TWO TREATED-COLOR SYNTHETIC RED DIAMONDS SEEN IN THE TRADE

By Thomas M. Moses, Ilene Reinitz, Emmanuel Fritsch, and James E. Shigley

Two dark brownish red faceted stones, recently submitted to the GIA Gem Trade Laboratory for standard origin-of-color reports, were found to be treated synthetic diamonds. This conclusion was based on observations of: patterns of zoned color, U.V. luminescence, and graining; metallic inclusions; and certain bands in the visible- and infrared-range absorption spectra. We believe that this is one of the first published reports of treated-color synthetic diamonds seen as faceted gems. For some of the gemological features described here, such as visible-range spectra with sharp absorption bands, this is one of the first reported occurrences in gem-quality synthetic diamonds.

In early July 1993, a diamond dealer submitted a 0.55ct dark brownish orangy red diamond (figure 1, left) to the New York office of the GIA Gem Trade Laboratory (GIA GTL) for a standard origin-of-color report. According to the client, this round brilliant-cut stone had been obtained on memo from a dealer in Bombay, India. In September, a 0.43-ct dark brownish red "radiant"-cut diamond (figure 1, right) was submitted in New York for a similar report by a separate client. Given the very high market value and the great rarity of natural-color "red" diamonds (see, e.g., Federman, 1992), these two stones were undoubtedly submitted to GIA GTL in hopes of receiving a favorable color description on a laboratory report. However, standard gemological examination quickly revealed that both stones were synthetic diamonds. In addition, their

ABOUT THE AUTHORS

182

Mr. Moses is director of identification and research, and Dr. Reinitz is a research scientist, at the GIA Gem Trade Laboratory in New York. Dr. Fritsch is manager of research, and Dr. Shigley is director of research, at the Gemological Institute of America, Santa Monica, California.

Acknowledgments: Sam Muhlmeister and Mike Moon, both of GIA Research, prepared the infrared spectra and the EDXRF analyses/visible spectra, respectively. Dr. Alan T. Collins, of the Physics Department at King's College, London, reviewed the draft manuscript and provided a number of helpful suggestions.

Gems & Gemology, Vol. 29, No. 3, pp. 182-190.

© 1993 Gemological Institute of America

gemological properties indicated that both had been color enhanced subsequent to synthesis.

To date, the GIA Gem Trade Laboratory has examined only a very few faceted synthetic diamonds that were submitted by members of the jewelry industry for a laboratory report (see also the brief mention of GIA GTL's examination of a 0.23-ct faceted Sumitomo synthetic vellow diamond in Fryer, 1987). With the announced commercial offering of Russian gem-quality synthetic diamonds for jewelry use (Catalano, 1993), however, it is likely that this situation will occur more frequently. Notification of the 0.55-ct faceted synthetic diamond and its gemological properties to other gem-testing laboratories was made through International Colored Gemstone Association (ICA) Laboratory Alert No. 74, dated August 9, 1993 (this alert also mentioned an untreated, 0.74-ct yellow synthetic diamond crystal examined by GIA GTL at a client's request at about the same time). The present article reports on the gemological properties of these two treated synthetic red diamonds and discusses how they compare with other synthetic diamonds examined to date.

BACKGROUND

The possibility of gem-quality synthetic diamonds entering the jewelry trade has been a concern ever since the first diamonds of a size and quality suitable for faceting were synthesized by General Electric in 1970. For more than two decades, researchers at GIA and elsewhere have been reporting regularly on the





Figure 1. Standard gemological testing at the GIA Gem Trade Laboratory in New York revealed that this 0.55-ct brownish orangy-red round brilliant cut (left) and this 0.43-ct brownish red "radiant" cut (right) are synthetic diamonds that have been treated to produce the red color. Photos by Shane F. McClure.

properties of gem-quality synthetic diamonds to address this industry concern (Crowningshield, 1971; Woods and Lang, 1975; Koivula and Fryer, 1984; Shigley et al., 1986, 1987, 1992, 1993a, 1993b; Burns et al., 1990; Kanda, 1990; Ponahlo, 1992; Burns and Davies, 1992; Clark et al., 1992; Rooney et al., 1993; Fritsch and Shigley, 1993). These articles have described various means for recognizing gem-quality synthetic, diamonds using both standard gem-testing equipment and more advanced instrumentation. Although synthetic diamonds with a red color have not been described in the gemological literature, there has been some scientific work on synthetic diamonds that are pink or red due to treatment by irradiation followed by annealing (see Collins, 1978; Collins, 1991, p. 667). The information on synthetic and treated synthetic diamonds reported in these articles, and our examination over many years of numerous natural-color diamonds, made possible the identification of the two synthetic diamonds reported here.

MATERIALS AND METHODS

We used standard gemological testing equipment as well as other laboratory instrumentation to characterize these faceted stones. The former included a gemological microscope, a long-wave (366 nm) and short-wave (254 nm) ultraviolet lamp unit (used in a darkened room), and a Beck prism spectroscope as well as a Discan digital-scanning diffraction-grating spectroscope (with the diamonds cooled using a spray refrigerant). We used a Pye-Unicam 8800 spectrophotometer to record absorption spectra at liquidnitrogen temperature over the range 250-850 nm, and Nicolet 510 and 60SX Fourier-transform infrared spectrometers to record infrared spectra over the range 400–10,500 cm⁻¹. Qualitative chemical analysis was carried out using a Tracor X-Ray energy-dispersive Xray fluorescence (EDXRF) system.

RESULTS

Microscopy. Color Zoning. When examined with 10× magnification, both samples exhibited very distinct color zoning (figures 2-4). Through the crown facets of the 0.55-ct stone, we observed the outlines of both square-shaped and superimposed cross-shaped light yellow areas surrounded by much larger areas of red color (figure 2 shows a portion of this color-zoning pattern). The cross-shaped pattern was approximately centered under the table facet. In general, the areas of yellow color were tabular, and they were much narrower than the red areas. When viewed through the pavilion facets of this stone, the color zoning was manifest, at four locations around the girdle (separated by 90°), as narrow light yellow zones surrounded by larger red areas (figure 3); this corresponds to looking down one of the four "arms" of the cross-shaped pat-

Figure 2. This view through the crown facets of the 0.55-ct red synthetic diamond shows the intersecting red and yellow zones. The latter appear slightly greenish due to their luminescence to visible light. Several groups of small metallic inclusions can also be seen. Photomicrograph by John I. Koivula; transmitted light, magnified 35×.

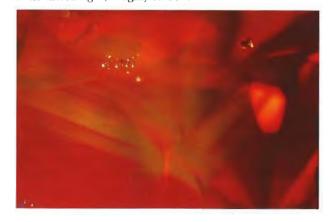




Figure 3. When the 0.55-ct stone was viewed through the pavilion facets parallel to the girdle, a narrow light yellow zone surrounded by larger red areas could be seen at four locations (separated by 90°) around the girdle. Photomicrograph by John I. Koivula; transmitted light, magnified 40×.

tern mentioned above. Similar kinds of red-yellow color zoning could also be seen through the crown and pavilion facets of the 0.43-ct stone (figure 4).

Graining. Using reflected light, we saw only one faint graining line on the table facet of the 0.55-ct stone. In contrast, we saw a faint pattern of surface graining and some parallel polishing "drag" lines on the table of the 0.43-ct stone (figure 5). In both stones, the color zones mentioned above were separated by planar boundaries marked by slight internal graining.

Inclusions. A large, rounded, opaque inclusion with a metallic (or reflective) appearance was readily visible beneath the table facet of the 0.55-ct stone (figure 6). It was accompanied by many smaller inclusions of similar appearance (again, see figure 2). Small metallic inclusions were also visible in the 0.43-ct stone, as was a large open cavity and an unusual square-shaped inclusion of uncertain identity seen through the table facet (figure 5). Because of these inclusions, both synthetic diamonds were attracted by a simple magnet. EDXRF chemical analysis of both stones revealed the presence of nickel and smaller amounts of iron (figure 7), presumably in large part from these metallic inclusions. Although GIA GTL does not issue quality-grading reports on synthetic diamonds, a natural diamond with eye-visible inclusions (such as the ones found

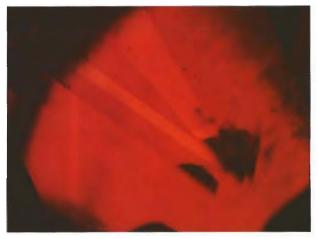
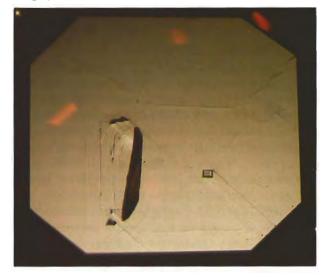


Figure 4. With magnification, the 0.43-ct red synthetic diamond showed a pattern of distinct red and narrow yellow zones separated by planar internal graining. Photomicrograph by John I. Koivula; transmitted light, magnified 40×.

in these synthetics) would receive an "Imperfect" clarity grade.

Ultraviolet Luminescence. The luminescence reaction visible from the crown facets of the 0.55-ct diamond to *both* long- and short-wave ultraviolet radiation was striking. In both cases, we saw two unevenly distributed colors of fluorescence: a very intense green and a moderately intense reddish orange.

Figure 5. A faint pattern of intersecting surface grain lines and some parallel polishing "drag" lines can be seen on the table facet of the 0.43-ct stone. Also visible is a large, open cavity and an unusual square-shaped inclusion. Photomicrograph by John I. Koivula; reflected light, magnified 15×.



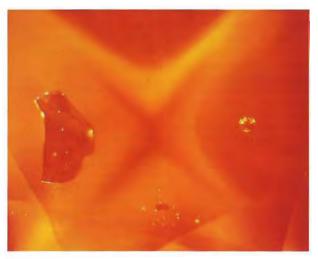
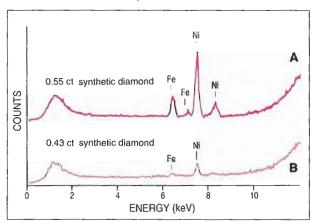


Figure 6. One large—and several smaller—opaque inclusions of flux metal lie beneath the table facet of the 0.55-ct red synthetic diamond. This photomicrograph also shows the distinctive pattern of color zones, with four yellow areas forming a "cross shape" that is surrounded by red areas. When the stone is illuminated by a strong visible light source, the yellow areas are seen to emit green luminescence. Photomicrograph by John I. Koivula; transmitted light, magnified 35×.

The pattern of green fluorescence was identical to that of the narrow yellow color zones described above (figure 6)—a combination of square and cross shapes (see figure 8). When the short-wave U.V. lamp was turned off, the green fluorescing regions continued to phosphoresce the same color briefly for several seconds. The moderately intense reddish orange fluorescence corresponded to only one small isolated point near the girdle under long-wave U.V., but to all the

Figure 7. These EDXRF spectra show the presence of both nickel (Ni) and iron (Fe) from the metallic inclusions in these two synthetic diamonds.



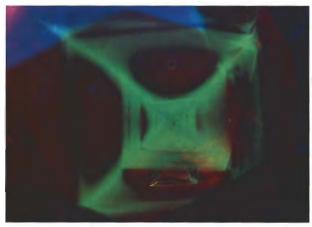


Figure 8. The crown facets of the 0.55-ct red synthetic diamond reveal an uneven, intense fluorescence to short-wave U.V. radiation. The combined square- and cross-shaped pattern of green fluorescence corresponds to the light yellow zones in the diamond; the moderate reddish orange fluorescence to the red areas in the stone. Photomicrograph by John I. Koivula; magnified 5×.

large, dark red areas under short-wave U.V (again, see figure 8).

The 0.43-ct stone also exhibited uneven U.V. luminescence, but in a different spatial pattern from that described above. The overall long-wave U.V. fluorescence was moderately intense, and the short-wave U.V. fluorescence was intense. In both cases, when the stone was viewed through the crown facets, there was a very small area of red fluorescence near the center of the table facet, which was surrounded by a narrow zone of green fluorescence. From the latter, narrow bands of moderate orange fluorescence pointed toward the four corners of the table facet, where there were square areas of stronger orange fluorescence. The remainder of the stone exhibited weaker orangy red fluorescence. When the U.V. lamp was turned off, we did not see any phosphorescence from the 0.43-ct stone.

We also observed moderate-intensity green luminescence in the yellow areas when the 0.55-ct diamond was illuminated with a strong visible light source (such as that provided by fiber-optic light with reflected or transmitted illumination; see figure 2). We did not see a similar luminescence in the 0.43-ct stone.

Spectroscopy. The visible-range absorption spectra of the two synthetic diamonds are shown in figure 9. Numerous sharp absorption bands occur between 400 and 800 nm in the spectrum of the 0.55-ct stone (figure 9A, table 1). Several of the bands between 500 and 660 nm were intense enough to be seen with a

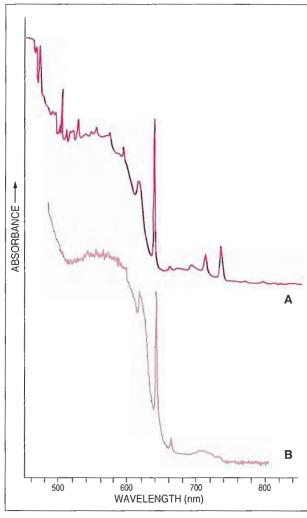


Figure 9. These visible-range absorption spectra were recorded at liquid-nitrogen temperatures for the 0.55-ct (A) and 0.43-ct (B) treated synthetic diamonds. A list of the bands present in both spectra, and their causes, are given in table 1. In the spectrum of the 0.55-ct stone, numerous sharp absorption bands can be seen between 460 and 800 nm; many of these were sufficiently intense to appear as sharp bands in a handheld spectroscope (i.e., at about 503, 527, 553, 595, 617, 637, and 658 nm), especially when the sample was cooled by use of spray refrigerant. No spectral features could be recorded below 460 nm because virtually all incident light was absorbed by the diamond itself. In the 0.43-ct synthetic diamond, only a few sharp bands are visible; the two at 637 and 658 nm are also present in the spectrum of the other diamond. No spectral features could be recorded below about 600 nm for the same reason as cited above.

handheld spectroscope, especially when the diamond was cooled.

Although the visible spectrum of the 0.43-ct stone (figure 9B) exhibited far fewer sharp absorption bands,

TABLE 1. Absorption bands present in the visible and near-infrared ranges of the spectrum of the 0.55-ct treated red synthetic diamond (with those seen in the 0.43-ct red synthetic diamond marked by an asterisk [*]), listed by decreasing wavelength.

Wavelength (rounded to closest nm)	Seen in handheld spectroscope (at low temperature)	Comments ^a
809		Visible in published spectrum but
792		not discussed in [a] Ni-related [a]
767		Visible in published spectrum but
101		not discussed in [a]
732		Ni- and N-related [a]
711		Ni- and N-related [a]
691		Ni- and N-related [a]
671		Ni- and N-related [a]
658*	Yes	Ni-related [b]
637*	Yes	"N-V" center typical of treated
037	165	pink diamonds [c]
617	Yes	"N-V" center, typical of treated
	162	pink diamonds [c]
614	Yes	"N-V" center, typical of treated
	168	pink diamonds [c]
595	Yes	Typical of treated diamonds [c]
595 575	Yes	Typical of treated diamonds [c]
3/3	162	diamonds [c]
553	Yes	Ni- and N-related [a]
547	Yes	Ni- and N-related [a]
540	162	Ni- and N-related [a]
527	Yes	Ni- and N-related [a]
520	res	Ni- and N-related [a]
518	Yes	Ni- and N-related [a]
516	165	Ni- and N-related [a]
511		Ni- and N-related [a]
503	Yes	
503	165	Ni- and N-related [a] and H3 center (always seen in
		, ,
502		treated pink diamonds) [c] Ni- and N-related [a]
494		Ni-related [b]
494		Ni- and N-related [a]
478		Ni- and N-related [a]
473		Ni- and N-related [a]
468		Ni- and N-related [a]
400		TNI- and IN-related [a]

^aReferences: [a] observed by Lawson and Kanda (1993a, 1993b) in nitrogen-containing synthetic diamonds, grown in Ni and subsequently annealed to 1600°–1990° C; [b] Collins and Spear, 1982: [c] Collins: 1982.

those observed are in wavelength positions similar to those seen in the other stone—in particular, at 637 and 658 nm. Besides sharp absorption bands, the visible spectra of both stones exhibited two additional features: an increasing absorption toward the violet, and a broad region of absorption extending from about 500 to 640 nm.

The mid-infrared absorption spectra (figure 10) reveal that both of these synthetic diamonds are a mixture of types. The 0.55-ct stone is type Ib + IaA + IaB (with IaA >> IaB, and Ia > Ib), while the 0.43-ct stone is type Ib + IaA +IaB (with IaA >> IaB, and Ib > Ia). For details on diamond types, see Fritsch and Scarratt (1992).

In addition, both stones showed absorption bands at 1050, 1450, and 1502 cm⁻¹ in their mid-infrared spectra (figure 10). Both also displayed a band at 4935 cm⁻¹ in their near-infrared spectra (which are not illustrated here). The 1450 and 4935 cm⁻¹ bands are referred to as H1a and H1b, respectively (Clark et al., 1956; Woods, 1984).

DISCUSSION

Comparison to Other Synthetic Diamonds. Certain gemological properties of synthetic diamonds differ from those of natural diamonds because of their different conditions of formation (for a recent review, see Burns and Davies, 1992). The observed zoning of color and U.V. luminescence, the pattern of graining, and the presence of metallic inclusions in these two stones are all typical of gem-quality colored synthetic diamonds described to date.

Conversely, these two synthetic diamonds displayed some features that are different from those that have been reported, not least of which is their red color. Thus far, the only commercially available gem-quality synthetic diamonds have been yellow, type-Ib material. They have been inert to long-wave U.V. radiation, and have lacked sharp absorption bands in their visible-range spectra (Shigley et al., 1986). The infrared spectra of these two red synthetic diamonds indicate that neither stone is a pure type-Ib diamond: both exhibit some type-Ia character. In addition, both fluoresced not only to short-wave but also, more importantly, to long-wave U.V. radiation, with a pattern of both green and orange colors that corresponds to the arrangement of internal growth sectors. Finally, both stones displayed sharp absorption bands between 500 and 660 nm, some of which were visible in a handheld spectroscope. None of these features has previously been reported for synthetic diamonds in the gemological literature.

We have examined two pieces of Sumitomo synthetic diamond that, after known irradiation and annealing, turned from yellow to orangy red. After treatment, they exhibited orange fluorescence to both long- and short-wave U.V. radiation (with the short-wave reaction more intense than the long-wave reaction). Their visible-range absorption spectra revealed sharp bands at about 575, 595, and 637 nm. Even after treatment, the infrared spectra indicated that one sample was still a pure type Ib, while the other was a mixture of Ib and minor IaB. The mid- and near-infrared spectra of both Sumitomo samples exhibited sharp bands at 1450 and 4935 cm⁻¹ after treatment.

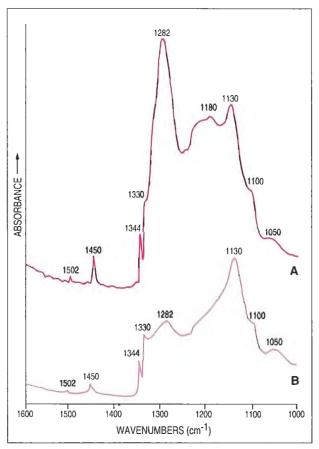


Figure 10. The "nitrogen region" (between 1344) and about 1000 cm⁻¹) of the mid-infrared absorption spectra of these two synthetic diamonds reveals that, unlike most synthetic yellow diamonds tested to date, they are not a pure type Ib. Type-Ib diamonds are characterized by a sharp band at about 1344 cm⁻¹, and a broader band at about 1130 cm⁻¹. Type-IaA diamonds have a band at approximately 1282 cm⁻¹, while type-IaB diamonds have bands at about 1330 and 1180 cm⁻¹ (see Field, 1992, p. 683). Thus, the 0.55-ct stone (spectrum A) is a mixture of type Ib + IaA + IaB (with IaA >> IaB, and Ia > Ib), and the 0.43-ct stone (spectrum B) is a type Ib + IaA + IaB (with IaA >> IaB, and Ib > Ia). The bands at 1502 and 1450 cm⁻¹ in both spectra are the result of annealing of these two irradiated synthetic diamonds (Clark et al., 1992, p. 43). The broad band at about 1050 cm-1 is due to a nitrogen-related defect (with N in a positive charge state) in the crystal structure of these diamonds that has been found only in synthetic diamonds (Lawson and Kanda, 1993a).

Visible- and Infrared-Range Absorption Spectra. As shown in table 1, the sharp absorption bands present in the visible-range spectra of these two synthetic diamonds arise from several different causes.

Scientific studies have shown that only nickel,

of the several transition metals that have been used as a flux for synthetic diamond growth, can give rise to sharp absorption bands in the visible-range spectrum of diamond (Collins and Spear, 1982; Lawson and Kanda, 1993a, 1993b). These Ni-related bands fall into two groups. The first group includes bands at 494 and 658 nm, which are present in the spectra of the asgrown Ni-containing synthetic diamond crystals (Collins and Spear, 1982; Collins et al., 1990). The second group contains a large number of bands between 460 and 800 nm, which are found in nitrogencontaining synthetic diamonds (grown in Ni) that have been annealed to 1600°–1900°C (Lawson and Kanda, 1993a, 1993b; again, see table 1).

Apart from those that are Ni-related, other sharp bands in the visible range result from laboratory treatment. The 503-nm (H3) band is known to result from irradiation and annealing (to 1400°-1700°C) of synthetic type-Ib diamonds, and is thought to be due to a vacancy trapped at a nitrogen A aggregate (two nearest neighbor substitutional N atoms; Collins, 1978, 1982, 1991). The 595-nm band is found in type-Ia and Ib diamonds that have been irradiated and then annealed to 800°-1000°C (Collins, 1982). Finally, there are several sharp bands that are typically seen in type-Ib diamonds that, after irradiation and annealing (to 800°C or more), turn from yellow to pink. These include the 575-nm band as well as the 637-nm band (with sidebands at 614 and 617 nm, all superimposed on a broad region of absorption between about 450 and 650 nm) produced by a defect known as the "N-V" center (a vacancy "V" trapped at a substitutional N atom; Davies and Hamer, 1976; Collins, 1978, 1982, 1991).

In the infrared spectra, the H1a and H1b bands (1450 and 4935 cm⁻¹)—as well as the band at 1502 cm⁻¹—are produced in type-Ib diamonds by irradiation and annealing above 800°C (Woods, 1984; Collins and Stanley, 1985; Collins, 1991; Clark et al., 1992, p. 43).

The presence of some or all of these spectral features in the two synthetic red diamonds allows us to make some inferences regarding their origin and treatment history. The presence of Ni-related sharp absorption bands confirms the results of EDXRF analysis that both samples are synthetic and were grown using a Ni-containing flux, since most of the sharp bands between 460 and 800 nm have no other known causes.

In the 0.55-ct stone, the bands indicative of irradiation and annealing include those at 503, 575, 595, and 637 nm in the visible spectrum, and those at

1450, 1502, and 4935 cm⁻¹ in the infrared spectrum. The 503-nm and 4935-cm⁻¹ features, along with the other bands in the mid-infrared spectrum, are evidence of some degree of nitrogen aggregation in this synthetic diamond. The numerous Ni-related sharp absorption bands in the visible spectrum suggest that this diamond either has a relatively high nickel content or, if it has a lower Ni content, it was heated after growth to temperatures above 1600°C, so these bands are especially prominent (A. T. Collins, pers. comm., 1993).

In the 0.43-ct stone, in contrast, only the 637-nm band seen in the visible spectrum, along with the bands at 1450, 1502, and 4935 cm⁻¹ in the infrared, are evidence of irradiation and annealing. Again, the 4935-cm⁻¹ feature, along with the other bands in the mid-infrared spectrum, are evidence of some degree of nitrogen aggregation (mainly A aggregates). The lack of the numerous, Ni-related sharp bands suggests that this synthetic diamond either contains relatively smaller amounts of nickel or was not annealed to such high temperatures (1600°–1900°C) as was the 0.55-ct stone.

Other bands in the mid-infrared revealed that the two stones exhibit some type-Ia character (mainly IaA; see caption, figure 10), which indicates that some nitrogen aggregates formed during treatment. In the spectra of both synthetic diamonds, the weak type-IaB features in the mid-infrared, and the lack of an H1c band (5165 cm⁻¹) in the near-infrared, confirm that only a limited number of nitrogen B aggregates (an even number of nearest-neighbor substitutional N atoms of undetermined structure; Woods, 1984; Collins and Stanley, 1985) formed during treatment in both stones (A. T. Collins, pers. comm., 1993). Aggregation of nitrogen atoms in a synthetic diamond has been documented during crystal growth (Kanda et al., 1990, for crystals produced in cobalt metal at temperatures of 1400°-1500°C) and during post-growth treatment (either by annealing alone at temperatures of 1700°-2400°C [Collins, 1980; Collins and Stanley, 1985, or by irradiation followed by annealing at temperatures of about 800°C [Collins, 1978]). From our data, we cannot conclude whether the observed N aggregation in these two stones resulted during crystal growth or post-growth treatment.

Cause of Color. Yellow-to-brown type-Ib diamonds, whether natural or synthetic, will turn pink to red (or purple) when subjected to treatment by irradiation and annealing (Collins, 1982; and our own experience—see previous Discussion section above). As

grown, synthetic diamond crystals do not exhibit a red color that results from impurities. This color is due to post-growth irradiation and annealing, as proved in these treated synthetic diamonds by certain spectral bands present.

Untreated natural pink-to-red diamonds are either type Ia or IIa (those that are treated are always partially type-Ib; Collins, 1982, and our own observations). The visible-range spectra of type-Ia diamonds of these colors show increasing absorption toward the ultraviolet (due to nitrogen). Superimposed on this are one or more sharp absorption bands of the "Cape series" (mainly the 415-nm band due to the N3 center, which consists of three nearest-neighbor substitutional N atoms). In addition, there is a broad absorption band centered at about 550 nm (Collins, 1982; Kane, 1987; Shigley and Fritsch, 1993). This latter broad band is thought to be due to a defect produced by plastic deformation (a small displacement of the carbon atoms along gliding planes in the diamond crystal structure) that can occur while the diamond is still in the earth (Collins, 1982).

Similarly, the visible-range spectra of untreated, natural type IIa diamonds of these colors exhibit a broad band between 500 and 600 nm, but lack the increasing absorption toward the ultraviolet and the sharp bands, both of which are due to nitrogen (Collins, 1982).

Except for the sharp bands (which make little contribution to the color), the visible spectra of the two treated red synthetic diamonds described here are similar in appearance to those of treated-color pink-to-red natural diamonds. There is increasing absorption toward the ultraviolet (due again to the singly substitutional nitrogen), and a broad absorption band between about 450 and 650 nm (due to the "N-V" center). This broad band, here the result of laboratory treatment, also gives rise to a pink-to-red color, since it reaches a maximum near 550 nm (similar in location to the broad absorption band in the spectra of untreated pink-to-red natural diamonds, which results from a different process; Collins, 1982).

Cause of U.V. Luminescence. The green fluorescence observed to correspond to the narrow yellow zones probably is due to the H3 center (503 nm), while the orange fluorescence from the more extensive red areas is probably due to the 575-nm absorption band (these observations have been confirmed by A. T. Collins, pers. comm., 1993).

Previous descriptions of yellow (untreated) synthetic diamonds reported a yellow or greenish yellow

fluorescence to short-wave U.V. radiation (Shigley et al., 1986, 1987). In all cases, these synthetic diamonds were pure type Ib with no evidence of a type-Ia character. In contrast, natural type-Ib yellow diamonds: (1) rarely react to U.V. radiation, but when they do, it is usually orange fluorescence to both long- and shortwave U.V. (Shigley et al., 1986); and (2) always exhibit some type-Ia character (again, observations confirmed by A. T. Collins, pers. comm., 1993). GIA and GIA GTL researchers are currently examining some yellow and greenish yellow, untreated and treated (annealing only), mixed type Ib + IaA synthetic diamonds from Russia that reveal only yellow to greenish yellow U.V. fluorescence. Thus, the orange U.V. luminescence observed in the two stones described here is almost certainly the result of irradiation and annealing, not of their mixed type Ib + IaA character. This possibility is supported by the orange fluorescence to both long- and short-wave U.V. of the two irradiated and annealed Sumitomo synthetic diamonds we examined. Furthermore, we have observed orange U.V. fluorescence in all treated-pink natural diamonds examined to date.

Comparison to Natural Diamonds. Some natural-color pink diamonds are type IIa (i.e., essentially lacking in nitrogen) and have an orange U.V. fluorescence (Collins, 1982). We have never seen a known treated pink diamond that is a type IIa. An increasing number of the pink-to-red natural-color diamonds that we have documented are type Ia and have a blue U.V. fluorescence. The color is primarily due to the broad absorption band centered at 550 nm (Collins, 1982; Shigley and Fritsch, 1993). None of these type-Ia natural diamonds has exhibited any type-Ib character. Thus, all known natural-color pink-to-red diamonds are readily distinguishable from the two stones described here (mainly on the basis of the distinctive features of the latter).

We have also documented some treated pink-tored type-Ib natural diamonds. They usually have evenly distributed color, and all exhibit the 575-, 595-, and 637-nm bands typical of treatment by irradiation and annealing. Although we examined two treated natural diamonds that were a mixed type Ib + IaA and exhibited uneven (pink/yellow) coloration and moderately strong orange fluorescence (to long- and short-wave U.V.), they did not display the pattern of color zoning, nor the nickel-related absorption bands, that were shown by the two stones described here and prove their synthetic origin.

CONCLUSION

These two red stones are the first treated-color synthetic diamonds that have been submitted to the GIA Gem Trade Laboratory by members of the trade. Although we do not know precisely where these synthetic diamonds were manufactured, their color zoning, U.V. luminescence behavior, and visible and infrared absorption spectra are very similar to those we have observed in synthetic diamonds grown in Russia (see, e.g., p. 207 of the Gem News section in this

issue). We have no evidence of, or information on, where they might have been treated.

Because such encounters with synthetic diamonds will undoubtedly increase in the future, colored diamonds must be examined with greater care than has been previously necessary. All those involved with selling or grading gem diamonds must know how to identify synthetic, and now treated synthetic, diamonds.

REFERENCES

- Burns R.C., Cvetkovic V., Dodge C.N., Evans D.J.F., Rooney M-L.T., Spear P.M., Welbourn C.M. (1990) Growth-sector dependence of optical features in large synthetic diamonds. *Journal of Crystal Growth*, Vol. 104, pp. 257–279.
- Crystal Growth, Vol. 104, pp. 257–279.

 Burns R.C., Davies G.J. (1992) Growth of synthetic diamond. In J.E. Field, Ed., The Properties of Natural and Synthetic Diamond, Academic Press, London, pp. 395–422.
- Catalano D.A. (1993) Chatham is entering the diamond business. National Jeweler, JA Hotline, July 25–28, pp. 1, 6.
- Clark C.D., Collins A.T., Woods G.S. [1992] Absorption and luminescence spectroscopy. In J.E. Field, Ed., The Properties of Natural and Synthetic Diamond, Academic Press, London, pp. 35–79
- Clark C.D., Ditchburn R.W., Dyer H.B. (1956) The absorption spectra of irradiated diamonds after heat treatment. *Procedures of the Royal Society*, Vol. A237, pp.75–89.
- Collins A.T. (1978) Migration of nitrogen in electron-irradiated type Ib diamond. *Journal of Physics C: Solid State Physics*, Vol. 11, pp. L417–L422.
- Collins A.T. (1980) Vacancy enhanced aggregation of nitrogen in diamond. *Journal of Physics C: Solid State Physics*, Vol. 13, pp. 2641–2650
- Collins A.T. (1982) Colour centres in diamond. *Journal of Genmology*, Vol. 18, No. 1, pp. 37–75.
- Collins A.T. (1991) Optical centers in synthetic diamond—a review. In R. Messier, J.T. Glass, J.E. Butler, R. Roy, Eds., Proceedings of the Second International Conference on New Diamond Science and Technology, Washington, DC, 23–27 September 1990, pp. 659–670.
- Collins A.T., Kanda H., Burns R.C. (1990) The segregation of nickel-related optical centers in the octahedral growth sectors of synthetic diamond. *Philosophical Magazine B*, Vol. 61, No. 5, pp. 797–810.
- Collins A.T., Spear P.M. (1982) Optically active nickel in synthetic diamond. *Journal of Physics D: Applied Physics*, Vol. 15, pp. L183–L187.
- Collins A.T., Stanley M. (1985) Absorption and luminescence studies of synthetic diamond in which the nitrogen has been aggregated. *Journal of Physics D: Applied Physics*, Vol. 18, pp. 2537–2545.
- Crowningshield R. (1971) General Electric's cuttable synthetic diamonds. Gems & Geniology, Vol. 13, No. 10, pp. 302–314.
- Davies G., Hamer M.F. (1976) Optical studies of the 1.945 eV vibronic band in diamond. *Proceedings of the Royal Society of London*, Vol. A348, pp 285–298.
- Federman D. (1992) The Hancock red diamond: Per-carat champion. *Modern Jeweler*, Vol. 91, No. 4, p. 34.
- Field J.E. (1992) The Properties of Natural and Synthetic Diamond. Academic Press, London, 710 pp.
- Fritsch E., Scarratt K. (1992) Natural-color nonconductive gray-toblue diamonds. *Gems & Gemology*, Vol. 28, No. 1, pp. 35–42. Fritsch E., Shigley J.E. (1993) The separation of natural from synthetic

- gem-quality diamonds on the basis of crystal growth criteria. *Journal of Crystal Growth*, Vol. 128, pp. 425–428.
- Fryer C.W. (1987) Gem trade lab notes: Synthetic diamond. Gems & Gemology, Vol. 23, No. 1, p. 44.
- Kanda H. (1990) Patterns observed in the cross sections of high pressure synthetic diamonds. New Diamond, pp. 58–62.
- Kanda H., Ohsawa T., Yamaoka S. (1990) Formation of nitrogen pairs in synthetic diamond during growth. In S. Saito, O. Fukunaga, M. Yoshikawa, Eds., Science and Technology of New Diamond, Terra Scientific Publishing Co., Tokyo, Japan, pp. 339–344.
- Kanc R.E. (1987) Three notable fancy-color diamonds: Purplish red, purple-pink, and reddish purple. Gems & Gemology, Vol. 23, No. 2, pp. 90–95.
- Koivula J.I., Fryer C.W. (1984) Identifying gem-quality synthetic diamonds: An update. *Gems & Gemology*, Vol. 20, No. 3, pp. 146–158.
- Lawson S.C., Kanda H. (1993a) Nickel in diamond: An annealing study. Diamond and Related Materials, Vol. 2, pp. 130–135.
- Lawson S.C., Kanda H. (1993b) An annealing study of nickel point defects in high-pressure synthetic diamonds. *Journal of Applied Physics*, Vol. 73, No. 8, pp. 3967–3973.
- Ponahlo J. (1992) Cathodoluminescence (CL) and CL spectra of De Beers' experimental synthetic diamonds. *Journal of Genmology*, Vol. 23, No. 1, pp. 3–17.
- Rooncy M-L.T., Welbourn C.M., Shigley J.E., Fritsch E., Reinitz I. (1993) De Beers near colorless-to-blue experimental gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 29, No. 1, pp. 38–45.
- Shigley J.E., Fritsch E. (1993) A notable red-brown diamond. *Journal of Gemmology*, Vol. 23, No. 5, pp. 259–266.
- Shigley J.E., Fritsch E., Kammerling R.C., Koivula J.E., Moses T.M. (1993a) Identifying faceted gem-quality synthetic diamonds. *Rapaport Diamond Report*, Vol. 16, No. 26, pp. 10–13.
- Rapaport Diamond Report, Vol. 16, No. 26, pp. 10–13.
 Shigley J.E., Fritsch E., Reinitz I. (1993b) Two near-colorless General Electric type-IIa synthetic diamond crystals. Gems & Gemology, Vol. 29, No. 3, pp. 191-197.
- Shigley J.E., Fritsch E., Reinitz I., Moon M. (1992) An update on Sumitomo gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 28, No. 2, pp. 116–122.
- Shigley J.E., Fritsch E., Stockton C.M., Koivula J.I., Frycr C.W., Kane R.E. (1986) The gemological properties of the Sumitomo gem-quality synthetic yellow diamonds. *Gems & Gemology*, Vol. 22, No. 4, pp. 192–208.
- Shigley J.E., Fritsch E., Stockton C.M., Koivula J.I., Fryer C.W., Kane R.E., Hargett D.R., Welch C.W. (1987) Gemological properties of the De Beers gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 23, No. 4, pp. 187–206.
- Woods G.S. (1984) Infrared absorption studies of the annealing of irradiated diamonds. *Philosophical Magazine B*, Vol. 50, No. 6, pp. 673–688
- Woods G.S., Lang A.R. (1975) Cathodoluminescence, optical absorption, and X-ray topographic studies of synthetic diamonds. Journal of Crystal Growth, Vol. 28, pp. 215–226.