NATURAL TYPE IA DIAMOND WITH A GREEN-YELLOW COLOR DUE TO NI-RELATED DEFECTS

Wuyi Wang, Matthew Hall, and Christopher M. Breeding

Commonly seen in HPHT-grown green synthetic diamonds, nickel-related defects were identified for the first time in a type Ia natural diamond with a strong green component. The 1.75 ct fancy green-yellow diamond showed a strong peak at 1332 cm^{-1} in the IR absorption spectrum, strong absorption from the 1.40 eV center and the associated ~ 685 nm band in the Vis-NIR spectrum, and extremely strong emissions from Ni-related defects in the photoluminescence spectra—all of which proved that nickel was the primary cause of the green color.

Nickel is widely used as a catalyst in high-pressure, high-temperature (HPHT) synthetic diamond growth processes. Consequently, Ni-related lattice defects are common in HPHT-grown synthetic diamonds, and can produce a green color component when the nitrogen concentration is sufficiently low (Lawson et al., 1998). The occurrence of trace amounts of Ni has also been confirmed in some natural diamonds—including, but not limited to, chameleon diamonds, yellow-orange diamonds colored by a broad absorption band at ~480 nm, H-rich diamonds, and even some colorless type IIa diamonds (Shigley et al., 2004; Hainschwang et al., 2005; and the present authors' unpublished research).

In a recent study, Wang and Moses (2007) provided the first evidence of Ni-related defects producing green color in a natural gem diamond: a 2.81 ct type IIa Fancy Intense yellowish green oval cut. However, the general role of Ni as a color-producing center in many natural diamonds remains unclear. Soon after studying the type IIa diamond noted above, the New York laboratory examined a type Ia natural diamond with a strong green color component that also proved to be the result of Ni-related defects.

Materials and Methods. A 1.75 ct cushion-cut diamond (figure 1) was submitted to the New York laboratory for a grading report and color graded Fancy green-yellow. To fully document that both the stone and the color were natural, we conducted standard gemological testing, fluorescence imaging (Diamond Trading Company [DTC] DiamondView), and detailed spectroscopic testing. Infrared absorption spectra were collected using a Thermo 6700 Fourier-transform infrared (FTIR) spectrometer (6000–400 cm^{-1}, 1 cm^{-1} resolution, up to 1,024 scans, at room temperature). UV-visible-near infrared (UV-Vis-NIR) spectra were collected with an Ocean Optics high-resolution spectrometer (Model HP-2000+, 250–1000 nm, 1 nm resolution, deu-

Figure 1. This 1.75 ct cushion-cut Fancy green-yellow diamond is colored mainly by Ni-related defects. Photo by Jian Xin (Jae) Liao.

See end of article for About the Authors and Acknowledgments.
GEMS & GEMOLOGY, Vol. 43, No. 3, pp. XXX–XXX.

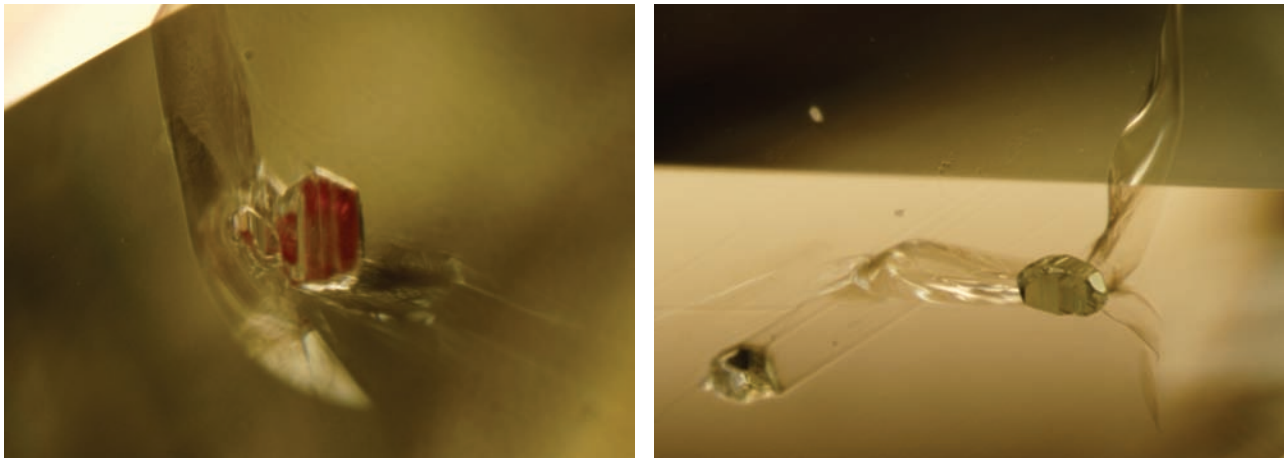


Figure 2. The presence of included crystals of reddish orange almandine-rich garnet (left, image width 1.35 mm) and pale green omphacite (right, image width 1.05 mm) demonstrates that this natural diamond crystallized in an eclogitic environment. Photomicrographs by W. Wang.

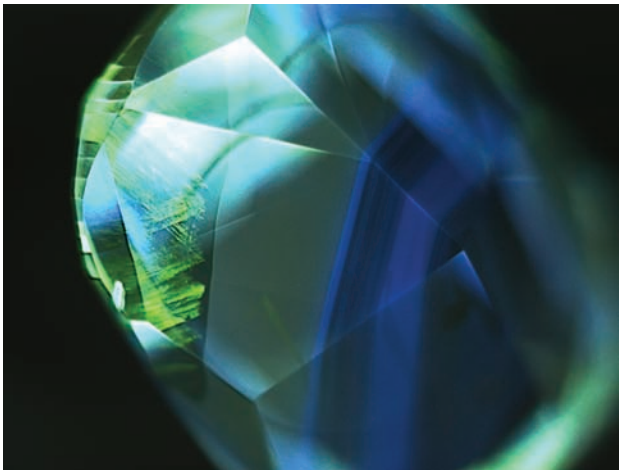
terium-tungsten-halogen source, at liquid-nitrogen temperature). Photoluminescence spectra were collected using a Renishaw InVia Raman microscope (488, 514, 633, and 830 nm laser excitations, various scan ranges, at liquid-nitrogen temperature). To test the diamond's color stability and any possible thermochromic properties, we heated it with an alcohol lamp to a temperature of approximately ~350°C.

Results and Discussion. Observation with a gemological microscope indicated that the green-yellow color was distributed evenly throughout the stone, with no evidence of treatment visible. Microscopy also revealed colorful euhedral mineral inclusions (100–150 mm in longest dimension) that were surrounded by small fractures. The reddish orange and pale green crystals (figure 2) were identified as almandine-rich garnet and omphacite, respectively, by Raman spectroscopy. The presence of natural mineral inclusions proved that the diamond was not synthetic. These inclusions are typical of diamonds from eclogitic environments (Meyer, 1987; Koivula, 2000). Furthermore, careful microscopic examination with various lighting configurations confirmed no coating was present.

The diamond fluoresced strong orangy yellow to long-wave UV radiation and moderate greenish yellow to short-wave UV; we did not observe any phosphorescence with standard handheld gemological UV lamps. When examined with the DTC DiamondView, the stone showed a large variation in fluorescence. Some zones displayed unevenly distributed linear green luminescence features. Other regions showed a moderate greenish yellow color. Still other parts of the stone displayed banded blue fluorescence (figure 3). Weak greenish yellow phosphorescence was also observed at the ultra-short wavelengths. The large variation in fluorescence colors and the absence of a typical HPHT-synthetic growth pattern confirmed that the diamond was natural.

The infrared absorption spectrum showed a clear band at 1282 cm^{-1}, indicating the diamond was type IaA; the nitrogen concentration was calculated to be about 36 ppm. Distinct absorption peaks were also noted at 3107 and 1405 cm^{-1}, showing the occurrence of hydrogen impurities. A relatively strong peak at 1332 cm^{-1} suggested that N^+ (which sometimes serves as a proxy for Ni content in diamond) might also be present. Isolated substitutional nitrogen acts as an electron donor, and some nickel-related defects are observed in the negatively charged state (Lawson et al., 1998). A strong 1332 cm^{-1} absorption is consistent with the detection of Ni-related defects in this diamond.

Figure 3. The green-yellow diamond showed distinctive zoned fluorescence in the DiamondView that also ruled out a synthetic origin. Areas of green, greenish yellow, and blue fluorescence occurred in different parts of the diamond. Image by W. Wang.



The Vis-NIR absorption spectrum (figure 4) showed weak but distinct absorptions between 350 and 370 nm (357.0, 360.2, 363.5, 367.0 nm; not shown in the figure) and 460 and 480 nm (468.0, 473.3, 477.4 nm). These features are identical to those reported for the type IIa, Ni defect?colored green diamond seen previously (Wang and Moses, 2007). These series of peaks are known to originate from Ni-related defects (Collins and Stanley, 1985; Lawson and Kanda, 1993a; Yelisseyev et al., 1996). Unlike the type IIa diamond, however, this type Ia stone exhibited additional weak absorptions at 415.2 nm (zero-phonon line [ZPL] of the N3 center and a common feature in type Ia diamonds) and 427.1 nm, but it lacked features in the 600–650 nm range (608.1, 637.5, 642.5 nm). An outstanding characteristic of the Vis-NIR absorption spectrum of the type Ia green-yellow diamond was the strong absorption of the 1.40 eV center (unresolved ZPL doublet at ~884 nm) and the associated ~685 nm band; it is well known that these are caused by interstitial Ni^+ (Isoya et al., 1990; Lawson and Kanda, 1993b). We also observed a sharp peak at 793.0 nm, another well-known Ni-related defect, but it was much weaker than the 884 nm peak. The 685 nm band was strong and broad, extending from 585 nm to about 735 nm, and efficiently blocked the transmission of red and orange light. Combined with a gradual increase in absorption from ~555 nm to the high-energy (low-wavelength) side due to unknown causes, the 685 nm absorption generated a transmission window centered at ~555–585 nm that resulted in the observed green-yellow bodycolor.

The photoluminescence spectrum collected with 830 nm laser excitation was dominated by the 883.1/884.8 nm doublet (i.e., the 1.40 eV center; figure 5). When 514 nm laser excitation was used, the spectrum exhibited a broad band centered at ~640 nm, with numerous sharp emissions superimposed between 560 and760 nm. These PL features are typically associated with the broad 480 nm absorption band that occurs in some natural yellow-orange diamonds and all chameleon diamonds, both of which reportedly contain Ni-related defects (Collins, 2001). However, these features are not believed to correlate directly with the 1.40 eV center. Unlike the green-yellow stone presented here, those types of diamonds do not show Ni-related defects in the Vis-NIR absorption spectrum. Spectroscopy also revealed that some common defects in type Ia natural diamonds (e.g., H3, H4, N-V centers) were not detected in this diamond.

Green color in natural diamonds can be introduced by a number of known defects or defect combinations, including absorptions from GR1, H2, and some hydrogen-related defects, and/or the fluorescence of the H3 defect (Collins, 1982; Collins, 2001). The absence of any of these centers and the almost exclusive occurrence of Ni-related defects (in particular the 1.40 eV center), strongly indicate that the green component of this diamond is caused by Ni.

A final interesting property that we noted about the green-yellow diamond is that when heated (~350°C), the stone changed color slightly to a more yellow (less green) hue. The original color was restored when we cooled the stone at room temperature for approximately 15 seconds.

Figure 4. Strong absorption from the 1.40 eV center (ZPL at ~884 nm) and the associated ~ 685 nm band are the dominant features in the Vis-NIR absorption spectrum of the 1.75 ct Fancy green-yellow diamond. The 1.40 eV center, caused by the interstitial charged-ion Ni^+, is the main cause of the diamond's green component.

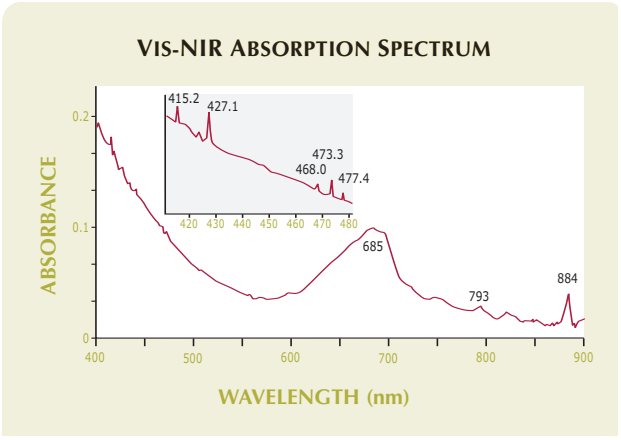
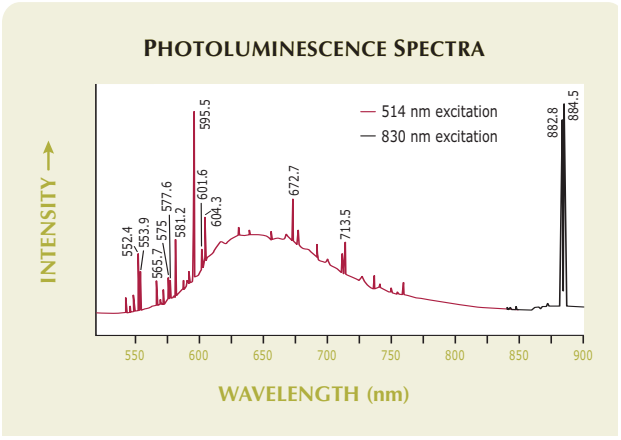


Figure 5. PL spectra confirmed the presence of extremely strong emissions from Ni-related defects (e.g., the 883.1/884.8 nm doublet). Numerous sharp emissions in the range 560–760 nm and a very broad luminescence band centered at ~640 nm strongly indicate an association between this diamond and natural yellow-orange and chameleon diamonds, which exhibit broad 480 nm absorption bands. The 640 nm feature is an emission band of an unknown defect that causes absorption at ~480 nm.



This weak thermochromicity, together with other gemological and spectroscopic similarities between this stone and chameleon diamonds, may indicate that Ni-related defects play a role in the thermochromic and photochromic diamond properties exhibited by both of these unusual types of diamonds.

Conclusions. Spectroscopic evidence from this rare type Ia gem diamond, as well as the yellowish green type IIa stone described recently, proves that Ni-related defects are directly responsible for the bodycolor. Diamonds colored by Ni may, in fact, be more common than has been believed, as reexamination of previously collected spectra seems to indicate. Therefore, nickel-related defects may represent another important cause of green color in natural diamonds.

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ACKNOWLEDGMENTS

The authors thank Dr. James Butler, of the Naval Research Laboratory, and Dr. Mark Newton and Dr. Christopher Welbourn, of the University of Warwick, for their constructive comments and suggestions, which helped improve this paper significantly. We are grateful to Thomas Moses, of the GIA Laboratory in New York, for discussions.

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