

Editors

Thomas M. Moses | Shane F. McClure

DIAMOND**Irradiated, with Green Color
Introduced by H2 Optical Center**

Several optical centers in diamond can result in green coloration. These include GR1 (zero-phonon line at 741 nm), fluorescence from the H3 center, some Ni-related defects, and unidentified but possibly hydrogen-related centers. In addition, the H2 optical center, which has its zero-phonon line at 986.3 nm in the infrared region, contributes to the green color of some HPHT-treated diamonds (see Summer 2007 Lab Notes, pp. 153–155). Although it is extremely rare for the H2 center to be the predominant contributor of green color, the New York laboratory recently examined one such diamond, which proved to be irradiated and annealed.

This 2.34 ct pear-shaped diamond was color graded as Fancy Deep yellow-green (figure 1). When observed under magnification with a strong light source, it appeared somewhat hazy compared to most natural gem diamonds. The color appeared evenly distributed throughout the whole stone. The mid-infrared spectrum showed strong type IaA absorptions, and no hydrogen-related peaks were detected. Also recorded was a weak absorption from the H1b defect (4935



Figure 1. This 2.34 ct Fancy Deep yellow-green diamond was identified as artificially irradiated and annealed. The green color is predominantly due to the H2 defect, an extremely rare occurrence.

cm⁻¹). UV-Vis-NIR spectroscopy at liquid-nitrogen temperature recorded absorptions due to the H2 defect (extremely strong), H3 (strong), and N3 (moderate). The same spectrum collected at room temperature (providing a direct reflection of a stone's bodycolor) showed a similar pattern, but the ZPL absorptions were poorly resolved, as expected (figure 2). No GR1 or 594 nm centers were detected. The sideband of the H2 center was extremely strong, extending well into the visible region and effectively blocking red and orange light. In combination with the H3 absorption, this created a transmission window in the 500–600 nm region, which explains the observed yellow-green bodycolor.

The gemological and spectro-

scopic features indicate that this diamond was artificially irradiated to improve its color. Before treatment, the stone very likely had a strong brown hue. Due to its high concentration of A-form nitrogen, significant amounts of H2 and H3 centers were introduced after irradiation and annealing. Annealing at high temperature (>1000°C) removed all GR1 and 594 nm centers but introduced large amounts of the H2 and H3 defects.

This specimen demonstrates that the H2 center can be the predominant contributor to a diamond's green color. This feature, present in such a high concentration, is more likely to occur after laboratory treatment.

Wuyi Wang and Emily Dubinsky

Large Multiple-Treated Pink

Pink diamonds with high saturation are very rare and highly valued. In recent years, a multiple-treatment process was developed to produce pink, red, or orange coloration in certain natural diamonds containing suitable impurities through the controlled introduction of lattice defects known as NV centers (Spring 2010 Lab Notes, pp. 51–52). Many diamonds treated in this fashion are now available in the gem market. Recently, the New York laboratory tested a very high-quality treated pink diamond, an excellent example of proper starting material and treatment conditions.

The 11.08 ct round brilliant was graded Fancy Vivid pink (figure 3), a very attractive but extremely rare color in nature. Microscopic observa-

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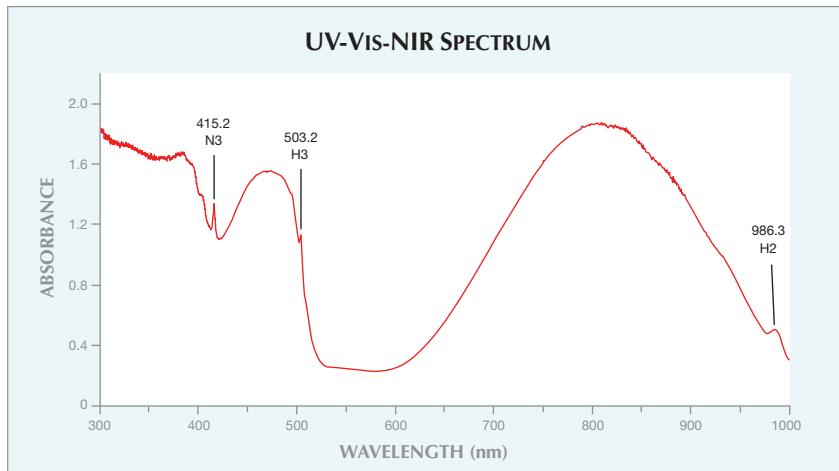


Figure 2. This room-temperature UV-Vis-NIR spectrum revealed extremely strong absorption from the H2 defect, as well as strong H3 and moderate N3 absorption. A transmission window created in the 500–600 nm region resulted in the yellow-green bodycolor.

tion revealed no observable fractures or inclusions. Instead, the diamond displayed moderate graining, which is consistent with a starting material that had a significant brown color component. This speculation was supported by the strong birefringence seen with a polarizing microscope. The diamond's color distribution was slightly patchy, but no concentration was observed at the culet. It showed

Figure 3. The Fancy Vivid pink color of this 11.08 ct diamond was produced by multiple treatments. The attractive coloration is the result of suitable starting material and proper treatment conditions.



very strong chalky orange fluorescence to both long- and short-wave UV radiation.

The mid-infrared absorption spectrum showed weak lines at 3107 and 1332 cm⁻¹, indicating a very low amount of B-form nitrogen impurity. A weak 1450 cm⁻¹ absorption [H1a] was also recorded. The UV-Vis spectrum collected at liquid-nitrogen temperature showed distinct peaks corresponding to NV centers with zero-phonon lines at 575 and 637 nm, as well as strong absorptions from irradiation-related centers such as 594, 741 (GR1), and 393 nm (ND1). Also recorded was a broad absorption band centered at 270 nm, attributed to isolated nitrogen. These gemological and spectroscopic features demonstrated that the color of the diamond was produced by multiple treatment processes. The initial high-pressure, high-temperature (HPHT) treatment would have effectively removed the unwanted brown color from the starting material and also introduced trace amounts (ppm level) of isolated nitrogen by disaggregating the preexisting B-form nitrogen. Subsequent irradiation and annealing would have turned part of the isolated nitrogen into NV centers, effectively blocking orange-yellow light and creating the pink color.

Few natural-color pink diamonds owe their coloration to NV centers. Separating these from their treated counterparts has become increasingly difficult because they share many similar features. While the intense color saturation itself is a strong indication of treatment, detailed spectroscopic analysis is essential for a conclusive identification.

Wuyi Wang and Kyaw Soe Moe

Coated Cat's-Eye GYPSUM

Any gem with elongated needle inclusions or a fibrous structure can produce chatoyancy when cut as a cabochon with the proper orientation. The Carlsbad laboratory recently received for identification a 30.45 ct translucent, saturated blue oval cabochon with an extremely sharp eye (figure 4). Standard gemological testing gave a spot RI of 1.56; the stone showed a moderately strong blue fluorescence to long-wave UV radiation and a weak blue reaction to short-wave UV.

While no particular gem came to mind during initial observation, the combination of saturated blue color and a sharp eye led us to suspect something too good to be true. This suspicion was confirmed during microscopic examination, which revealed a uniform fibrous structure and a blue coating on the top portion of the cabochon (figure 5). Decol-

Figure 4. This 30.45 ct blue oval cabochon proved to be a coated cat's-eye gypsum.





Figure 5. A blue color coating was clearly visible on the surface of the gypsum cabochon. Image width: 1.0 mm.

orized areas related to surface damage provided further evidence of a superficial color coating (figure 6). The base of the cabochon had a colorless coating that was easily observed, as a portion of it had delaminated from the substrate. The underlying material was very soft and easily scratched by a metal probe.

Raman spectroscopy of the top and bottom coatings gave results consistent with a polymer resin, and the substrate material was identified as gypsum. This was the first example of a color-coated cat's-eye gypsum examined in GIA's laboratory.

Amy Cooper and Phil York

Figure 6. Decolorized areas corresponding to surface damage confirmed that the blue color of the gypsum cabochon resulted from the thin coating, which was identified as a polymer resin by Raman spectroscopy. Image width: 4.3 mm.



Figure 7. This $26.99 \times 17.90 \times 7.25$ mm pearl has a unique mushroom shape (left). Underneath the cap of the specimen are arching radial structures reminiscent of the "gills" found in some actual mushrooms (right).



Mushroom PEARL

In July 2012, the New York laboratory received a most unusual pearl for examination. The $26.99 \times 17.90 \times 7.25$ mm specimen bore an uncanny likeness to a mushroom, consisting of a bell-shaped cap atop a narrower stem (figure 7, left). Interestingly, arching radial structures very reminiscent of the "gills" found in actual mushrooms were observed under the cap (figure 7, right). The pearl's brown color further added to the mushroom effect.

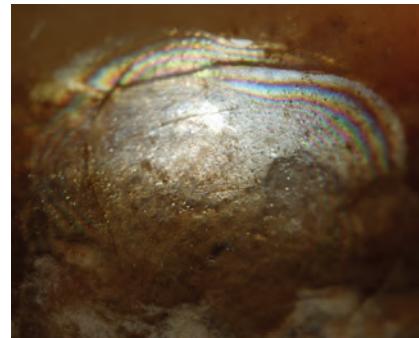
After digital imaging, the pearl was examined with the microscope (figure 8). It displayed a non-nacreous porcelaneous surface, with a noticeable flame structure at the top of the cap and a very subtle flame structure on the stem (figure 8, left). The flame structure at the end of the cap inter-

sected in a few small patches. The widest section of the pearl as well as the base of the stem showed a mottled growth pattern and coloration, which may have obfuscated any flame structure in those areas.

Microradiography revealed a denser growth structure along the center (lengthwise) of the pearl and visibly less compact layered growth in the widest area of the cap (figure 9). This growth structure in the cap made it more fragile than the top and base of the pearl; minor fracturing and chipping were seen along the rim with the microscope, including a number of iridescent liquid-filled inclusions slightly below the surface (figure 8, right).

Raman spectroscopy showed an aragonite peak, and chemical analysis by energy-dispersive X-ray fluorescence (EDXRF) indicated the presence

Figure 8. The pearl in figure 7 displays a subtle flame structure on the stem (left, image width ~7 mm). The widest section of the cap contains iridescent fractures just below the surface (right, image width ~7 mm).



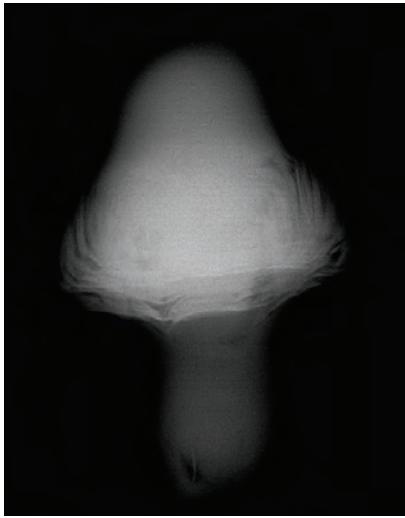


Figure 9. Microradiography reveals a denser growth structure down the length of the pearl and a visibly less compact layered growth structure in the widest part of the cap.

of Ca, as expected for a pearl. The absence of pigment and color concentrations indicated that the color was natural. The surface appearance, primarily the intersecting flame structure and liquid inclusions, pointed to a mollusk of the *Cassis* genus (i.e., a large marine snail). Although we had no way to confirm this through testing, the owner said it reportedly came from a *Cassis cornuta* mollusk found in the Indonesian archipelago.

While a pearl from a mollusk of the *Cassis* genus is uncommon in its own right, the shape of this specimen is what made it truly remarkable. Its striking resemblance to a mushroom has not been observed by GIA in any other pearl, from any mollusk species.

Akira Hyatt

amond grading laboratories (C. Even-Zohar, "Synthetics specifically 'made to defraud,'" *Diamond Intelligence Briefs*, Vol. 27, No. 709, May 21, 2012, pp. 7281–7283). In June 2012, 10 diamonds submitted to GIA's Hong Kong laboratory were identified as CVD-grown synthetics. Overall, they appeared comparable to top-quality natural counterparts. These round brilliants ranged from 0.30 to 0.35 ct, with F–H color grades (figure 10). Microscopic examination showed no fractures or inclusions, but did reveal weak graining and tiny pinpoints. Accordingly, their clarity grades ranged from VVS₁ to VVS₂, and one sample received a VS₁. The specimens were essentially inert to long-wave UV radiation and displayed a very weak yellow to green-yellow fluorescence to short-wave UV.

Infrared absorption spectroscopy identified all 10 synthetic diamonds as type IIa. Common features in CVD synthetics, such as isolated nitrogen absorption at 1344 cm⁻¹ and hydrogen-related absorptions at 3123 and 3107



Figure 11. In the DiamondView, all 10 synthetic diamond samples displayed moderate green fluorescence and distinctive CVD growth striations.

cm⁻¹, were not recorded. However, photoluminescence spectra collected at liquid-nitrogen temperature with various laser excitations showed very strong [Si-V]⁰ emissions at 736.6 and 736.9 nm, as well as strong peaks from N-V centers at 575.0 and 636.9 nm and an H3 emission at 503.2 nm. The DiamondView revealed moderate green fluorescence (attributed to the H3 optical center) and typical CVD growth striations (figure 11). Weak blue phosphorescence was also observed in each sample in the DiamondView.

Figure 10. These 10 CVD synthetic diamonds (0.30–0.35 ct, with F–H color) were recently identified in GIA's Hong Kong laboratory.



SYNTHETIC DIAMOND CVD Synthetic Diamonds Identified in Hong Kong Laboratory

Synthetic diamonds grown by the chemical vapor deposition (CVD) process are becoming more common in the jewelry market, and since mid-2012 they have shown up in major di-

These gemological and spectroscopic features are similar to those observed in Gemesis CVD synthetic diamonds (W. Wang et al., "CVD synthetic diamonds from Gemesis Corp.," Summer 2012 *GeG*, pp. 80–97), suggesting that post-growth annealing at high temperature was applied to improve their color and possibly their transparency.

Shun Yan Wong, Wai Kar Carmen Lo, and Terry Poon

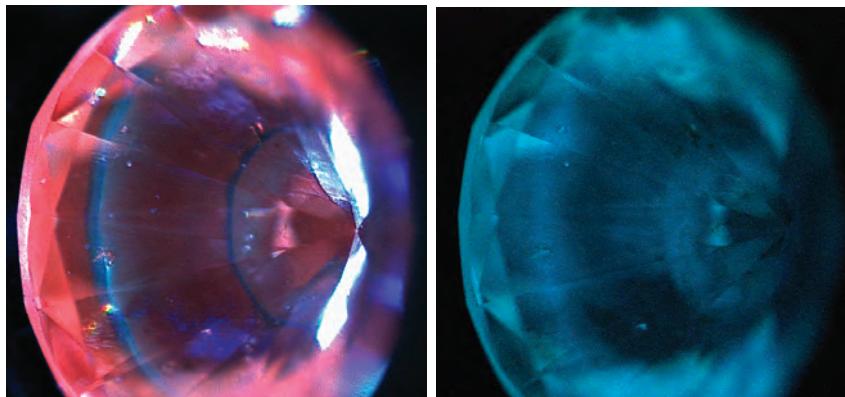


Figure 13. The type IIb CVD synthetic's DiamondView fluorescence image (left) showed regions of orangy red and blue fluorescence, including two distinctive blue concentric rings. The DiamondView also revealed mottled purple areas that are typical of some CVD synthetics. The unusual rings of fluorescence correspond to the strongest phosphorescence (right).

Type IIb CVD Synthetic Diamond

Gem-quality synthetic diamond grown by chemical vapor deposition is rarely encountered among the stones submitted for a GIA diamond report. Rarer still are type IIb CVD specimens—most are type IIa. Until recently, only one type IIb CVD synthetic had been submitted (Summer 2008 Lab Notes, pp. 158–159).

In April 2012, the Carlsbad laboratory examined a 0.25 ct round brilliant with Faint brown (L) color and I₁ clarity (figure 12). The sample showed strong graining with magnification, and it fluoresced very weak yellow to long-wave UV radiation and weak orange to short-wave UV. No phosphorescence or electrical conductivity was observed. Its DiamondView reac-

tion was marked by moderately strong orangy red and mottled purple regions and two unusual concentric rings of blue fluorescence (figure 13, left). DiamondView imaging also showed moderate blue phosphorescence, with the areas of strongest phosphorescence corresponding to the blue-fluorescing rings (figure 13, right). The growth conditions leading to this unusual pattern are unknown. Nevertheless, similar luminescence colors and mottled purple areas have been seen previously in CVD synthetics (e.g., W. Wang et al., "Latest-generation CVD-grown synthetic diamonds from Apollo Diamond Inc.," Winter 2007 *GeG*, pp. 294–312).

The infrared absorption spectrum revealed no detectable nitrogen, as expected since most CVD synthetic diamonds are nominally type IIa. Yet we did observe weak absorption at 2800 cm⁻¹ from trace amounts of boron. It is unclear whether the boron was doped intentionally. The Vis-NIR spectrum, collected at liquid-nitrogen temperature, showed a gradual increase in absorption toward shorter wavelengths, which imparted the brown color. Type IIb diamonds usually show a gradual increase in absorption toward longer wavelengths, resulting in a blue color. Additionally, this synthetic diamond produced strong absorption from the

Si-V defect (doublet at 736.6/736.9 nm), which was also manifested as a very strong photoluminescence (PL) emission. Si-V is a common, often diagnostic defect in CVD synthetic diamond. Although nitrogen was not observed in the sample's IR absorption spectrum, the more sensitive PL technique (514 nm excitation, collected at liquid-nitrogen temperature) displayed strong emissions from neutral and negatively charged N-V centers (zero-phonon lines at 575 and 637 nm, respectively).

All of the spectroscopic and gemological features confirmed this was a type IIb CVD synthetic diamond. The specimen was unusual due to its boron content and distinctive DiamondView characteristics.

Although type IIb CVD synthetic diamonds are produced for industrial purposes, and the boron can cause a blue color (e.g., P. M. Martineau et al., "Identification of synthetic diamond grown using chemical vapor deposition [CVD]," Spring 2004 *GeG*, pp. 2–25), gem-quality type IIb CVD synthetics are quite rare, and the two examples submitted to GIA so far have shown brown coloration. As CVD technology continues to evolve, though, the gem trade will likely see blue type IIb versions in the future.

Sally Eaton-Magaña

Figure 12. This 0.25 ct round brilliant with L color and I₁ clarity proved to be a type IIb CVD synthetic diamond.



Lead Glass-Filled SYNTHETIC RUBY

Recently examined in the Carlsbad laboratory was an 11.52 ct purplish red cushion mixed cut (figure 14). Gemological testing confirmed the material was corundum, based on its RI values of 1.760–1.769 and hydrostatic SG of 3.98. The sample fluoresced strong red when exposed to long-wave UV radiation, and strong to moderate red to short-wave UV. Observation with a desk-model spectroscope revealed a distinct spectrum consistent with ruby.

While these initial observations were quite standard, microscopic examination revealed details out of the ordinary. A network of uniformly patterned fractures was consistent with those often seen in quench-crackled corundum. These fractures showed a moderately prominent orange-to-blue flash effect (figure 15), small clusters of whitish devitrification products, and flattened gas bubbles—all indicators of lead glass-filled corundum. EDXRF spectroscopy confirmed the presence of lead. Notably, the gem contained subtly curving striae (again, see figure 15), which proved it was a flame-fusion synthetic ruby. Unlike a similar glass-filled synthetic ruby ex-

amined in the New York laboratory (see Fall 2007 Lab Notes, pp. 250–251), no orange fluorescence was observed in the glass-filled fractures.

Lead glass-filled ruby has been in the market for several years, and flame-fusion synthetic ruby for much longer, but this was the first example of a lead glass-filled flame-fusion synthetic ruby seen in the Carlsbad laboratory. It is unclear why anyone would knowingly produce this gem material, which currently represents the lowest standard in the realm of lead glass filling.

Nathan Renfro

Red TAAFFEITE Crystal

A 1.56 g red hexagonal crystal (figure 16) was recently submitted to the Carlsbad laboratory for a ruby report. As the hexagonal shape and red color were consistent with ruby, it would be easy to assume the crystal was corundum. The specimen was reported to be from Myanmar.

We could not obtain an RI measurement due to the rough surface, but standard gemological testing using a desk-model spectroscope showed fine lines in the red end of the spectrum. When exposed to long- and short-wave UV radiation, the sample fluoresced moderate and weak red, respectively. The crystal's hydrostatic SG was 3.62, which eliminated ruby as a possibility.

Figure 14. This 11.52 ct synthetic ruby proved to be filled with lead glass.



Figure 15. Curved striae and an orange-to-blue flash effect were observed in the sample, identifying it as a flame-fusion synthetic ruby filled with lead glass. Image width: 3.6 mm.

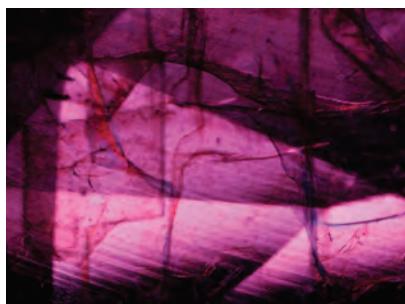


Figure 16. This 1.56 g rough hexagonal crystal was identified as taaffeite. While taaffeite is a rare mineral in any color, the red variety is extremely scarce.

Raman analysis identified the crystal as taaffeite (spectra are available in the GeG Data Depository at gia.edu/gandg). The vibrant red color is presumed to be caused by chromium, which is incorporated into the aluminum sites of other aluminum oxide minerals (e.g., corundum and spinel) to produce red coloration. The presence of Cr was confirmed by EDXRF analysis, and is consistent with the fine lines observed in the red region of the visible spectrum.

While taaffeite is occasionally seen in the laboratory, the color is usually grayish purple. Red varieties of this rare mineral are extremely scarce (see Spring 1990 Gem News, pp. 102–103), and examining this moderately sized specimen was certainly an unusual opportunity.

Nathan Renfro and Laurent Massi

PHOTO CREDITS:

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