CHARACTERIZATION OF A SYNTHETIC NANO-POLYCRYSTALLINE DIAMOND GEMSTONE

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A potential new synthetic gem material in the form of a faceted 0.88 ct brownish yellow nano-polycrystalline diamond (NPD) has undergone a full gemological examination, including detailed spectroscopic analysis, for the first time. While the material's implications for the gem industry are still unknown, NPD's optical characteristics along with manufacturing improvements make it a potentially important synthetic for gemologists to be aware of, even though very few samples have been faceted and future production costs and availability for gem purposes are uncertain. Features seen with magnification may provide an indication of its nano-polycrystalline nature, and the identification of this material can be confirmed by spectroscopy and other advanced testing methods. NPD is an entirely new kind of synthetic diamond, and its development illustrates the ongoing research on diamond properties for a number of important applications beyond the field of gemology.

Synthetic nano-polycrystalline diamond (NPD) may be one of the most important developments in synthetic diamond production in recent years. This transparent brownish yellow material is produced not by CVD or traditional HPHT synthesis methods, but rather in a multi-anvil press by a sintering process that converts high-purity graphite directly into synthetic diamond. According to the developer of the process, the conversion time averages 10–20 minutes (though can be less than 10 minutes) at 15 gigapascals and 2,300–2,500°C (T. Irifune, pers. comm., 2012). These pressures and temperatures are far higher than those used in the HPHT syn-

thesis of single-crystal diamond. The material consists of randomly oriented nanoscale-sized synthetic diamond crystallites that have been bonded tightly together to form what may be thought of as an ultra-hard synthetic diamond ceramic.

A recent article by Skalwold (2012) documented a transparent 5 mm NPD sphere, and served as means to introduce this new synthetic diamond's development and some of its properties. Soon after that article was published, Dr. Tetsuo Irifune, director of Ehime University's Geodynamics Research Center (GRC), once again offered one of the authors (EAS) an exclusive opportunity to study this unique material. This time the specimen was a 0.88 ct faceted round brilliant (figure 1). In collaboration with researchers at GIA, an analysis of its gemological and spectroscopic properties was undertaken to establish gem identification criteria. Further work on this material will be conducted by author EAS and by GIA as more samples become available.

Figure 1. This 0.88 ct synthetic nano-polycrystalline diamond, produced by direct conversion from graphite at high temperatures and pressures, represents a completely new type of transparent gem material. Photo by Robert Weldon.

See end of article for About the Authors and Acknowledgments.

GEMS & GEMOLOGY, Vol. 48, No. 3, pp. 188–192,
<http://dx.doi.org/10.5741/GEMS.48.3.188>.

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As initially reported by Skälwold et al. (2012), while this transparent gem material shares some similarities with natural and synthetic single-crystal diamond, it also has properties that are sufficiently distinctive to be recognizable by gem-testing laboratories. Given that there are only five known faceted samples in existence, the opportunity to characterize it with the assistance of a gemological laboratory was a singular opportunity.

PRODUCTION

Relatively swift advancements have been made in the manufacturing process of NPD. In less than a decade since the successful production of this material was first reported (Irifune et al., 2003), improvements have resulted in relatively large pieces suitable for a number of applications, most notably for diamond anvils used in high-pressure research. For this purpose, two NPD cylinders are produced per week, generally measuring 6.5–9 mm in diameter and 6.5–8 mm in length (a maximum of 10 mm in each dimension is possible). But if the GRC's Botchan multi-anvil press were to produce only NPD, up to 10 cylinders could be made each week. The pieces recovered from the press have a slight surface texture, caused by the tantalum cap-

In Brief

- Synthetic nano-polycrystalline diamond (NPD) consists of nanoscale-sized synthetic diamond crystallites bonded together using an HPHT sintering process.
- A 0.88 ct brownish yellow round brilliant, one of five faceted NPD gems currently in existence, was characterized for this report.
- Key identifying properties include a hazy, roiled appearance and distinctive mid-IR, visible-range, and photoluminescence spectra.
- This sample was cut from early production, and future NPD material may not show the same diagnostic features.

sule in which the graphite-to-NPD conversion takes place (see figure 4 of Skälwold, 2012). These cylinders are cut by a combination of specialized lasers and polishing techniques. The material requires nontraditional cutting and polishing methods because of its polycrystalline nature and polishing hardness. Unlike natural and other synthetic diamonds, NPD is uniformly hard in all directions at the macro scale (although hardness varies on the nano scale).

TABLE 1. Basic gemological properties of the NPD sample.

Color	Fancy Deep brownish yellow
Clarity	Slightly Included (SI ₁)
Appearance	Slightly hazy or cloudy
Luster	Adamantine
Refractive index	Over the limits of the standard refractometer
Specific gravity	3.52
UV fluorescence	
Long-wave	Moderate chalky reddish orange
Short-wave	Weak reddish orange
Phosphorescence	None observed
Magnetic attraction	None observed
Diamond testers	
Presidium	Positive for diamond
DiamondSure	Referred for further testing; not "passed" as natural diamond
Magnification	Roiled appearance; one black and numerous pinpoint inclusions; patchy clouds of color zoning

Efforts are now under way at the GRC to produce colorless NPD. Marketing of the material is still in its infancy, and pricing for industrial use has yet to be established (T. Irifune, pers. comm., 2012).

MATERIALS AND METHODS

A 0.88 ct round brilliant studied for this report measured $6.13 \times 6.10 \times 3.78$ mm. It was graded for color and clarity using standard GIA procedures. Basic gemological properties were collected (table 1), and additional testing was performed with a Presidium GEM Mini-DiamondMaster and a DTC DiamondSure screening device. The sample was examined with a Nikon SMZ-1500 binocular gemological microscope under several lighting configurations. Deep-ultraviolet (~230 nm excitation) fluorescence images were captured using a DTC DiamondView instrument.

Visible absorption spectra were recorded with the sample cooled to liquid-nitrogen temperature (~77 K) using a custom-made Ocean Optics high-resolution spectrometer. Infrared absorption spectra were recorded with a Thermo-Nicolet Magna IR 760 spectrometer, while Raman and photoluminescence (PL) spectra were measured with a Renishaw InVia Raman spectrometer. PL spectra were recorded at liquid-nitrogen temperature using four excitation wavelengths (325, 488, 514, and 633 nm).

Figure 2. The NPD sample displayed some interesting visual features attributed in part to the polycrystalline nature of the material. Small whitish pinpoint inclusions (A, image width 1.7 mm) were scattered throughout the specimen. A dark inclusion (B, image width 0.65 mm) was observed but could not be identified with Raman analysis. Also observed were a mottled uneven coloration (C) and a finely textured roiled appearance (D, image width 3.6 mm). Photomicrographs by N. Renfro.

RESULTS AND DISCUSSION

The GIA color and clarity grades, as well as basic gemological properties, are shown in table 1. With magnification, we observed numerous whitish pinpoint inclusions along with a single larger black inclusion, patchy clouds of color zoning, and a roiled appearance (figure 2). This last feature was much like the effect sometimes seen in the hessonite variety of grossular, and it appeared to cause the sample's slight haziness when viewed in the face-up position. The black inclusion showed a dominant broad Raman peak at 1078 cm^{-1} , but we were unable to identify a mineral phase from the spectrum. Observation with crossed polarizing filters showed a cross-hatched or tatami-like strain pattern in several orientations, with no apparent variation in the color, intensity, or distribution of the pattern depending on direction (figure 3). While the hazy, roiled appearance is quite unusual, visual features alone should not be considered completely diagnostic for NPD, but rather as indications that laboratory testing is needed.

Fluorescence imaging using the DiamondView showed orangy red luminescence with an irregular structure (figure 4). This unusual patchy appearance bears some resemblance to the networks or "webs" often seen in fluorescence images of natural type II diamonds. The orangy red luminescence seems to arise from boundaries between what appear to be larger aggregates of the nano-crystallites. This distinctive lumi-

nescence is similar in appearance and color to that generated by N-V optical centers in diamond.

We reexamined the sample with the microscope to look for evidence of the nano-crystallite aggregates. Inserting a quarter-wave plate and observing the birefringence while rotating the sample showed that most

Figure 3. When examined between crossed polarizing filters, the NPD sample displayed a cross-hatched or tatami-like pattern of low-order (dark gray) interference colors. Unlike similar birefringence seen occasionally in natural diamonds, it remained consistent in color and distribution regardless of the sample's orientation. Photomicrograph by N. Renfro; image width 4.4 mm.

Figure 4. When examined in the DiamondView, the NPD sample showed unevenly distributed orange red luminescence. Irregular darker areas of varying size are surrounded by the luminescence, which seems to originate along boundaries that may correspond to aggregated domains of nano-crystallites. Images by David Nelson; field of view is 3.5 mm (right).

of the birefringence was due to strain within the individual domains that correspond to those seen with the DiamondView. The strain in each of the domains was almost certainly low, causing no more than first-order gray and white interference colors. The sample also showed evidence of a global strain birefringence superimposed on the individual domain birefringence, and it too was first-order gray and white (W. A. Bassett, pers. comm., 2012).

Spectroscopy. The NPD sample's absorption spectra were distinct from those of natural diamond. Absorption features corresponding to the mid-infrared one-phonon region of diamond were observed (figure 5),

Figure 5. The NPD sample's mid-infrared spectrum reveals an absorption pattern unlike that of natural or synthetic diamond, especially in the region below 1500 cm^{-1} . This portion of the spectrum contains features that may be due to nitrogen, although diamond type could not be determined from them. There are no features in this spectrum that suggest the presence of boron or hydrogen.

but nitrogen aggregation state and diamond type could not be determined because the spectrum was different from that of type I and type II diamond (Breeding and Shigley, 2009). No evidence of hydrogen or boron impurities was observed in the mid-infrared spectrum.

The visible spectrum displayed increasing absorption toward the blue region, as well as two absorption bands at approximately 612 and 667 nm (figure 6). This increasing absorption is responsible for the sample's brownish yellow color. The two absorption bands are likely associated with the orange red fluorescence, but the assignment of the defect(s) causing these two bands is unclear. Luminescence features of similar energies reported in CVD synthetic diamond (Dischler, 2012, pp. 108–109) have been attributed to $[\text{N-V}]^0$ and $[\text{N-V}]^-$ centers. Further investigation will be required to determine if these are indeed the same

Figure 6. The visible spectrum of the NPD sample displays increasing absorption toward the blue region, which gives rise to its brownish yellow color. Absorption bands at 612 and 667 nm of unclear origin may be related to the orange red luminescence observed with the DiamondView.

Figure 7. This photoluminescence spectrum of the NPD sample, obtained with 514 nm laser excitation, displays the same two spectral features seen in the visible spectrum at 612 and 667 nm, along with some weaker bands of unknown origin.

optical defects responsible for the fluorescence shown by the NPD material.

Photoluminescence spectra recorded with the four laser excitations displayed weak but similar luminescence features at several wavelengths. The spectrum recorded with 514 nm excitation (figure 7) exhibited the same two peaks at 612 and 667 nm that were recorded in the visible absorption spectrum.

As reported by Sumiya et al. (2009), the characteristic brownish yellow color of NPD is thought to be caused by lattice defects within each crystallite due to

plastic deformation resulting from the HPHT conditions used for its production. Further investigation is necessary to confirm the cause of color in this material.

CONCLUSIONS

Until now, gem-quality synthetic diamonds with good transparency have all reportedly consisted of single-crystal material. This examination of a transparent faceted synthetic nano-polycrystalline diamond marks a fundamental change. The distinctive properties of this material should be readily identifiable with routine gemological testing. The observation of a roiled appearance within a diamond-like specimen, though not diagnostic, should alert gemologists that advanced testing is required.

The authors stress that the sample reported here is only one example from a rapidly improving technology. It was faceted from early production and not destined for applications where clarity, polish, and uniformity are a priority. Therefore, visual observations of this particular sample do not necessarily apply to all NPD specimens. This underscores the need for advanced laboratory testing and ongoing research as more material becomes available.

While NPD has been developed primarily for high-tech applications that require superior hardness and toughness, the present sample illustrates its potential as a gemstone. In the future, successful efforts to improve or remove color, either during production or with post-production treatment, may expand NPD's viability as a gemstone.

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ACKNOWLEDGMENTS

The authors are grateful to Dr. Tetsuo Irifune, director of the Geo-

dynamics Research Center at Ehime University (Matsuyama, Japan), for generously loaning the faceted NPD sample and for insights regarding its nature. For their assistance and helpful discussion, we also thank: Dr. William A. Bassett, professor emeritus of geology at Cornell University; Dr. Steven D. Jacobsen, associate professor of earth and planetary sciences at Northwestern University in Evanston, Illinois; David Christie of IMR Test Labs in Lansing, New York; and Al Gilbertson, John I. Koivula, David Nelson, and Robert Weldon of GIA in Carlsbad.

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