Characterization of a Synthetic Nano-Polycrystalline Diamond Gemstone

Elise A. Skalwold, Nathan Renfro, James E. Shigley, and Christopher M. Breeding

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 synthesis 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.

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As initially reported by Skalwold 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.

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 × 6.10 × 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).

**TABLE 1. Basic gemological properties of the NPD sample.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Fancy Deep brownish yellow</td>
</tr>
<tr>
<td>Clarity</td>
<td>Slightly Included (SI1)</td>
</tr>
<tr>
<td>Appearance</td>
<td>Slightly hazy or cloudy</td>
</tr>
<tr>
<td>Luster</td>
<td>Adamantine</td>
</tr>
<tr>
<td>Refractive index</td>
<td>Over the limits of the standard refractometer</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.52</td>
</tr>
<tr>
<td>UV fluorescence</td>
<td></td>
</tr>
<tr>
<td>Long-wave</td>
<td>Moderate chalky reddish orange</td>
</tr>
<tr>
<td>Short-wave</td>
<td>Weak reddish orange</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>None observed</td>
</tr>
<tr>
<td>Magnetic attraction</td>
<td>None observed</td>
</tr>
<tr>
<td>Diamond testers</td>
<td></td>
</tr>
<tr>
<td>Presidium</td>
<td>Positive for diamond</td>
</tr>
<tr>
<td>DiamondSure</td>
<td>Referred for further testing; not “passed” as natural diamond</td>
</tr>
<tr>
<td>Magnification</td>
<td>Roiled appearance; one black and numerous pinpoint inclusions; patchy clouds of color zoning</td>
</tr>
</tbody>
</table>

Notes & New Techniques
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 luminescence 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
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), 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 orangy 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 [N-V]0 and [N-V]– centers. Further investigation will be required to determine if these are indeed the same.
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 rolled 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.

REFERENCES


ABOUT THE AUTHORS

Ms. Skalwold (elise@nordskip.com) is a gemologist and author involved in research and curating at Cornell University in Ithaca, New York. Mr. Renfro is a staff gemologist, Dr. Shigley is a distinguished research fellow, and Dr. Breeding is a research scientist, at GIA in Carlsbad.

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