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Fancy Dark Brown-Yellow Zoned Type IIa/IIb DIAMOND

Type IIb diamonds are very rare; type IIb diamonds in brown hues are even rarer. While zoned type IIa/IIb diamonds have been reported (see, e.g., Lab Notes: Fall 1993, p. 199; Summer 2005, pp. 167–168), they are also far from common. Therefore, the combination of properties exhibited by the diamond in figure 1, which was sent to the Carlsbad laboratory for a Colored Diamond Grading Report, is remarkable.

The 3+ ct pear shape was color graded Fancy Dark brown-yellow. No color zoning was visible with magnification, even when the stone was immersed in methylene iodide. Internal graining was colorless and weak. The diamond was inert to both long- and short-wave ultraviolet (UV) radiation from a standard gemological UV lamp, and exhibited no phosphorescence. When examined between crossed polarizers, it exhibited a dense “tatami” pattern, with strong localized strain surrounding a crystal (the only solid inclusion observed). The stone also exhibited feathers and indented naturals.

Editors' note: All items are written by staff members of the GIA Laboratory.

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The mid-infrared (IR) spectra (figure 2) clearly showed the presence of two diamond types: IIa and IIb. When the pear shape was oriented such that the shoulder end was sampled, the resulting spectrum was typical of type IIa diamond with no absorption from boron or nitrogen impurities. However, when the point end was sampled, the spectrum exhibited bands at 2930 and 2801 cm^{-1} , which are characteristic of boron in type IIb diamond. This IIb spectrum was similar to that of a Fancy Dark greenish yellow-brown type IIb diamond examined at the New York laboratory in 2005 (again, see figure 2), though the boron peaks in the 2008 sample were less intense.

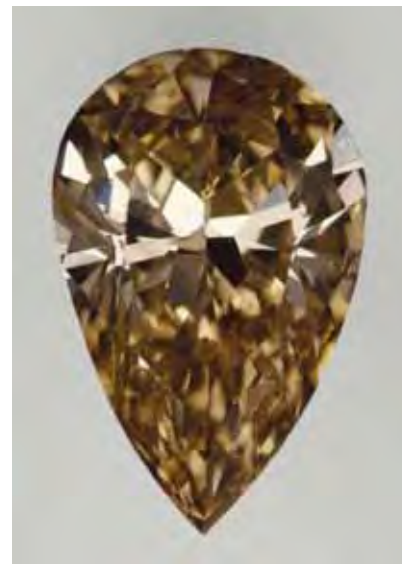
The ultraviolet-visible-near infrared (UV-Vis-NIR) spectra gathered from the present stone were typical of brown type IIa diamonds; absorption increased toward the blue end of the spectrum. This is in contrast to the visible spectra for blue type IIb diamonds, in which absorption increases toward the red end (A. T. Collins, “The colour of diamond and how it may be changed,” *Journal of Gemmology*, Vol. 27, No. 6, 2001, pp. 341–359).

In the DiamondView, the type IIa portions showed blue fluorescence and no phosphorescence, while the IIb regions exhibited much weaker blue fluorescence (figure 3) and short-lived weak blue/white phosphorescence. Boundaries between zones were irregular—in some places linear and in others jagged (figure 4, left). The IIa portions of the stone exhibited “mosaic” disloca-

tions (figure 4, right), which are typical in natural IIa and IIb diamonds (e.g., P. M. Martineau et al., “Identification of synthetic diamond grown using chemical vapor deposition [CVD],” Spring 2004 *Gems & Gemology*, pp. 2–25). Additionally, a “flame” or “wave” structure observed in the fluorescence of the IIb region was replicated in the phosphorescence for that region.

Since boron acts as an electron acceptor, type IIb diamond is classified as a semiconductor. When the electrical conductivity of the zoned diamond was

Figure 1. This 3+ ct Fancy Dark brown-yellow diamond was found to be distinctly type zoned (IIa and IIb).



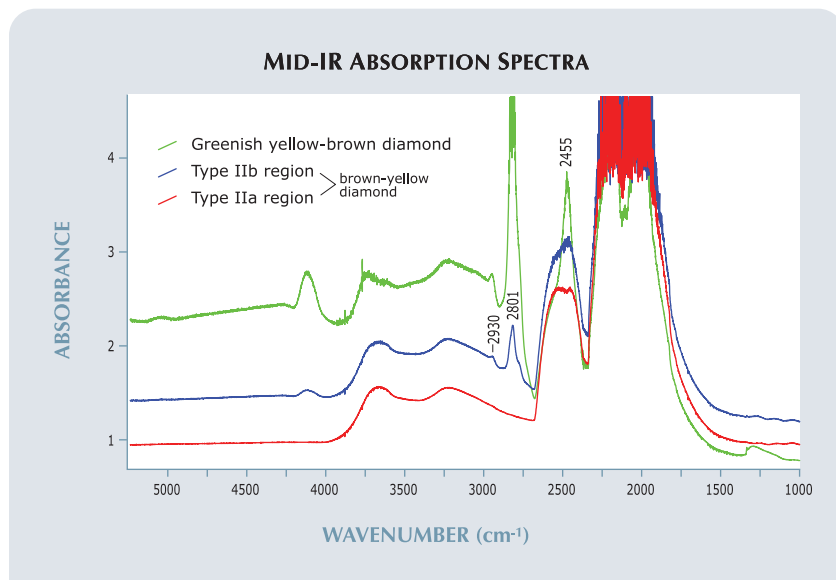


Figure 2. The mid-IR absorption spectra of the brown-yellow diamond in figure 1 indicate the presence of type IIa and IIb zones. Also shown for comparison is the spectrum of a greenish yellow-brown type IIb stone.

tested, the shoulder end (IIa) did not conduct, while the point end (IIb) was weakly conductive. This observation was not, in itself, conclusive, since type IIb diamonds are not homogeneously conductive, but it did correlate with the mid-IR and DiamondView results.

Photoluminescence (PL) spectra collected with a 488 nm laser revealed the presence of the 3H peak (503.5 nm), which has been reported before in type IIb diamonds (e.g., Fall 2004 Lab Notes, pp. 241–242). This peak occurred in

spectra from both regions of the stone, but it was stronger in the IIb region. Spectra collected using three other laser wavelengths indicated that the stone was of natural color. Raman spectroscopy (514.5 nm excitation) was used to try to identify the crystal inclusion, but no match could be found. This was unfortunate, since knowledge of the mineral might have provided valuable information pertaining to the origin of this exceptional diamond.

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Figure 4. The boundaries between the type zones are linear in some places and jagged in others (left); the type IIa regions in the diamond also show the subtle mottled appearance of “mosaic” dislocations (right).



Figure 3. This DiamondView image of the pavilion of the pear shape clearly shows the different type zones: moderate blue fluorescence for the type IIa region, and weak blue for the IIb zone.

HPHT-Treated CVD SYNTHETIC DIAMOND Submitted for Dossier Grading

Gems & Gemology has reported on synthetic diamonds grown by the chemical vapor deposition (CVD) method for several years (e.g., W. Wang et al., “Gem-quality synthetic diamonds grown by a chemical vapor deposition [CVD] method,” Winter 2003, pp. 268–283; P. M. Martineau et al., “Identification of synthetic diamond grown using chemical vapor deposition [CVD],” Spring 2004, pp. 2–25; and W. Wang et al., “Latest-generation CVD-grown synthetic diamonds from Apollo Diamond Inc.,” Winter 2007, pp. 294–312). CVD synthetic diamonds have been submitted to the GIA lab (e.g., Lab Notes: Spring 2008, pp. 67–69, and Summer 2008, pp. 158–159), but those samples were as-grown, even though high-pressure, high-temperature (HPHT) treatment of CVD synthetics is well known.

The 0.21 ct round brilliant in figure 5 was recently submitted for Diamond Dossier grading. Standard testing identified it as a CVD synthetic. It was graded near colorless (GIA does not use



Figure 5. This 0.21 ct CVD synthetic diamond was found to be HPHT treated.



Figure 6. The HPHT-treated CVD synthetic diamond shows weak birefringence in shades of gray, in contrast to the high-order interference colors previously documented in as-grown samples. Note the pinpoint inclusions. Field of view 1.73 mm.



Figure 7. DiamondView imaging of the synthetic diamond shows blue-green fluorescence with yellow-green striations, consistent with reports for HPHT-treated CVD synthetic diamonds.

letter grades on synthetic diamond reports) and VVS, with the clarity grade based on pinpoint inclusions. Between crossed polarizers, it exhibited weak birefringence in shades of gray (figure 6). In comparison, the as-grown sample described in the Spring 2008 Lab Note showed strong birefringence with high-order interference colors, consistent with the samples examined by Wang et al. (2007).

The sample was inert to long-wave UV radiation but fluoresced weak yellow to short-wave UV. In the DiamondView, it fluoresced blue-green, with yellow-green striations (figure 7), and exhibited weak blue phosphorescence. The fluorescence color was similar to the green luminescence of HPHT-treated nitrogen-doped CVD synthetic diamonds reported by Martineau et al. (2004), and it contrasted distinctly with the orangy pink to orangy red hues of the as-grown CVD synthetics described in the previous Lab Notes. The striations are growth phenomena, and are typical of CVD synthetic diamonds (see, e.g., Martineau et al., 2004).

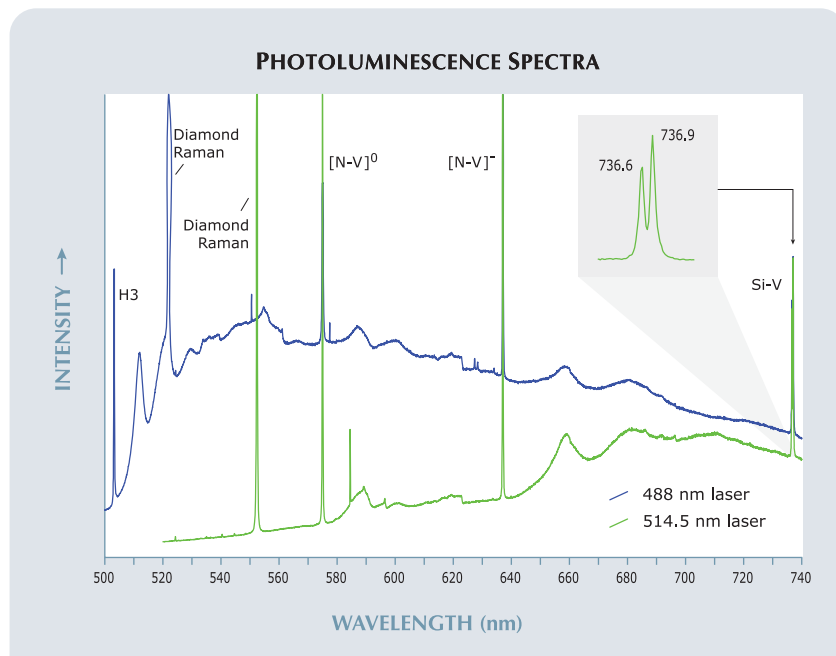
The mid-IR spectra established that the sample was type IIa. Neither of the hydrogen-related peaks at 3123 and 3107 cm^{-1} was detected. Martineau et al. (2004) stated that the former would be removed by HPHT treatment, while the latter could appear *after* HPHT treatment. A weak peak was observed at 1332 cm^{-1} , consistent with the near-colorless sam-

ples described by Wang et al. (2007).

Photoluminescence spectra collected at liquid-nitrogen temperature (~ 77 K) with 488 and 514.5 nm laser excitation (figure 8) exhibited a very

large peak doublet at 736.6/736.9 nm, due to the silicon-vacancy (Si-V) defect. Correspondingly, a very small doublet was recorded in the UV-visible spectrum at ~ 737 nm; the spectrum was otherwise featureless but with absorption rising toward the

Figure 8. The PL spectra (at 488 and 514.5 nm laser excitation) of the HPHT-treated CVD synthetic diamond show a very large Si-V doublet at 736.6/736.9 nm.



blue region, as is typical of a near-colorless type IIa diamond.

The Si-V defect was originally considered indicative of CVD synthetic diamonds; however, recent work has shown that the defect also exists in some natural colorless and near-colorless diamonds (C. M. Breeding and W. Wang, "Occurrence of the Si-V defect center in natural colorless gem diamonds," *Diamond and Related Materials*, Vol. 17, 2008, pp. 1335–1344). Large peaks were observed at 575.0 and 637.0 nm (the zero-phonon lines [ZPLs] of the nitrogen-vacancy centers [N-V]⁰ and [N-V]⁻, respectively), consistent with CVD synthetic diamond (see, e.g., Wang et al., 2003). In contrast to the as-grown CVD synthetic diamonds documented in the two earlier Lab Notes, the PL spectra for this diamond did not exhibit a 596.5/597.0 nm doublet. Again, this is consistent with the HPHT-treated CVD synthetic diamonds discussed by Martineau et al. (2004). The 488 nm spectrum did display a large peak at 503.1 nm—the H3 ZPL—associated with nitrogen. This is also consistent with the results of Martineau et al. (2004), and contrasts with the relative lack of H3 peaks in the near-colorless as-grown CVD synthetic diamond samples investigated by Wang et al. (2007). It appears that the H3 defect is introduced during HPHT annealing.

We have seen very few HPHT-treated CVD-grown synthetic diamonds in the laboratory, but the criteria discussed above allowed us to successfully identify this sample.

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QUARTZ with Secondary Covellite Dendrites

The discovery of some unusual dendritic inclusions in two transparent faceted quartz gems sent to the laboratory for examination helped us make a connection between two separate notes previously published in *Gems & Gemology*. The first of these (Spring 2005 Lab Notes, pp. 47–48) described thin hexagonal platelets of the copper sulfide covellite in colorless and smoky quartz,

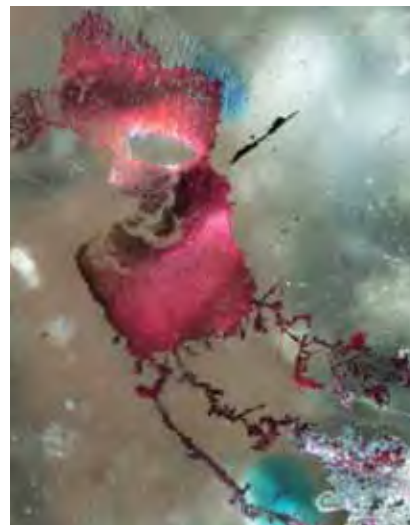
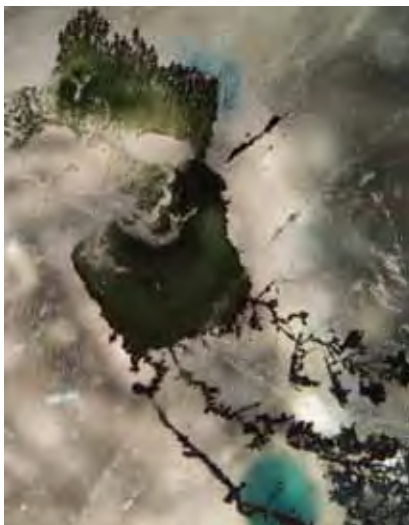


Figure 9. Discovered in colorless quartz reportedly from Paraíba State, Brazil, this dendrite is grayish green in transmitted light (left). In reflected light (right), it shows strong metallic pink reflectance, suggesting it is covellite, which was confirmed by Raman analysis. Note the blue gilalite inclusions in the background. Field of view 4.39 mm high.

said to be from Minas Gerais, Brazil. The material was being marketed as "pink fire" quartz due to the intense pink reflectivity of the numerous tiny covellite inclusions. These appeared to be primary to the formation of the host, since they were not associated in any way with surface-reaching cracks. As is characteristic for thin crystals of covellite, these inclusions also appeared grayish green in transmitted light.

The second report (Fall 2005 Gem News International, pp. 271–272) dealt with inclusions of a blue-to-green mineral in quartz, which occurred as jellyfish-like radiating clusters. This mineral was identified as gilalite, a hydrated copper silicate. The quartz was stated to have come from the Brazilian state of Paraíba, and is often sold as "Paraíba" quartz.

Our recent examination of the two faceted quartz gems, which are reportedly from the same locality that produced the gilalite inclusions, proved interesting, as both contained obvious black-appearing dendrites that were green in transmitted light (figure 9, left), with a bright pink reflectance color (figure 9, right). This was the same reaction previously reported for

hexagonal platy covellite inclusions, which suggested that these dendrites were also covellite. Moreover, one of the gems contained inclusions of gilalite (identified by their appearance) as well, indicating the presence of copper in the system. The dendrites were situated along surface-reaching fracture planes, proof that they formed after the quartz had crystallized.

Since the broad edges of the inclusions had been polished through and were exposed at the surface, these dendrites made ideal targets for Raman microanalysis, which confirmed that they were covellite. Covellite is known to be a secondary copper mineral in copper deposits, so the discovery of these dendrites as fillings in quartz was not surprising, even though such secondary inclusions in quartz have not been reported before.

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Induced Copper Contamination of TOURMALINE

In recent years, Gem Identification has received numerous requests to analyze tourmalines for the presence of copper,

since (justifiably or not) copper-bearing tourmalines generally command significantly higher prices in the marketplace than their non-cuprian counterparts. Such analyses are typically conducted on surface and near-surface areas of the faceted gems.

Since we are dealing with the detection of trace elements (in parts per million), we invariably face the problem of accidental or deliberate surface contamination. As the experiments described below indicate, this can be accomplished either by polishing a tourmaline on a copper lap, or by soaking the stone (faceted or in its rough state) in a concentrated solution of a copper salt such as copper sulfate. Accidental contamination from a copper lap is a very real possibility, since copper laps are often used to polish gems such as tourmalines.

To demonstrate the potential for this contamination, we started with two small (1–2 ct) faceted “watermelon” tourmalines and analyzed them by energy-dispersive X-ray fluorescence (EDXRF). Neither stone showed any copper peaks. We then rubbed the tourmalines 10 times in a circular motion against a flat copper lap, using moderate thumb pressure. When we repeated the EDXRF analyses, a clear signal for copper appeared.

At this point, we examined the tourmalines with a gemological microscope. We did not see any surface-reaching pits or cracks in the first tourmaline, only fine polishing lines. Nor did we see any evidence of copper on or in its surface.

The other stone had no eye-visible surface defects, but it did have a surface-reaching crack across the table that picked up minute amounts of microscopic copper when it was rubbed against the lap. In standard darkfield illumination, this contaminant was seen as thin black smudges that resembled the typical surface dirt often seen in such cracks (figure 10, left), but fiber-optic illumination revealed the metallic nature and copper color of the contaminant (figure 10, right). In light of these results, it seems clear that if copper laps are used to polish tourmalines, there is a possibility of accidental (or—though difficult to prove—deliberate) contamination.

This brings us to intentional contamination of tourmaline using concentrated copper salt solutions. The salt we chose for the experiment was copper sulfate, since chalcantite (the mineral name for naturally occurring copper sulfate) was readily available. We have no reason to believe that any other cop-

per salt in concentrated solution would not have worked just as well.

For this experiment, we selected another small (3 ct) faceted tourmaline with a few surface-reaching features—growth tubes and cracks—that did not detract significantly from its outward appearance. We also treated an ~7.5 ct piece of rough gem-quality tourmaline that had a nice greenish blue color that was not copper related.

Again, we first analyzed both samples using EDXRF; no copper was detected in either of them. Next, we warmed both samples in the light well of a gemological microscope and dropped them into the concentrated copper sulfate solution, which had been cooled in a refrigerator. This created a mild vacuum, which allowed the copper sulfate solution to enter any surface openings in the test subjects. After the solution had reached room temperature, we removed the tourmalines and hand-dried them with paper towels. Again, we repeated the EDXRF analyses.

Both tourmalines had absorbed enough copper solution to produce a visible copper signal on their EDXRF spectra. The copper peaks in the rough sample were not nearly as strong as the signal from the faceted stone, as expected. Although copper sulfate solution has an obvious blue color, no color from the solution was observed in either sample.

In analyzing tourmaline for copper, GIA uses a cleaning protocol that eliminates the potential for errors resulting from such contamination. These experiments underscore the importance of cleaning test samples thoroughly before analysis, and being aware of the very real possibility of surface contamination if unexpected elements are detected during analysis.

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Figure 10. The crack across the table of this tourmaline readily picked up minute traces of copper when the stone was rubbed against a flat copper lap. In standard darkfield illumination (left), the copper looks like typical smudges of black dirt. However, with surface-incident fiber-optic illumination (right), the metallic nature and copper color of the contaminant are clearly seen. Field of view 0.9 mm.

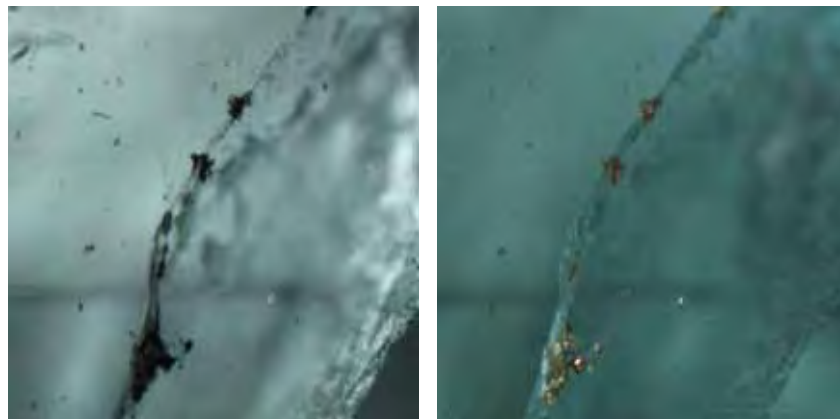


PHOTO CREDITS

Robison McMurtry—1 and 5; Karen M. Chadwick—3, 4, 6, and 7; John I. Koivula—9 and 10.