether in nature or in the laboratory), while most of the gemological criteria used to separate natural- from treated-color diamonds are based on features related to the annealing step in the treatment process. Recently, it was reported that two sharp bands in the near-infrared region (referred to as H1b and H1c) are characteristic of annealing of laboratory-irradiated type Ia diamonds in the yellow to brown range (Woods, 1984; Woods and Collins, 1986). This article is the first report of the observation of the H1b and H1c lines in treated green diamonds (figure 1).

BACKGROUND

Green coloration is produced in diamonds when high-energy radiation (e.g., electrons, neutrons, gamma or alpha rays, etc.) removes carbon atoms from their original positions in the diamond crystal structure, thereby creating vacancies (called the GR1 [General Radiation] center, with a sharp absorption band at 741 nm). These vacancies absorb light in the red portion of the spectrum. Inasmuch as most nitrogen-containing diamonds already absorb in the violet end of the spectrum, this leaves a transmission "window" in the green. The GR1 center can be created by irradiation either in nature or in the laboratory. Thus, its presence is not proof of laboratory treatment.

Gemologists have used various criteria in the past to separate natural- from treated-color green diamonds. Recent observations have shown these criteria to be wrong in some cases, although they may be correct in others.

Specifically, many gemologists have noted that treated green diamonds commonly have an unattractive brownish or grayish ("olive" or "tourmaline") green hue, in contrast to the purer, more attractive green of the natural stones (G. R. Crowningshield, 1957 and pers. comm., 1987). In 1957, Crowningshield stated that "unless green *naturals* are present on a dark-green diamond . . . few dealers today accept as natural any dark-green stones." At that time, dark green in diamonds was associated with treatment, and only the few pale green stones with green naturals encountered were believed to be of natural color. Today, however, it appears that more light green stones are available on the market. This may be due to the fact that treaters are currently using electron and other irradiation technologies which may produce a greater proportion of stones that are light green, as compared to the darker green associated with the older method of treatment in a nuclear reactor

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Figure 1. The two treated green diamonds described in this article weigh 0.17 ct (left) and 0.19 ct (right). Photo by Robert Weldon.

(R. T. Liddicoat, pers. comm., 1988). In the course of our study of colored diamonds, we have observed sufficient overlap in color between the two groups to suggest that color alone is not a reliable separation criterion.

In addition, except for cases of cyclotron and radium treatment (see, e.g., Nassau, 1984), where the green color is concentrated in lines or spots, the color of treated green diamonds is generally homogeneous throughout the stone. This is not always the case for natural diamonds (some of which have only a green outer "skin"). Again, though, this characteristic cannot serve as conclusive evidence.

Green or brown spots, thought to be the result of α-radiation bombardment (Vance and Milledge, 1972), may also be present on the surface of a natural green diamond crystal. Called "irradiation stains" by gemologists, they are sometimes observed at the girdle or culet of a faceted stone, close to the original surface of the diamond. To our knowledge, they cannot be induced by laboratory irradiation (except by exposure to radium salts, a process that is easy to detect because of the remnant radioactivity). Therefore, these spots have suggested to some gemologists that the green body color of the diamond is also of natural origin. However, some near-colorless diamonds also have (natural) brown or green irradiation stains, and these stones, too, may be turned green by irradiation in the laboratory.

The presence of a prominent 595-nm absorption line (traditionally called the "5920"), first reported by Dugdale (1953), has been associated with the treatment of yellow diamonds (Crowningshield, 1957). In some rare cases, this line has even been observed in the spectra of treated green diamonds (G. R. Crowningshield, pers. comm., 1988). However, this line has been observed in a number of natural-color diamonds as well, including some green stones (Crowningshield, 1957; Anderson, 1963; Scarratt, 1979; Cottrant and Calas, 1981; Collins, 1982; Guo et al., 1986). From these observations on color, color distribution, irradiation stains, and spectral bands, one can readily understand why it may be difficult to determine whether the color in a diamond is natural or the result of treatment.

However, a breakthrough in the separation of some natural-color from treated-color diamonds was achieved recently (Woods, 1984; Woods and Collins, 1986; Collins et al., 1986). In particular, two sharp absorption bands in the near-infrared region at about 4935 cm^{-1} (2026 nm) and 5165 cm^{-1} (1936 nm), called respectively H1b and H1c, have been associated with the annealing of known laboratory-irradiated type Ia diamonds in the yellow to brown color range. Neither band has ever been observed in natural-color diamonds. We report here the first observation of either of these infrared bands in green diamonds known to be treated (as stated by M. Fuchs, pers. comm., 1987).

MATERIALS AND METHODS

The treated diamonds loaned to us for study are two dark grayish green round brilliants that weigh 0.17 and 0.19 ct (figure 1). The optical absorption spectra of the two stones were obtained with a Pye-Unicam 8800 spectrophotometer (at low temperature, 120K) as well as a Beck prism spectroscope mounted on a GIA GEM Instruments spectroscope base. The infrared absorption data were obtained

with a Nicolet 60SX Fourier Transform infrared spectrometer, covering the energy range from 400 to 25,000 cm^{-1} (see Fritsch and Stockton, 1987, for more details on this instrument).

RESULTS

The gemological properties of the two stones are summarized in table 1, but they are not sufficient to provide a useful conclusion. The color of each of these stones falls within the range that has been observed for treated green diamonds (as mentioned above). The larger stone displays an internal planar brown graining and an otherwise homogeneous green body color (figure 2), which suggests that this stone was brownish before irradiation. The smaller stone does not exhibit such colored graining. The optical absorption spectra of both stones (as observed with the Pye-Unicam 8800) display a strong to moderate GR1 (figure 3), a moderate 595 nm, and moderate H3 (503 nm) and H4 (496 nm) lines (which are sometimes referred to collectively by gemologists as the "4980–5040 pair"). Both stones are "green transmitters"; that is, they fluoresce green to a concentrated beam of visible light transmitted through the stone. This property has been noted in natural and treated diamonds of various colors, and our observations suggest that it is associated with the defect that gives rise to the H3 band. The near-infrared spectrum shows a weak but definite H1b band for the larger stone, and moderately intense, sharp, H1b and H1c bands for the smaller one (figure 4). Both are type Ia diamonds (containing aggregated nitrogen atoms).

TABLE 1. Gemological and spectral properties of the two treated dark grayish green diamonds.

Property	0.19 ct stone	0.17 ct stone
Gemological		
Fluorescence to U.V. radiation:		
Long-wave	Strong yellowish green	Weak green
Short-wave	Very weak green	Very weak green
Fluorescence to transmitted visible light	Strong green	Moderate to strong bluish green
Internal graining	Moderate to strong brown planar	None observed
Optical absorption spectrum, hand spectroscope (nm)	Moderate sharp 496–503 nm, weak sharp 595	Strong 415, weak 478, moderate sharp 496–503
Advanced Spectroscopy		
Low-temperature optical absorption spectrum (nm)	Moderate 496 (H4) and 503 (H3), moderate 595, strong 741 (GR1)	Moderate 415, weak 478, moderate sharp 496 (H4) and 503 (H3), weak 595, moderate 741 (GR1)
Type	IaA + B (moderate nitrogen content)	IaA + B (high nitrogen content)
Near-infrared absorption	H1b	H1b, H1c

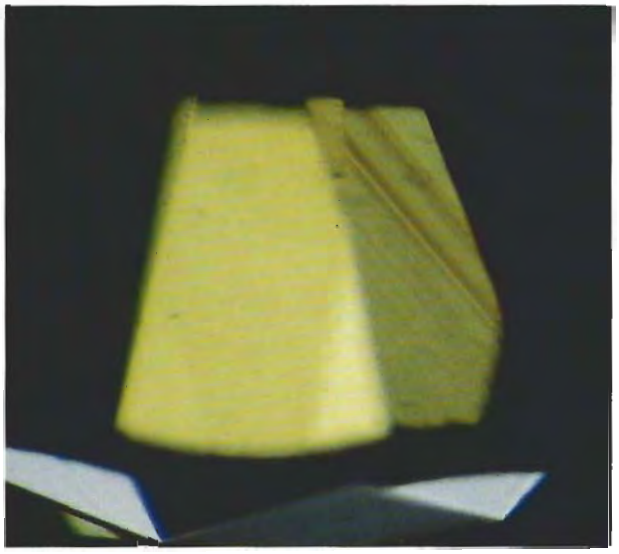

Figure 2. Brown planar graining in the otherwise homogeneous green 0.19-ct diamond indicates that the stone was brownish in color before it was irradiated. Magnified 10×; photomicrograph by John Koivula.

DISCUSSION AND CONCLUSION

Woods and Collins (1986) demonstrated that the H1b and H1c bands are related to the intense annealing (at least 650°–700°C) of irradiated diamonds. Thus, it is most unexpected to find these bands in green diamonds, because the green color usually is changed to yellow by such annealing. Although Mr. Fuchs does not know the exact details of the treatment these stones received, he indicated that it is likely that they were originally irradiated and heat treated in an attempt to get a "canary" yellow color; then, when the new color was deemed unsatisfactory, the stones were subsequently re-irradiated to green. So far, there has been no evidence of the H1b and/or H1c lines appearing in any colored diamonds other than

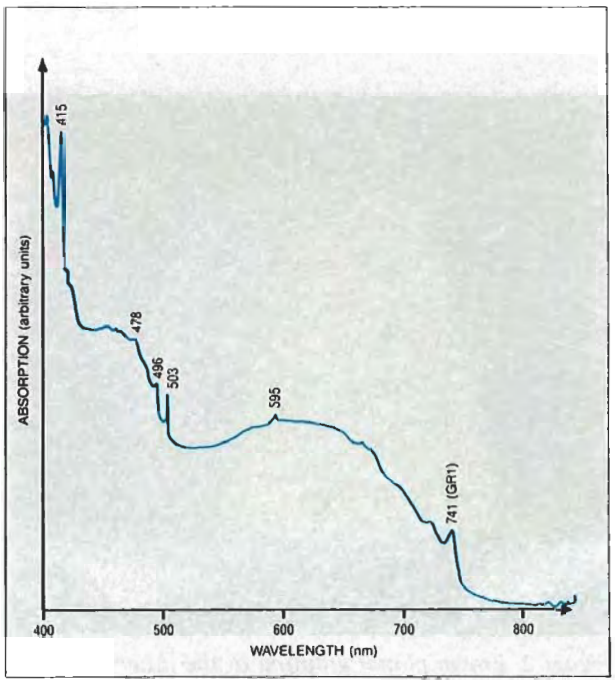

Figure 3. This optical absorption spectrum of the 0.17-ct treated green diamond was taken at 120 K (−243°F).

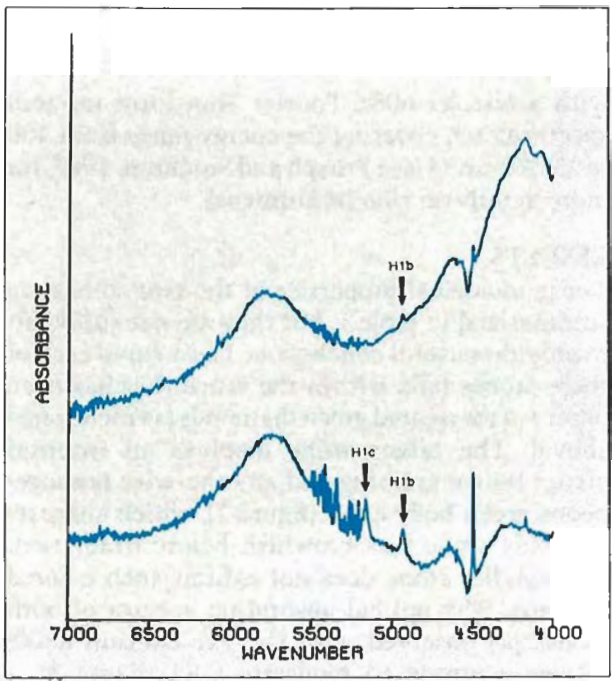

Figure 4. The near-infrared absorption spectra of the two treated diamonds (top = 0.19 ct stone, bottom = 0.17 ct stone) show the presence of the H1b and H1c lines (arrows).

those treated in a laboratory. Thus, the observation of the H1b and/or H1c lines seems to be one of the few reliable means at this time to identify treatment in a green diamond, although it may be applicable only in rare instances as represented by the two stones we studied.

Note added in proof: Shortly after the H1b and/or H1c bands were observed in the two treated green diamonds discussed here, we observed these bands in another green diamond, which had been submitted to the East Coast Gem Trade Laboratory. This 0.58-ct grayish yellow-green stone exhibited a strong green fluorescence to transmitted light, a greenish yellow fluorescence to ultraviolet radiation, a weak 595-nm line in the visible range, and both the H1b and H1c lines in the near infrared. We concluded, therefore, that the green color of the stone was the result of treatment.

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