The Rhodesian Star: An Exceptional Asteriated Diamond

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The physical and optical properties of an exceptional asteriated diamond called *The Rhodesian Star* are described in detail. The stone shows a dramatic six-lobed star pattern formed by a dark grey cloud that strongly contrasts with the diamond's light greenish grey-yellow body colour. Analysis by various optical and spectroscopic methods identified the growth of the diamond as mixed-habit cuboid-octahedral, with the lobes forming the star pattern corresponding to cuboid growth sectors. These sectors are rich in hydrogen and nickel and are full of microscopic inclusions, possibly consisting of voids that are partially filled with graphite.

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Introduction

'Asteriated' diamonds contain a star-shaped cloud of light-scattering inclusions, and they used to be quite rare (Wang and Mayerson, 2002; Darley et al., 2009). With the discovery of enormous diamond deposits in Zimbabwe in 2006 and the appearance of such stones in the international markets around 2011, these diamonds have become more common. In very rare cases, attractive, well-defined star-shaped patterns are seen in complete diamond octahedra without the need to cut them into slices to make the star pattern more visible. Such is the case for the diamond studied for this report (Figure 1), named *The Rhodesian Star* after the old nomenclature of Zimbabwe. It is extremely likely that the diamond was mined in that country, since rough diamonds of similar appearance and properties are virtually unknown from other localities.

Asteriated diamonds from historical sources (Brazil and India) were described by Rondeau et al. (2004) using samples dating from 1802 to 1844. They characterized such diamonds as nitrogen-rich, with mixed-habit cuboid-octahedral growth and enrichment of hydrogen and nickel in the cuboid sectors. The correlation between symmetrical clouds and high hydrogen content was also pointed out by Wang and Mayerson (2002). Virtually all asteriated diamonds have a near-colourless to light brown or brown-yellow body colour with a somewhat darker brown-to-grey star pattern. The pattern always consists of two stars with three-fold symmetry, hence a six-fold star can be seen in complete octahedra. When such diamonds are sliced to enhance the contrast between the cloud and the surrounding diamond, patterns with two, three, four or six lobes can be seen (e.g., Figure 2).

Until now only a very few attractive complete octahedra of asteriated diamonds have appeared in the market and been analysed by a laboratory. This study reports the physical and optical properties of an exceptional 11.38 ct asteriated diamond: The Rhodesian Star.

Figure 1: The Rhodesian Star, a spectacular 11.38 ct asteriated diamond, is positioned here to show the star pattern reflected through four of the polished octahedral faces. Photo by E. Vadaszi.

Background

When the diamond was purchased by one of the authors (EV) in early 2014, it had windows polished on the octahedral faces in order to make the star pattern more visible, since its surface had an otherwise sandblasted look. Such matte-surfaced diamonds are common from Zimbabwe, and they typically also have a thick translucent-to-opaque green to nearly black crust. The original weight of the diamond was indicated to be close to 14 ct, and the polishing of the windows reduced it to a little over 13 ct.

After purchase, the stone's eight octahedral faces were repolished to display the star pattern to the best extent possible. Since polishing precisely parallel to the octahedron is virtually impossible due to diamond's greatest hardness along this plane (Kraus and Slawson, 1939), the faces were polished slightly oblique to the original octahedral surfaces. The polishing process was a very noisy and rather long process that took five full days. The boundaries between the octahedral faces were left with their original sandblasted appearance, hence resembling the surface of a nicely bruted girdle.

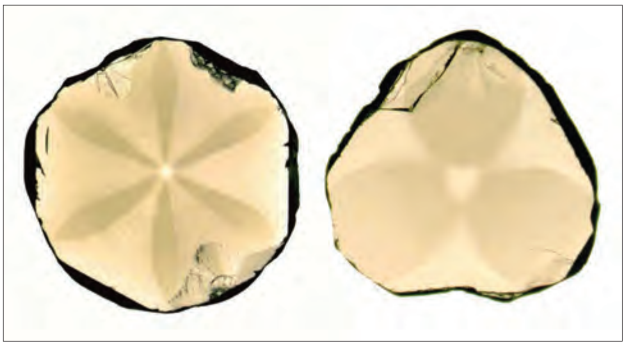
The result of this work is a unique and spectacular asteriated diamond weighing 11.38 ct and measuring 13.57 × 13.52 × 13.51 mm, of light greenish grey-yellow colour. The dark grey star-shaped cloud is much sharper and shows a far higher contrast than any other asteriated diamond that these authors are aware of.

Materials and Methods

The diamond was analysed at the Liechtenstein branch of GGTL Laboratories. The inclusions and strain pattern were visualized using a Leica M165C trinocular microscope, equipped with a Leica DFC420 CCD camera with a resolution of 5 megapixels. The strain pattern was analysed with the stone immersed in alcohol between crossed polarizing filters.

The luminescence of the diamond was observed in 254 nm short-wave (SW) and 365 nm long-wave (LW) radiation from a 6 W UV

Figure 2: Asteriated diamonds are commonly sliced to best display their star patterns. These two diamond slices in the collection of the French National Museum of Natural History date from 1844 and originate from India. Reprinted with permission from Rondeau et al. (2004).



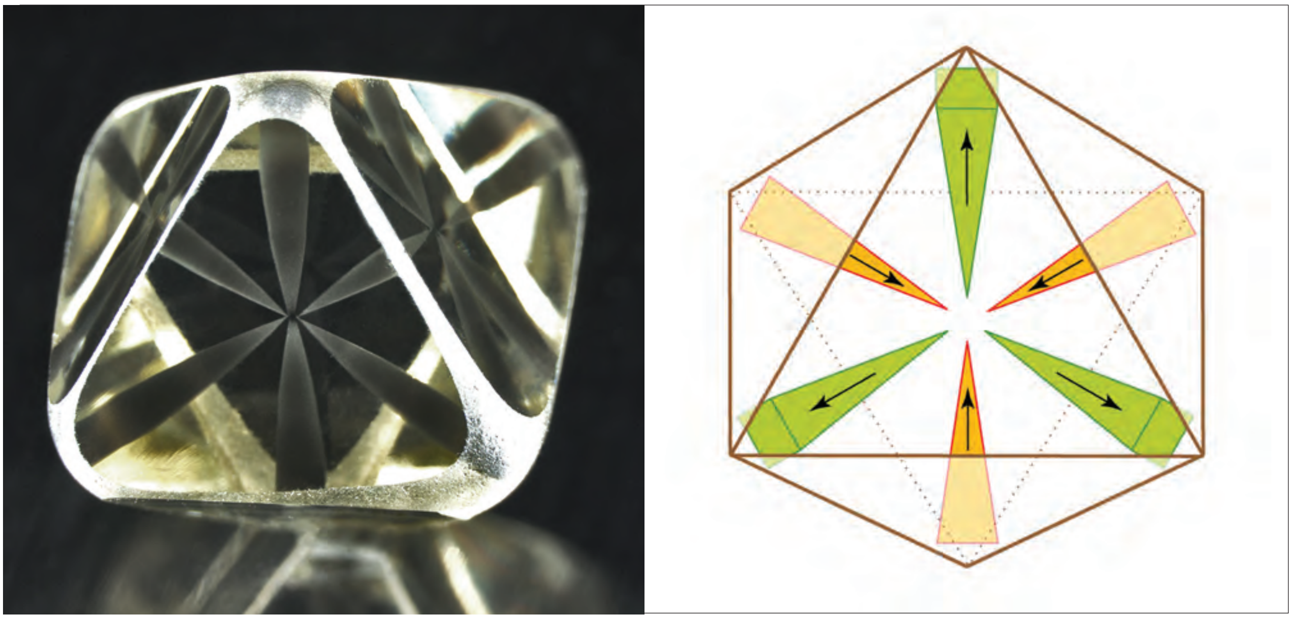


Figure 3: The star pattern shows exceptionally high contrast to the rest of the diamond (left, photo by T. Hainschwang). On the right is a graphical representation of the two sets of three-fold stars, which shows the pattern seen in The Rhodesian Star.

lamp (model UVP UVSL-26P). The luminescence was also observed in broadband UV using three different excitation bands (LW band 1: 300–410 nm; LW band 2: 355–375 nm; SW/LW band: 250–350 nm) from a GGTL DFI luminescence microscope using a suitably filtered 300 W full-spectrum xenon lamp. The luminescence images recorded with the GGTL DFI system were acquired with a Leica DFC450 C CCD camera with a resolution of 5 megapixels and the CCD sensor thermoelectrically cooled with a delta of −20°C compared to the surrounding temperature. Infrared spectra were recorded in transmission mode with a resolution of 4 cm^{-1} on a PerkinElmer Spectrum 100S Fourier-transform infrared spectrometer equipped with a thermoelectrically cooled DTGS detector, using a 5× beam condenser, over a range of 8500–400 cm^{-1}, with 100–500 scans.

Photoluminescence spectra were recorded on a GGTL system using 405, 473, 532 and 635 nm laser excitations, and a high-resolution echelle-type spectrograph by Catalina Scientific equipped with an Andor Neo sCMOS camera with a resolution of 5 megapixels, thermoelectrically cooled to −40°C. The system was set up to record spectra in the range of 350–1150 nm with an average resolution of 0.04 nm. All photoluminescence spectra were recorded with the diamond cooled to 77 K by direct immersion in liquid nitrogen.

Ultraviolet-visible–near infrared (UV-Vis-NIR) spectra were recorded on a GGTL D-C 3 spectrometer system using a combined xenon, tungsten-halogen and LED light source. A quadruple-channel spectrometer with a Czerny-Turner monochromator and a thermoelectrically cooled CCD detector was employed, with an average resolution of 0.3 nm. The spectrum was measured with the diamond placed in an integrating sphere of 15 cm diameter and cooled to about 77 K (−196°C).

Results and Discussion

Visual Observation and Microscopy

The asteriated pattern is caused by the combination of two stars, each showing the typical three-fold symmetry of diamond (Figure 3). The stars are oriented in different planes, so when they are viewed with magnification only one star is in focus at a time (Figure 4).

The tiny black inclusions forming the star patterns in some asteriated diamonds have been identified with Raman spectroscopy as highly crystalline graphite (Rondeau et al., 2004). The dark appearance and strong contrast of the lobes in The Rhodesian Star are due to a high density of such grey-to-black microscopic inclusions (Figure 5). The exact nature of these inclusions

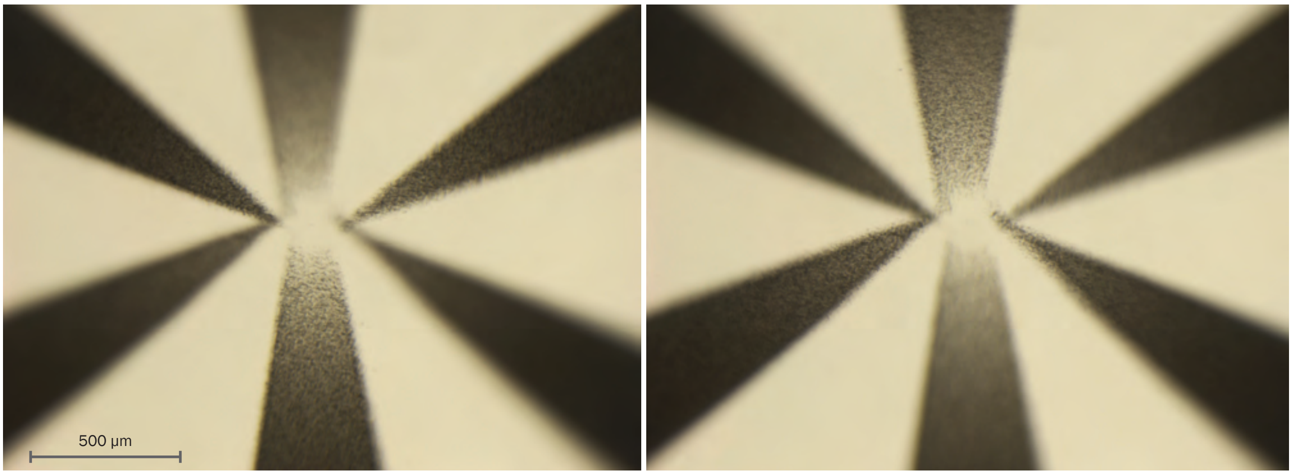


Figure 4: Each three-lobed star in the diamond originates from a separate plane, so only one star is in focus at a time when viewed with magnification. Photomicrographs by T. Hainschwang.

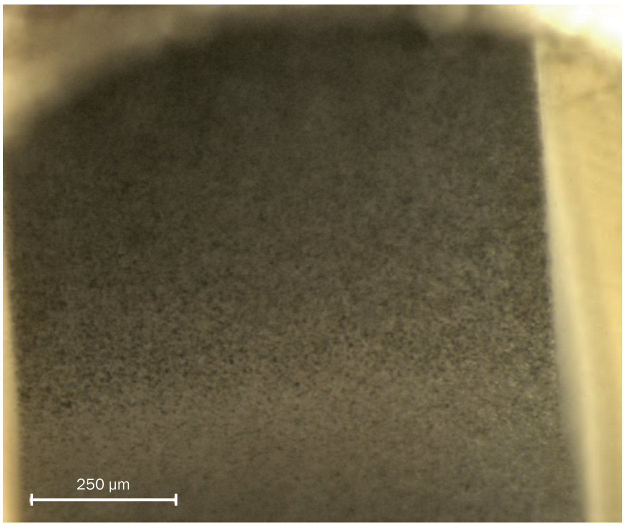


Figure 5: The dark appearance of the star pattern in the diamond is caused by microscopic particles that probably consist of voids that are partially or completely filled by graphite. Photomicrograph by T. Hainschwang.

was not determined due to time restraints when testing the diamond, but it is likely that they consist of voids that are partially or completely filled by graphite (cf. Klein-BenDavid et al., 2007).

Also observed in The Rhodesian Star were dark green radiation stains (Figure 6). Such stains are—as the name indicates—related to radiation and are characteristic for many natural rough diamonds (Nasdala et al., 2013). The stains on The Rhodesian Star are of natural origin. Similar stains may be observed in laboratory-irradiated diamonds treated by direct contact with radium salts, but such stains typically have a perfectly round shape, in contrast to the irregular shape of the stains in naturally irradiated diamonds (Hainschwang and Notari, 2014). The latter stains are caused by natural alpha radiation, and because of the low penetration depth of alpha particles, they are always limited to an area very near the surface. As determined by optical microscopy combined with the measurement capability of the Leica DFC450 C CCD camera, the depth of the stains in this diamond was found to be 5–10 µm. The presence of the pristine green radiation stains shows that the diamond has not been exposed to heat above 400–500°C, since such stains turn brown upon annealing (Nasdala et al., 2013).

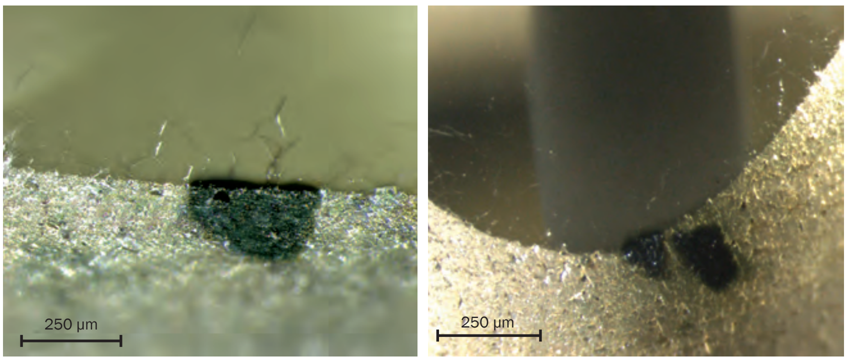


Figure 6: Several irregularly shaped dark green radiation stains on the surface of the diamond clearly show that it was exposed to natural alpha radiation and that it has not been heated to more than 400–500°C during the polishing process. Photomicrographs by T. Hainschwang.

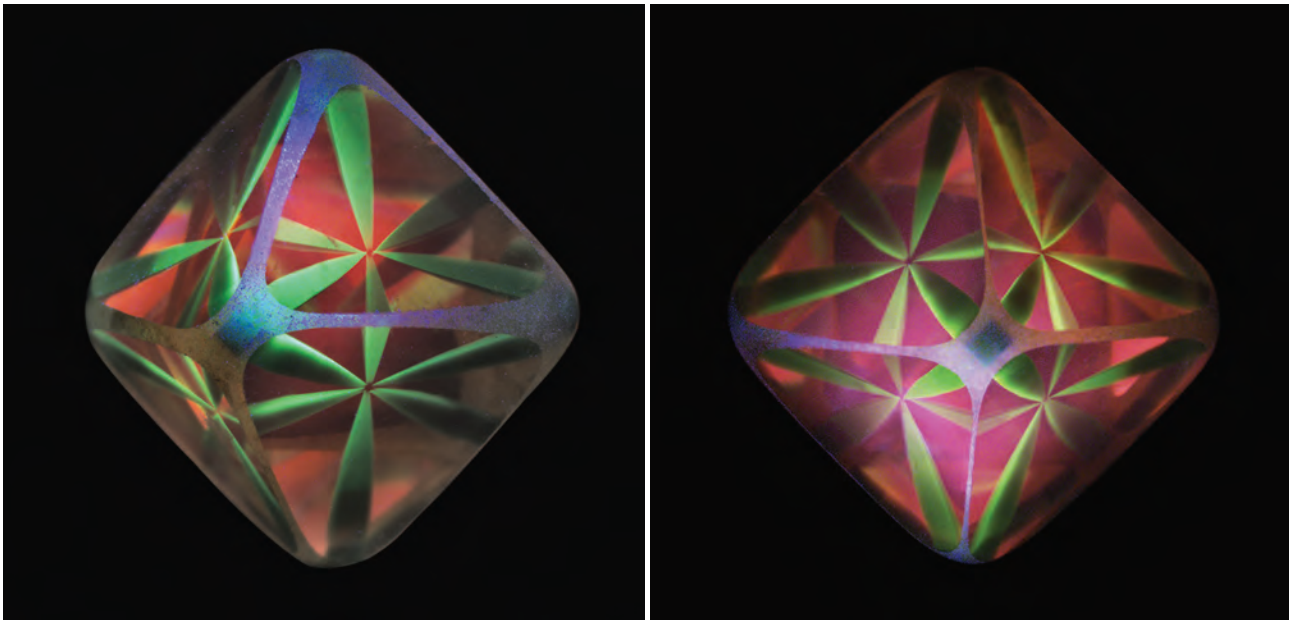


Figure 7: The Rhodesian Star displays beautiful luminescence patterns when exposed to the strong broadband UV excitation of the GGTL DFI fluorescence microscopy system (left = 300–410 nm and right = 355–375 nm excitation). Photos by T. Hainschwang.

While radiation stains are known in diamonds from many deposits, they are especially prominent in diamonds from Zimbabwe, which is the likely origin of this diamond.

Luminescence

Luminescence imaging is a technique where a material is typically excited by a UV source and its emission colours are observed.

The Rhodesian Star shows no apparent fluorescence under standard long- and short-wave UV lamps. However, when exposed to a high-power UV source such as the GGTL DFI fluorescence microscope, the stone exhibits a spectacular fluorescence pattern (see Figures 7– 9 and the cover of this issue). The star pattern glows green while the rest of the diamond luminesces pink-orange to purple-pink, depending on the specific UV excitation band used: 250–350 nm excitation causes pink-orange PL, 300–410 nm produces orangy pink PL, and 355–375 nm excites purple-pink PL.

UV excitation reveals that the lobes forming the star pattern have a square cross-section, which is particularly apparent at the corners of the octahedron (Figure 8). The square shape could lead to the conclusion that the lobes correspond to cube sectors such as those present in synthetic diamond. However the sectors almost certainly are of cuboid growth, a rather common form that exists

Figure 8: In this luminescence image (250–350 nm excitation), the square cross-section (and hence the cuboid nature) of a lobe of The Rhodesian Star is evident at the corner of the diamond octahedron. Photomicrograph by T. Hainschwang.

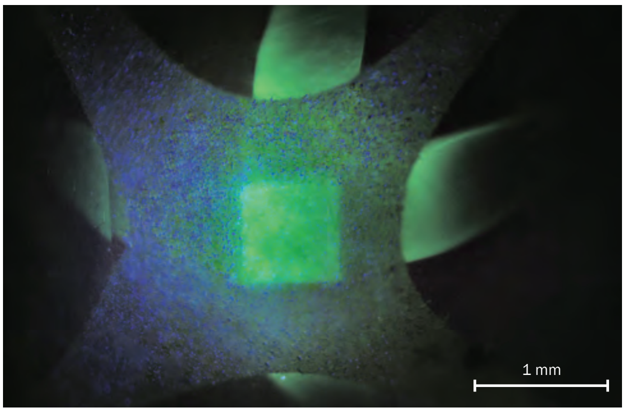
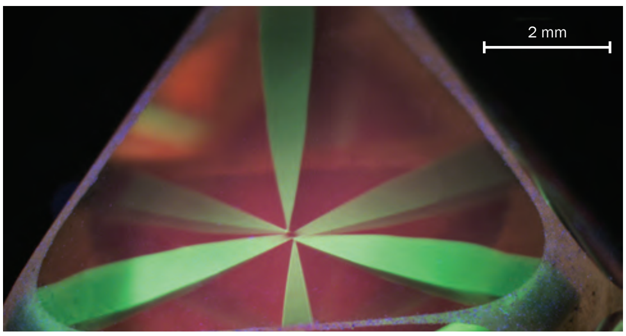


Figure 9: This close-up view of the luminescence of The Rhodesian Star under 250–350 nm excitation displays the green-luminescing lobes, which follow the cuboid directions of the diamond. Photomicrograph by T. Hainschwang.



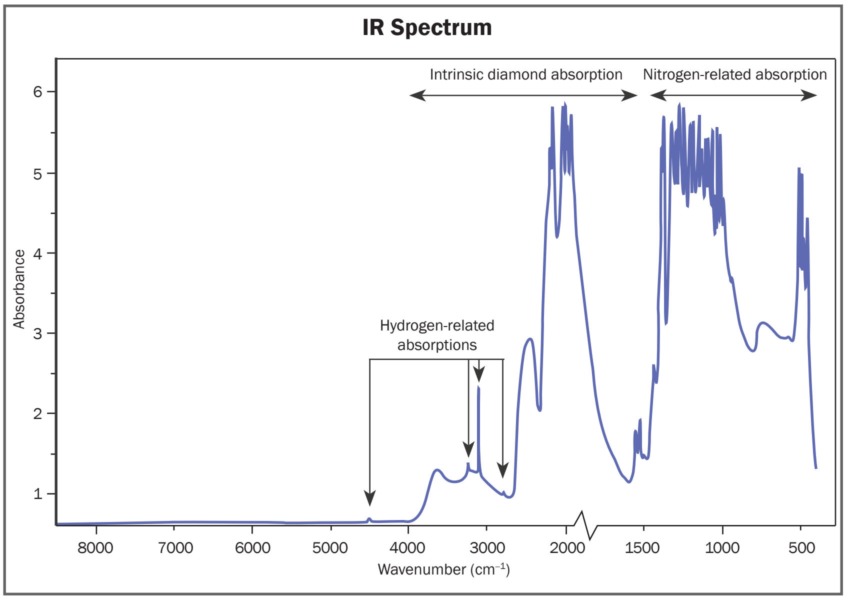


Figure 10: The infrared spectrum of The Rhodesian Star shows it is a type IaA>B diamond with very high nitrogen and moderate hydrogen content.

only in natural diamond. Cuboid sectors are known to be typically rich in hydrogen and nickel-related defects (Lang et al., 2004). These nickel-related defects are responsible for the green luminescence in these sectors (see PL Spectroscopy section for more details). A sketch of the two three-fold stars observed in this diamond, and the square cross-section of the lobes, is shown in Figure 3.

Infrared Spectroscopy

Infrared spectroscopy is a well-known method used to distinguish different diamond types based on the presence or absence of substitutional nitrogen and/or boron impurities and the aggregation state of the nitrogen. The presence of hydrogen also can be confirmed by this technique, and certain radiation-related defects can be detected.

The infrared spectrum of The Rhodesian Star characterizes the stone as a type IaA>B diamond (Figure 10); hence the A-aggregate form of nitrogen dominates the B-aggregate form of nitrogen. The stone contains very high concentrations of nitrogen and moderate amounts of hydrogen. The nitrogen content could not be properly determined; due to the thickness of the diamond and its enriched nitrogen content, the necessary nitrogen absorptions (482 cm^{-1} for A aggregates and 1010 cm^{-1} for B aggregates) could not be properly resolved. Infrared spectra recorded from the individual sectors show that by far most of the hydrogen is located within the 'star' cuboid sectors.

UV-Vis-NIR Spectroscopy

Performed at low temperature (–196°C, with the sample immersed in liquid nitrogen), UV-Vis-NIR spectroscopy is useful for detecting many important defect centres in diamond. Among these are the N3/N2 centres, which are responsible for the yellow coloration of many diamonds, and several radiation-related defects such as GR1, the 594 nm centre, etc.

The Rhodesian Star shows a standard cape spectrum, with distinct N3 and N2 absorptions at 415.2 and 478 nm, respectively. Several radiation-related features also can be seen, such as GR1 at 741.2 nm (caused by the neutral carbon vacancy), 3H at 503.5 nm and the 594 nm centre (Figure 11). These absorptions are rare in untreated natural diamond—with the exception of naturally irradiated green to greenish blue stones—although they have been found to be rather common in untreated diamonds from Zimbabwe (Breeding, 2011; Crepin et al., 2011). These rough stones often have a thick very dark green 'skin' from natural irradiation, and although the vast majority of the diamonds have a mixed brown/yellow body colour in their transparent core, they show minor traces of natural radiation damage in their spectra.

PL Spectroscopy

Laser-excited PL spectroscopy is a very sensitive method for detecting the defects responsible for the observed luminescence. The diamond sample is immersed in liquid nitrogen, and the

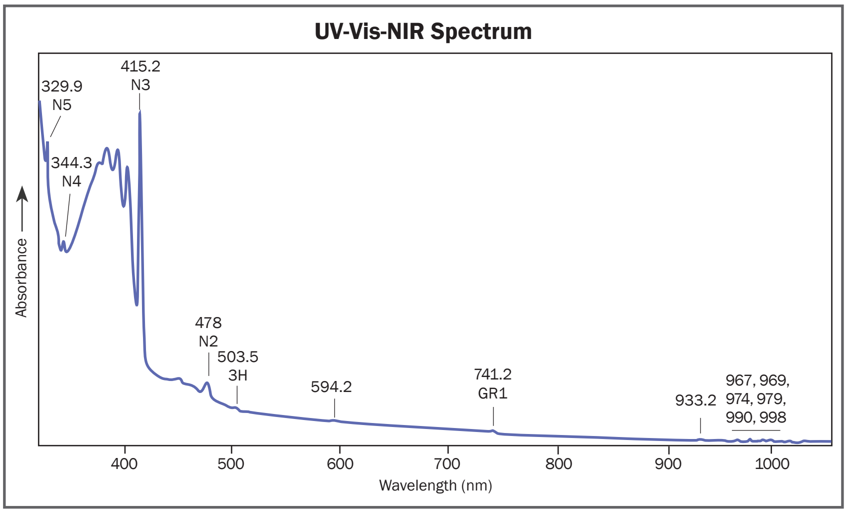


Figure 11: The UV-Vis-NIR spectrum of The Rhodesian Star indicates that its light greenish grey-yellow body colour originates from strong N3/N2 absorption combined with GR1 absorption. The overall slight green hue originates from surface-related green coloration caused by natural radiation exposure. The path length of the beam through the GR1-damaged surface is very short, so absorbance of the GR1 band is very low. Several other absorptions, such as the 594.2 nm peak, also indicate that the stone experienced exposure to radiation.

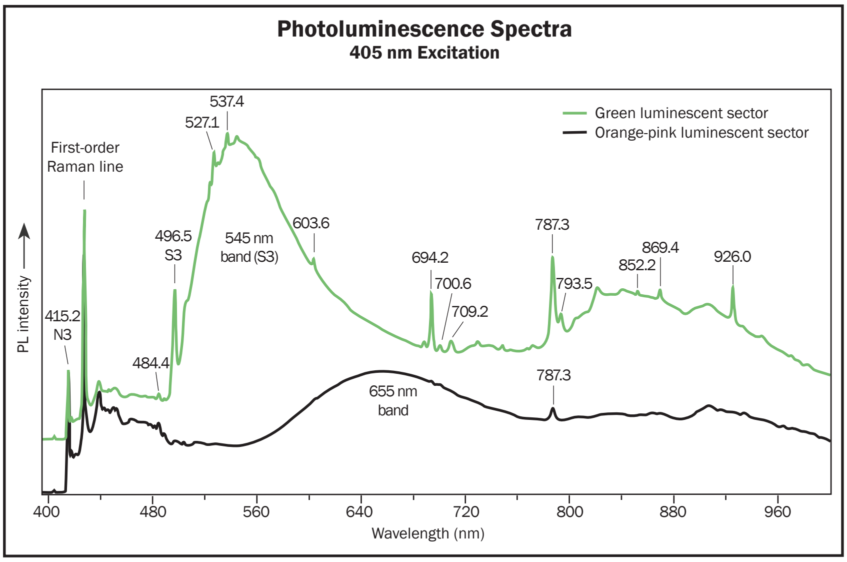


Figure 12: The PL spectra of the differently luminescing sectors of The Rhodesian Star obtained with 405 nm excitation show that the green PL of the lobes is due to strong nickel-related (S3) defect luminescence, while the orange-pink PL from the octahedral sectors originates from a broad emission band of unknown origin centred at 655 nm. The spectra clearly show that the cuboid sectors are rich in nickel while the octahedral sectors are not.

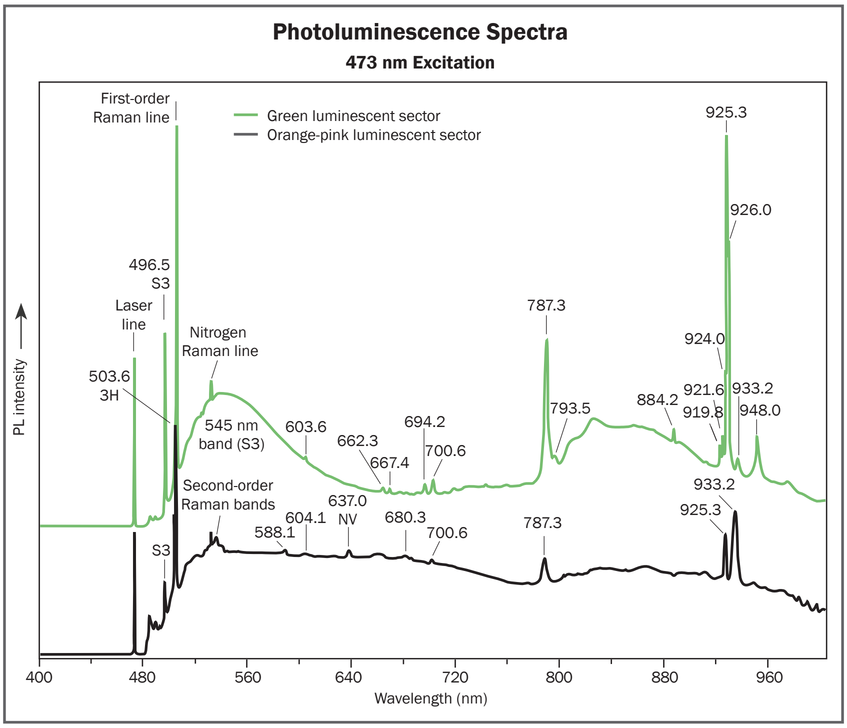


Figure 13: As with the 405 nm laser, PL spectroscopy of The Rhodesian Star obtained with 473 nm excitation shows that the green PL of the lobes originates from strong S3 defect luminescence. The extremely broadband emission seen in the octahedral sectors indicates a much different PL colour than was seen with 405 nm and strong UV excitation; the colour most closely resembles 'beige' or some sort of brown hue. The cuboid sectors are richer in nickel defects than the octahedral sectors. (The nitrogen line is produced by Raman scattering from the liquid nitrogen surrounding the specimen.)

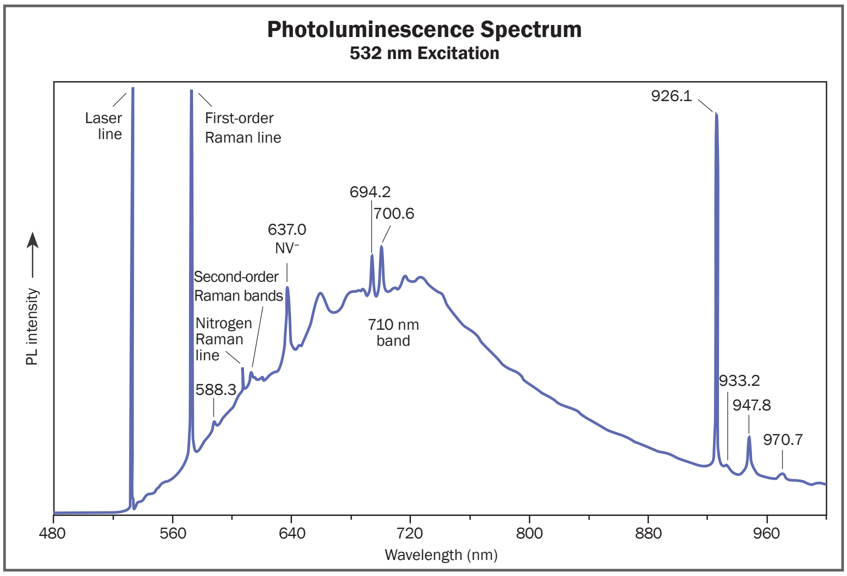


Figure 14: The PL spectrum of The Rhodesian Star obtained with 532 nm excitation is characterized by a broad band centred at 710 nm, along with distinct NV⁻ centre PL and several nickel-related emissions (possibly including those in the 900–950 nm range). Both growth sectors in the diamond were simultaneously excited by the laser when recording this spectrum. (The nitrogen line is produced by Raman scattering from the liquid nitrogen surrounding the specimen.)

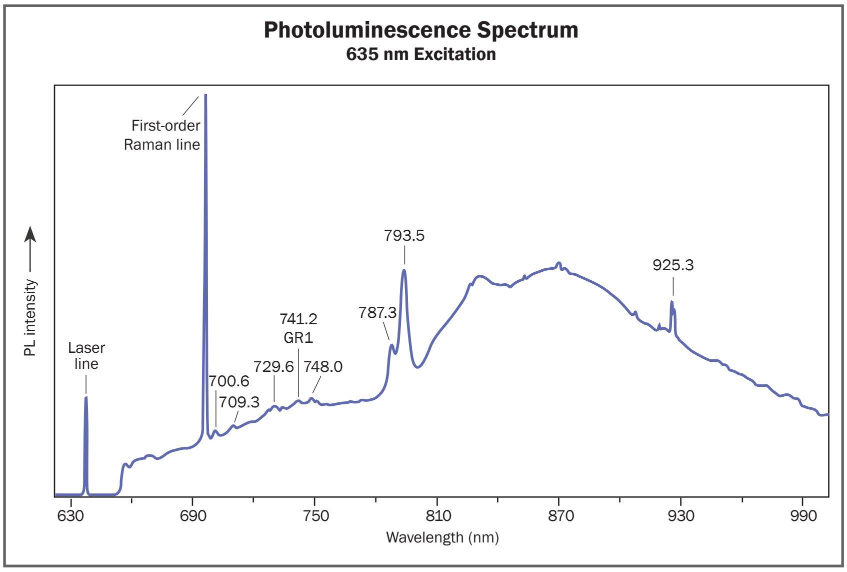


Figure 15: The PL spectrum of The Rhodesian Star obtained with 635 nm excitation is characterized by several nickel-related defects, with those at 787.3 and 793.5 nm being particularly intense. Both growth sectors in the diamond were simultaneously excited by the laser when recording this spectrum.

luminescence is produced using laser excitation of various wavelengths. The resulting luminescence is measured by a high-resolution spectrometer and plotted as a spectral curve.

The Rhodesian Star was tested with four different lasers (405, 473, 532 and 635 nm; Figures 12–15). Using 405 and 473 nm excitations, differences in PL luminescence between the octahedral and cuboid growth sectors could be depicted in the corresponding spectra. However, it was not possible to measure the green luminescence in the 'star sector' using the 532 or 635 nm excitations, because these wavelengths are longer than 500 nm and therefore do not excite the centre responsible for the green PL.

The green luminescence of the star-shaped cloud is caused by the S3 centre, which is a nickel-related defect that can be seen as a sharp line at 496.5 nm and a broad band centred at 545 nm (Kanda and Watanabe, 1999; Figure 12). This defect is characteristic of diamonds of mixed cuboid-octahedral growth, and is mainly present in the cuboid sectors of natural diamonds (Welbourn et al., 1989; Lang et al., 2004; Hainschwang, 2014). It is the predominant defect in so-called re-entrant cube mixed-habit cuboid-octahedral natural diamonds (Hainschwang et al., 2013). It is also characteristic of HPHT synthetic diamonds grown using a nickel-iron solvent, particularly after annealing, but may be found in as-grown synthetic diamonds produced using relatively high temperatures. However, in synthetic diamonds the defect is predominant in octahedral growth sectors (Kupriyanov et al., 1999).

The orange-red to orange-pink luminescence of the rest of the diamond is caused by an unknown defect that is seen as a broad emission band centred at 655 nm (using 405 nm laser excitation; Figure 12).

Many of the other emission bands and lines detected with the four lasers can also be assigned to nickel-related defects (Zaitsev, 2001), such as those at 694.2, 700.6, 787.3 and 793.5 nm (again, see Figures 12–15). The causes of the PL features above 900 nm are unknown, although the 926.1 nm emission has been tentatively assigned to a nickel-related defect (Hainschwang et al., 2005). It is possible that the other lines from around 900 to 950 nm are nickel-related as well, with the exception of the 933.2 nm feature which is very probably nitrogen related. This line shows up in absorption and also in luminescence when the N3 and N2 absorptions are intense.

With the exception of a very weak GR1 feature at 741.2 nm (Figure 15) and an NV^- centre emission at 637.0 nm (Figure 14), no radiation-related features were detected by PL spectroscopy. The straightforward detection of many radiation-related features with absorption spectroscopy and the quasi-non-detectability of these defect centres by PL spectroscopy can be explained by the fact that they are present only in the upper few microns of the stone. Since the PL spectra were taken from either the lobes or from the bulk of the diamond—without the use of a microscope—the radiation-related PL from the surface was not well excited and thus not detected.

The very sensitive method of photoluminescence spectroscopy clearly shows that the sectors containing the star pattern originate from nickel-rich cuboid growth, while the rest of the diamond consists of normal octahedral growth that is poor in defects other than nitrogen.

Conclusions

The Rhodesian Star is a superb example of an asteriated diamond. Gemmological testing has demonstrated that the star pattern is the result of cuboid-octahedral growth and that the grey-to-black particles are restricted to the cuboid sectors only. Spectroscopy confirmed that hydrogen and nickel defects are confined to the cuboid sectors, as previously documented in such diamonds. The spectacular luminescence patterns seen when the diamond is exposed to a high-power UV source are the result of nickel-related defects (S3) in the cuboid sectors, which are responsible for the bright green PL. The orange-red to purple-pink luminescence of the octahedral portions of the crystal originate from a broadband emission from unknown defect(s). Although it is extremely rare to see such luminescence with the use of standard UV lamps, the purple to nearly red luminescence is actually quite common in natural diamonds when they are exposed to intense UV excitation from our GGTL DFI fluorescence microscope. While orange-to-red PL (excited by UV to violet light) is known from various types of emission centres, the only well-characterized defects known to produce this luminescence are the NV^- and NV^0 centres, although it is very rare for them to emit strong PL in untreated diamonds.

The properties of The Rhodesian Star—particularly its surface texture and appearance, and the spectral data such as the radiation-related defects—indicate that its origin is Zimbabwe, which is one of the best-known sources for asteriated diamonds.

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