G&G

Lab Notes

Editors
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UV-Reactive OPAL

A pair of milky white polished opals, weighing 2.66 and 2.48 ct, were recently examined at the Carlsbad laboratory (figure 1). Spot RI readings of 1.44 and 1.43, respectively, were consistent with opal. The stones were placed under long-wave ultraviolet light (LWUV) as part of the routine testing.

Figure 1. Note the milky white color of these two polished opals before exposure to long-wave ultraviolet light.

Upon removal from the UV light source, it was apparent that the opals' color had changed to a bright orangy red. Further gemological testing confirmed that the specimens had been impregnated with an unknown photochromic substance that changed color when exposed to UV light. The color change (figure 2) occurred after approximately one minute of exposure. The orangy red color faded completely about five minutes after removal from the UV source. Furthermore, when the specimens were placed near a window, sunlight provided enough UV radiation to fully induce the orangy red color. This reversible and repeatable effect, known as tenebrescence, is occasionally seen in natural materials, most notably hackmanite. Exposure to the light of an incandescent bulb faded the color faster, which is another property of tenebrescence. Exposure to short-wave UV did not produce any visible effect on the color.

The fact that hydrophane opal allows foreign substances to be introduced has already been established (N. Renfro and S. McClure, "Dyed purple hydrophane opal," Winter 2011 *G&G*, pp. 260–270). This was in the context of dyeing with a substance that altered the appearance of the bodycolor, but did not change color in the presence of UV light. Impregnating opal with a UV-reactive chemical to make the opal appear to be tenebrescent has not been previously documented. Whether the substance used to impregnate the opals affected the original color or transparency is not known, nor is the stability of the treatment.

Figure 2. The same two opals are shown after exposure to long-wave UV.

Troy Ardon

Assembled "PEARL" Filled with Wire

The excitement of being the first person to observe a pearl's interior is always foremost in one's mind when performing microradiography tests on a newly submitted specimen. Baroque pearls in particular have a higher probability of revealing something unusual (see Fall 2013 Lab Notes, pp. 172–173), since they often contain internal voids that are ideal for filling if exposed by damage or excessive drilling.

A light yellow and cream baroque pearl (figure 3), weighing 10.97 ct and measuring 12.74 × 11.60 × 11.14 mm, was recently submitted with seven others to the Bangkok laboratory for a GIA Quality Assurance Report, which provides rapid identification for sorting goods. Prior to microradiography, the pearl immediately appeared suspect because it was circled by an eye-visible band that indicated some "work" had likely been carried

Editors' note: All items were written by staff members of GIA laboratories.

Gems & Gemology, Vol. 50, No. 1, pp. 66–71,
http://dx.doi.org/10.5741/GEMS.50.1.66.

Figure 3. In this 10.97 ct baroque pearl, a suspect ring circling the surface is clearly visible.

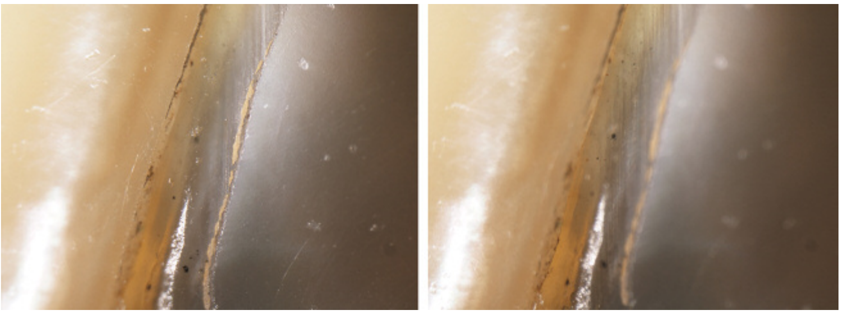
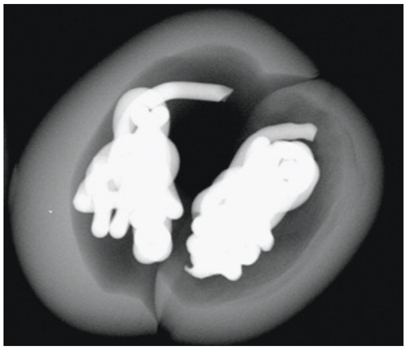


Figure 4. The area between the two parts assembled to form the "pearl" revealed creamy areas of deterioration where the bonding agent met the pearl components (left) and very small black impurities of an unknown nature trapped within the agent (left and right). Magnified 70×.

out. This was confirmed by examination with a loupe and microscope, which revealed a lustrous, transparent bonding agent. Small black impurities of an unknown nature were present in the bonding agent (figure 4). The type of work performed on the pearl was instantly confirmed by microradiography (figure 5). Looking at the microradiograph, it was obvious that two coiled wire fillings had been placed in the void between two hollow pearl pieces.

This is not the first time that metal wire has been encountered in pearls (see K. Scarratt, "Notes from the Laboratory," *Journal of Gemmology*, Vol. 20, 1986, p. 95), but it appears to be the first time two different hollowed halves have been assembled with a piece of wire in each. While there is little doubt that this specimen was fabricated to increase its weight and create a "single" pearl, the alterations were so severe that they removed critical internal structure, making the components difficult to identify. The two specimens may have been natural pearls with internal voids, bead-cultured pearls with voids around the bead (as is common), non-bead cultured pearls, or any combination of these. We therefore concluded that the "pearl" should be described as "undetermined" but filled.

Figure 5. The internal structure revealed two very distinct pieces of coiled wire (metal is radio-opaque) within voids whose outlines did not match. The mismatched outlines helped prove that two separate specimens were combined to form the new "pearl."



Nanthaporn Somsa-ard and Areeya Manustrong

CVD SYNTHETIC DIAMOND with Unusual DiamondView Image

Over the last several years, CVD-grown synthetic diamonds have evolved rapidly in overall quality, including size and clarity. GIA's laboratory frequently documents new, sometimes subtle developments in this material.

Recently a 0.32 ct, G-color CVD synthetic (figure 6) was submitted to the Carlsbad laboratory. DiamondView imaging (figure 7) showed a few interesting characteristics. Most of the sample displayed a deep blue fluorescence, a feature typically derived from the N3 optical center and often observed in natural diamonds. CVD-grown synthetic diamonds usually have either a greenish blue or an orange to red fluorescence, depending on whether they have been treated to generate high concentrations of NV centers. The deep blue, N3-related fluorescence is so prevalent among mined diamonds that the color itself can often verify that a diamond is not synthetic. In addition to the deep blue color of the fluorescence, its visual pattern closely resembled the dislocation networks commonly seen in natural-origin type IIa diamonds rather than the striations caused by stepwise growth in CVD synthetics (P.M. Martineau et al., "Identification of synthetic diamond grown using chemical vapor deposition [CVD]," Spring 2004 *G&G*, pp. 2–25).

Figure 6. This G-color, 0.32 ct CVD-grown synthetic showed DiamondView features typically associated with a natural origin.

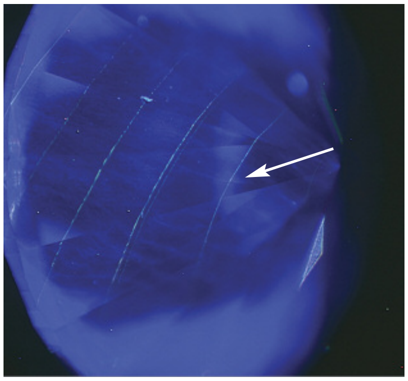


Figure 7. In addition to blue fluorescence, the CVD synthetic's DiamondView image displayed yellow-green fluorescence lines indicating the stop/start cycling that occurred during the growth process.

Taken together, the blue fluorescence and apparently random patterning closely resemble DiamondView images of natural-origin type IIa diamonds. This indicates that CVD manufacturers are becoming quite adept at mimicking natural growth. It is unclear whether this resemblance was a deliberate goal or a by-product of advances in CVD growth; regardless, the blue fluorescence for this CVD synthetic diamond does not appear to derive from the N3 center. Photoluminescence (PL) spectroscopy, collected with 325 nm excitation, showed only a very weak peak at 415.2 nm.

Yet this stone also contained two features that clearly indicated its synthetic origin: a large concentration of the Si-V center at 737 nm, revealed by PL spectroscopy, and the pronounced yellow-green parallel lines in the DiamondView image.

These parallel lines, with a nearly uniform spacing of approximately 0.8 mm in this sample, are created when the CVD reactor undergoes stop and start cycles during growth. These cycles create a temporary change in chemical composition, especially at the growth interface. Willems et al. ("Exploring the origin and nature of luminescent regions in CVD synthetic diamond," Fall 2011 *G&G*, pp. 202–207) proposed that a change in surface roughness promotes the incorporation of impurities, which alters the fluorescence and creates new dislocations.

Four PL spectra were collected from these yellow-green lines and from the blue-fluorescing regions, using 488 nm laser excitation and normalized to the Raman peaks. The relative intensities of the peak areas from both regions were averaged to compare the optical defects that altered the fluorescence. The H3 center at 503.2 nm, the NV centers at 575 and 637 nm, and the Si-V center at 737 nm all showed higher concentrations along the yellow-green lines. These vacancy-related defects increased by a factor of approximately 1.5 for NV^0 and Si-V, 3 for NV^-, and 5 for H3, indicating a higher presence of vacancies at the growth interface. Several sequential growth runs were likely necessary to achieve high CVD quality, leaving behind these fluorescence lines as evidence of synthetic origin.

Sally Eaton-Magaña

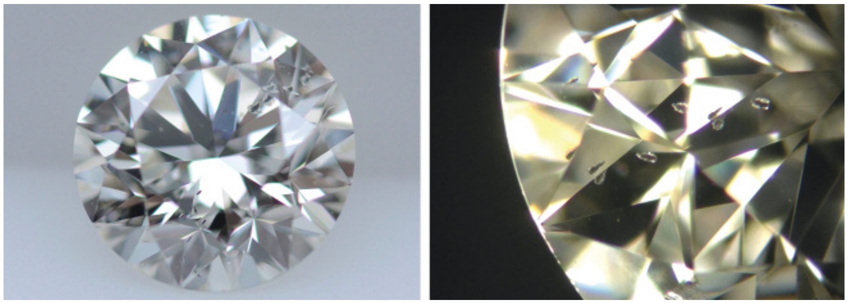
Round CVD SYNTHETIC DIAMOND Over 1 Ct Identified in Hong Kong Lab

In the past ten years, CVD synthetic diamonds have showed significant improvements in quality and size (Martineau et al., Spring 2004 *G&G*, pp. 2–25; Wang et al., Winter 2003 *G&G*, pp. 268–283; Wang et al., Summer 2012 *G&G*, pp. 80–97). Their color and clarity can be comparable with top natural counterparts, but for the most part they are still small. CVD gem-quality synthetic diamonds over 1 ct are occasionally reported in the trade, usually in fancy shapes with limited depth.

Recently, a round-brilliant specimen, identified as a CVD synthetic diamond, was submitted to the Hong Kong laboratory for grading service. It weighed 1.20 ct (6.70 × 6.72 × 4.30 mm), with a color grade of L, a clarity grade of SI_2, and a cut grade of Very Good. This specimen resembled well-cut natural round diamonds (figure 8, left), with a few black inclusions of irregular shape clearly observable under the microscope (figure 8, right).

Infrared absorption spectroscopy identified it as type IIa. A very weak absorption at 1344 cm^{-1} was attributed to isolated nitrogen in the diamond lattice (figure 9). Based on the absorption intensity (0.014 cm^{-1}) of this peak, the total concentration of isolated nitrogen was well below 1 ppm. Occurrence of trace isolated nitrogen was the major optical center responsible for the L color observed. No hydrogen-related absorption was observed at either 3107 or 3123 cm^{-1} using infrared absorption spectroscopy. Photoluminescence (PL) spectra at liquid nitrogen temperature with 532 nm laser excitation showed the $[Si\text{-}V]^-$ doublet emissions at 736.6 and 736.9 nm (figure 10), a characteristic feature of CVD synthetic diamond. Weak emissions from N-V centers at 575.0 nm and 637.0 nm were also recorded. Fluorescence images collected using the Diamond-

Figure 8. Left: This 1.20 ct CVD synthetic round brilliant had a color grade of L, a clarity grade of SI_2, and a cut grade of Very Good. Right: The 6.7 mm specimen contained a few black inclusions with irregular shapes.



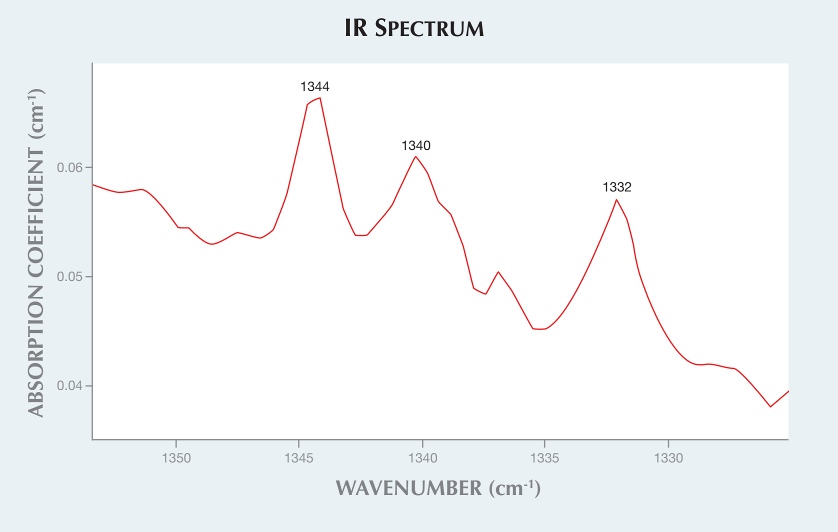


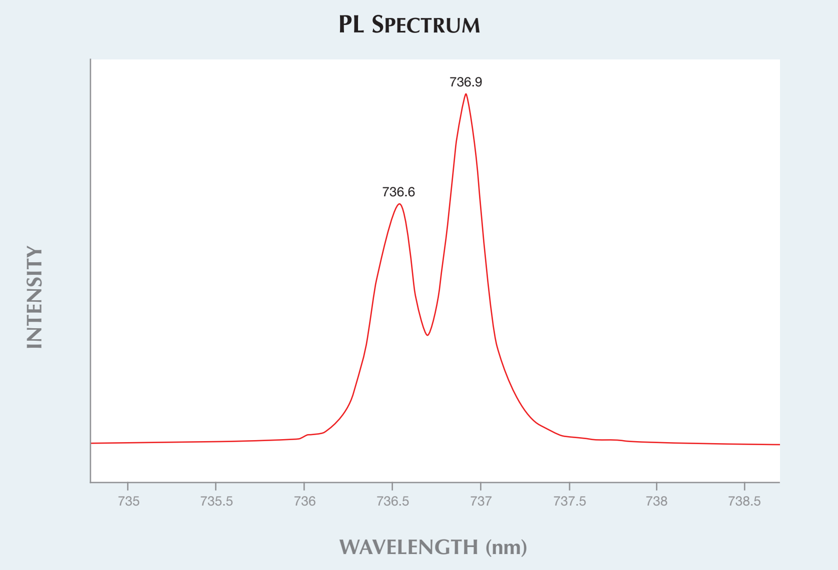
Figure 9. The CVD synthetic diamond's infrared absorption spectrum showed a weak peak at 1344 cm^{-1}. This feature, attributed to the isolated nitrogen impurity, was responsible for the L color grade.

View showed green fluorescence with characteristic CVD growth striations (figure 11). All these gemological and spectroscopic observations, very similar to those of Gemesis specimens (Wang et al., 2012), confirmed this was a CVD synthetic diamond. It was annealed at high pressure and high temperature (HPHT) to improve its color appearance.

As this sample shows, CVD technology has reached a new milestone, with the growth of crystals thick enough to consistently cut well-proportioned round brilliants. It is highly likely that we will see more gem-quality CVD synthetic diamonds over 1 ct in the trade.

Carmen "Wai Kar" Lo, Ping Yu Poon, and Shun Yan Wong

Figure 10. A photoluminescence spectrum collected at liquid nitrogen temperature using 532 nm laser excitation revealed a strong emission doublet at 735.6 and 735.9 nm, indicating a $[Si\text{-}V]^-$ *optical center.*



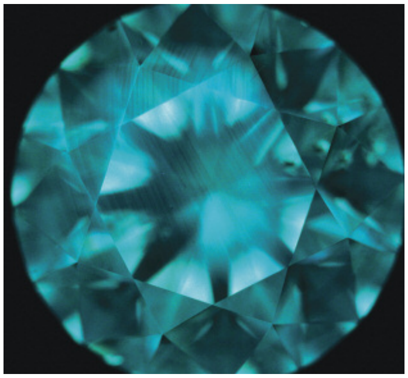


Figure 11. Observed in the DiamondView, the 6.7 mm synthetic diamond showed typical striations indicative of CVD growth.

Fancy Black NPD SYNTHETIC DIAMOND

As reported previously in *Gems & Gemology*, nano-polycrystalline diamond (NPD) growth technology is one of the most significant new developments in diamond synthesis (see E.A. Skalwold, "Nano-polycrystalline diamond sphere: A gemologist's perspective," Summer 2012 *G&G*, pp. 128–131). The material is completely transparent and comparable to natural diamond, while tougher than natural diamond or previous synthetic diamonds. NPD could pose a challenge to the natural diamond industry once these goods, particularly higher-quality transparent samples, enter the consumer market.

Recently, the New York laboratory tested a small, black marquise-cut stone for identification and color origin. At first glance, the 0.9 ct translucent specimen (figure 12) resembled a typical black diamond submitted to the lab for identification and color origin. One must be careful to separate such stones from synthetic moissanite. This marquise, however, revealed unusual properties strikingly similar to those of the NPD synthetic diamonds reported on by Skalwold, as well as other previously tested samples. These previously studied specimens were transparent with a yellow to brown range of color.

Unlike natural diamond, the stone in question was heavily included with graphite crystals. The

Figure 12. This 0.9 ct marquise proved to be a synthetic nano-polycrystalline diamond (NPD), the first one detected by a gemological laboratory.

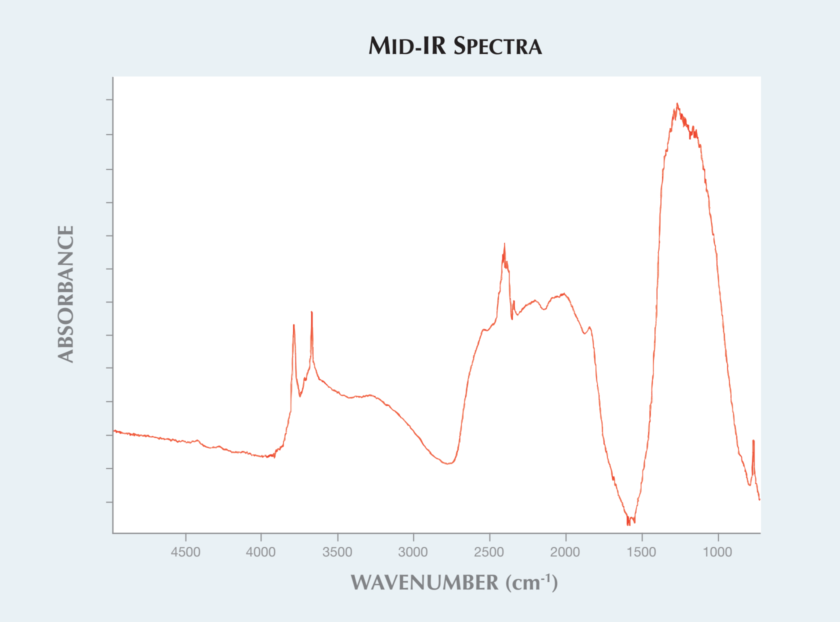
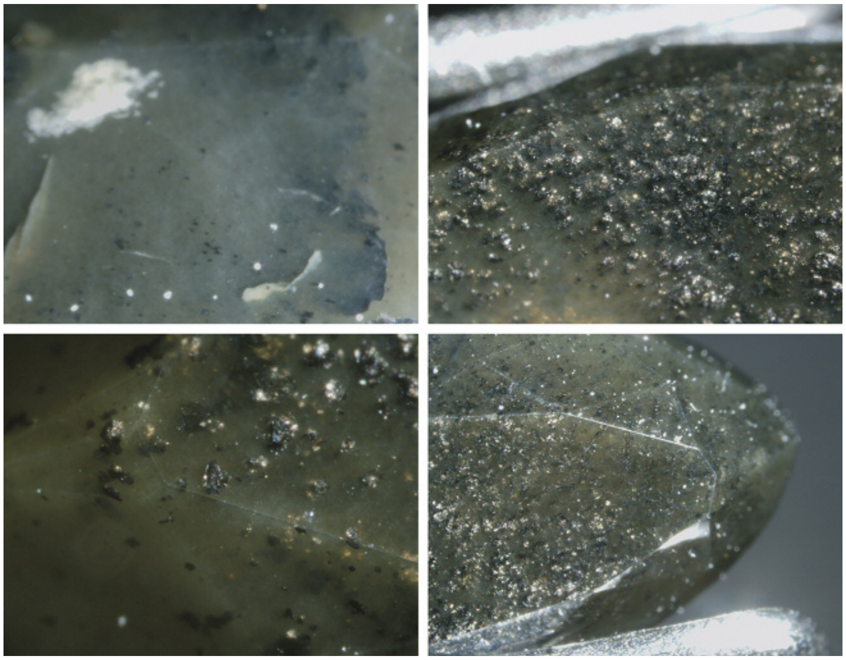


Figure 14. The mid-infrared spectrum of the synthetic NPD displayed peaks at approximately 3727 and 3611 cm^{-1}.

matrix hosting the inclusions had a murky yellowish color (figure 13). Using diffuse reflectance, we obtained a mid-infrared absorbance spectrum strikingly similar to that of the NPD synthetic diamonds reported in the aforementioned article. We observed the diagnostic diamond absorption peaks at approximately 2000 cm^{-1} and absorption in the one-phonon region, possibly due to nitrogen impurity. Peaks at approximately 3727 and 3611 cm^{-1} were also observed, as in the previously tested NPD samples (figure 14). Raman spectroscopy is a common and useful technique in identifying a gem diamond. Due to the nano-sizes of the crystals that compose the aggregated sample, a Raman shift is usually not detectable in NPD using visible-light laser excitations. The same feature was observed in this specimen.

Figure 13. Photomicrograph images of the heavily included synthetic diamond showed an abundance of graphite inclusions and a murky yellowish matrix. Fields of view (clockwise from top left): 1.5, 3.1, 1.5, and 4.1 mm.



Further analysis using the DiamondView instrument revealed a fluorescence pattern and structure that was, again, very similar to earlier NPD samples (figure 15). Raman analysis showed a broad band at approximately 1350 cm^{-1} and a weak band at about 1580 cm^{-1}; these are assigned as D- and G-bands, respectively (S. Odake et al., "Pulsed laser processing of nano-polycrystalline diamond: A comparative study with single crystal diamond," *Diamond and Related Materials*, 2009, Vol. 18, pp. 877–880). Odake reported the two bands in NPD samples grown from high-purity graphite at a temperature of 2600K and a pressure of 15 GPa; both are caused by nanocrystalline graphite or amorphous carbon. Unlike Odake's samples, which showed G- and D-bands of equal intensity, ours showed a strong D-band with a weak G-band. We measured Raman spectra at many different locations but

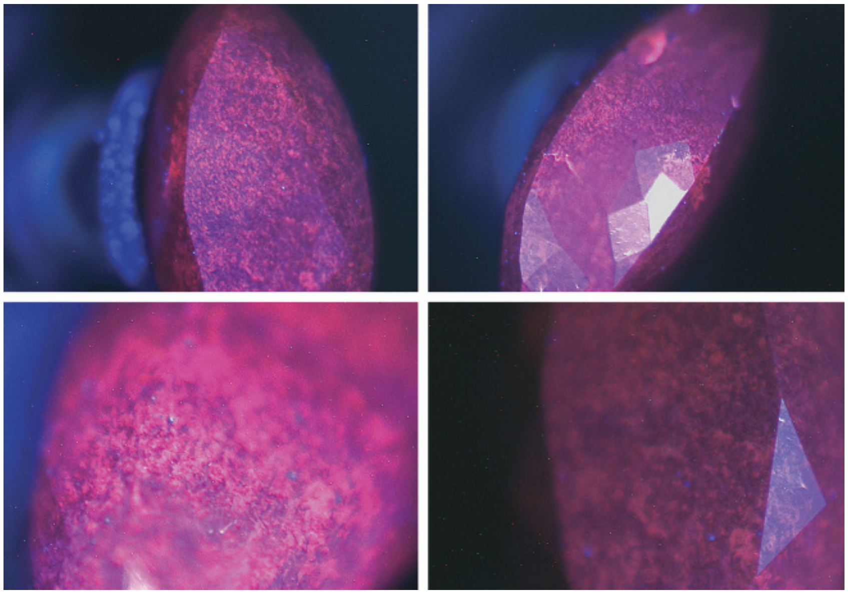


Figure 15. DiamondView images of the synthetic NPD exhibited a distinct fluorescence pattern.

did not observe the diamond Raman band at 1332 cm^{-1}, an absence Odake also reported.

Testing and observations revealed the diamond to be an NPD synthetic diamond, the first detected by a gemological laboratory.

Paul Johnson and Kyaw Soe Moe

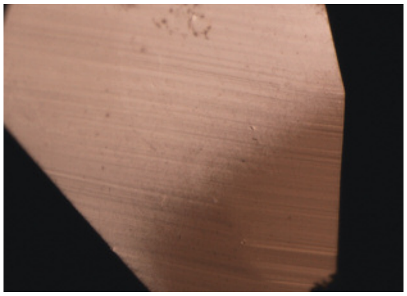
Titanium-Coated TANZANITE

Five faceted violetish blue stones, ranging from 0.39 to 0.82 ct (figure 16), were recently submitted to the Carlsbad laboratory for identification service. Standard gemological testing revealed a refractive index of 1.689–1.700 for all five samples. When observed using polarized light, each displayed a medium pleochroism. Specific gravity, measured using the hydrostatic method, was 3.37. These properties were consistent with tanzanite.

Figure 16. These five tanzanite samples (0.39–0.82 ct) proved to be color-coated with titanium.

Microscopic examination showed that the material was relatively free of inclusions, but showed areas of abrasion along pavilion facet junctions. Observed using reflected light, the pavilion of each stone showed a significantly higher luster than the crown. Some individual facets even showed a variation in luster due to an unevenly distributed color coating (figure 17). When the samples were examined using diffuse transmitted light, the facet junctions and several chipped spots appeared much less saturated, which was also consistent with a color coating (figure 18).

Figure 17. This upper portion of a pavilion facet, examined in reflected light, shows a much higher luster than the lower, uncoated portion. Field of view 1.22 mm.



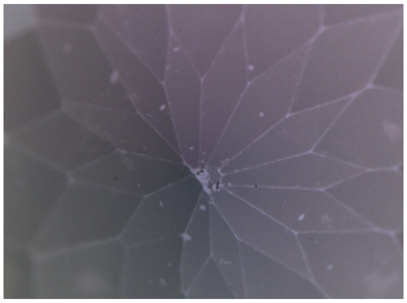


Figure 18. The coating on this tanzanite's pavilion has been worn away along the facet junctions and in some small chipped areas, revealing the less-saturated violet color of the tanzanite underneath. Field of view 2.90 mm.

Because tanzanite with a cobalt coating has previously been reported (S.F. McClure and A.H. Shen, "Coated tanzanite," Summer 2008 *G&G*, pp. 142–147), all tanzanites submitted to the lab are routinely checked by energy-dispersive X-ray fluorescence (EDXRF) and microscopic examination. These five stones were also checked by EDXRF, but no cobalt was detected; however, all five showed a significant signal for titanium on their pavilions. No titanium was detected on the crowns. LA-ICP-MS was also used to confirm that the coated area contained significant titanium.

While color-enhancing coatings on tanzanite are occasionally seen at GIA's laboratory, this is the first time we have examined tanzanite that has been color coated with titanium.

Amy Cooper and Nathan Renfro

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