TREATED-COLOR PINK-TO-RED DIAMONDS FROM LUCENT DIAMONDS INC.

Wuyi Wang, Christopher P. Smith, Matthew S. Hall,
Christopher M. Breeding, and Thomas M. Moses

Lucent Diamonds has developed a new treatment process for natural type Ia diamonds that produces colors ranging from pink-purple through red to orangy brown, using a multi-step process that involves HPHT annealing, irradiation, and low-pressure annealing at relatively lower temperatures. Those stones that achieve a predominant pink-to-red or purple color are marketed as "Imperial Red Diamonds." Gemological properties and characteristic spectra are presented for 41 diamonds, representing the range of colors produced thus far. These treated-color natural diamonds can be readily identified by internal graphitization and surface etching seen with magnification, distinctive color zoning, and reactions to long- and short-wave UV radiation. The color is caused primarily by the absorption of the (N-V)$^-$ center, with further influence from the (N-V)^0, H3, H4, and N3 centers. Other characteristic infrared and UV-visible absorption features include the H1a, H1b, H1c, 6170 cm^{-1}, and, frequently, 594 nm bands. This type of defect combination is not known in naturally colored diamonds.

Historically, diamonds in the pink-to-red color range have been among the most highly prized. In nature, most pink-to-red, brown, and purple colors (and combinations thereof) in diamond have been attributed to the development of defect centers caused by shear stress and plastic deformation. These defects, which gemologists describe as colored "graining," were formed after the growth of the gem was complete and either prior to or during the diamond's ascent to the earth's surface (see, e.g., Orlov, 1977; Collins, 1982; Fritsch, 1998; Moses et al., 2002). Many of the world's most famous diamonds owe their color to this mechanism, including such notable stones as the 0.95 ct Hancock Red, the 5.11 ct Moussaieff Red, the 59.60 ct Steinmetz Pink, and the 128.48 ct Star of the South.

As a result of the prestige and value associated with these colors, attempts have been made since antiquity to impart a pink-to-red coloration to diamonds. In the earliest times, topical coatings were used to achieve this goal; however, such coatings were not stable and could be readily removed. The first treatment to induce a more stable hue in this range was introduced in the 1950s, when irradiation with high-energy electrons began to be applied experimentally to modify the color of natural diamonds. On rare occasions, a brownish pink to red hue would result when certain diamonds were irradiated in this manner and subsequently annealed (Crowningshield, 1959; Crowningshield and Reinitz, 1995). It was only significantly later, during the mid- to late 1980s, that scientists realized the stones that changed color in this manner were type Ib diamonds, which contain single substitutional nitrogen impurities (Fritsch, 1998; Shigley et al., 2004). More recently, high pressure/high temperature (HPHT) annealing of type IIa diamonds has been shown to change the color of some brown diamonds to hues in the purplish pink to brown-pink range (Hall and Moses, 2000).

See end of article for About the Authors and Acknowledgments.

GEMS & GEMOLOGY, Vol. 41, No. 1, pp. 6–19.

Figure 1. Treated-color "Imperial Red Diamonds" are being produced by Lucent Diamonds of Denver, Colorado. Shown here are three loose stones (0.15–0.33 ct) and a selection of fine jewelry demonstrating the possibilities of these gems. The ring is set with a 1.25 ct diamond, while the bracelet and necklace feature 0.38 and 0.34 ct diamonds, respectively. The ring is courtesy of John Atencio Designer Jewelry, Denver; the bracelet and necklace are both courtesy of Avirom Associates, Boulder, Colorado. Photo © Harold & Erica Van Pelt.

The latest entrant into this specialized arena of treated-color diamonds is Lucent Diamonds Inc., a U.S. corporation based in Denver, Colorado. This company has specialized in the production of synthetic diamonds and the HPHT treatment of natural and synthetic diamonds since 1995. During the 2004 Tucson shows, Lucent Diamonds unveiled a new color series of treated-color natural diamonds, which they are marketing under the name "Imperial Red Diamonds" (figure 1). The treatment employs a complex, multiple-step procedure that is effective with only certain types of natural diamonds or HPHT-grown synthetic diamonds (A. Grizenko and V. Vins, pers. comms., 2004). Following the show, we contacted Lucent Diamonds to borrow samples in the full range of colors produced, so they could be examined and tested. From our study of several of these diamonds, we determined that a number of standard gemological and spectroscopic features will readily distinguish these stones as being diamonds of a natural origin (i.e., not synthetic) with treated color.

Lucent Diamonds first began applying this process to type Ib synthetic diamonds. Subsequently, they experimented with naturally grown diamonds. To date, more than 1,000 natural diamonds have been treated in this manner, resulting in a dominant pink, red, purple, or brown color appearance. However, diamonds with a dominant brown appearance are excluded from the "Imperial Red Diamond" group, so only a small portion of the stones are sold under that trade name (A. Grizenko, pers. comm., 2005). Continued developments in the pre-screening of diamonds that can be treated successfully by this process have improved the percentage output of pink-to-red or purple stones, while they have confirmed the scarcity of appropriate natural-origin starting material. Mr. Grizenko projects that within a year, they will have achieved a stable production of 50 carats of "Imperial" diamonds per month. Given the rarity of natural-color intense pink-to-red diamonds, even such relatively small numbers may have a significant impact on the availability of diamonds in this color range (natural or treated) in the gemstone and jewelry market.

MATERIALS AND METHODS

A total of 41 diamonds (see, e.g., figure 2) were provided by Lucent Diamonds for this study. They ranged from 0.14 to 0.91 ct and are representative of

Figure 2. This group of 12 stones (0.14–0.65 ct) represents the range of colors Lucent Diamonds is marketing as "Imperial Red Diamonds." These treated-color natural-origin diamonds have been produced by a new treatment method, which involves HPHT annealing, irradiation, and low-pressure annealing at relatively lower temperatures. Photo © Harold & Erica Van Pelt.

the color range that is currently being produced by this process (A. Grizenko, pers. comm., 2005).

Color grades were determined by experienced colored-diamond color graders using the standard conditions and methodology of GIA's color grading system for colored diamonds (King et al., 1994). Internal features were observed with a standard binocular microscope using a variety of lighting techniques. Reactions to ultraviolet radiation were checked in a darkened room with a conventional four-watt combination long-wave (365 nm) and short-wave (254 nm) lamp. All of the stones were also examined using a Diamond Trading Company (DTC) DiamondView deep-ultraviolet (<230 nm) luminescence imaging system (Welbourn et al., 1996). A handheld spectroscope was used to view absorption features in the visible range, with the samples at both room temperature and low temperature.

All the samples were also analyzed using several other spectroscopic techniques. Absorption spectra in the ultraviolet to visible (UV-Vis) range were recorded with a Thermo-Spectronic Unicam UV500 spectrophotometer over the range 250–850 nm with a sampling interval of 0.1 nm. The samples were mounted in a cryogenic cell and cooled using liquid nitrogen. Infrared absorption spectra were recorded in the mid-infrared (6000–400 cm^{-1}, 1 cm^{-1} resolution) and near-infrared (up to 11000 cm^{-1}, 4 cm^{-1} resolution) ranges at room temperature with a Thermo-Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer, equipped with KBr and quartz beam splitters. In collecting absorption spectra in the near-infrared range, the lower energy side was extended to 2700 cm^{-1} to cover the three-phonon region of diamond absorption, which—like the two-phonon region absorption in the middle-infrared region—can be employed to calibrate the absorption intensity of other defects. A 6× beam condenser focused the incident beam on the sample, and a total of 1,024 scans (per spectrum) were collected to improve the signal-to-noise ratio.

Low-temperature photoluminescence (PL) spectra were recorded using a Renishaw 1000 Raman microspectrometer with an Argon-ion laser at two different laser excitations: 488.0 nm (for the range 490–850 nm) and 514.5 nm (for the range 517–850 nm). PL spectra of 15 stones were also collected using a Diode laser (780 nm) for the range 782–1000 nm. The samples were cooled by direct immersion in liquid nitrogen. Up to three scans were accumulated in some cases to achieve a better signal-to-noise ratio.

RESULTS

Visual Appearance. All the samples had an obvious coloration that ranged from pink/red to purple and brown, as well as combinations thereof (again, see figure 2). In the face-up position, all samples appeared homogeneously colored; however, when viewed face-down, a few samples revealed subtle to more distinct uneven coloration (see below). When color graded, the majority of the samples fell within a relatively small area of color space. These are in the GIA hue ranges of purple-red to orangy red (figure 3), as well as in a rather confined area of tone and saturation.

Microscopic Characteristics. *Internal and Surface Features.* A broad range of internal characteristics were noted, including predominant octahedral growth sectors and color zoning, as well as a variety of natural mineral inclusions. Although these indicated that the diamonds had grown naturally (i.e., were not synthetic), they also showed evidence of strong alterations due to treatment in a laboratory.

Figure 3. This color wheel illustrates the range of hues of most of the diamonds treated by the new method. The samples examined were given the following GIA color grades: Fancy Deep pink, brownish pink-purple, brown-pink, and pink-brown; Fancy purplish red, brownish purplish red, brownish purple-red, reddish brown, and brown-red; and Fancy Dark reddish brown, red-brown, and orangy brown. Brown colors, which depend on the degree of tone relative to the saturation of the hue, are not represented in this diagram.

In several of the samples, we observed precipitation of graphite at the interface between euhedral mineral inclusions and the host diamond, leading to the formation of large dark gray to black inclusions that had a very coarse surface texture (figure 4). The euhedral morphology of these inclusions was comparable to olivine or garnet, two very common inclusions in natural diamonds, and was distinctly different from that of metallic inclusions in synthetic diamonds. Although the identification of these inclusions was difficult due to the fact that they are covered entirely with graphite, their coarse texture and appearance was very distinctive. Some of the graphitized inclusions were also associated with stress fractures that had a similar texture and appearance (figure 5). Cleavages revealed inner surfaces that had been etched (figure 6), and a few stones displayed severely etched areas or facets on or adjacent to the girdle that had not been repolished (figure 7).

Strain. Most of the samples showed weak to moderately intense strain when they were viewed with

Figure 4. A very coarsely textured graphitization of the diamond surrounding naturally occurring mineral inclusions and along associated stress fractures was commonly seen in many of the Lucent samples. The graphitization was induced by the HPHT treatment conditions. The morphology of the mineral inclusions resembles that of olivine or garnet, which occur as inclusions only in natural diamonds; the metallic inclusions seen in many synthetic diamonds have a very different shape and appearance. Photomicrograph by C. P. Smith; magnified 62×.

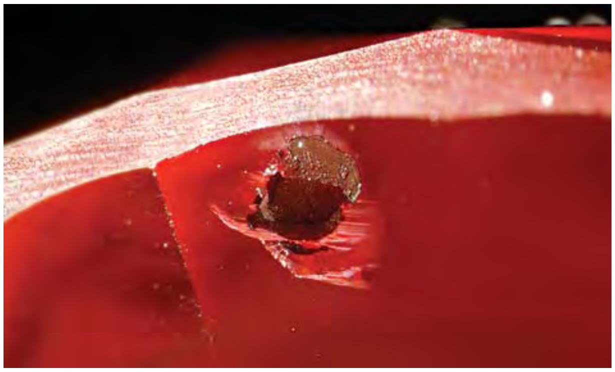


Figure 5. Graphitization was also evident along internal stress fractures. Typically, these stress fractures displayed a narrow, highly reflective fringe along the outermost extension of the fracture that was probably induced by the expansion pressure created when the walls of the stress fractures converted to graphite. Photomicrograph by C. P. Smith; magnified 58×.

Figure 6. Cleavages that reached the surface exhibited distinct etching along their full extent. Such etching is also evidence of HPHT treatment. Photomicrograph by C. P. Smith; magnified 52×.

the microscope between crossed polarizing filters. For the most part, the strain was in banded patterns that followed the octahedral growth zoning, exhibiting predominantly gray-to-blue interference colors (figure 8). A few samples, however, revealed higher levels of strain that were associated with mottled or "cellular" patterns (figure 9), similar to the patterns seen in natural-color type Ia pink-to-red or purple diamonds (see, e.g., figure 15 in King et al., 2002, p. 140).

Internal Growth Structures and Color Zoning. Some of the most characteristic features of these diamonds can be seen in their color zoning and its relation to the internal growth structures. In these stones, thick or extended regions of color were seen to conform to internal growth structures (i.e., various crystal faces). Visually, this resulted in various color concentrations that were a combination of straight and angular, including color zoning that appeared very irregular because of internal regions that had a more complex growth history. In addition, typically these color zones exhibited sharp,

Figure 7. Small, severely etched areas were present on or near the girdles of several samples, indicating that the damage caused by certain phases of the treatment process had not been completely removed by repolishing. This kind of coarse etching is unlike what may be encountered when etching takes place in nature. Photomicrograph by C. P. Smith; magnified 50×.

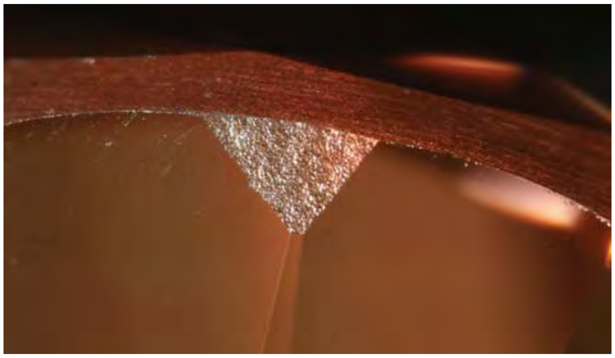


Figure 8. Most of the samples exhibited relatively weak to moderately intense strain when viewed between crossed polarizing filters. The banded pattern shown here follows the octahedral growth planes. This type of strain is not seen in HPHT- or CVD-grown synthetic diamonds, providing additional confirmation that these Lucent diamonds are naturally grown. In addition, this type of strain is not typical of natural-color type Ia pink-to-red or purple diamonds. Photomicrograph by C. P. Smith; magnified 22×.

Figure 9. A few of the samples exhibited a higher degree of strain, in a mottled or "cellular" pattern, similar to that seen in natural-color natural diamonds in this color range (but not encountered in synthetic diamonds). Photomicrograph by C. P. Smith; magnified 32×.

Figure 10. All the samples showed characteristic color zoning that was homogeneous or followed straight to angular growth sectors. In some samples, the zoning was subtle, occurring as highly saturated and less-saturated zones of the same hue. This is distinctly different from the colored graining evident in natural-color pink to red, purple, and brown diamonds, which is due to plastic deformation–related defects. Photomicrograph by C. P. Smith; magnified 40×.

clearly defined color boundaries. Such color zoning is very different from that encountered in natural-color pink-to-red diamonds, where localized color concentrations relate to colored "graining" that is caused by plastic deformation (see Discussion section below).

The color zoning of the Lucent samples typically ranged from pink to purple-pink and brown to purple-brown of varying saturation. In a few of the samples, this color zoning was rather subtle and typically consisted of more highly saturated pink zones bordered by less-saturated zones of the same hue (figure 10). In other samples, however, the color zoning was much more obvious, consisting of saturated zones of pink-to-red color bordered by growth sectors that were paler pink to near-colorless (figure 11). A few of the diamonds had all three types of color zoning: consisting of regions or

Figure 11. In this sample, the color zoning is more obvious, concentrated within complex, naturally occurring growth sectors. Here, saturated pink zones occur adjacent to paler pink to near-colorless growth sectors that for the most part follow octahedral crystal faces. Again, this form of pink-to-red color zoning is distinctly different from the linear pink-to-red graining that typically extends in only one direction in natural-color diamonds of this hue, Photomicrograph by C. P. Smith; magnified 48×.

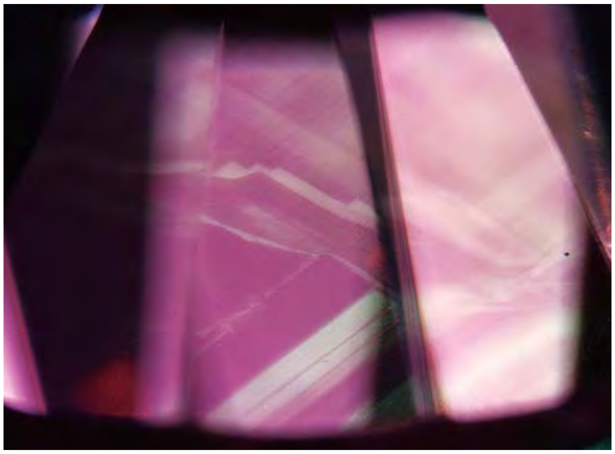
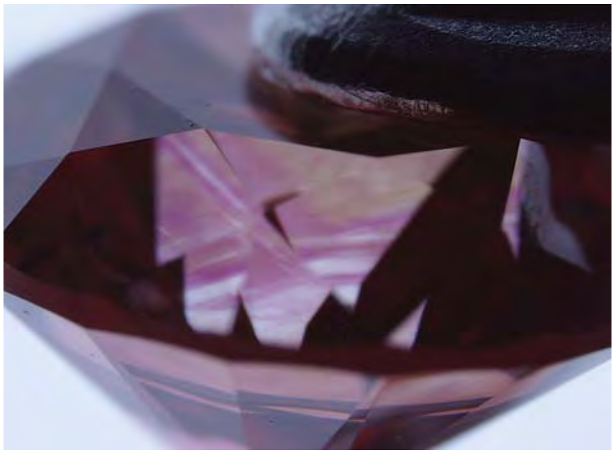


Figure 12. A few diamonds contained distinct pink-to-red zones in some areas, with brown and near-colorless zones in others. Photomicrograph by C. P. Smith; magnified 28×.



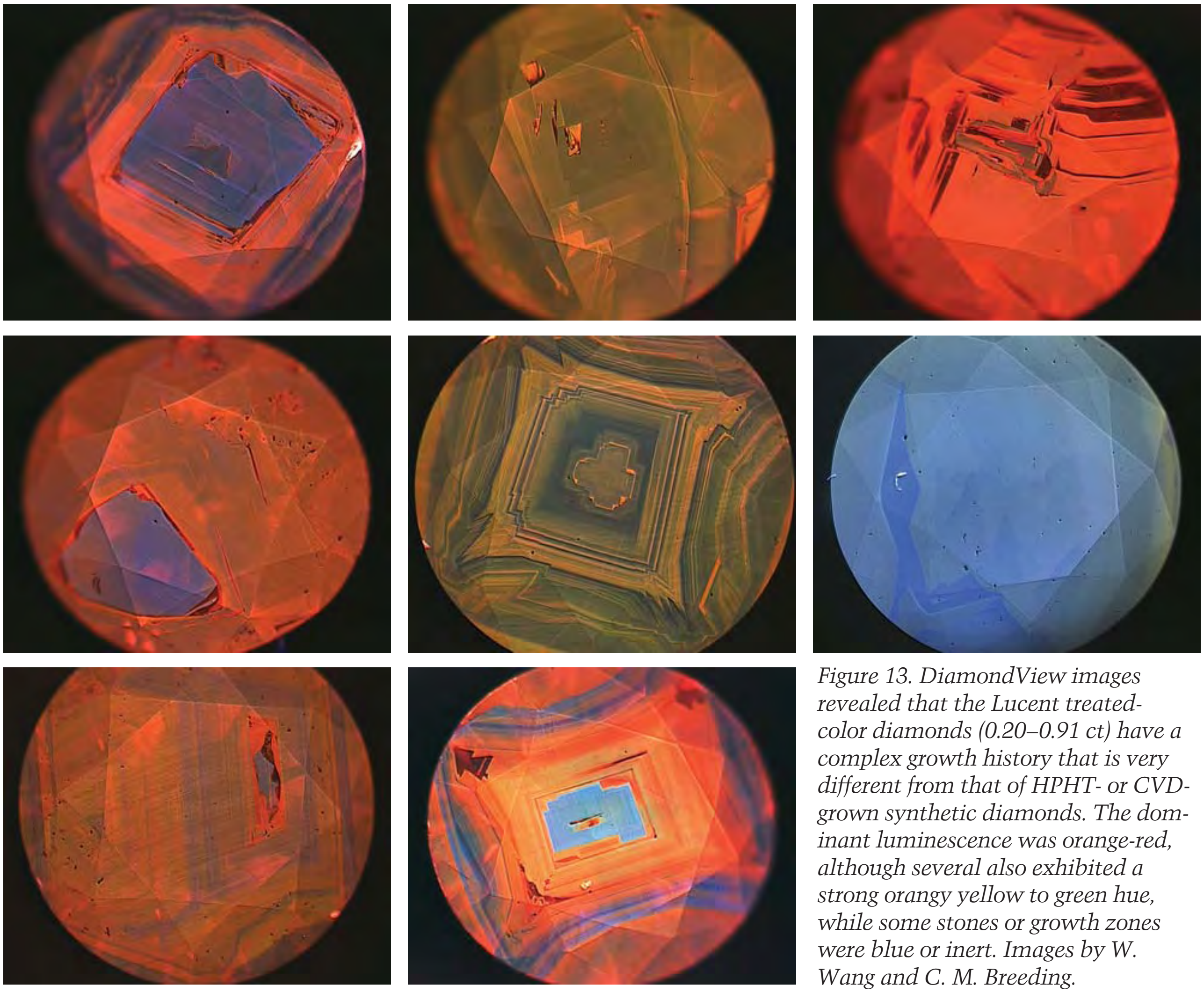


Figure 13. DiamondView images revealed that the Lucent treated-color diamonds (0.20–0.91 ct) have a complex growth history that is very different from that of HPHT- or CVD-grown synthetic diamonds. The dominant luminescence was orange-red, although several also exhibited a strong orangy yellow to green hue, while some stones or growth zones were blue or inert. Images by W. Wang and C. M. Breeding.

growth sectors that were saturated pink to purple-pink, brown to purple-brown, and pale pink to near-colorless (figure 12).

DiamondView Imaging. The luminescence images of the stones we examined revealed complex growth patterns (figure 13), as expected for natural diamonds. An orange-red fluorescence color dominated most growth sectors, while some other areas were orangy yellow to green, blue, or just dark in appearance. The confinement of the strong orange fluorescence to growth sectors was consistent with the color zoning observations described above. These patterns are a direct reflection of the large variation in the type and concentration of defects, as well as of the complex growth history, of most natural diamonds. Neither the fluorescence nor the growth features that are characteristic of synthetic diamonds (see, e.g., Wang et al., 2003; Shigley et al., 2004) were observed in these stones, which confirmed their natural origin. The observed patterns are mostly attributed to octahedral {111} growth planes.

Visible Luminescence. There are certain defect centers in diamond that yield luminescence to visible light (refer to the UV-Vis-NIR Spectroscopy and Raman PL Spectroscopy sections below). When these centers are strong enough, distinctive luminescence may be seen in a microscope, a loupe, or even with the unaided eye if the stones are viewed with a strong light source. All the stones we examined exhibited a green luminescence to visible light that ranged from moderate to very strong; it was rather homogeneous in some samples, while heavily zoned in others (figure 14). This green luminescence is related to H3 emission centered at 503 nm. A strong orange-red luminescence was also seen in all samples. This luminescence relates to $(N\text{-}V)^-$ emission centered at 637 nm and was variable in appearance,

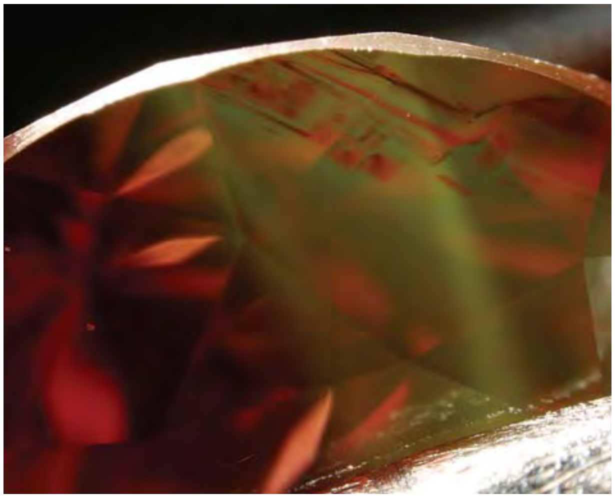


Figure 14. Green luminescence to visible light (related to the H3 center) was seen in all samples. In most samples, this luminescence followed the internal growth structures, as with the stepped octahedral zoning seen here. In some, however, the green luminescence was more evenly distributed throughout. Photomicrograph by C. P. Smith; magnified 35×.

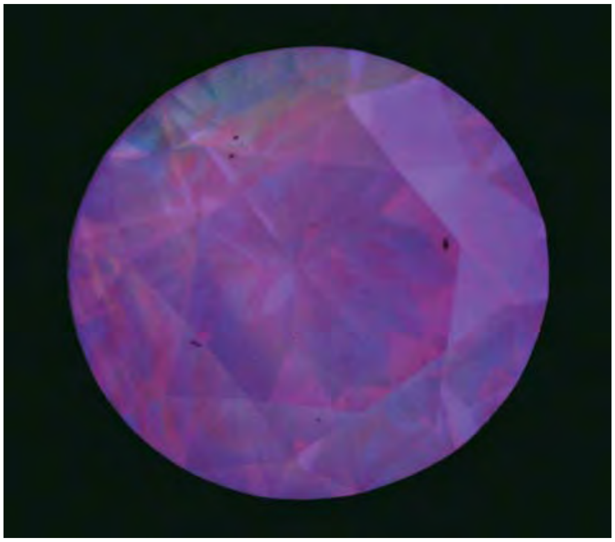
ranging from homogeneous to an alignment with the internal growth structures. In addition, a few samples also displayed zones of yellow luminescence attributed to $(N\text{-}V)^0$ emission centered at 575 nm. When all three luminescence colors were present in the same stone, they made for a very colorful image of the internal growth structures (figure 15), which we had not encountered previously.

Figure 15. Strikingly, when exposed to a strong light source, several of the samples exhibited all three luminescence colors—green, orange-red, and yellow—producing a combination of colors unlike any the authors had seen previously in a natural-color diamond. Photomicrograph by C. P. Smith; magnified 27×.

Fluorescence. All the samples displayed a distinctive, moderate-to-strong, very chalky fluorescence reaction when exposed to either long- or short-wave UV radiation. In general, these diamonds revealed combinations of yellow, green, and orange fluorescence on exposure to long-wave UV, although a couple of samples also exhibited blue fluorescence. With close inspection, zoning (often subtle) could be seen between the different colors (figure 16). To short-wave UV, these diamonds displayed a rather consistent moderate-to-strong orange and yellow fluorescence. In most samples, the orange fluorescence dominated, and the yellow could be seen in only certain areas, such as near the culet (figure 17). No phosphorescence was evident in any of the samples following exposure to long- or short-wave UV.

UV-Vis-NIR Spectroscopy. Overall, of the 41 stones included in this study, most revealed similar absorption features in the ultraviolet to visible and near-infrared regions of the spectrum, although certain variations were noted (figure 18). The most dominant series of bands included strong absorptions at 415 nm (N3), 503 nm (H3), 575 nm $(N\text{-}V)^0$, and 637 nm $(N\text{-}V)^-$, which were evident in all the samples. Of these, the absorption at 637 nm was consistently the most intense. A weak absorption at 496 nm (H4) was recorded

Figure 16. This image reveals the typical, chalky long-wave UV fluorescence of the "Imperial" treated-color diamonds, which results from a combination of orange, yellow, and green fluorescing zones. Such a reaction is not seen in natural-color pink-to-red and purple diamonds. Photomicrograph by C. P. Smith; magnified 10×.



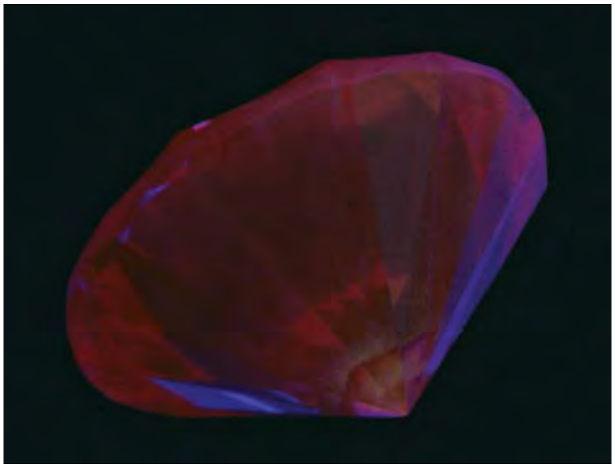


Figure 17. The reaction to short-wave UV of these diamonds is also highly indicative of the treatment, displaying a consistent moderate-to-strong orange and yellow fluorescence. In most samples, the orange fluorescence dominated; the yellow was seen only in certain areas, such as near the culet in this sample. Photomicrograph by C. P. Smith; magnified 10×.

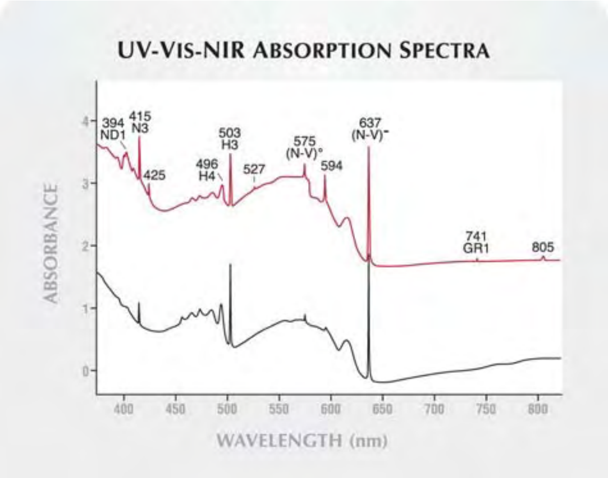


Figure 18. The absorption spectra through the ultraviolet, visible and near infrared regions show strong absorption features from several defect centers including the N3, H3, $(N\text{-}V)^0$, and $(N\text{-}V)^-$, which are typical of these treated-color diamonds. These absorption features combine to produce a transmission "window" in the red region, which is responsible for the pink/red coloration of these stones. In addition, absorptions with varying intensities at 394 (ND1), 425, 496 (H4), 527, 594, 741 (GR1), and 805 nm were also observed in several of the samples. The upper spectrum is from a 0.40 ct purplish pink diamond, and the lower spectrum is from a 0.41 ct brown-pink diamond. The spectra are offset vertically for clarity.

in most samples (31 total); in only one of these was the H4 stronger than the H3. Half the samples had absorption at 594 nm that varied greatly in intensity from one sample to the next . In most cases, this band was weak to moderate, but it was extremely strong in three samples. In those samples where we detected the 594 nm absorption, we also typically recorded a weak 741 nm (GR1) absorption, as well as a weak 805 nm absorption. However, the 805 nm band also occurred in some stones that did not reveal either the 594 nm or GR1 features. Several of the samples that had both the 594 nm and GR1 also showed weak absorptions at 425 and 527 nm; five of these showed a very weak absorption at 394 nm (ND1).

When the samples were cooled and viewed with a standard handheld spectroscope, similar features were noted, consisting of strong, sharp lines at 415, 503, and 637 nm in all the samples, as well as sharp, weak-to-moderate lines at 575 and 594 nm in many of them.

IR Spectroscopy. All the diamonds we tested proved to be type Ia. The concentrations and relative aggregation states of nitrogen varied significantly between samples (figure 19). Absorption features at 1280 and 1215 cm^{-1} are attributed to nitrogen in the A-aggregate form (nitrogen atoms in pairs), and those at 1170 and 1010 cm^{-1} are attributed to nitrogen in the form of B-aggregates (four nitrogen atoms surrounding a common vacancy). In general, the concentration of A-aggregates was significantly higher than B-aggregates. This trend held true for all except seven of the samples, where the nitrogen was dominantly in the B-aggregate form. Using a spectral fitting calibration against the two-phonon absorption of diamond, we estimated the total nitrogen content to range from 23 to 322 ppm. In addition, most of the samples displayed weak-to-moderate absorption bands at 3107 and 1405 cm^{-1}, which are related to hydrogen impurities. Interestingly, the samples with nitrogen predominantly in the B-aggregate form also revealed significantly stronger hydrogen absorption.

A relatively strong absorption at 1450 cm^{-1} (H1a—an interstitial nitrogen atom; Woods, 1984) and a weak absorption at 1344 cm^{-1} related to isolated nitrogen impurities (type Ib component) were recorded in all samples. Again using spectral fitting

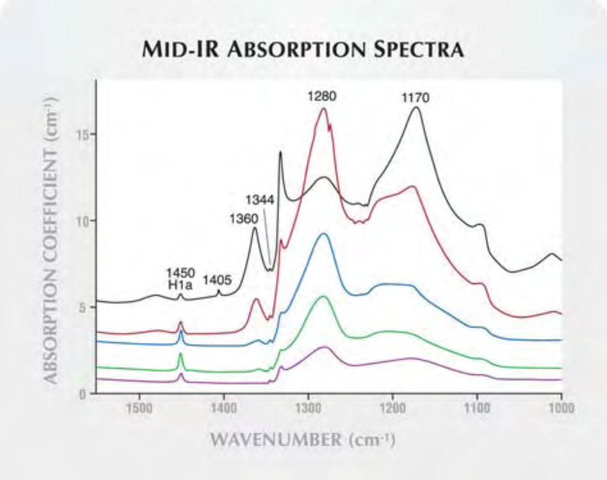


Figure 19. These representative absorption spectra in the mid-infrared range illustrate the large variation in nitrogen concentration of these treated-color diamonds. All of the stones in this study were classified as type Ia, and most are dominated by the A-aggregate form of nitrogen. However, a few samples (e.g., black line) contained more B-aggregates than A-aggregates. Also note the relatively strong H1a absorption at 1450 cm^{-1}, and the weak absorption at 1344 cm^{-1}, which is related to isolated nitrogen. Very weak absorptions at 1358 and 1355 cm^{-1} were also observed in those samples that had little or no platelet peak absorption at ~1360 cm^{-1}. The spectra are offset vertically for clarity.

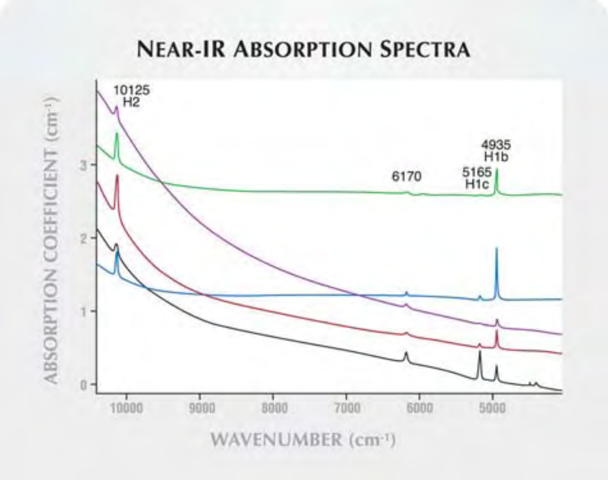


Figure 20. Strong H1c and/or H1b absorption lines, as well as a sharp peak at 6170 cm^{-1}, are features commonly seen in the near-infrared absorption spectra of these treated-color diamonds. A very strong H1c occurred in another sample, which was dominated by the B-aggregate form of nitrogen (black curve). A moderately strong H2 absorption was observed in all samples. The spectra are offset vertically for clarity.

techniques, we calculated the intensity of the H1a absorption at around 0.2–1.2 cm^{-1} and estimated the concentration of isolated nitrogen at 3–28 ppm. Another common feature of varying intensity was the nitrogen platelet peak at ~1360 cm^{-1}. In the samples in which this peak was absent or very weak, two very weak absorptions at 1358 cm^{-1} (intensity of 0.04 to 0.1 cm^{-1}) and 1355 cm^{-1} (0.04 to 0.1 cm^{-1}) were also evident.

In the near-infrared region (figure 20), the dominant features included strong absorptions at 5165 cm^{-1} (H1c) and/or 4935 cm^{-1} (H1b). The relative intensity of the H1b to H1c was determined to be proportional to the diamond's nitrogen aggregation state (see, e.g., Collins et al., 1986). In those diamonds that were dominated by A-aggregates, virtually no H1c was detected, whereas the diamond with B>>A aggregations of nitrogen exhibited a much stronger H1c absorption than H1b. A moderate-to-strong H2 (negatively charged N-V-N center) absorption at ~10125 cm^{-1} (987.7 nm) was also seen in all samples, with an intensity that varied from 0.05 to 0.6 cm^{-1} (majority >0.2 cm^{-1}). The intensity of the H2 absorption had a direct correlation to the concentration of A-aggregates. In one sample, the intensity of the H2 was 0.5 cm^{-1} correlated to an A-aggregate concentration of 143 ppm. Another sample with an A-aggregate concentration of only 10 ppm had an H2 absorption intensity of only 0.1 cm^{-1}. Another sharp, relatively strong absorption was recorded at 6170 cm^{-1} in all the samples tested. The occurrence of this absorption in diamond was reported only very recently (see further comments below; De Weerdt and Anthonis, 2004). To date, no correlation is evident between the 6170 cm^{-1} peak and the presence of H1a, H1b, or H1c.

Raman PL Spectroscopy. Low-temperature photoluminescence spectra revealed dominant PL bands of the same wavelength as the absorption bands recorded with the spectrophotometer. In addition to the strong emissions from the H3, (N-V)^0, and (N-V)$^-$ centers, we also noted H4 emission at 496 nm of variable intensity in all the samples (figure 21). For those samples that were nearly pure type IaA, the H4 luminescence was the weakest. At 535 nm another weak intensity band was also commonly recorded. A weak but sharp emission at 588 nm was

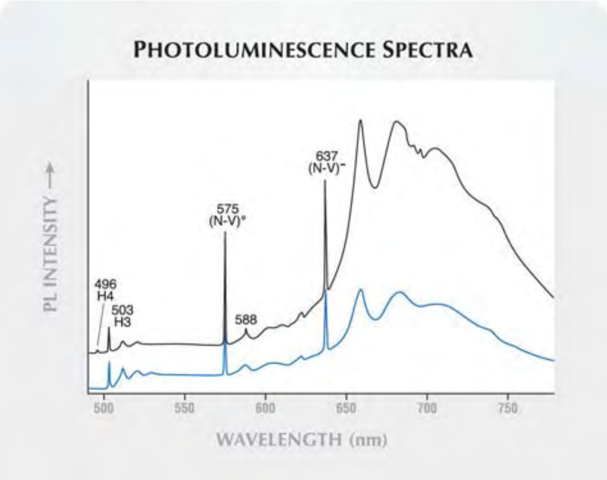


Figure 21. Photoluminescence spectra collected using an Ar-ion laser (488 nm excitation) exhibited strong emissions at 503, 575, and 637 nm. Weak luminescence peaks were also observed in some samples at 496, 535, and 588 nm. The spectra are offset vertically for clarity.

evident using both the 488 and 514 nm laser excitations. This independent 588 nm emission typically was superimposed onto the broad side band of 575 nm (N-V)^0. The 588 nm emission was observed in 22 of the samples; the GR1 and 594 nm features were also detected in the absorption spectra of these same samples.

DISCUSSION

The Treatment Method. A recent patent by one of the Russian scientists associated with Lucent Diamonds describes the methods by which red color may be produced in diamonds in a laboratory (Vins, 2004). The technique consists of generating isolated nitrogen in natural type Ia diamond via HPHT conditions (6–7 GPa at over 2150°C), followed by irradiation using a high-energy electron beam and further annealing in a vacuum at a temperature no lower than 1100°C. Based on the results of our analyses, it is evident that the Lucent "Imperial" pink to red treated-color diamonds we have examined have been processed by a similar method. This is based on several standard gemological and spectroscopic features.

First, the severe graphitization and etching seen with magnification clearly indicate that these diamonds were exposed to HPHT conditions. In addition, the presence of isolated nitrogen in the infrared spectrum is consistent with the de-aggregation of nitrogen defects under similar conditions (see, e.g., Fisher and Spits, 2000), although the presence of isolated nitrogen alone is not proof of HPHT treatment. Further evidence of irradiation-induced defects is provided by the 594, 637, and 741 (GR1) absorptions in these type IaAB diamonds with a Ib component. The presence of the H1b and/or H1c bands in the near-infrared region is also consistent with annealing subsequent to irradiation. When a type Ia irradiated diamond is annealed at around 1000°C, the 594 nm center is removed, thus producing H1b and/or H1c lines (Collins, 1982). Also important is the presence of a much less stable defect in some of the samples, the ND1, which is removed at temperatures above 500°C (Zaitsev, 2001). When this band occurs in combination with the 594 nm band as well as H1b and H1c absorptions, it is indicative of a multi-step process involving HPHT annealing, irradiation, and relatively lower temperature, low pressure annealing.

In the patent, the overall nitrogen concentration is described as exceeding 800 ppm. However, during the course of our investigation, we determined that the total nitrogen concentration in the diamonds we tested was 23–322 ppm.

Characterization of the Samples. The majority of the diamonds were darker in tone and higher in saturation than the natural-color diamonds we have encountered in this hue range. However, there were two samples—a Fancy Deep pink and a Fancy Deep brown-pink—that closely resembled the appearance of natural-color diamonds.

The mineral inclusions we observed with magnification identified the diamonds as being naturally grown. However, the heavily graphitized and etched features also clearly indicated that these stones had been exposed to high pressure/high temperature (HPHT) processing. The larger, more massive, coarsely textured black to dark gray inclusions were foreign minerals that experienced severe graphitization of the diamond at the interface between the included crystal and the diamond host. The HPHT conditions were also responsible for the graphitization along internal fractures and the etching observed along surface-reaching cleavages and in those areas at the surface that were not repolished following treatment. It is important to note that graphitization may take place naturally in diamond; however, such natural inclusions are very different in appearance from these samples. It also should be noted that, depending on the specific HPHT conditions, there may be significantly less graphitization and etching in some treated samples.

In type Ia natural diamonds, naturally occurring pink-to-red and purple coloration is clearly associated with zones exhibiting plastic deformation. As a result, when such stones are viewed between crossed polarizing filters, they typically reveal very high levels of strain (see, e.g., figure 15 in King et al., 2002, p. 140). The strain visible in these treated-color samples was significantly weaker. In only a few of the Lucent samples did the strain levels approach what is typical for their natural-color counterparts.

The thick and extended regions of color zoning that were present in these samples occurred in a variety of straight, angular, and irregular patterns. Such color zoning is very different from that encountered in natural-color pink-to-red diamonds, which is visible as straight, parallel color zones that extend in only one direction and typically do not have sharp boundaries (see, e.g., Koivula, 2000, p. 92).

The DiamondView imaging accentuates the complex growth structure of these natural diamonds, which involves the development of primarily octahedral {111} growth planes. The large variation in fluorescence colors (red, orange, yellow, blue, and green) as well as the dark areas where no fluorescence was evident, is a direct reflection of the specific type and concentration of defects before treatment and the resultant reconfiguration of the defects by the treatment process. These features are markedly different from those of synthetic diamonds created by HPHT or CVD techniques, and they confirm the natural origin of these samples (Wang et al., 2003; Shigley et al, 2004).

When illuminated by a strong light source, green (H3) luminescence has been seen in many naturally colored, as well as artificially colored, diamonds (Fritsch, 1998; Reinitz et al., 2000). (It is often referred to as "transmission luminescence," though this is not strictly correct.) A weak orange-red luminescence due to N-V centers may be seen in some natural-color pink diamonds; however, it is more commonly associated with treated-color pink-to-red diamonds with moderate to high color saturation (see, e.g., Shigley et al., 2004). Nevertheless, we had not previously witnessed the combination of green (H3), orange-red $(N\text{-}V)^-$, and yellow $(N\text{-}V)^0$ visible luminescence seen in these treated-color diamonds. Nor have we encountered in natural-color pink-to-red diamonds the strong, chalky orange, green, and yellow fluorescence to long-wave UV that was evident in these treated stones.

The "Imperial" treated-color diamonds in this study owed their color to the absorption of N-V centers positioned at 575 and 637 nm, with some influence from other absorption features. The introduction of a relatively high concentration of H3/H4 defects, which absorb blue-green light, is essential to generate a pure red hue. If the H3/H4 absorptions are not strong enough, a distinct purple hue will be developed, as was observed in some of the stones we tested. High concentrations of the A/B form of nitrogen are necessary to generate H3/H4 defects during treatment. Additionally, if the absorption of the N-V centers is not strong enough relative to the absorption of the H3 and H4 centers, then brown colors develop.

In contrast, the vast majority of natural-color pink-to-red diamonds owe their hue to a broad absorption band centered at approximately 550 nm (e.g., Collins 1982; King et al., 2002; Moses et al., 2002). To date, we are not aware of any reports of the artificial introduction of the 550 nm band in type I natural diamonds. We have examined a small number of natural-color pink diamonds that owe their color to N-V centers. Typically, these diamonds are rather pale in color and are classified as type IIa. However, we have not observed strong H3 or N3 absorption in such diamonds.

The physics responsible for the 588 nm peak visible in the PL spectra of some samples is not fully understood (Zaitsev, 2001). On initial consideration, there seemed to be some correlation between the occurrence of this peak and the color saturation of the diamonds. After further investigation, however, we found that the 588 nm emission may also be observed in some natural green-yellow diamonds that have high concentrations of H3 centers.

The 6170 cm^{-1} absorption in the infrared is another little-known defect. Its occurrence, reported in previous publications and the present study, is closely related to irradiation and annealing, either naturally or in the laboratory. De Weerdt and Anthonis (2004) first reported a peak at 6172 cm^{-1} in a treated diamond and, based on their experiments, suggested that it resulted from a complex treatment process. In addition, Hainschwang et al. (in preparation) have correlated a band at 6165 cm^{-1} to the presence of H1c centers in irradiated and annealed diamonds. In this study of a large set of samples, we found no such correlation. However, those samples with the strongest 6170 cm^{-1} band in general had very weak H1b/H1c bands and relatively stronger 594 nm absorption. In unpublished data from ongoing research at GIA, we have recorded the occurrence of this band (with position varying slightly from 6170 to 6168 cm^{-1}) in a few naturally irradiated diamonds as well. A few of those natural-color stones displayed green radiation stains. All these observations indicate that the 6170 cm^{-1} absorption represents a defect that may be introduced via irradiation and annealing processes, either in the laboratory or in nature. Consequently, we do not consider the presence of this band as conclusive of color treatment on its own.

Although we did not perform stability testing per se, we concluded—based on the kinds of defects observed and their concentrations—that the colors produced by the multiple-step treatment process described here are both stable and permanent to normal conditions of wear and care. In addition, we did not detect any residual radioactivity.

IDENTIFYING CHARACTERISTICS

A number of standard gemological properties and advanced analytical features will readily identify that these stones are naturally grown and their color has been artificially induced. The fact that they were grown in nature can be confirmed by the presence of characteristic mineral inclusions and distinctive internal growth structures, as well as by the lack of the inclusion features and growth structures typical of HPHT- and CVD-grown synthetic diamonds. With standard gemological techniques, the artificial coloration can be identified by the strongly altered inclusion features in combination with the differences in appearance of the pink-to-purple or brown color zoning in these samples as compared to the colored graining in natural-color diamonds. In addition, with a standard handheld spectroscope, the distinctive combination of strong 415, 503, and 637 nm absorption lines, as well as weak-to-moderate 575 and 594 absorption lines, clearly identifies the treated origin of the color. Furthermore, the unique long- and short-wave UV fluorescence reactions are clear indicators that this material has been treated.

The more advanced analytical techniques also revealed some interesting identification criteria that appear to be unique to this process. The occurrence of trace isolated nitrogen, together with H3 and H2 centers, are some of the common features related to HPHT treatment, whereas defects such as H1a, H1b, H1c, $(N\text{-}V)^-$, 594 nm, $(N\text{-}V)^0$, H3, and H4 commonly occur in diamonds that have been exposed to radiation. Although these defects may occur in natural-color diamonds, we have not seen a known natural-color diamond that has all of these features. The absorption at 6170 cm^{-1}, although not proof, may also suggest color treatment.

CONCLUSION

Naturally colored diamonds in the pink-to-red hue range are some of the most exotic and expensive gemstones. At auction, such diamonds have achieved as much as US$895,000 per carat (Balfour, 2000). As a result, various forms of treatment have been applied in attempts to recreate these highly desirable colors. Previously, these ranged from simple topical coatings (e.g., Moses et al., 2004) to move advanced techniques such as irradiation of type Ib diamonds (Crowningshield, 1959; Crowningshield and Reinitz, 1995) and HPHT annealing of type IIa diamonds (e.g., De Beers Industrial Diamonds et al., 2001).

Most recently, Lucent Diamonds has introduced treated-color pink-to-red natural diamonds into the marketplace under the trade name "Imperial Red Diamonds." The Lucent group began developing the technology to produce these stable colors on a commercial basis toward the end of 2003, and they first offered them for sale in the summer of 2004. Our investigations confirmed that a combination of treatment techniques, including HPHT annealing and irradiation, are applied to induce the coloration in these diamonds, consistent with the process described by Vins (2004). They can be readily identified by their distinctive inclusion features, color zoning, and long- and short-wave UV fluorescence, as well as by their unique combination of spectroscopic features.

ABOUT THE AUTHORS

Dr. Wang is research scientist, Mr. Smith is director of identification services, Mr. Hall is manager of analytical research services, and Mr. Moses is vice president of identification and research at the GIA Gem Laboratory in New York. Dr. Breeding is research scientist at the GIA Gem Laboratory in Carlsbad, California.

ACKNOWLEDGMENTS: The authors are grateful to Alex Grizenko, president of Lucent Diamonds Inc., for supplying specimens for this study, and to Dr. Victor Vins, research and development manager of New Diamonds of Siberia, Novosibirsk, Russia, for many helpful discussions. They also thank John King and Joshua Cohn, of the GIA Gem Laboratory in New York, for careful color grading observations and useful discussions.

REFERENCES

Balfour I. (2000) *Famous Diamonds*. Christie, Manson & Woods, London.

Collins A.T. (1982) Colour centres in diamond. *Journal of Gemmology*, Vol. 18, No. 1, pp. 37–75.

Collins A.T., Davies G., Woods G.S. (1986) Spectroscopic studies of the H1b and H1c absorption lines in irradiated, annealed type-Ia diamonds. *Journal of Physics C: Solid State Physics*, Vol. 19, pp. 3933–3944.

Crowningshield G.R. (1959) Highlights at the Gem Trade Lab in New York. *Gems & Gemology*, Vol. 9, No. 9, pp. 268–270.

Crowningshield G.R., Reinitz I. (1995) Gem Trade Lab Notes: Treated-color pink diamond. *Gems & Gemology*, Vol. 31, No. 2, pp. 121–122.

De Beers Industrial Diamonds, Spits R.A., Burns R., Fisher D. (2001) *High Temperature/Pressure Color Change of Diamond*. International (PCT) patent application WO 01/72404A1, filed April 2.

De Weerdt F., Anthonis A. (2004) A new defect observed in irradiated and heat treated type Ia diamonds. *The 55th Diamond Conference*, July 5–7, 2004, Warwick, England, p. 17.

Fisher D., Spits R.A. (2000) Spectroscopic evidence of GE POL HPHT-treated natural type IIa diamonds. *Gems & Gemology*, Vol. 36, No. 1, pp. 42–49.

Fritsch E. (1998) The color of diamond. In G. E. Harlow, Ed., *The Nature of Diamonds*, Cambridge University Press, Cambridge, U.K., pp. 23–47.

Hainschwang T., Fritsch E., Notari F., Massi L. (in preparation) The properties of irradiated and annealed diamonds exhibiting an undescribed near-infrared absorption.

Hall M., Moses T. (2000) Gem Trade Lab Notes: Diamond—blue and pink HPHT annealed. *Gems & Gemology*, Vol. 36, No. 3, pp. 254–255.

King J.M., Moses T.M., Shigley J.E., Liu Y. (1994) Color grading of colored diamonds in the GIA Gem Trade Laboratory. *Gems & Gemology*, Vol. 30, No. 4, pp. 220–242.

King J.M., Shigley J.E., Guhin S.S., Gelb T.H., Hall M. (2002) Characterization and grading of natural-color pink diamonds. *Gems & Gemology*, Vol. 38, No. 2, pp. 128–147.

Koivula J.I. (2000) *The Microworld of Diamonds*. Gemworld International, Northbrook, IL.

Moses T., King J.M., Wang W., Shigley J.E. (2002) A highly unusual 7.34 carat Fancy Vivid purple diamond. *Journal of Gemmology*, Vol. 28, No. 1, pp. 7–12.

Moses T., Smith C., Wang W., Hall M. (2004) Topical coating on diamonds to improve their color: A long history. *Rapaport Diamond Report*, Vol. 27, No. 20, pp. 91–93.

Orlov Yu. L. (1977) *The Mineralogy of Diamond*. Wiley Interscience, New York, pp. 128–131.

Reinitz I.M., Buerki P.R., Shigley J.E., McClure S.F., Moses T.M. (2000) Identification of HPHT-treated yellow to green diamonds. *Gems & Gemology*, Vol. 36, No. 2, pp. 128–137.

Shigley J.E., McClure S.F., Breeding C.M., Shen A.H., Muhlmeister S.M. (2004) Lab-grown colored diamonds from Chatham Created Gems. *Gems & Gemology*, Vol. 40, No. 2, pp. 128–145.

Vins V.G. (2004) *The Technique of Production of Fancy Red Diamonds*. Russian Federation patent 2237113, filed June 26, 2003, issued Sept. 27, 2004. [in Russian]

Wang W., Moses T., Linares R., Hall M., Shigley J.E., Butler, J. (2003) Gem-quality synthetic diamonds grown by a chemical vapor deposition (CVD) method. *Gems & Gemology*, Vol. 39, No. 4, pp. 268–283.

Welbourn C.M., Cooper M., Spear P.M. (1996) De Beers natural versus synthetic diamond verification instruments. *Gems & Gemology*, Vol. 32, No. 3, pp. 156–169.

Woods G.S. (1984) Infrared absorption studies of the annealing of irradiated diamonds. *Philosophical Magazine B*, Vol. 50, pp. 673–688.

Zaitsev A.M. (2001) *Optical Properties of Diamond*. Springer-Verlag, Berlin, 502 pp.