2009 LAB NOTES

Editors
Thomas M. Moses and
Shane F. McClure
GIA Laboratory

CUBIC ZIRCONIA Reportedly Coated with Nanocrystalline Synthetic Diamond

It has been two decades since *G&G* first reported on cubic zirconia with a thick diamond-like coating (Spring 1987 Gem News, p. 52) and E. Fritsch et al. commented on the remote possibility of growing a thinner monocrystalline film on cubic zirconia (CZ) that would give the thermal conductivity of diamond ("A preliminary gemological study of synthetic diamond thin films," Summer 1989 *G&G*, pp. 84–90). Recently, the GIA Laboratory had the opportunity to study some new, commercially available samples of cubic zirconia reported to be coated with nanocrystalline synthetic diamond (typically defined as having grain sizes less than 500 nm). Serenity Technologies (Temecula, California) and Zirconmania (Los Angeles) supplied the lab with material they market as EternityCZ and Diamond-Veneer, respectively.

The Serenity Technologies website claims it is "virtually impossible to visually identify EternityCZ as anything but a diamond. The only way to positively identify EternityCZ is by its weight, hardness and chemical component" (www.serenitytechnology.com). It also states that the RI and dispersion change due to the nanocrystalline diamond coating. Zirconmania makes similar claims about Diamond-Veneer (http://diamondveneer.net).

Figure 1. This 0.31 ct cubic zirconia from Serenity Technologies is reportedly coated with nanocrystalline synthetic diamond.

Figure 2. In reflected light, the coating on the surface of this 2.36 ct cubic zirconia is clearly visible. Also, the chips look conchoidal, in contrast to the typical step-like appearance of diamond. Field of view 1.7 × 1.3 mm.

We examined 14 round brilliant samples from Serenity (0.29–0.32 ct; e.g., figure 1) and four from Zirconmania (0.13–2.36 ct). Seventeen of the specimens corresponded to the D range on the GIA diamond color grading scale; the last was equivalent to an E.

All the analyses we performed successfully identified the samples as diamond simulants. Microscopic examination with darkfield illumination revealed the orange pavilion flash typical of CZ. All also tested as "not diamond" with a thermal conductivity diamond tester and the DiamondSure instrument. All the specimens showed chips, in various sizes, which appeared conchoidal, not step-like as one might expect for diamond. Additionally, all the samples revealed the presence of a coating on the crown and pavilion when viewed in reflected light (figure 2). The coating's appearance varied within facets and particularly at the

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facet junctions. Finally, the coating could be scratched with a corundum (Mohs 9) hardness point—therefore, it did not seem to add significantly to the CZ's durability.

SG values ranged from 5.91 to 5.96, as calculated by the DiaVision noncontact measuring device. This range coincides with the reported SG of 5.95 for yttrium-stabilized CZ (M. O'Donoghue, Ed., *Gems*, 6th ed., Butterworth-Heinemann, Oxford, UK, 2006). We were unable to measure the RI of the coated CZs using a standard gemological refractometer, but "read-through" observations, which provide a relative approximation of RI, yielded results more consistent with CZ than diamond.

Raman, photoluminescence (PL; at 325, 488, 514, and 830 nm laser excitations), and Fourier-transform infrared (FTIR) analyses using standard techniques revealed no peaks associated with diamond. The Raman and FTIR spectra matched those of CZ. Although we have not yet had an opportunity to determine the thickness of the coating, it appears to be too thin to contribute significantly to the spectra dominated by the underlying material.

The results of our tests establish that these EternityCZ and Diamond-Veneer samples are easily separated from diamond. Characterization of the coating material is the focus of ongoing research. If the coating material is nanocrystalline synthetic diamond, it does not take much imagination to predict that natural diamond, instead of CZ, might be used as a future substrate material to improve the appearance or the color of the stone (see, e.g., Summer 1991 Gem News, pp. 118–119). Should such a treatment become commercially available, it could be far more difficult for gemologists to identify.

Sally Eaton-Magaña and Karen M. Chadwick

DIAMOND

Assemblages of K-Feldspar, Hematite-Magnetite, and Quartz in Etch Channels

Most minerals seen in diamond occur as single crystals. Rarely have we encountered inclusions of mineral assemblages formed at conditions outside the diamond stability field. Recently, the New York laboratory examined a group of five diamonds (1.67–3.70 ct) submitted together by a single client. These stones contained dark sectorial clouds, as well as numerous etch pits and etch channels. Three of the diamonds were color graded Fancy black, and the other two were graded Fancy Dark brown. Infrared spectroscopy showed a relatively high concentration of hydrogen in all the stones, which is the likely cause of the sectorial clouds that produced the dark colors.

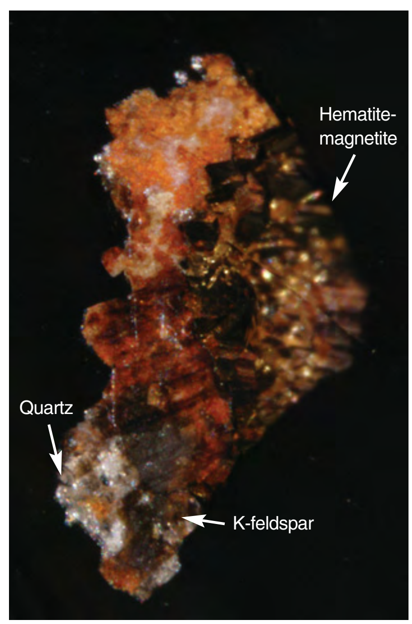
Figure 3. This 2.46 ct Fancy black diamond contained dark sectorial clouds as well as assemblages of mineral inclusions, which formed in etch channels.

Of greatest interest were the assemblages of mineral inclusions seen in the etch pits and channels of all the diamonds. Microscopic examination revealed these as opaque dark brown, transparent gray, and transparent near-colorless to white materials. The largest assemblage (~1.1 × 0.5 × 1.0 mm)—observed in a 2.46 ct oval modified brilliant-cut Fancy black diamond (figure 3)—consisted of four minerals (figure 4) in an etch channel that broke the surface at the crown shoulder. Raman spectroscopy identified the opaque dark brown portion, which made up most of this assemblage, as a mixture of hematite and magnetite. The bottom part of this mixture was totally enclosed in the diamond and showed well-formed stepped surfaces. The transparent gray inclusions were identified as K-feldspar, and the white inclusions were quartz.

A 1.67 ct cut-cornered rectangular step-cut Fancy Dark brown diamond contained an assemblage almost as large (~0.9 × 0.6 × 0.5 mm), which broke the surface of the pavilion near a corner. Raman spectroscopy identified this assemblage as a mixture of hematite-magnetite and quartz.

The presence of dark sectorial clouds in all five stones suggested that these diamonds could have formed in a similar environment. Since quartz and K-feldspar would not be stable in the high-temperature and high-pres-

Figure 4. This assemblage of hematite-magnetite, K-feldspar, and quartz crystallized in an etch channel of the diamond in figure 3 as secondary inclusions. The orange color is likely due to iron staining from weathering of the iron-bearing hematite-magnetite. Field of view 0.8 mm.



sure stability field of diamond, these assemblages could only have formed at conditions outside the diamond stability field, such as within the continental crust, where these minerals are stable. Furthermore, the well-developed crystalline quality and morphology of these included minerals suggest formation and growth after the diamond was brought to a relatively shallow depth in the earth.

Most of the mineral inclusions we observe in the laboratory are protogenetic or syngenetic inclusions formed within the diamond stability field. These assemblages provide excellent examples of epigenetic mineral inclusions that formed outside the diamond stability field and are typically associated with crustal processes.

Wai L. Win and Ren Lu

Clarity Grading Radiation Stains

Radiation stains can appear as green or brown patches in diamond. They are typically associated with naturals, indented naturals, feathers, or etch features, and are thought to be caused by exposure to radioactive elements in a near-surface, low-temperature environment. Radiation stains are green when they form and can turn brown if the diamond is subjected to relatively high temperatures, such as those that occur during the polishing process. Their impact on a diamond's clarity grade depends on whether or not they penetrate the surface of the stone.

Recently, the New York laboratory examined a 1.01 ct round brilliant cut submitted for grading. An etch channel extended into the diamond from a bezel surface; it was identifiable by its distinct elongated form and angular outline, as well as the growth markings along its edges (figure 5). Spherical brown zones were visible reaching beyond the etch channel in two areas. Their unusual appearance, color, and relationship to the etch channel immediately identified them as radiation stains. They probably formed when radioactive particles lodged in the etch channel, affecting only those areas.

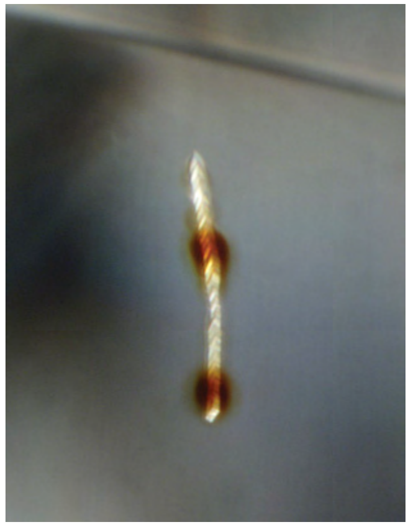


Figure 5. The two brown patches of color in this etch channel, shown here at 100× magnification, are radiation stains. The etch channel was visible at 10× magnification; as a result, these stains were considered inclusions for the purpose of clarity grading.

To assess the effect of a radiation stain on a diamond's clarity grade, the grader must first determine if the stain is an inclusion or a blemish. While all radiation stains penetrate into the diamond to a certain extent, they are only considered inclusions if the penetration is visible at 10× magnification, as was the case with the stains illustrated here. Otherwise, the staining is treated as a blemish, which has only a minor effect on the clarity grade.

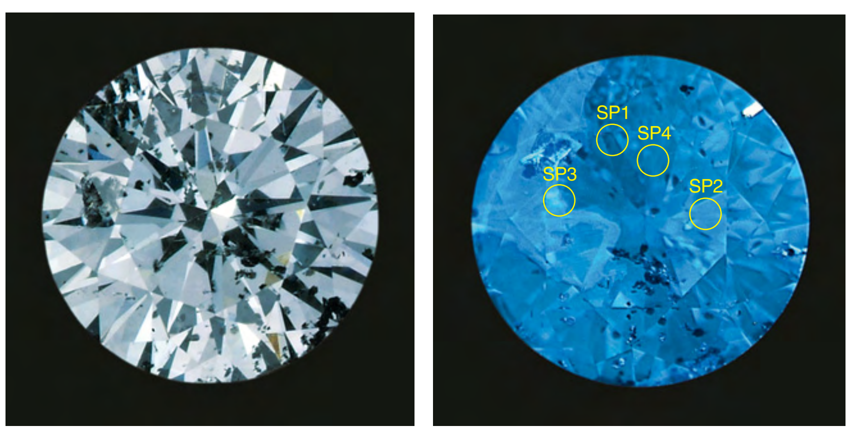
Vincent Cracco and Alyssa Grodotzke

Rare Mixed Type (Ia/IIb) Diamond with Nitrogen and Boron Centers

Type IIb diamonds are among the rarest and most valued of all natural diamonds. Their characteristic blue color originates from a very low concentration of boron impurities, which is also responsible for their distinctive properties (see, e.g., J. M. King et al., "Characterizing natural-color type IIb blue diamonds," Winter 1998 *G&G*, pp. 246–268). In general, type IIb diamonds do not have the quantity and variety of inclusions often observed in type I and some type IIa diamonds, which are differentiated by the presence (type I) and relative absence (type IIa) of nitrogen impurities.

The New York laboratory recently examined a very rare natural type IIb diamond with a noticeable type Ia component. This 0.17 ct round brilliant cut was graded Fancy Light grayish blue (figure 6, left). Numerous

Figure 6. This 0.17 ct Fancy Light grayish blue type IIb diamond (left) contained unusual amounts of nitrogen and hydrogen, characteristic of a type Ia diamond. The DiamondView fluorescence image (right) shows the heterogeneous distribution of boron (darker blue areas represented by spots 1 and 4) and nitrogen (lighter blue areas represented by spots 2 and 3).



graphite particles were the only inclusions observed. Electrical conductivity, as measured with a gemological conductometer, was consistent with that of a typical type IIb diamond. The stone showed very weak blue fluorescence to long-wave ultraviolet (UV) radiation and was inert to short-wave UV. It showed both blue and red phosphorescence, as is typical of natural IIb stones. DiamondView images revealed zones with various hues of blue fluorescence (figure 6, right), which suggested a heterogeneous distribution of defects and impurities.

The mid-infrared spectrum (figure 7) had a dominant IIb character, with a boron component indicated by a band at ~2801 cm^{-1}. However, evidence of a nitrogen component with both A and B aggregates was clearly present in the 1280–1170 cm^{-1} region, indicating a type Ia nature as well. A noticeable amount of hydrogen was also observed at 3107 and 1405 cm^{-1}, which—to the best of this contributor's knowledge—is the first time hydrogen has been directly observed in a natural type IIb diamond. The relative intensities of the boron, nitrogen, and hydrogen bands varied noticeably among the regions sampled. Unfortunately, the nature of our infrared system and the shape of the stone did not allow us to correlate the different IR features to specific regions that were indicated by the DiamondView image.

However, we were able to correlate low-temperature PL spectra at 325, 488, and 514 nm excitations to those specific regions (figure 8). This technique allowed us to probe point-by-point for the presence or absence of nitrogen-related features, effectively mapping the stone's type IIb and Ia regions. Specifically, PL spectra taken from the lighter blue region (spots 2 and 3 in figure 6, right) showed nitrogen features typical of type Ia stones, such as the N3, H3, H4, and NV^0 centers; spectra from the darker blue regions (spots 1 and 4) exhibited virtually none of these features, correlating to type IIb. This PL mapping allowed a rare direct observation of the N3 defect at 415 nm (along with H3, H4, and NV^0) in a mostly type IIb stone, which is quite noteworthy because the N3 defect is considered the key feature in the distinction of type I from type II diamonds.

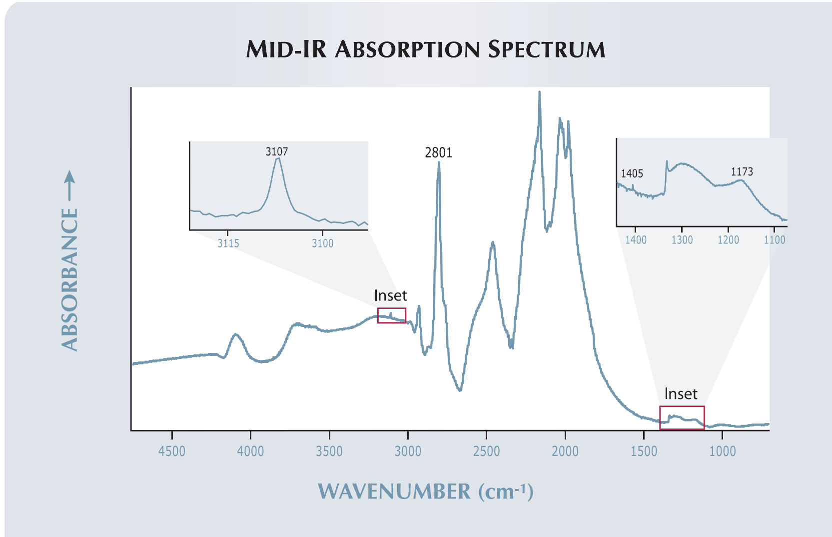
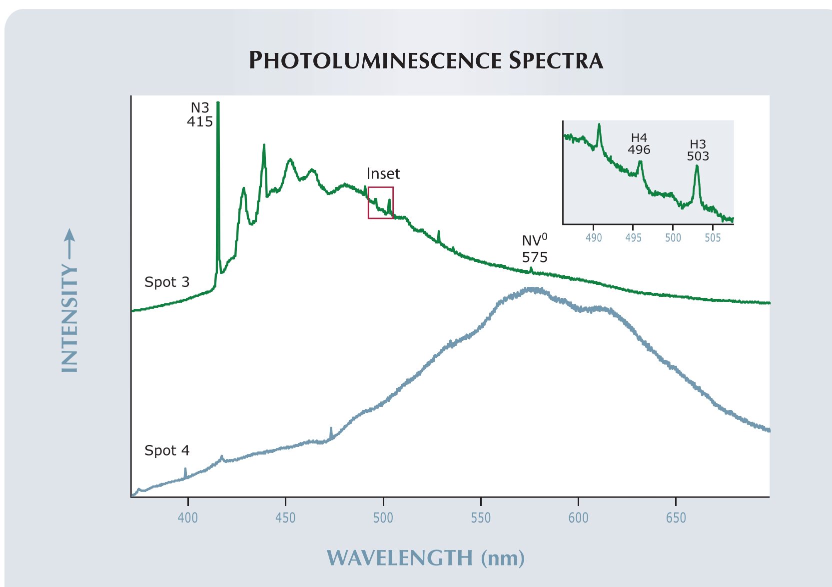


Figure 7. The mid-IR spectrum of the 0.17 ct diamond shows a dominantly type IIb nature, with a boron-related band near 2801 cm^{-1}, but also—see insets—evidence of a type Ia nature, with nitrogen (e.g., the 1173 cm^{-1} band, correlating to B-aggregates) and hydrogen (3107 and 1405 cm^{-1}) impurities.

Figure 8. Taken at 325 nm UV wavelength, low-temperature PL spectra collected from the lighter blue areas (spots 2 and 3) in figure 6 showed optical centers (e.g., N3, H3, H4, and NV^0) consistent with type Ia diamonds, whereas spectra from the darker blue areas (spots 1 and 4) were free of these nitrogen features, which is consistent with a type IIb diamond.



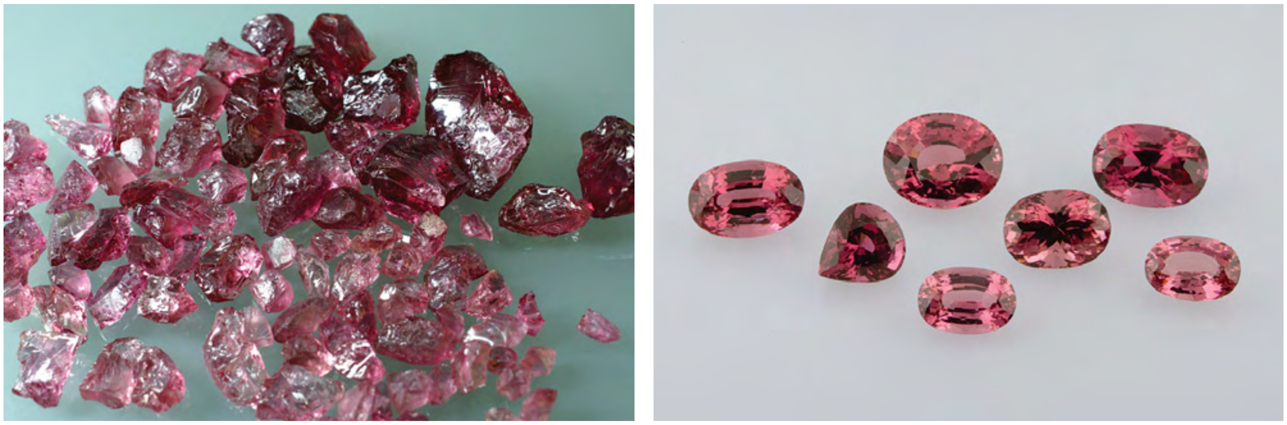


Figure 9. The parcel of rough spinel on the left, reportedly from Tajikistan, contains pieces weighing up to 48.5 g. The seven faceted spinels on the right (9.04–28.16 ct) were fashioned from some of this rough.

Mixed-type diamonds with a type IIb component have been examined previously at the GIA Laboratory (e.g., Lab Notes: Summer 2000, pp. 156–157; Summer 2005, pp. 167–168; and Winter 2008, pp. 364–365). However, type IIb diamonds with an extensive type Ia component have been observed only rarely. The mixed-type nature indicates a substantial change in the geochemical environment during the diamond's crystallization. Further analysis of the available data may shed light on the interaction between boron, carbon, nitrogen, and hydrogen, and their impact on the spectral and physical properties.

Ren Lu

Purplish Pink SPINEL from Tajikistan—Before and After Cutting

In December 2007, Pakistan-based client Syed Iftikhar Hussain submitted a parcel of spinel rough reportedly from Tajikistan (figure 9, left). These 84 samples, the largest weighing 48.5 g, exhibited varying saturations of purplish pink color. Little has been written on the properties of Tajik spinel (see, e.g., J. I. Koivula and R. C. Kammerling, "Examination of a gem spinel crystal from the Pamir Mountains," *Zeitschrift der Deutschen Gemmologischen Gesellschaft*, Vol. 38, 1989, pp. 85–88), so in November 2008 the Bangkok laboratory was fortunate to have an opportunity to briefly examine seven stones that the client had faceted from this parcel (figure 9, right).

Figure 10. Among the inclusions observed in the rough spinels were a fine euhedral crystal (left, magnified 75×) and crystals with white particulate trails forming "comet tails" (right, magnified 35×).

Most of the original rough consisted of broken pieces, and only a few showed the octahedral crystal forms typical of spinel. We could not perform accurate RI measurements because of the lack of flat surfaces, so we had to rely on other tests. The hydrostatic SG measurements, spectra seen with a handheld spectroscope, polariscope reactions, and UV fluorescence were consistent with spinel. These observations were further substantiated by PL spectroscopy (514 nm laser excitation at room temperature) on the largest piece, which proved it was natural spinel. The most prominent inclusions seen in the samples were euhedral crystals, needles, and crystals with white particulate trails forming "comet tails" (figure 10).

After the rough was cut, we obtained standard gemological properties for the seven faceted stones. The results were fairly consistent: RI—1.712–1.713, SG—3.59–3.62, strong red fluorescence to long-wave UV radiation and weak red to weak-to-moderate orange (some with a chalky greenish cast) fluorescence to short-wave UV, and a characteristic "organ pipe" spectrum (with some general absorption in the orange/yellow and part of the green region) seen with the

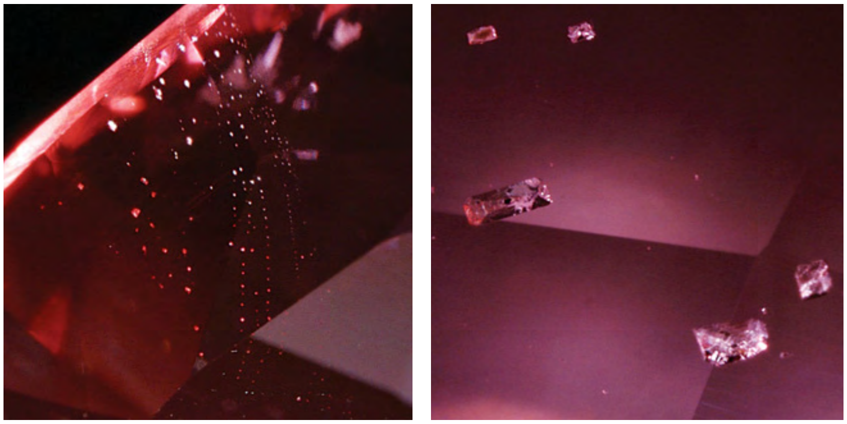


Figure 11. One of the faceted spinels contained a plane of negative crystals (left, magnified 50×) and a group of euhedral crystals (right, magnified 20×).

spectroscope. While the refractive indices were almost identical to that of the crystal detailed by Koivula and Kammerling (and a Tajik spinel reported in the Spring 1989 Lab Notes, pp. 39–40), the SGs varied slightly.

Since the cleanest pieces of rough were likely selected for faceting, it was no surprise that six of the cut stones showed few inclusions. The 11.96 ct pear shape hosted the most internal features, which consisted of a plane of octahedral negative crystals and some euhedral crystals (figure 11). Tiny negative crystals were only faintly visible in one other stone. Unfortunately, there was no time to identify inclusions in either the rough or cut spinels with Raman spectroscopy. The PL spectrum of the pear-shaped stone closely matched that of the rough sample.

Nicholas Sturman

PHOTO CREDITS
Robison McMurtry—1; Karen M. Chadwick—2; Jian Xin (Jae) Liao—3, 6 left; Wai L. Win—4; Jason Darley—5; Ren Lu—6 right; Ken Scarratt—9 left, 10; Suchada Kittayachaiwattana—9 right; Nicholas Sturman—11.