

Unusual Polyphase Inclusions In CORUNDUM

The New York laboratory recently identified some inclusions in corundum that have not previously been reported in the gemological literature. While examining a 3.79 ct unheated blue sapphire of metamorphic origin, we noted a small, transparent, surface-reaching crystal, which Raman analysis identified as zircon. Much to our surprise, the high-powered microscope built into the Raman instrument showed numerous (>10) inclusions within the zircon crystal (figure 1). We noted several transparent rounded inclusions, a few euhedral crystals, and a reddish material. Raman analysis of the rounded features showed peaks associated with CO₂, while the spectrum from the reddish regions indicated the presence of hematite. We had never before observed such “inclusions within inclusions” of zircon in sapphire.

As part of GIA's continuing effort to provide country-of-origin determinations for corundum, the New York laboratory has been characterizing more than 500 unheated corundum samples known to be from the Winza region of

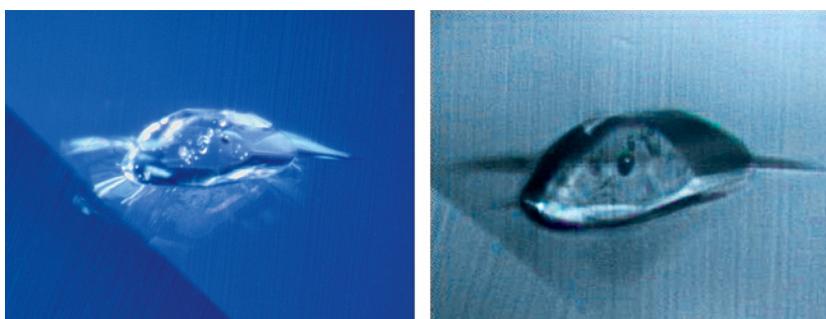


Figure 1. The zircon crystal (~210 μm long, left) in an unheated blue sapphire has inclusions of its own that are visible at higher magnification (right).

Tanzania. During this project, we found what we believe to be diaspore on the basis of Raman analysis (figure 2); we also detected hematite in two samples (figure 3). Although polyphase

Figure 2. The large white inclusion in this pink sapphire from Winza, Tanzania, had a Raman spectrum consistent with diaspore. Field of view ~0.5 mm.



inclusions in corundum from Winza have been characterized previously (D. Schwarz et al., “Rubies and sapphires from Winza, central Tanzania,” Winter 2008 *G&G*, pp. 322–347; A. Peretti, “Winza rubies identified,” *Contributions to Gemology*, No. 7, 2008, www.gemresearch.ch/journal/No7/No7.htm), we believe this is the first time diaspore and hematite have been identified as components of inclusions from this locality.

David Kondo

DIAMOND Black Diamond with Solid CO₂ Micro-Inclusions and Phosphorescent Zones

Also recently examined at the New York lab was the 0.45 ct natural-color black heart-shaped diamond shown in figure 4 (left). Microscopic observa-

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

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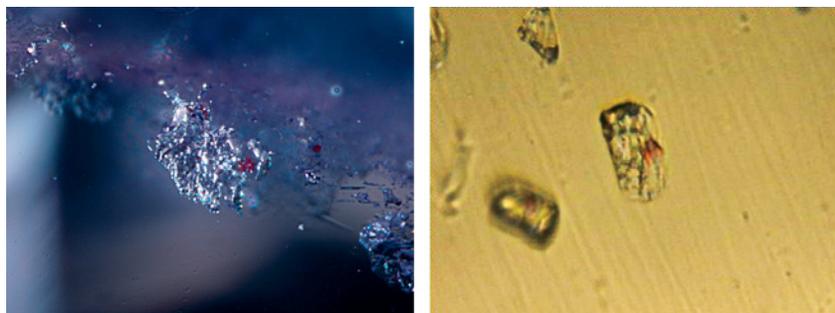


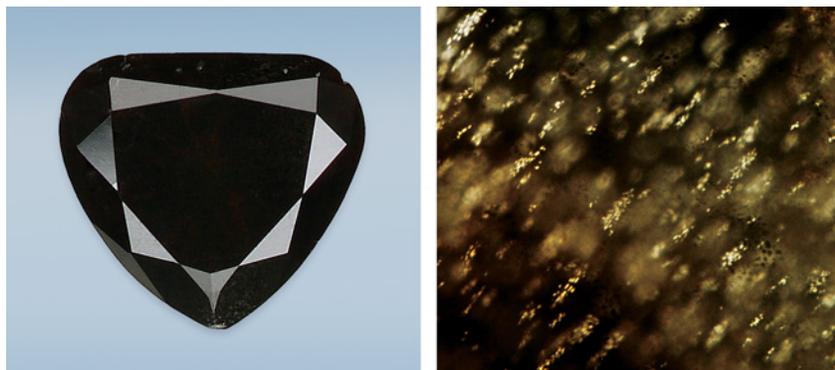
Figure 3. For these inclusions in a violetish blue sapphire (left) and a pink sapphire (right, taken with a Raman microscope)—both from Winza—Raman spectra for the red regions matched hematite. Fields of view 1.2 and 0.15 mm, respectively.

tion revealed an abundance of clouds, and higher magnification showed clusters of round, disc-like inclusions ~32 μm across (figure 4, right). This is the first time we had observed such features in a black diamond, which derives its color from its inclusions.

Due to time constraints, we did not have the opportunity to identify these inclusions using Raman microspectroscopy. However, the mid-infrared (IR) spectrum demonstrated that the diamond's major impurity was solid CO_2 , with dominant absorption peaks at ~2370 and ~658 cm^{-1} (figure 5). Features associated with micro-inclusions such as silicates and apatite also were observed, at 1055 and 575 cm^{-1} , respectively (though not visible in figure 5). Sharp absorption bands at 871 and 721 cm^{-1} , together with a broad

band at 1430 cm^{-1} , suggested the presence of carbonates. Quartz absorption bands detected at 798 and 779 cm^{-1} were shifted from their normal positions. This diamond also contained hydrous components, as revealed by a broad band at ~3220 cm^{-1} that indicated asymmetric OH^- stretching (see D. A. Zedgenizov et al., "Carbonatitic melts in cuboid diamonds from Udachnaya kimberlite pipe [Yakutia]: Evidence from vibrational spectroscopy," *Mineralogical Magazine*, Vol. 68, No. 1, 2004, pp. 61–73). Another broad band at ~1713 cm^{-1} may be related to the H_2O -bending mode. Small hydrogen bands were observed at 4703 and 3107 cm^{-1} . These features are not common in gem-quality diamonds. Absorption bands in the 1300–1000 cm^{-1} region suggested this was a type Ia stone.

Figure 4. This 0.45 ct black diamond (left) contains abundant microscopic clouds. With high magnification (112.5 \times), clusters of round, disc-like inclusions are also seen (right).



When examined with the strong ultra-short-wave (~225 nm) ultraviolet radiation of the DiamondView, most of the stone fluoresced strong yellowish green, but there were three rectangular nonfluorescent zones (figure 6, left). Unlike the rest of the diamond, these zones exhibited strong phosphorescence (figure 6, right). Photoluminescence (PL) spectroscopy using 488 and 633 nm lasers showed similar features for both these zones and the fluorescent areas, but a few PL bands—such as at 511, 572, 696.2, and 739 nm—were observed only in the nonfluorescent zones. The assignment for these bands is not clear, but they may be related to the unusual phosphorescence. The clouds in the diamond were confined to the {100} crystal plane in the dominant yellowish green fluorescent area, while the phosphorescent zones were formed in {111} directions.

This black diamond offered a valuable opportunity to study the geologic conditions of diamond growth. The micro-inclusions of solid CO_2 and water—which we have seen only rarely in gem-quality diamonds—suggested that this diamond formed from carbonate-rich melts. Internal pressure from these volatiles caused the quartz absorption bands to shift, which further suggests that these micro-inclusions were trapped during the diamond's growth.

Paul Johnson and Kyaw Soe Moe

Fancy Vivid Blue HPHT-Treated Diamond

As we have noted previously, many natural type IIb blue diamonds have gray or brown overtones that can be removed by high-pressure, high-temperature (HPHT) annealing, thus enhancing the blue color (see, e.g., Spring 2010 Lab Notes, pp. 51–52). Recently, the New York laboratory examined one such diamond with a hue more saturated than most other HPHT-treated blue diamonds we have tested.

The 3.81 ct pear-shaped diamond

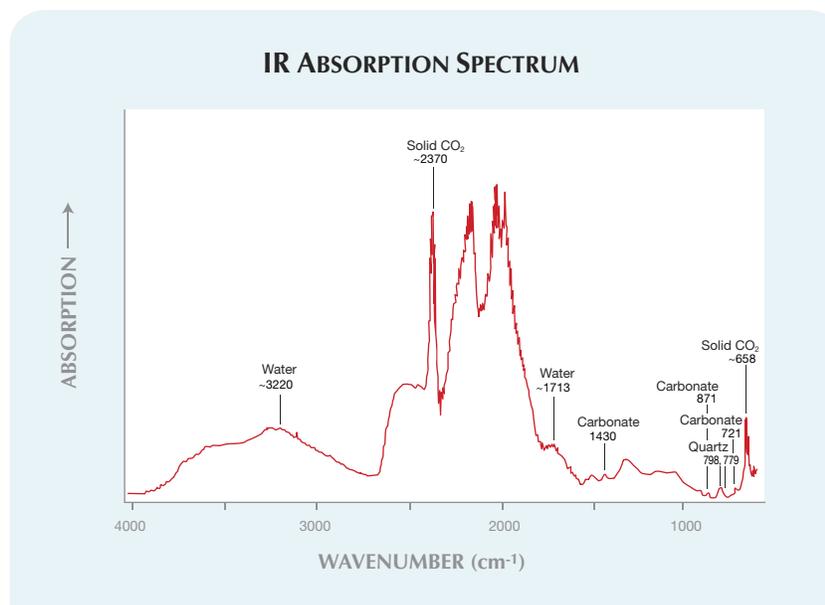


Figure 5. The IR spectrum of this natural-color black diamond demonstrates the presence of various micro-inclusions, such as solid CO₂, carbonates, quartz, and water.

(13.24 × 9.22 × 5.42 mm) was graded Fancy Vivid blue and displayed even color distribution (figure 7). The highly saturated hue in combination with well-balanced transparency was reminiscent of a fine blue sapphire.

Two tiny graphite flakes were seen when the stone (clarity graded VS₂) was examined through the pavilion. No graining was detected. The diamond was inert to conventional long- and short-wave UV radiation. Only a

weak blue fluorescence and very weak blue phosphorescence were visible with the strong ultra-short-wave UV radiation of the DiamondView; these less intense reactions are clearly different from those of most natural-color or HPHT-treated type IIb diamonds.

The mid-IR spectrum showed strong boron-related absorptions (such as a peak at ~2800 cm⁻¹), which are typical of type IIb diamond. We established that the diamond was HPHT



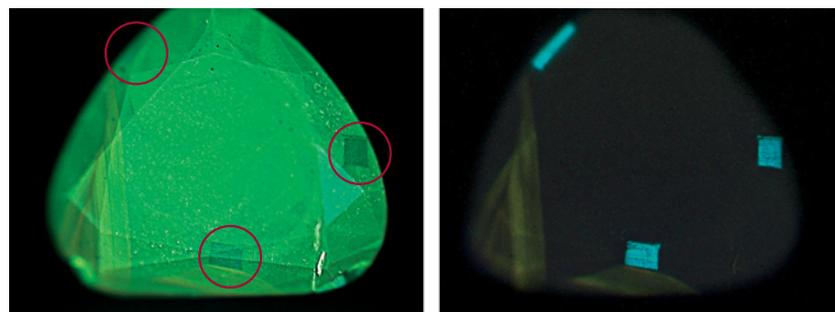
Figure 7. This 3.81 ct Fancy Vivid blue type IIb diamond was identified as HPHT treated.

annealed on the basis of its gemological properties and PL spectra collected at liquid-nitrogen temperature with laser excitations from UV to IR.

The color of an HPHT-treated diamond can be affected by many factors, such as the chemical purity of the starting material, the treatment conditions, and even the cut. In our experience, extremely attractive colors such as that seen in this diamond are rare. This is the fourth-largest Fancy Vivid blue HPHT-treated diamond GIA has graded to date. The largest weighed more than 7.5 ct.

Wuyi Wang

Figure 6. In the DiamondView, the black diamond displays strong yellowish green fluorescence except for three nonfluorescent rectangular zones (left). However, these rectangular zones show strong phosphorescence, while the rest of the diamond does not (right).



Interesting Display of the H3 Defect in a Colorless Diamond

Type IIa diamonds contain few impurities and usually show little variation in their gemological and spectroscopic characteristics. However, fluorescence imaging with the strong ultra-short-wave UV radiation of the DiamondView occasionally reveals interesting internal features. Recently, a 2.24 ct pear-shaped diamond (11.63 × 7.43 × 4.34 mm) was submitted to the New York laboratory for grading. IR absorption spectroscopy confirmed that the

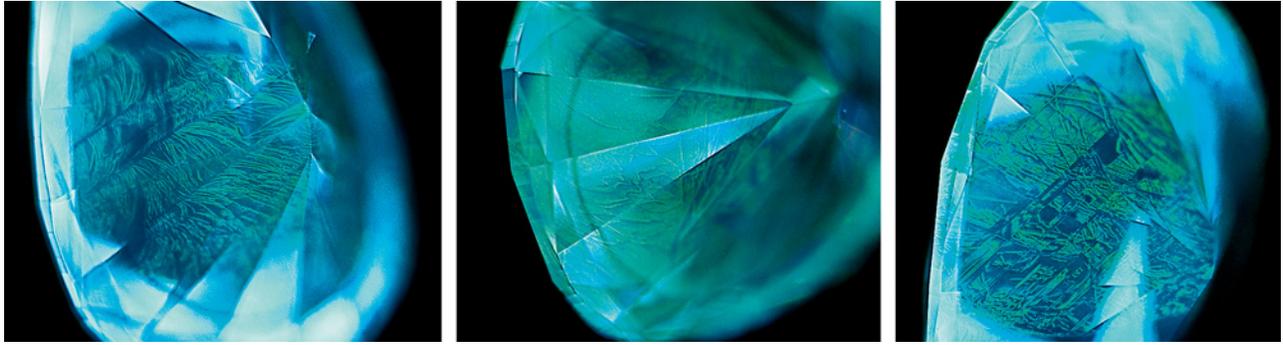


Figure 8. These DiamondView images of a 2.24 ct colorless type IIa diamond display the H3 defect in fern-like (left), flame-like (center), and distorted vein (right) structures.

E-color, internally flawless stone was a typical type IIa diamond, with no impurity-related defects.

A striking feature displayed in the DiamondView was the stone's dominant blue fluorescence with unusual green patterns. Depending on the direction of observation, these green regions showed fern-like, flame-like, or distorted vein structures over the entire pavilion (e.g., figure 8). We also observed strong blue phosphorescence in the DiamondView.

PL spectroscopy at liquid-nitrogen temperature with 488 nm laser excitation showed relatively strong emission from the H3 optical center with a zero-phonon line (ZPL) at 503.2 nm, weak emission from NV⁰ at 575.0 nm, and a sharp peak at 648.2 nm (figure 9). The 648.2 nm emission is very likely a boron-related defect, and type IIa diamonds with this emission often display strong blue phosphorescence. The unusually strong H3 emission, together with the distinctive patterns observed in the DiamondView, demonstrated that the green fluorescence is caused by the H3 optical center (see, e.g., Spring 2010 Lab Notes, pp. 49–50).

Such an interesting pattern of H3 distribution in a type IIa diamond is rare. The formation mechanism is not fully understood, but it could be related to the presence of lattice impurities (such as A-form nitrogen and vacancies) in a specific crystal orientation.

Erica Emerson and Wuyi Wang

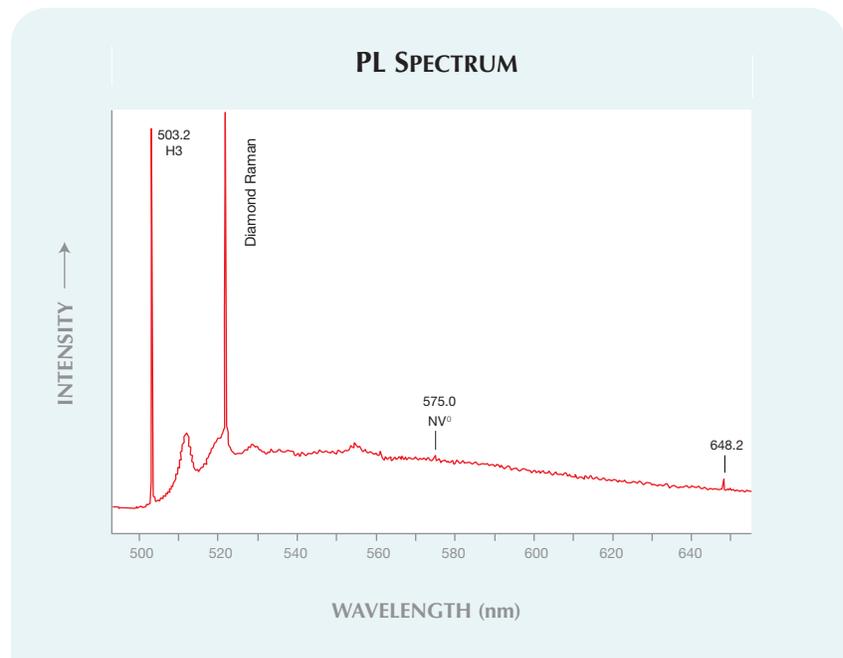
CVD SYNTHETIC DIAMOND Over One Carat

Single-crystal synthetic diamonds grown by chemical vapor deposition (CVD) are occasionally submitted to the GIA Laboratory for identification and grading reports. For the first time, the New York laboratory has identified a near-colorless CVD synthetic diamond larger than one carat that was submitted for grading.

The 1.05 ct pear shape (9.81 × 5.95

× 3.06 mm) was color-graded as equivalent to G (figure 10). In addition to pinpoint inclusions, it contained some feathers and fractures along the girdle, and its clarity grade was equivalent to I₁. No fluorescence was observed when it was exposed to conventional long- and short-wave UV radiation. The mid-IR absorption spectrum showed no absorption in the one-phonon region and no hydrogen-related absorption, which classified it as type IIa. (It is unusual to

Figure 9. The 2.24 ct colorless diamond's PL spectrum shows a relatively strong emission from the H3 center.



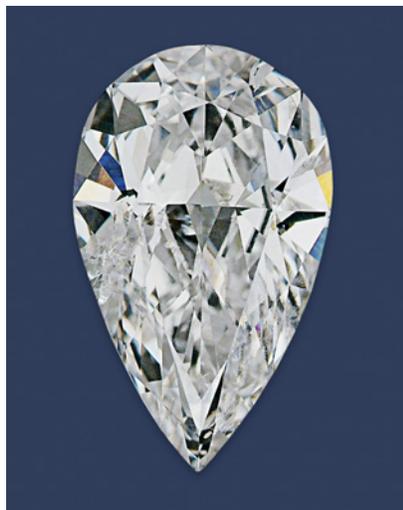


Figure 10. This G-color CVD synthetic diamond weighs 1.05 ct.

encounter a “white” CVD-grown diamond without H-related absorption at 3123 cm^{-1} .) Images taken with the DiamondView showed strong pink fluorescence with some irregularly shaped areas of blue fluorescence (figure 11). PL spectra collected at liquid-nitrogen temperature with laser excitations from the UV to IR regions revealed features typical of CVD synthetic diamond: strong emissions from NV centers, a doublet at 596.5 and 597.1 nm, and $[\text{Si-V}]^-$ doublet

Figure 11. When exposed to the strong short-wave UV radiation of the DiamondView, the 1.05 ct CVD synthetic diamond displays strong pink fluorescence with irregular areas of blue.



emissions at 736.6 and 736.9 nm. The gemological and spectroscopic features confirmed that this sample was a CVD synthetic diamond.

It is clear that larger, better-quality CVD synthetic diamonds are being produced as there is continued improvement in the growth techniques.

Wuyi Wang and Kyaw Soe Moe

Synthetic Diopside in Manufactured GLASS

Manufactured glasses are familiar gem simulants, and are usually identifiable by included gas bubbles. If the glass has begun to devitrify, however, it may contain natural-appearing crystalline inclusions, so identification may be confusing for all but the most experienced gemologists. Devitrification usually occurs in colored glasses, which contain additional elements that increase the likelihood of developing crystals. These crystals typically nucleate on gas bubbles or foreign particles in the glass (J. I. Koivula, “A photolexicon of inclusion-related terms for today’s gemmologist: Part 27,” *Canadian Gemmologist*, Vol. 17, No. 2, 1996, p. 40).

The Carlsbad laboratory recently

Figure 12. Synthetic diopside crystals decorate an elongated colorless rod of synthetic wollastonite in a piece of manufactured glass. Magnified 70 \times .



examined an unusual example of this phenomenon. The standard gemological properties (RI of 1.52 and hydrostatic SG of 2.55) were consistent with manufactured glass. The piece displayed three distinct color zones: greenish blue, green, and essentially colorless. The colorless zone ran through the green area and contained numerous well-formed blocky green crystals, several of which had strongly saturated green cores (e.g., figure 12). Raman analysis identified the crystals as diopside. Because these green synthetic diopside crystals only occurred in the colorless area, they appeared to have caused a “chromophore cannibalization” effect on the originally green glass, rendering those portions of the sample colorless. Energy-dispersive X-ray fluorescence analysis of the host confirmed the presence of chromium, the likely chromophore of both the green portion of the glass and the synthetic diopside crystals.

Also present were elongated colorless crystals, which Raman analysis identified as wollastonite. These appeared to be the initial devitrification product, followed by the synthetic diopside crystals, which were commonly distributed along the length of the synthetic wollastonites (again, see figure 12). Irregularities along the synthetic wollastonite crystals likely served as nucleation sites for the synthetic diopside.

While synthetic wollastonite has been reported previously in manufactured glass (H. A. Hänni et al., “A glass imitation of blue chalcedony,” *Journal of Gemmology*, Vol. 27, No. 5, 2001, pp. 275–285), this is the first time we have seen synthetic diopside as a devitrification product.

Nathan Renfro and John Koivula

Green Be-Diffused SAPPHIRE

Beryllium diffusion can produce a wide range of colors in corundum. The Carlsbad laboratory routinely encounters blue, yellow, orange, pink, and red examples. Green is one of the more

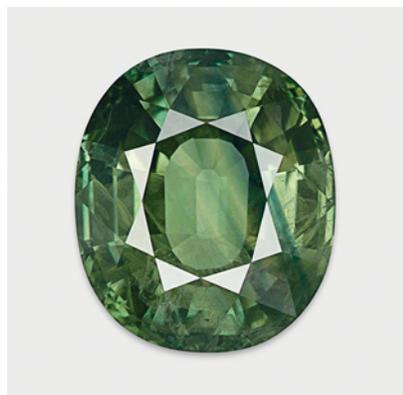


Figure 13. Chemical analysis revealed that this 14.20 ct green sapphire had been treated by beryllium diffusion.

unusual colors for this material, especially in larger sizes, but we recently examined a 14.20 ct sample that was beryllium diffused (figure 13).

The standard gemological properties for this stone were consistent with corundum. Microscopic examination revealed particulate clouds, flux-healed “fingerprints,” discoid-like fractures, and planar growth features. The desk-model spectroscope showed strong iron-related absorption centered at 450 nm. As expected, immersion displayed alternating blue and yellow color zones, a common feature in green sapphires.

Beryllium diffusion was first detected in the early 2000s because of surface-conformal color zoning in orangy pink to pinkish orange sapphires. However, the vast majority of Be-diffused corundum currently being processed does not show this type of zoning because the stones are diffused all the way through. Nevertheless, microscopic examination can offer clues to the likelihood of Be diffusion, such as synthetic overgrowth, significantly altered crystal inclusions, and localized blue zones of internal diffusion (caused by the release of Ti from inclusions such as rutile into the Fe-containing corundum host). While these clues alone are not proof of Be diffusion, their presence does suggest high-temperature heat treatment (see J. L. Emmett et al., “Beryllium diffu-

sion of ruby and sapphire,” Summer 2003 *G&G*, pp. 84–135).

The GIA Laboratory uses laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) to test all heat-treated corundum for the presence of beryllium. This stone, which had features consistent with heat treatment, was no exception. LA-ICP-MS indicated an average Be concentration of just over 13 ppmw (27 ppma), enough to dramatically alter the color.

The appearance in the marketplace of this large green Be-diffused sapphire reinforces the need to send all suspect stones to a qualified laboratory for chemical analysis. Microscopic evidence of high-temperature treatment can raise suspicion of Be diffusion, but chemical analysis by a technique capable of detecting traces of Be is necessary to confirm the treatment.

Nathan Renfro

Heat-Treated SPINEL

This spring, the New York laboratory examined a 17.02 ct reddish orange oval modified brilliant (figure 14) that was singly refractive, had an RI of 1.719 and SG of 3.59, and displayed a series of chrome lines with the desk-model spectroscope—all properties consistent with spinel. Magnification revealed

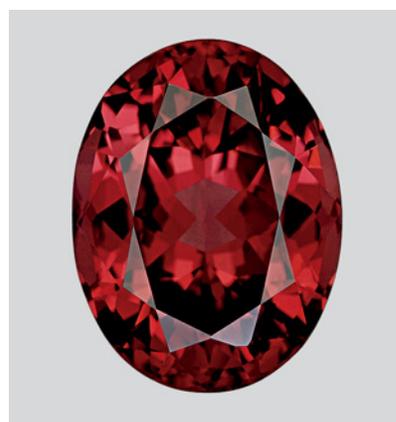
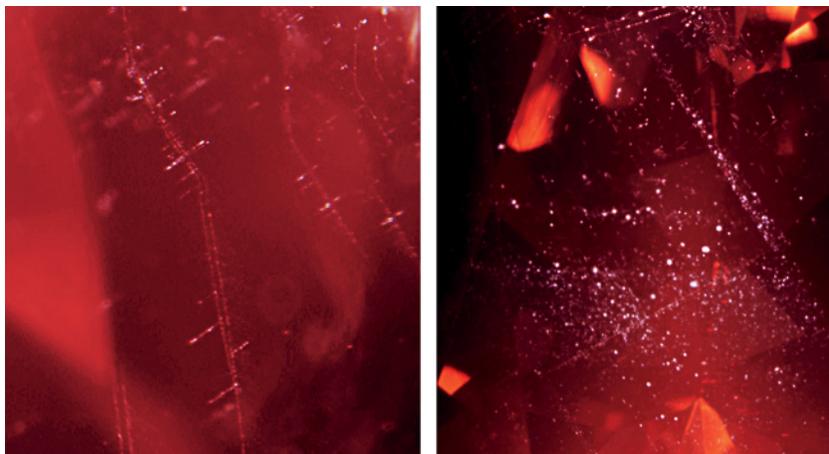


Figure 14. Based on standard gemological observations and advanced testing, this 17.02 ct reddish orange oval modified brilliant was identified as a heated natural spinel.

particulates and strings of minute inclusions (figure 15). These were reminiscent of boehmite in spinel (see E. J. Gübelin and J. I. Koivula, *Photoatlas of Inclusions in Gemstones*, Opinio Verlag, Basel, Switzerland, 1986, p. 375), which suggested a natural origin. A few small expansion halos or “blebs” emanating from the strings of inclusions indicated that the stone might have been subjected to heat.

Since first experimenting on heat-treated Tanzanian spinels in 2005, the GIA Laboratory has tested several hun-

Figure 15. The internal features observed in the reddish orange spinel were limited to particulates and strings of minute inclusions.



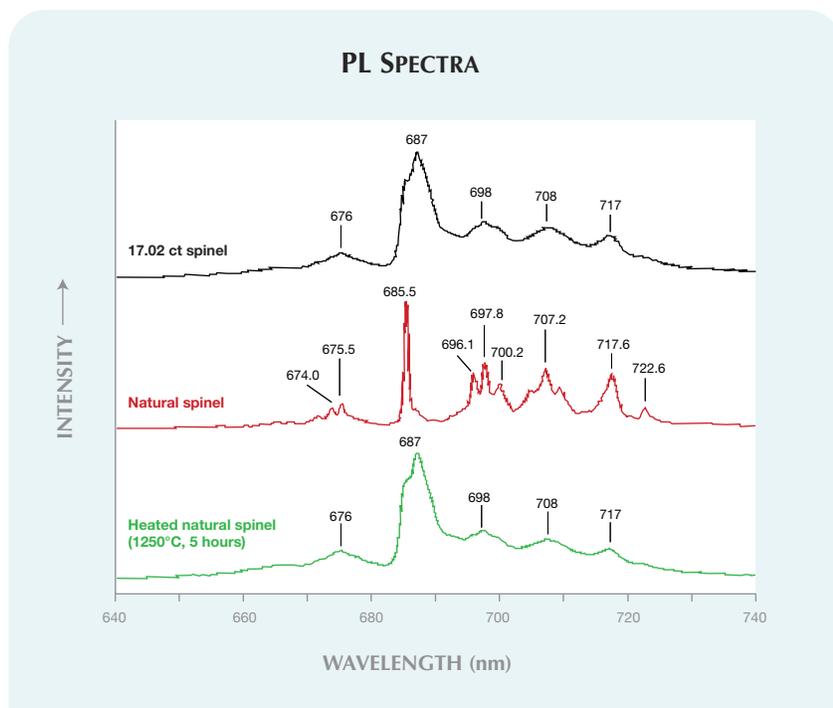


Figure 16. PL spectra display a clear difference between unheated and heated natural Cr-bearing spinels. The spectra were collected using 514.5 laser excitation, except for the heated natural spinel (which employed a 488 nm laser, with no effect on the peak width).

dred other samples (see S. Saeseaw et al., "Distinguishing heated from unheated natural spinels: A short review of ongoing research," March 22, 2009, www.gia.edu/research-resources/news-from-research). Our research has shown that unheated natural Cr-bearing (pink-to-red) spinel can be distinguished from synthetic or heated spinel through room-temperature photoluminescence spectroscopy. Cr-related emission peaks in unheated stones are usually very sharp. With heat treatment, these become broad bands due to conversion of the crystal structure from "ordered" to "disor-

dered." We performed PL spectroscopy on the 17.02 ct stone using 514.5 nm laser excitation. The broad chromium emission bands observed at 676, 687, 698, 708, and 717 nm indicated either a natural spinel that had been heat treated (figure 16) or a synthetic spinel. In contrast, a well-defined "organ-pipe" structure of the emission bands is typical of unheated natural Cr-bearing spinel (S. Muhlmeister et al., "Flux-grown synthetic red and blue spinels from Russia," Summer 1993 *G&G*, pp. 81–98).

To make the further separation of heated natural spinel from synthetic

spinel in the absence of diagnostic inclusions, chemical analysis by LA-ICP-MS can be used. In general, synthetic materials have a purer chemical composition than their natural counterparts. We detected significant amounts of impurities—including Li (77 ppm by weight), Be (32.6 ppm), Mn (243 ppm), and Ga (67 ppm)—in this sample. Concentrations of these elements in synthetic pink-to-red spinels are extremely low or not detectable.

Based on the gemological, spectroscopic, and chemical testing, we identified this stone as natural spinel with "indications of heating." It is our understanding (from the gem trade and our own research) that heat treatment may improve the clarity of some spinels, though not their color. The relative lack of inclusions suggests that this stone was heated to improve its clarity.

David Kondo, Riccardo Befi, and
Donna Beaton

Erratum

The Winter 2009 Lab Note "Diamond with flower-shaped cloud" (p. 290) erroneously stated that the hydrogen cloud followed the "{111} crystallographic direction." It should have read "{100} crystallographic direction." *Gems & Gemology* regrets the error.

PHOTO CREDITS

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