

# THE GEMOLOGICAL PROPERTIES OF RUSSIAN GEM-QUALITY SYNTHETIC YELLOW DIAMONDS

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*A group of gem-quality synthetic diamonds, grown in Russia using the "BARS" apparatus and now being sold for jewelry use, is examined. Study of seven yellow (five faceted, 0.11–0.51 ct) to orangy or brownish yellow as-grown samples, and three yellow to greenish yellow samples (all faceted, 0.14–0.21 ct) reportedly treated by post-growth annealing at high pressure and temperature, revealed distinctive gemological properties. These include: color and luminescence zoning, metallic inclusions, graining, and sharp visible-range absorption bands (some seen with a handheld spectroscope).*

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**D**evelopments in diamond synthesis make it increasingly likely that gem-quality synthetic diamonds will soon become available in the jewelry marketplace. Only a few months ago, Chatham Created Gems of San Francisco, California, announced that they would soon begin marketing synthetic diamonds from Russia for jewelry use ("Beware: Russia sells man-made diamonds," 1993). The quantity will be limited at first (see Nassau, 1993, for an analysis of the potential for synthetic diamond production in Russia), and subsequent Chatham statements have indicated that the original announcement was probably premature (Costan, 1993). Nevertheless, positive identification of any synthetic diamond is essential to maintaining confidence and integrity in the gem diamond industry.

In late 1990, GIA researchers had their first opportunity to examine synthetic diamonds produced in Russia (Koivula and Kammerling, 1991). Then, in May of 1992, one of the authors (NVS) provided GIA Research with 10 Russian gem-quality synthetic diamonds for detailed study. Most recently, in November 1993, we obtained four Russian yellow synthetic diamonds directly from the Chatham company. Independent of this research, during the latter half of 1993, the GIA Gem Trade Laboratory identified several synthetic diamonds among stones submitted by members of the jewelry industry for standard "origin of color" reports. Some of the cut stones found to be synthetic also appeared to have been treated by irradiation and subsequent heating (see International Colored Gemstone Association [ICA] Lab Alert No. 74, dated 13 August 1993; Moses et al., 1993a, 1993b). Evidence (cited in these references) suggests that all of the synthetic diamonds seen in GIA GTL recently, both

Figure 1. These synthetic diamonds—two as-grown crystals (0.78 and 0.88 ct), three as-grown faceted stones (0.18–0.51 ct), and two faceted stones treated at high pressure and temperature (0.14–0.21 ct)—were manufactured in Novosibirsk, Russia. They represent the core sample of this study. Photo by Robert Weldon.



the as-grown yellow crystals and faceted stones and the red treated samples, are of Russian origin.

We report here on a detailed gemological study of the 10 gem-quality synthetic diamonds—seven "as-grown" yellow to orange or brownish yellow (two crystals and five faceted samples; see figure 1), and three reportedly treated yellow to greenish yellow (all faceted; see figure 1)—received in 1992. All were produced in Novosibirsk (a major technological city in southern Siberia, located approximately 3,000 km east of Moscow). We believe from the properties observed that the four yellow to orange or brownish yellow synthetic diamonds recently loaned to GIA by Chatham Created Gems in late 1993, and the three yellow synthetic diamond samples seen briefly by GIA researchers in late 1990, represent the same type of synthetic diamond production. The three yellow to greenish yellow synthetic diamonds described here were reportedly heat treated ("annealed") at high pressure after synthesis in Novosibirsk to alter their color and to study other effects of annealing. We do not know their color before treatment, although we believe it was in the same range as the seven as-grown samples. Note that little information has been published on

Russian synthetic diamonds treated by high-pressure/high-temperature annealing (Malogolovets et al., 1991; Teslenko, 1993); for brevity, such stones are referred to here simply as "HPHT treated."

Although all of the Russian synthetic diamonds described here are easily identifiable, some of their gemological characteristics (such as their ultraviolet luminescence and optical absorption spectra) differ significantly from what we and others have reported so far for yellow synthetic diamonds of other manufacture that are suitable for jewelry use.

## BACKGROUND

Since 1971, gem researchers have regularly reported on the gemological properties and identifying characteristics of gem-quality synthetic diamonds (Crowningshield, 1971; Koivula and Fryer, 1984; Shigley et al., 1986, 1987, 1992, 1993a, 1993b; Ponahlo, 1992; Rooney et al., 1993; Koivula et al., 1993). Information on synthetic diamonds suitable for faceting has also appeared elsewhere in the scientific literature (see, e.g., Woods and Lang, 1975; Sunagawa, 1984; Burns et al., 1990; Lang and Moore, 1990; Collins, 1990; Kanda, 1990; Fritsch and Shigley, 1993).



Figure 2. A "split sphere" apparatus is used to grow synthetic diamond crystals at Novosibirsk. Left: This view of the apparatus opened reveals the internal spherical cavity, which holds the two sets of anvils and the central high-pressure cell. Right: The same apparatus is in a closed configuration at the start of an experiment to grow diamond crystals. Photos provided by N. V. Sobolev.

As discussed in these references, the gemological identification of synthetic diamonds is based on the conditions of diamond growth in the laboratory, which differ significantly from those in nature (in particular, growth time, chemical composition within the growth system, rapidity of cooling from high temperature, etc.). For example, with growth from a flux metal or alloy, metallic inclusions may become trapped in the synthetic diamond during crystallization. Furthermore, laboratory synthesis produces diamond crystals with a morphology different from that of natural gem diamonds. In particular, the synthetic diamond crystals we have examined always exhibit cube, and sometimes exhibit dodecahedral and trapezohedral, internal growth sectors (and external morphology), in addition to the octahedral sectors found in both natural and synthetic gem diamonds (Sunagawa, 1984; Shigley et al., 1987). The presence of several growth sectors,

potentially containing different types and amounts of impurities, can lead to zonations of color, luminescence, and graining in synthetic diamonds that are different from those seen in natural diamonds.

The reports mentioned earlier have described synthetic diamonds grown by General Electric, Sumitomo Electric Industries, and (on an experimental basis) by the De Beers Diamond Research Laboratory. All of these manufacturers use the "belt" type of growth equipment (see Strong and Wentorf, 1972; Bundy et al., 1973; Nassau, 1980, pp. 170–193). However, the Russian synthetic diamonds described here were grown using a different apparatus. As a result, some of their gemological properties are different from those reported for these other productions. Nevertheless, they are sufficient to identify these stones as synthetic diamonds by means of standard gem-testing equipment and techniques.

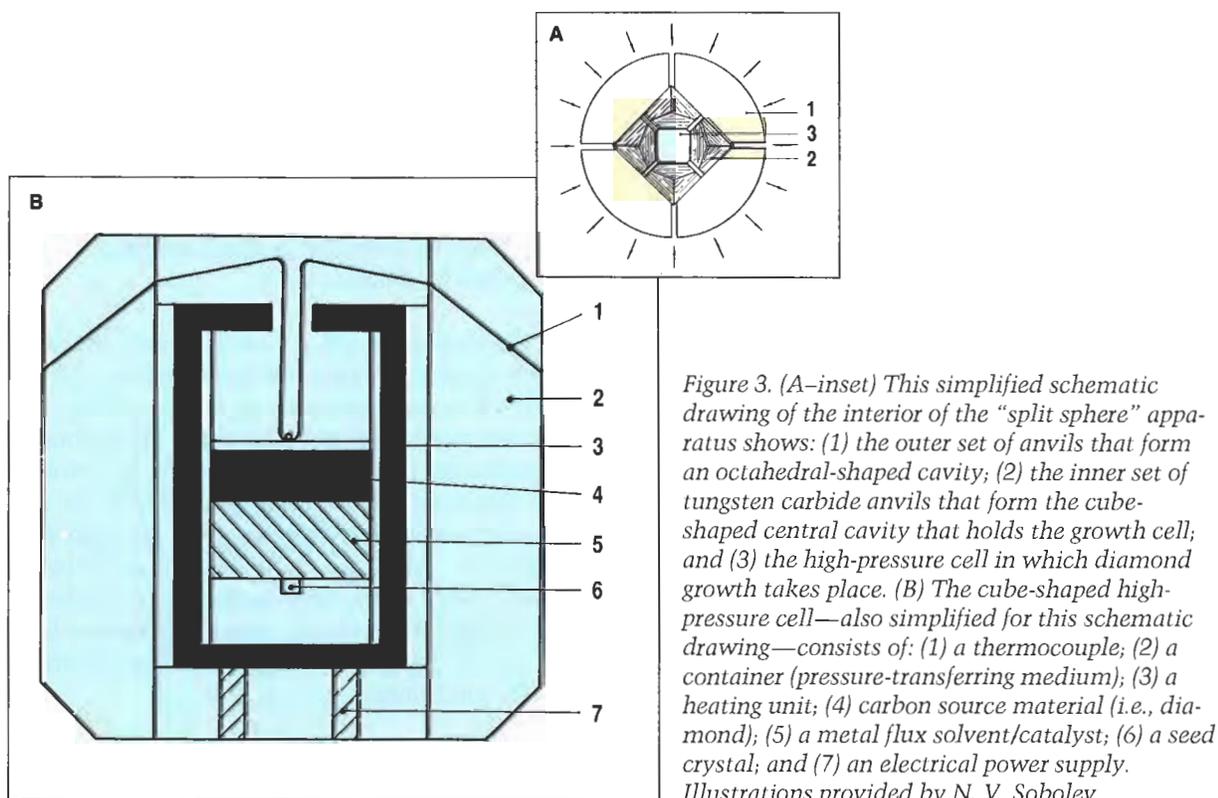
## GROWTH MECHANISM

The only economical process for growing large (1+ ct) single crystals of synthetic diamond is still the high-pressure/high-temperature flux method. General Electric, Sumitomo Electric, and De Beers researchers all use a reaction vessel in what is referred to as a "belt" type of apparatus mounted in a high-pressure hydraulic press, although the design details of their respective equipment apparently differ (see Nassau, 1980, pp. 170–193). When a metal solvent/catalyst is used as a flux, typical growth conditions are 1400° to 1600°C and 50 to 60 kbar. Such conditions are within the field of temperatures and pressures where diamond is the stable phase of carbon. With this type of equipment and these conditions, diamond crystals are produced by the "temperature gradient" or "reconstitution" technique (for more information, see Strong and Wentorf, 1972, 1991; Bundy et al., 1973; Burns and Davies, 1992). Growth periods for a 1-ct diamond crystal are reportedly on the order of five days or more (Shigley et al., 1986, 1987).

At Novosibirsk, synthesis of large, single diamond crystals is accomplished using a different type of high-pressure/high-temperature apparatus,

known as the "split sphere" (also referred to by the Russian acronym "BARS"; Pal'yanov et al., 1990; Yelissev et al., 1992a, 1992b). In this type of growth apparatus, pressure is applied to two sets of anvils (figures 2 and 3). The outer set of eight anvils forms an octahedron-shaped cavity. Within this space, an inner set of six additional anvils is positioned to form a cube-shaped central cavity that contains the high-pressure cell in which the diamond crystals are actually grown (again, see figure 3). Diamond crystal growth experiments have been conducted at pressures of about 55 to 65 kbar and temperatures in the range of about 1350° to 1700°C. Transition metals (Fe, Ni, Mn, etc.) and their alloys are used as solvents/catalysts. The best-quality cuboctahedral crystals (grown up to 1.5 ct) reportedly have been obtained using growth rates of not more than 5 mg/hr. Thus, the conditions of pressure, temperature, time, and flux composition are similar to those used in the "belt" type of growth apparatus. However, the growth cell in the BARS equipment is smaller than that in the typical belt-type growth apparatus, so there is less space available to grow synthetic diamonds.

Experiments have also been carried out at



Novosibirsk and elsewhere in Russia to study the effects of additional heating (or "annealing") at high pressure on synthetic diamonds produced using the BARS equipment (see Malogolovets et al., 1991; Teslenko, 1993). These experiments were conducted using the same "split sphere" growth apparatus. These researchers report that heating for four to five hours at up to 2000° to 2200°C and 70 to 80 kbar can both affect the color of the synthetic diamonds and produce changes in their visible and infrared absorption spectra. We do not know the exact treatment procedure used on the three yellow to greenish yellow synthetic diamonds described here, their condition before treatment, or whether the treatment was carried out before or after the samples were faceted.

## MATERIALS AND METHODS

Ten synthetic diamonds were included in this study (see table 1 for descriptions of each) and subjected to all key tests. The four additional samples loaned by Chatham Created Gems (also in table 1) and the three yellow crystals seen in 1990 have the

same gemological properties as the first seven in table 1; they are not discussed further here.

We used standard gemological testing equipment, including a binocular gemological microscope, a long-wave (366 nm) and short-wave (254 nm) Ultraviolet Products U.V. lamp unit (in a darkened room), and both a Beck prism and a Discan digital-scanning diffraction-grating spectroscope. Pye-Unicam 8800 and Hitachi U-4001 spectrophotometers were used to record absorption spectra at room and liquid-nitrogen temperatures over the range 250–850 nm. A Nicolet 60SX Fourier-transform infrared spectrometer was used to record infrared spectra over the range 400–25,000 cm<sup>-1</sup>. Qualitative chemical analysis was carried out using a Tracor X-ray energy-dispersive X-ray fluorescence (EDXRF) system. The cathodoluminescence photos were taken using a Nuclide ELM-2B luminoscope. Luminescence spectra were obtained using a Milton Roy SLM Aminco AB2 series luminescence spectrometer. Excitation was used with a bandpass of 4 nm, and emission was recorded with a bandpass of 1 nm.

## RESULTS

In contrast to the sample groups of gem-quality yellow synthetic diamonds we had examined before, the Russian samples described here exhibit greater variation in their gemological properties. In this section, we will describe the more representative features we have observed—some of which are merely indicators of synthesis, while others are proof. We emphasize that not all of these features are present in all 10 samples. Thus, they should not necessarily all be expected in other samples of this kind of synthetic diamond.

**Color.** The colors of all 10 samples and the four Chatham synthetic diamonds are listed in table 1, using GIA's current terminology for describing the color of fancy-color natural diamonds. The colors in these stones are similar to those of the Sumitomo and De Beers synthetic diamonds (Shigley et al., 1986, 1987), although the cause of the greenish yellow color is different (see later discussion). However, to our knowledge, none of the synthetic diamonds described in the above references had been exposed to post-growth high-heat/temperature treatment conditions.

**Morphology.** Each of the two crystals in the study sample (and the three pieces of similar material

**TABLE 1.** Russian gem-quality synthetic diamonds examined during this study.

Sample no.	Weight (ct)	Shape	Color <sup>a</sup>	Clarity <sup>b</sup>
<b>As-grown</b>				
21476	0.78	Crystal <sup>c</sup>	Y	
21477	0.26	Round brilliant	oY	VS <sub>2</sub>
21478	0.88	Crystal <sup>d</sup>	brY	
21481	0.20	Rectangle	oY	SI <sub>1</sub>
21484	0.18	Hexagon	oY	VS <sub>1</sub>
21485	0.51	Square	Y	VS <sub>1</sub>
21486	0.11	Hexagon	oY	VS <sub>2</sub>
<b>HPHT-treated</b>				
21474	0.17	Rectangle	gY	SI <sub>1</sub>
21475	0.14	Round brilliant	gY	I <sub>1</sub>
21480	0.21	Emerald	Y	VS <sub>1</sub>
<b>As-grown samples loaned by Chatham Created Gems</b>				
21635	0.53	Princess	oY	I <sub>1</sub>
21636	0.11	Round brilliant	Y	VVS <sub>1</sub>
21637	0.32	Crystal <sup>c</sup>	brY	
21638	1.02	Crystal <sup>d</sup>	brY	

<sup>a</sup>Color: Y—yellow, gY—greenish yellow, oY—orange yellow, brY—brownish yellow.

<sup>b</sup>Clarity: Although the GIA Gem Trade Laboratory does not issue grading reports on synthetic diamonds, the faceted samples shown here (if natural) would receive these clarity grades on the basis of their inclusions and other clarity characteristics.

<sup>c</sup>Flattened cuboctahedron.

<sup>d</sup>Modified cuboctahedron.

seen by us in late 1990) exhibited a combination of octahedral, cube, dodecahedral, and/or trapezohedral faces in different relative sizes and arrangements (see figures 1 and 4; for further information on the crystal morphology of natural and synthetic diamonds, see Sunagawa, 1984). The crystal morphology observed on these crystals is the same as that reported on other productions of synthetic diamonds (Shigley et al., 1986, 1987).

**Microscopy.** Examination of these Russian synthetic diamonds with a gemological microscope revealed many of the same kinds of diagnostic features we have reported previously in other gem-quality synthetic diamonds.

**Color Zoning.** One of the two crystals displayed an even yellow color. The other (no. 21478) exhibited some color zoning, with areas of lighter and darker yellow that were separated by graining (best seen using fiber optic illumination).

With only one exception (no. 21484), each of the faceted stones also displayed some form of uneven color zoning (as has been the case with other yellow synthetic diamonds; see Shigley et al., 1986, 1987, 1992). The appearance of the color zoning in a particular sample was influenced not only by the faceted shape and the viewing conditions, but also—more importantly—by the arrangement and relative sizes of the internal growth sectors in the original crystal, their orientation with respect to the faceted shape, and the amount of the growth sectors that remain after faceting. Color zoning was especially prominent in the HPHT-treated samples (see figures 5 and 6).

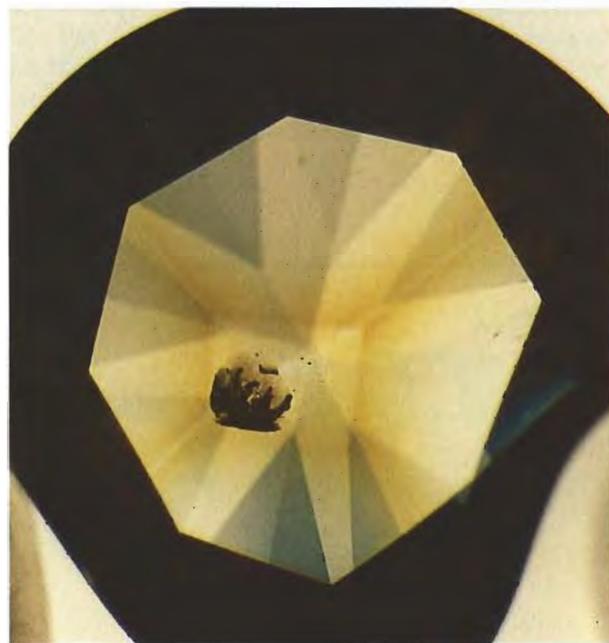
When most visible, this zoning appears (in transmitted light) as a near-colorless to light yellow, square or rectangular, central area surrounded by darker yellow areas, the latter often in a four-fold symmetric arrangement. Some typical patterns are illustrated in figure 7. In most cases, the position of the zoning appeared to correspond to the pattern of graining and uneven U.V. luminescence (see below).

**Graining.** We observed various patterns of surface and/or internal graining in all of the faceted Russian synthetic diamonds, although the surface graining was more difficult to see. For example, figure 8 shows an octagonal, or "stop sign," surface graining pattern on the table facet of the HPHT-treated synthetic diamond no. 21480 (for comparison, see pho-



Figure 4. This 0.78-ct synthetic diamond crystal (no. 21476) shows the arrangement of crystal faces and the location of the seed (the black-appearing square area) on the octahedral face at the base of the crystal. Photomicrograph by John I. Koivula.

Figure 5. Distinct color zoning is seen when 0.14-ct HPHT-treated synthetic diamond no. 21475 is immersed in methylene iodide and viewed perpendicular to the girdle through the pavilion facets. Note the yellow outline of the rectangular area near the center. At each of the four corners of this area, a narrow yellow zone (slightly darker along both sides, and lighter along the center) projects outward toward the edge of the sample. The black-appearing area near the center is a metallic inclusion. Photomicrograph by John I. Koivula.



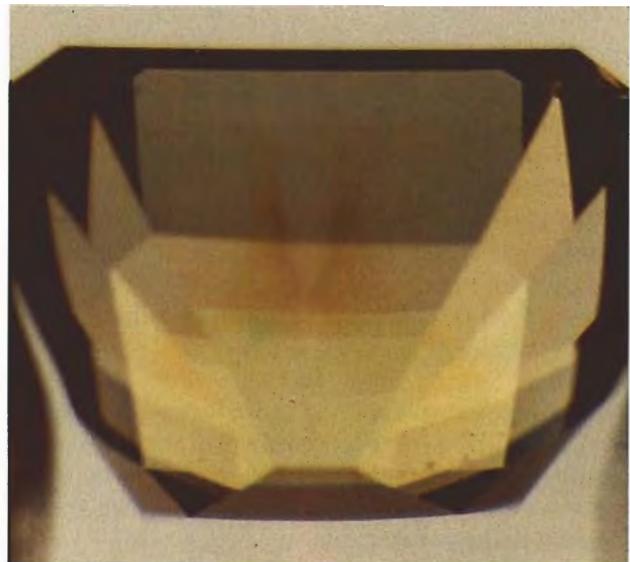
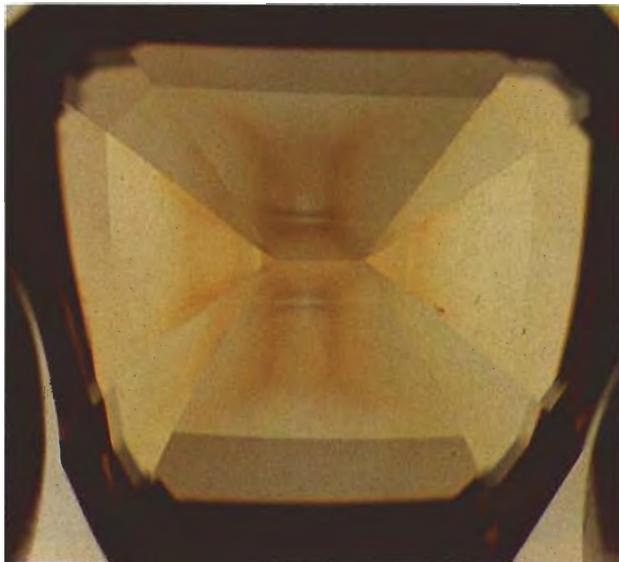


Figure 6. Distinct color zoning is also seen when 0.17-ct HPHT-treated sample 21474 is immersed in methylene iodide and viewed through the culet and the pavilion facets (left). Near the center, a square-shaped area is outlined in yellow. As the sample is rotated toward the girdle (right), a position is reached where this central area appears to broaden toward the crown facets. Photomicrographs by John I. Koivula.

tos in Shigley et al., 1986, 1987). This same sample revealed a pattern of internal graining in the form of a rectangle with graining lines projecting outward from each corner (figure 9; similar to the patterns described for color zoning). Other patterns, such as intersecting graining lines (or planes), were seen in other samples (see, e.g., figures 10 and 11).

*Inclusions.* Large rounded or elongate inclusions with a metallic luster were present in several of the faceted stones and both crystals (figures 12 and 13). In addition, most of the faceted stones exhibited numerous tiny pinpoint inclusions (figure 14). Most of the samples displayed a weak attraction to a sim-

ple magnet, and some showed none at all. We could not establish any relationship between the strength of the magnetic attraction and the size or number of the metallic inclusions present in a given sample.

EDXRF chemical analyses of the samples revealed the presence of nickel (Ni) and iron (Fe) in all but one of them (no. 21485, which contained only Ni), with the X-ray peak for Ni always being more intense than that for Fe (figure 15). Both elements have been reported previously in synthetic diamonds (see Shigley et al., 1987, 1992; Burns and Davies, 1992; Rooney et al., 1993). As expected, we noted no differences in the EDXRF spectra of the as-grown and HPHT-treated samples.

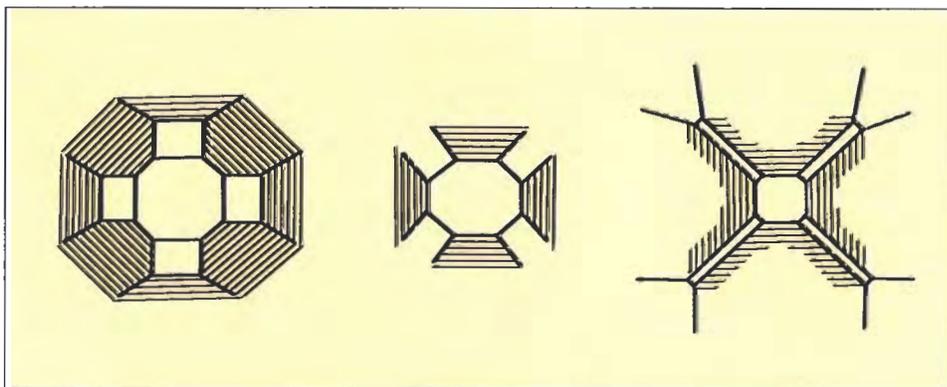
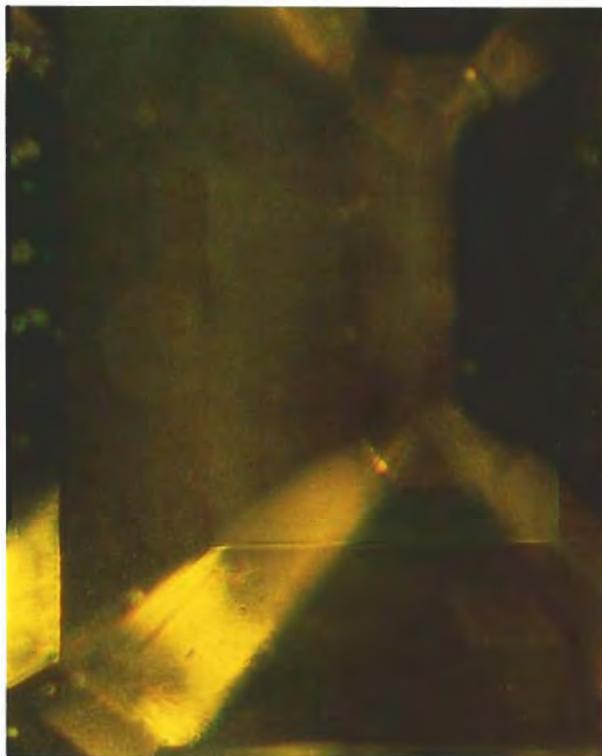
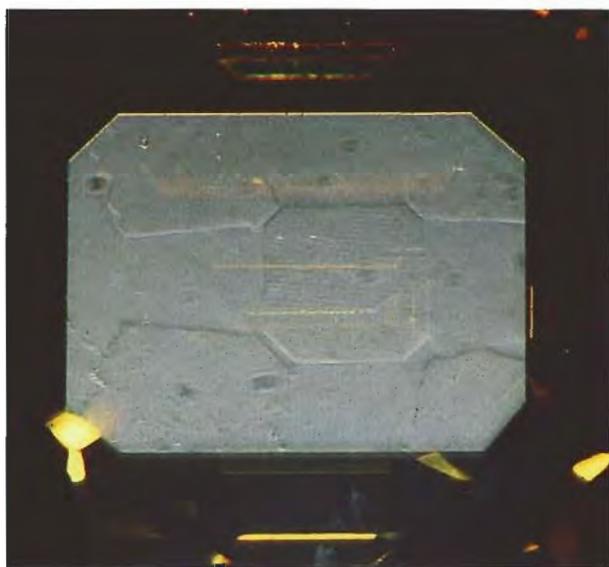


Figure 7. These three configurations are typical of color and luminescence zoning seen in the Russian synthetic diamonds examined. Patterns intermediate between these, or representing only a portion of one of them, have also been observed.

*Appearance in Polarized Light.* Examination of crystal no. 21476 with crossed polarizing filters revealed an anomalous birefringence (i.e., "strain") pattern in the form of a black or gray cross. Faceting of such a crystal might lead to more distorted-appearing anomalous birefringence where the cross pattern can no longer be recognized. In general, the eight faceted samples exhibited only weak anomalous birefringence in patterns that were usually difficult to see because of the small size of the samples and the fact that they were faceted.

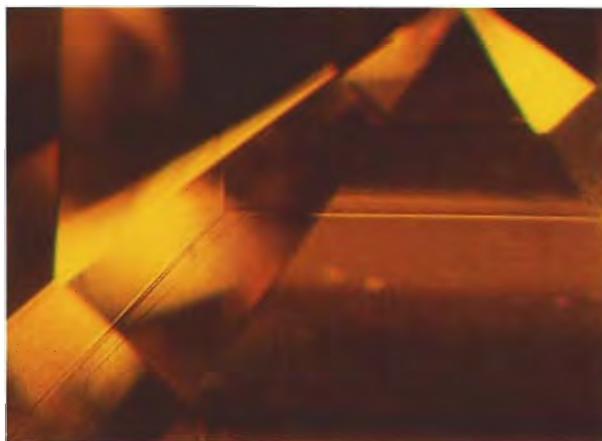
**Ultraviolet Luminescence.** The U.V. luminescence of the 10 samples is summarized in table 2. Since luminescence in these synthetic diamonds occurs mostly in certain internal growth sectors or at the borders between sectors, the luminescence color and intensity that one observes may depend on the orientation of the sample and, for a cut stone, how the faceted shape intersected the growth-sector pattern of the original crystal (again, see figure 7). The observations we describe below are based on what we saw for those growth sectors of the sample that luminesced most intensely.

*Figure 8. Indirect reflected light reveals octagonal surface graining on the table facet of HPHT-treated sample 21480. This octagon, from which four "arms" emanate, marks the intersection of the plane of the table facet and the arrangement of internal growth sectors in the synthetic diamond. The same growth-sector arrangement is visible in the cathodoluminescence pattern. Photomicrograph by John I. Koivula; magnified 25 $\times$ .*



*Figure 9. In sample 21480, internal graining is evident as a rectangular area seen beneath the table facet. Graining lines also project outward from each corner of the rectangle. The green seen in some parts of the sample is caused by luminescence to visible light. Note also the tiny pinpoint inclusions. Photomicrograph by John I. Koivula; magnified 35 $\times$ .*

*Figure 10. Internal graining, in the form of intersecting lines, is visible through the pavilion facets of sample 21485. Similar graining patterns were seen beneath each of the four corners of the pavilion. Photomicrograph by John I. Koivula; magnified 25 $\times$ .*



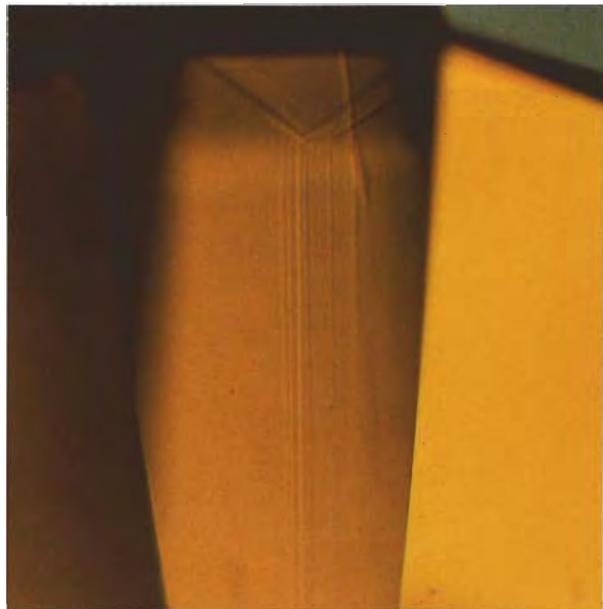


Figure 11. A different kind of internal graining, also in the form of intersecting lines, is seen through the pavilion facets of the same synthetic diamond shown in figure 10. Photomicrograph by John I. Koivula; magnified 40 $\times$ .



Figure 13. This group of elongate, metallic inclusions beneath the crown facets of sample 21481 is typical of the metallic inclusions seen in some of the faceted Russian synthetic diamonds. Photomicrograph by John I. Koivula; magnified 35 $\times$ .

In contrast to previous reports on other yellow synthetic diamonds (see, e.g., Shigley et al., 1986, 1987, 1992), only one as-grown sample (no. 21485) was inert to long-wave U.V. radiation but fluoresced to short-wave U.V. (this sample, incidentally, is the purest type-Ib sample; see discussion of infrared spectroscopy below). For all seven as-grown samples, the fluorescence to short-wave U.V. was

Figure 12. Opaque inclusions of flux metal (largest, 0.9 mm long) are seen here near the outer edge of crystal no. 21476. The elongate, rounded shape is characteristic of this kind of metallic inclusion in synthetic diamonds. Photomicrograph by John I. Koivula; magnified 20 $\times$ .



Figure 14. This large metallic inclusion, accompanied by numerous pinpoint inclusions, was seen beneath the table facet of HPHT-treated sample 21475 (see also figure 5). Note the rectangular area marked by graining; the border of this rectangular area is outlined by sectors that luminesce green to visible light. Photomicrograph by John I. Koivula; magnified 35 $\times$ .



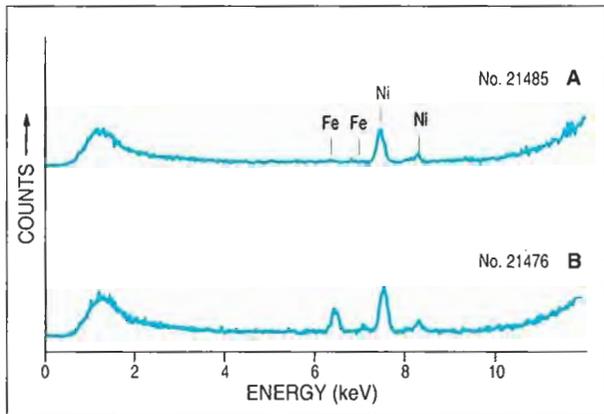
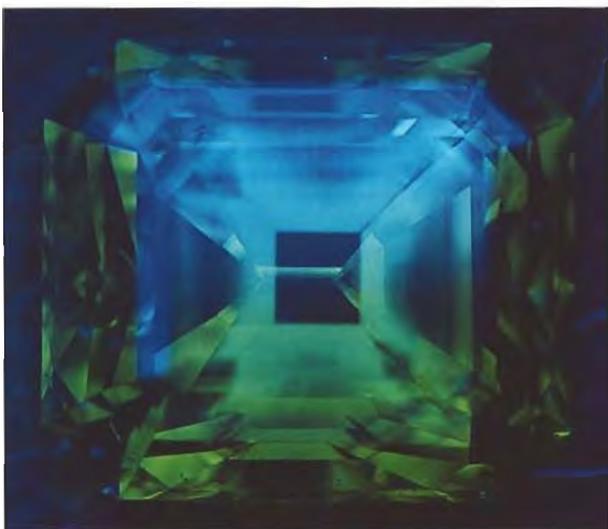


Figure 15. These two EDXRF spectra show the presence of nickel (Ni) and/or iron (Fe) in the metallic inclusions in these synthetic diamonds.

more intense than or equal to the long-wave U.V. reaction. However, all three HPHT-treated samples fluoresced more intensely to long-wave than to short-wave U.V. radiation, and their fluorescence to both wavelengths was greater than that of the as-grown samples (again, see table 2). Furthermore, these three samples exhibited moderate to strong yellow phosphorescence when either U.V. lamp

Figure 16. Zoned long-wave U.V. fluorescence was observed in faceted as-grown Russian yellow synthetic diamond no. 21481. Some internal growth sectors (at the center and near the corners) are inert, but others fluoresce greenish yellow. The blue color is a reflection from the U.V. lamp off the crown facets. Photomicrograph by John I. Koivula.



was turned off. Figures 16 and 17 illustrate the uneven distribution of the U.V. luminescence that is typical of these synthetic diamonds. This pattern is similar, again, to that observed for the color zoning and graining.

**Luminescence Spectroscopy.** A three-dimensional plot of the emission as a function of excitation wavelength for sample 21480 (HPHT treated) is shown in figure 18. The greenish yellow fluorescence of the Russian synthetic diamonds appears in the emission spectrum as a broad band with an

TABLE 2. Ultraviolet luminescence of the Russian synthetic diamonds examined.

Luminescence behavior	As-grown crystals	As-grown cut stones	HPHT-treated cut stones
<b>Long-wave U.V. fluorescence</b>			
Color	Yellow	Greenish yellow to yellow	Greenish yellow
Intensity	Weak	Weak to strong <sup>a</sup>	Very strong
Appearance	Turbid <sup>b</sup>	Turbid	Turbid
Distribution	Uneven <sup>c</sup>	Uneven	Uneven
<b>Long-wave U.V. phosphorescence</b>			
Color	None	None	Yellow
Intensity			Moderate to strong
Duration			30–45 sec.
<b>Short-wave U.V. fluorescence</b>			
Color	Yellow	Yellowish green to green	Yellowish green
Intensity	Weak	Weak to strong	Strong
Appearance	Turbid	Turbid	Turbid
Distribution	Uneven	Uneven	Uneven
<b>Short-wave U.V. phosphorescence</b>			
Color	None	None <sup>d</sup>	Yellow
Intensity			Moderate to strong
Duration			30–60 sec.

<sup>a</sup>As-grown sample 21485 was inert to long-wave U.V. radiation.

<sup>b</sup>A turbid appearance is also known as "chalky" fluorescence.

<sup>c</sup>An uneven distribution indicates that the fluorescence emission is related to the arrangement of internal growth sectors in the diamond. Some sectors fluoresce with a weak to strong intensity, while other sectors are inert.

<sup>d</sup>As-grown sample 21486 exhibited moderate yellow phosphorescence for about 30 seconds when the short-wave U.V. lamp was turned off.

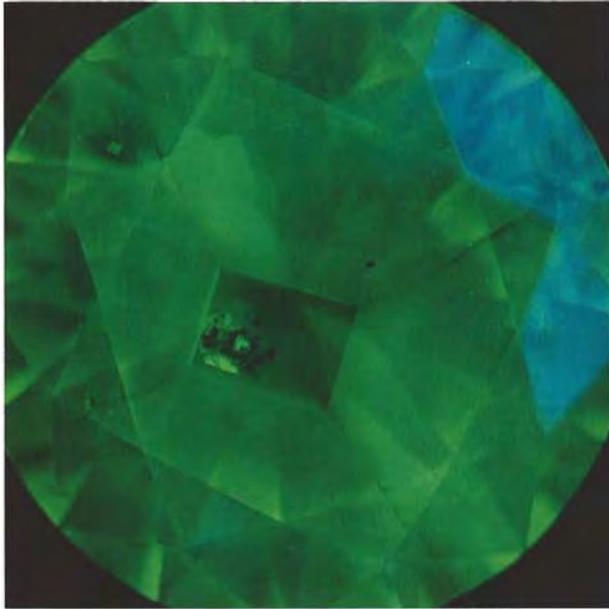


Figure 17. Zoned long-wave U.V. fluorescence was observed in greenish yellow HPHT-treated Russian synthetic diamond no. 21475. When compared to the pattern of color zoning (see figure 5), the darker yellow areas appear to be fluorescing greenish yellow, while the central colorless area is inert. The blue color is a reflection from the U.V. lamp off several crown facets. Photomicrograph by John I. Koivula.

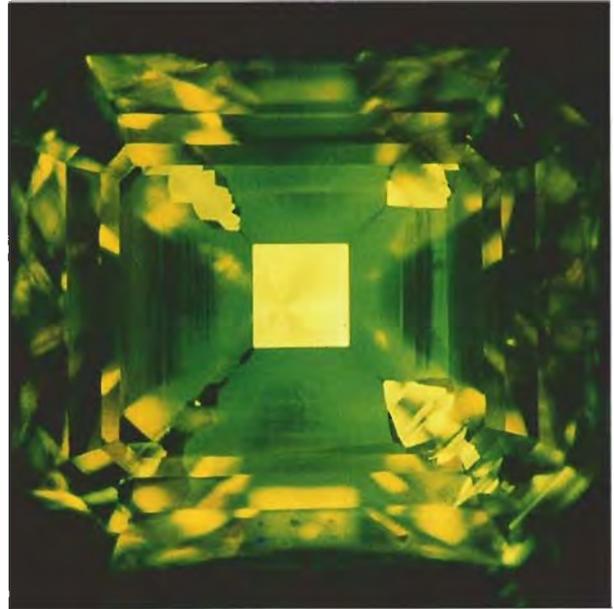


Figure 19. Cathodoluminescence of faceted yellow synthetic diamond sample 21481 (compare figure 16) readily reveals the arrangement of internal growth sectors, with some sectors at the center and the four corners luminescing yellow, and others emitting a greenish yellow. Note that the sectors that are not fluorescing to U.V. radiation in figure 16 are luminescing yellow here.

apparent maximum at around 550 nm. Small "dips" on the broad band seen in all the emission spectra are due to superimposed features that closely correspond to those noted in the absorption spectrum of the diamond at room temperature. Additional

weak, sharp emissions were seen at approximately 748, 776, and 795 nm (not visible in figure 18 because of the vertical scale used). The general shape of the emission spectrum, and therefore the color of the fluorescence, remain essentially the

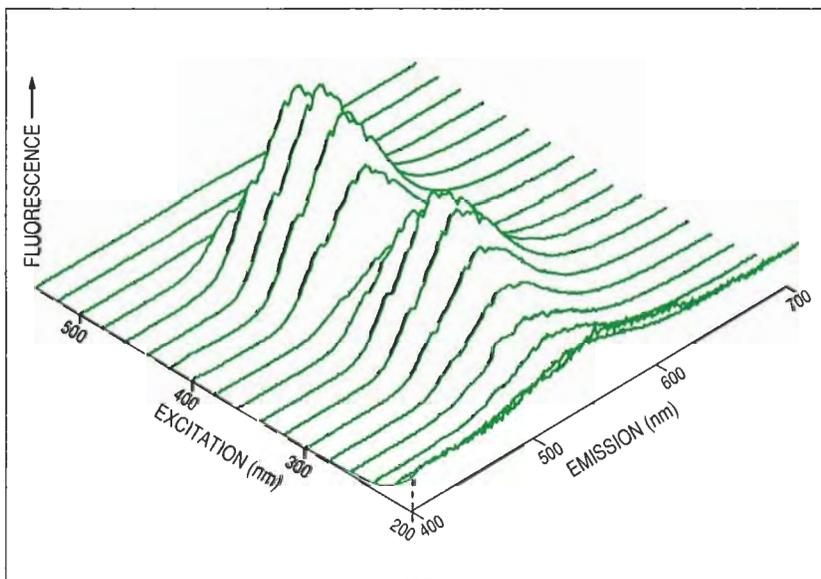


Figure 18. This three-dimensional plot shows the evolution of fluorescence emission (axis on the right) in HPHT-treated sample 21480 as a function of the excitation wavelength (axis on the left). Note that the general shape of the emission stays the same even when the excitation is changed. Artifacts at once and twice the excitation wavelength have been removed for clarity.

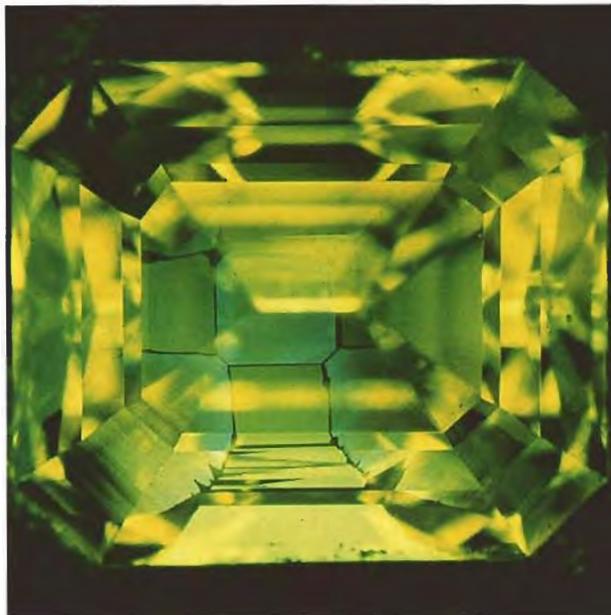


Figure 20. With cathodoluminescence, the different internal growth sectors in HPHT-treated synthetic diamond no. 21480 are seen to luminesce various colors that reveal the arrangement of sectors. Note that the same octagonal pattern seen in the surface graining of this stone (figure 8) is evident in the cathodoluminescence pattern, since both features are related to growth sectors.

same even when the excitation wavelength is changed. However, one can see that the emission intensity is stronger at the 365-nm excitation than at the 255-nm excitation. This confirms that the fluorescence is stronger to long-wave (365 nm) than to short-wave (255 nm) U.V. radiation. Maximum emission intensity is reached for excitation wavelengths of about 350 and 450 nm. The latter is situated in the visible range. Therefore, this diamond actually luminesces more intensely when excited with visible light in the blue range (about 450 nm) than when excited with U.V. radiation.

**Cathodoluminescence.** When exposed to a beam of electrons in a vacuum chamber, these synthetic diamonds emit cathodoluminescence. Typically, the uneven cathodoluminescence pattern, which closely resembles the U.V. fluorescence pattern, is directly related to the arrangement of internal growth sectors (see, e.g., figures 19 and 20). As we and others have reported previously, it is easier to see the growth sectors in a synthetic diamond with cathodoluminescence than with other luminescence techniques (see Woods and Lang, 1975; Shigley et al., 1987; 1993a; Lang and Moore, 1990; Ponahlo, 1992), because the luminescence that aris-

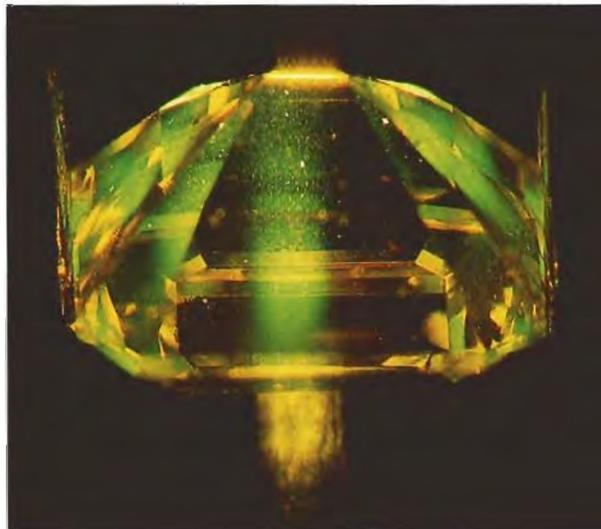


Figure 21. Green luminescence (also referred to as "transmission luminescence") is seen when faceted HPHT-treated sample 21480 is positioned over a strong visible (in this case fiber optic) light. Small pinpoint inclusions within the synthetic diamond are also highlighted. This luminescence to visible light was weaker in the other samples. Photomicrograph by John I. Koivula; magnified 10 $\times$ .

es from the electron beam is more intense than that produced by exposure to U.V. radiation. Consequently, it is an excellent identification tool for this material.

**Luminescence to Visible Light.** All but two (as-grown nos. 21478 and 21484) samples also exhibited an unevenly distributed, weak to moderate intensity, green luminescence when they were positioned over a strong source of visible light (figure 21). It followed the general pattern observed for the other kinds of luminescence; areas that luminesced greenish yellow most strongly to both U.V. and visible light also had a darker yellow body color. We have not seen similar luminescence to visible light in other yellow synthetic diamonds (Shigley et al., 1986, 1987, 1992). Note also that the sample with the most intense green luminescence to visible light (no. 21480) still had a yellow body color. Thus, this luminescence makes no significant contribution to the body color of any of these samples.

**Luminescence to X-rays.** When exposed to X-rays (80 keV, 40 mA), the 10 samples emitted little if any luminescence as compared to a yellow, type-IaA, natural diamond (which luminesced weak yellow). This result is generally consistent with that

reported by Koivula and Fryer (1984, p. 151) for G.E. yellow synthetic diamonds.

**Absorption Spectroscopy (Handheld).** In yellow synthetic diamonds examined previously (Crowningshield, 1971; Koivula and Fryer, 1984; Shigley et al., 1986, 1987), no sharp absorption bands were visible when the samples were viewed with a handheld spectroscope, even after the samples were cooled. However, all except two (nos. 21484 and 21486, both as-grown) of the Russian synthetic diamonds did exhibit one or more sharp absorption bands that could be seen with a spectroscope when the samples had been cooled to low temperature with a spray refrigerant (for further information on this technique, see Hofer and Manson, 1981). Table 3 includes a compilation of these sharp absorption bands. Note that the ease with which sharp bands can be seen will vary depending on factors such as the type of spectroscope used and the sample's viewing position. In addition, locations of sharp bands seen with a spectroscope can usually only be estimated. Thus, each absorption band listed in table 3 is shown with an accurate wavelength value, determined with the spectrophotometer, to prevent confusion with the information presented below.

The visible spectra for each of the seven as-grown samples displayed increasing absorption toward the ultraviolet, beginning at somewhere between 450 and 500 nm. Those for the two crystals and three of the five as-grown faceted stones also displayed a sharp absorption band, with weak-to-moderate intensity, at about 658 nm. An additional weak sharp band around 637 nm was observed in the spectrum of sample 21485; one at approximately 527 nm was seen in sample 21481.

The handheld spectroscope revealed quite different visible spectra for the three HPHT-treated synthetic diamonds. All three samples exhibited much less absorption below 450 nm, plus a number of sharp absorption bands between 470 and 600 nm when they were cooled with a spray refrigerant. The bands observed in each of the three samples were as follows: no. 21474—473, 477, 478, 481, and 547 nm; no. 21475—473, 478, 481, 547, and 553 nm; and no. 21480—473, 478, 481, 503, 511, 518, 527, 547, and 553 nm.

**Ultraviolet-Visible Absorption Spectrometry. As-Grown Samples.** Figure 22A presents the room-temperature absorption spectrum of an as-grown

**TABLE 3.** Absorption bands seen in the ultraviolet, visible, and near-infrared spectra of the Russian synthetic diamonds, listed by decreasing wavelength.

Wavelength (rounded to closest nm)	U <sup>a</sup>	T <sup>b</sup>	Handheld spectroscope (at LT) <sup>c</sup>	Comments
792	Y	Y		Ni-related <sup>d,f,g</sup>
767		Y		Visible in published spectrum but not discussed <sup>d</sup>
732	Y			Ni- and N-related <sup>d,f</sup>
711	Y			Ni- and N-related <sup>d,f</sup>
691	Y			Ni- and N-related <sup>d,f</sup>
671	Y			Ni- and N-related <sup>d</sup>
660	Y	Y		
658	Y		Yes	Ni-related <sup>e,f</sup>
649	Y			Ni-related <sup>e</sup>
647	Y			Ni-related <sup>e</sup>
639	Y	Y		
637	Y		Yes	Ni-related <sup>e</sup>
627	Y			Ni-related <sup>e</sup>
623		Y		
617	Y			Ni-related <sup>e</sup>
607		Y		
592		Y		
582		Y		
563		Y		
553	Y	Y	Yes	Ni- and N-related <sup>d</sup>
547	Y	Y	Yes	Ni- and N-related <sup>d</sup>
540		Y		Ni- and N-related <sup>d,f</sup>
527	Y	Y	Yes	Ni- and N-related <sup>d,f</sup>
520		Y		Ni- and N-related <sup>d</sup>
518		Y	Yes	Ni- and N-related <sup>d</sup>
516	Y	Y		Ni- and N-related <sup>d</sup>
511	Y	Y	Yes	Ni- and N-related <sup>d</sup>
506		Y		
503		Y	Yes	Ni- and N-related <sup>d,f</sup>
500	Y	Y		Ni- and N-related <sup>d</sup>
494	Y	Y		Ni-related <sup>e</sup>
491		Y		Ni- and N-related <sup>d</sup>
481		Y	Yes	Ni- and N-related <sup>d</sup>
478		Y	Yes	Ni- and N-related <sup>d</sup>
477		Y	Yes	Ni- and N-related <sup>d</sup>
473	Y	Y	Yes	Ni- and N-related <sup>d</sup>
468	Y	Y		Ni- and N-related <sup>d</sup>

<sup>a</sup>U: Observed in the spectral curves of the as-grown samples (figures 23A–23B).

<sup>b</sup>T: Observed in the spectral curves of the HPHT-treated samples (figures 23C–23D).

<sup>c</sup>Absorption bands visible with either a Beck or Discan spectroscope when the sample is cooled to low temperature with a spray refrigerant.

<sup>d</sup>Observed by Lawson and Kanda (1993a, 1993b) in nitrogen-containing synthetic diamonds that were grown in nickel and subsequently annealed to 1600°–1900°C.

<sup>e</sup>Observed by Collins and Spear (1982).

<sup>f</sup>Observed by Yelissev et al. (1992) in nitrogen-containing synthetic diamonds that were grown in nickel-iron.

<sup>g</sup>Observed by Vins et al. (1991) in nitrogen-containing synthetic diamonds that were grown in nickel-iron and subsequently annealed above 1400°C.

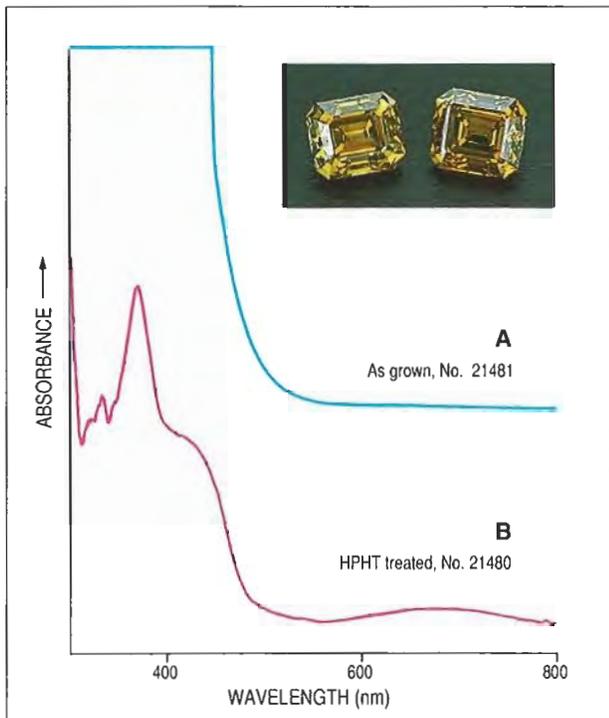


Figure 22. The room-temperature absorption spectra of orangy yellow as-grown sample 21481 (stone at right in photo) and yellow HPHT-treated sample 21480 (stone at left) reveals increasing absorption toward the ultraviolet, which gives rise to the yellow color in both synthetic diamonds. Less absorption below about 500 nm in the HPHT-treated sample explains why it is lighter yellow than the as-grown sample. The broad absorption region between 600 and 800 nm causes the green component in the color of some of the samples. Although too weak in spectrum B to affect sample 21480, it was sufficiently intense in the spectra of HPHT-treated samples 21474 and 21475 to produce a greenish yellow body color. The two spectra are offset vertically for clarity; both have been normalized by dividing the measured absorption by the path length of light through each sample.

sample. The yellow color is caused by an absorption that continuously increases from the near-infrared toward the ultraviolet, becoming very intense at wavelengths less than 550 nm.

The low-temperature absorption spectra in figure 23 illustrate the variety of sharp absorption bands noted in all of these synthetic diamonds (again, see table 3). In the seven as-grown samples, the important spectral features can be categorized as follows:

1. A weak, sharp band at 527 nm, present in two samples (see, e.g., figure 23A).
2. A group of up to six bands, from 617 to 658 nm, with intensities that were always in the same relative proportion to one another. One or more bands of this group were present in all the as-grown samples. The strongest band, and sometimes the only one visible in the spectrum, is at 658 nm (again, see figure 23A and B). The remaining bands are at 617, 627, 637, 647, and 649 nm.
3. A group of four distinct, moderately broad absorption bands from 671 to 732 nm (with the last being the most intense) that were observed in three of the as-grown samples. The bands are at 671, 691, 711, and 732 nm. One or more of the bands in this group were present in the spectra of all the as-grown samples.
4. Weak, sharp bands at 468, 473, 494, and 500 nm, seen in only one sample.
5. A weak, sharp band at 792 nm seen in the spectra of two samples.

*HPHT-Treated Samples.* The spectra of the HPHT-treated synthetic diamonds were quite distinctive, and featured an even greater number of absorption bands. Comparison of the two room-temperature spectra in figure 22 shows that, for like sample thicknesses, the HPHT-treated sample exhibits less absorption in the region where there was "total absorption" for the as-grown samples (i.e., below about 550 nm). Therefore, HPHT-treatment increases the transparency of these synthetic diamonds in the 300 to 500 nm range. In particular, two broad absorption bands, one at about 400 nm and one with an apparent maximum at about 425 nm, are present in figure 22B. The general shape of the absorption is a continuous increase toward the ultraviolet, which again explains the dominant yellow color.

Superimposed on this dominant feature is the broad band with an apparent maximum at 700 nm. It is particularly well defined in the spectra of the greenish yellow samples (see figure 23C). This broad band, and the more intense absorption below 550 nm, are responsible for the transmission "window" in the greenish yellow region of the spectrum (at about 560 nm) and, hence, the greenish yellow color of sample nos. 21474 and 21475. This broad band is weaker in the spectrum of sample 21480

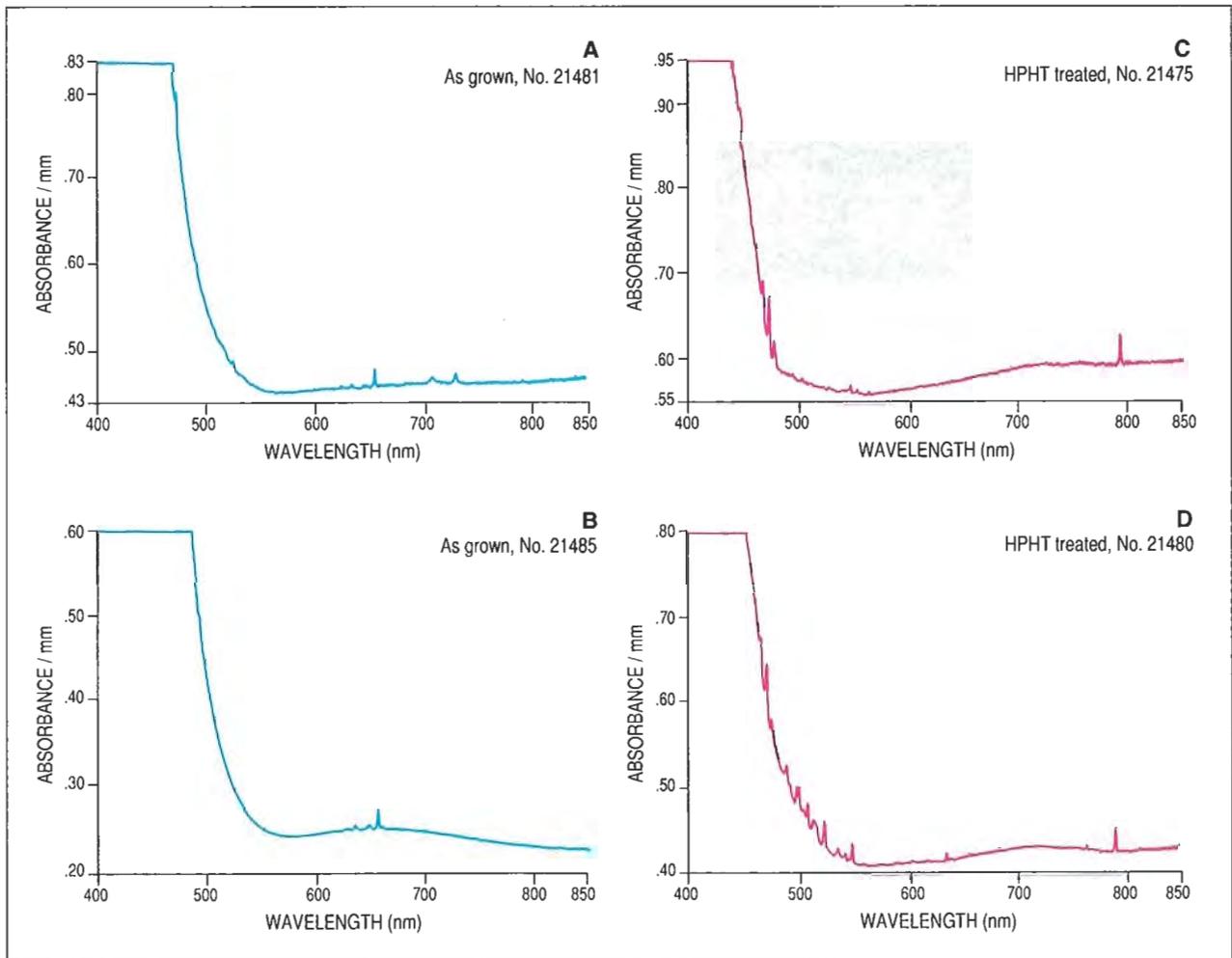


Figure 23. These visible-range absorption spectra of two yellow as-grown and two HPHT-treated Russian synthetic diamonds were recorded at liquid-nitrogen temperature. In addition to the increasing absorption toward the ultraviolet and the weak broad absorption region centered at about 700 nm (evident in spectra B, C, and D), all four spectra display a number of sharp absorption bands, which are listed in table 3. To normalize the absorbance values for the four spectra, we divided them by the appropriate approximate path length of light through the sample. Because of the vertical scale chosen to illustrate these four spectra, some weak absorption bands described in the text, and listed in table 3, may not be visible here.

(figures 22B, 23D), which may explain why this sample is yellow and not greenish yellow.

The spectra of the HPHT-treated samples, like those of their as-grown counterparts, show a number of sharp bands in the visible and near-infrared ranges, although most of these bands are at different positions (again, see the four spectra in figure 23), and there are even more of them. We noted the following bands in the spectra of the HPHT-treated samples:

1. A single sharp band at about 494 nm, seen in two samples (figures 23C and D).
2. A series of sharp bands that span the wave-

length range from 460 to 660 nm. At least part of this series of bands is present in the spectra of all three HPHT-treated samples. In sample 21480, in which these absorptions were most intense, we were able to distinguish 25 sharp bands (see table 3 and figure 23D), as well as an apparently unrelated weak band at 767 nm. The more intense of these absorption bands can be seen with the handheld spectroscope (using a spray refrigerant). Although some of them might be close to absorption lines seen in the spectra of natural colored diamonds (such as the H3 absorption band at 503 nm), the pattern that

the bands form in the spectra of synthetic diamonds is unique, and helps identify them as part of the system under discussion.

3. The 792-nm absorption, which was observed only as a weak feature in two as-grown samples, was present in the spectra of all of the HPHT-treated samples as a sharp, relatively intense peak (figures 23C and D), even at room temperature.

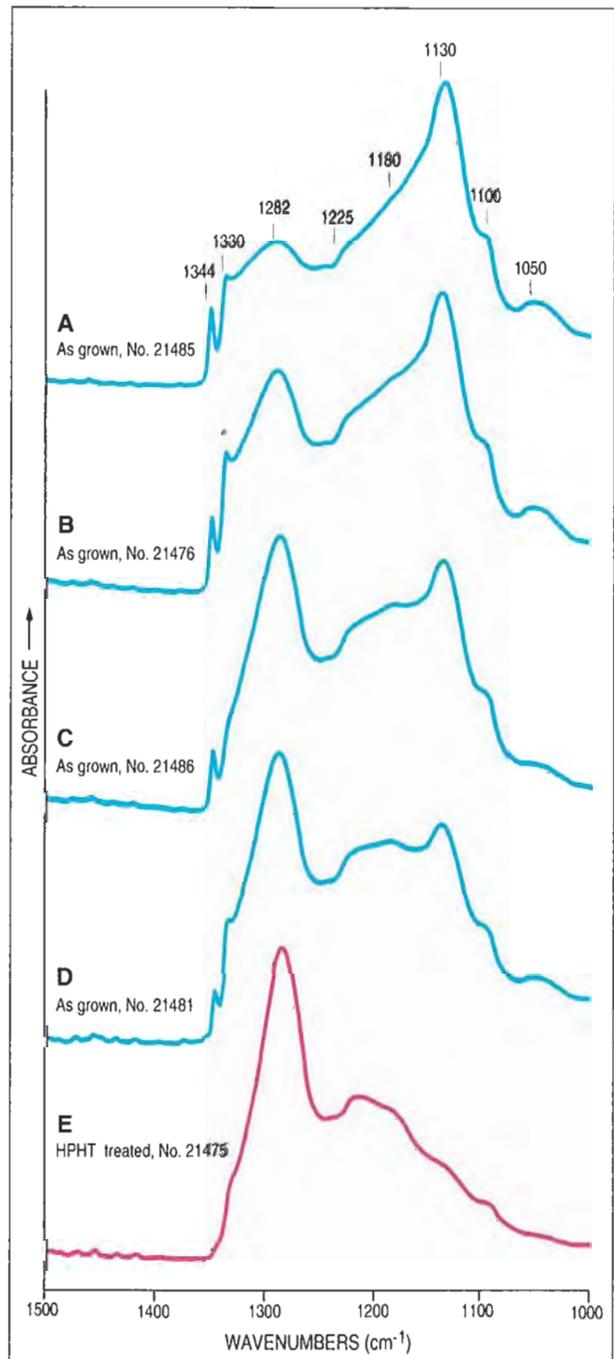
The spectra of the HPHT-treated samples did not show the group of six bands, with the strongest peak at 658 nm, that was described above for the as-grown samples.

**Infrared Absorption Spectroscopy.** The mid-infrared absorption spectra of selected Russian synthetic diamonds are partially illustrated in figure 24. All as-grown samples showed a mixture in variable proportions of type-Ib (singly substitutional nitrogen) and type-IaA (paired nitrogen atoms) diamond. In addition, the infrared spectra of several of the as-grown samples revealed some weak type-IaB features. Since the peak heights of the absorptions in the "nitrogen region" (approximately 1344 to 1000  $\text{cm}^{-1}$ ) are equal to or less than those of the neighboring intrinsic diamond absorptions (between approximately 3900 and 1400  $\text{cm}^{-1}$ ), it appears that these synthetic diamonds contain only moderate amounts of nitrogen. A feature at 1050  $\text{cm}^{-1}$  was

observed in all of the as-grown samples, but was absent from the spectra of HPHT-treated stones.

In contrast, all of the HPHT-treated samples proved to be nearly pure type-IaA diamond. The presence of a weak, residual 1344  $\text{cm}^{-1}$  peak indicates that only a very small proportion of type-Ib nitrogen remains in the HPHT-treated samples.

Figure 24. These mid-infrared absorption spectra (in the "nitrogen region") of four as-grown synthetic diamonds and one HPHT-treated sample reveal the different diamond types represented. Type-Ib diamonds are characterized by a sharp band at about 1344  $\text{cm}^{-1}$  and a broader band at 1130  $\text{cm}^{-1}$ . Type-IaA diamonds have a broad band at about 1282  $\text{cm}^{-1}$  and weaker bands at about 1225 and 1180  $\text{cm}^{-1}$ . Type-IaB diamonds have a sharp band at about 1330 and a broader band at about 1180  $\text{cm}^{-1}$  (see Field, 1992, p. 683). The spectra of the four as-grown synthetic diamonds show a range from an almost-pure type-Ib (A) to a mixture of type-Ib with, finally, a dominant component of type-IaA (D). Spectra A, B, and D also show a minor type-IaB component. The spectra of the three HPHT-treated stones are identical to one another in this region of the infrared, and are typical of an almost pure type-IaA diamond (E). The five spectra have been offset vertically for clarity.



## DISCUSSION

**Comparison to Other Synthetic Diamonds.** Overall, we observed much greater variability from sample to sample in the Russian synthetic diamonds we studied than in any previous group of gem-quality synthetic diamonds. This is probably because of the growth technique used, and the fact that only one stone may be grown at a time, with considerable variability possible between production runs. Even so, we observed that these Russian synthetic diamonds have some gemological properties that are similar to, and some that are different from, other yellow and greenish yellow synthetic diamonds that we have examined.

For example, we have seen the yellow and greenish yellow colors described here in other synthetic diamonds (although, as discussed below, produced by different factors). In addition, the cube, dodecahedral, and trapezohedral faces identified on the Russian synthetic diamonds have also been reported on crystals of other gem-quality synthetic diamonds (Shigley et al., 1986; 1987; see also Rooney et al., 1993). The identification of cube faces and related internal growth sectors proves that these Russian samples are synthetic.

The color zoning, graining, and weak anomalous birefringence patterns seen in these Russian samples (but varying somewhat from one sample to the next) are generally similar to what we have observed in other yellow synthetic diamonds; thus they remain diagnostic identification features. Note, however, that the patterns of color zoning differ somewhat from those we have illustrated previously, probably because of the growth conditions used in Novosibirsk.

Metallic inclusions are among the most conspicuous diagnostic features of gem-quality synthetic diamonds (Shigley et al., 1986, 1987). In other yellow synthetic diamonds, we typically observed these metallic inclusions near the outer edges of the crystals (where they were subject to removal by faceting). In these Russian synthetic diamonds, however, the metallic inclusions were also frequently located deep within the crystals, often near the original seed. This was also true with the yellow and treated-red synthetic diamonds examined recently that we also believe to be of Russian origin (see Moses et al., 1993a, 1993b).

We never observed long-wave U.V. fluorescence of any intensity in other yellow synthetic diamonds, although almost all did exhibit weak-to-strong short-wave U.V. fluorescence, often zoned in

intensity, primarily yellow to greenish or orangy yellow (Shigley et al., 1986, 1987). Thus, these Russian samples (both as-grown and HPHT treated) are the first synthetic diamonds we have examined that display long-wave U.V. fluorescence, in this case weak to very strong yellow to greenish yellow. (For the HPHT-treated samples, the fluorescence is more intense to long-wave than to short-wave U.V.; the reverse is true for the as-grown samples.) Thus, a simple check for short-wave, with no long-wave, U.V. fluorescence will not permit rapid identification of these Russian samples (in contrast to other yellow synthetic diamonds). Nonetheless, the uneven intensity of the U.V. fluorescence (and, similarly, of the cathodoluminescence) still reveals the different internal growth sectors characteristic of synthetic diamonds.

U.V. fluorescence is closely related to diamond type. Among our samples, pure type-Ib diamonds show no long-wave U.V. fluorescence. As the proportion of type-IaA increases, so does the intensity of the long-wave U.V. fluorescence. When the type-Ib and type-IaA components are roughly equal, the intensity of fluorescence to both long- and short-wave U.V. is roughly equal. The fluorescence behavior of the three HPHT-treated samples is typical of type-Ia diamond with no significant type-Ib component.

The three HPHT-treated samples, and one as-grown sample (no. 21486), exhibited moderate to strong yellow phosphorescence to both short- and long-wave U.V. Previously, we noted weak yellow phosphorescence to short-wave U.V. from the greenish yellow De Beers synthetic diamonds (Shigley et al., 1987) and from portions of one of the two 5-ct color-zoned yellow Sumitomo synthetic diamond crystals (Shigley et al., 1992).

Also distinctive of the Russian synthetic diamonds is the weak to moderate green luminescence to visible light seen in most of our samples, a feature we have not seen in other synthetic diamonds. This luminescence may be due to Ni-related defects present only in these Russian samples.

**Cause of Color and Spectral Features.** *U.V.-Visible Absorption.* The general increase in absorption toward the ultraviolet in the as-grown material is typical of type-Ib synthetic yellow diamonds (see Shigley et al., 1986, 1987). It produces a brownish to orangy yellow color. The lighter yellow color of all three HPHT-treated diamonds is due to the reduced absorption in the 400- to 500-nm range. The green-

ish component of the color of two of these stones is contributed by the additional broad absorption band with an apparent maximum at about 700 nm. This band is very weak in the as-grown samples, and so has little if any effect on their color. Because the absorption of this band in the HPHT-treated samples is not overwhelmed by the "type-Ib" nitrogen-related absorption, it plays a more important role in the coloration of these samples. Combined with the increasing absorption toward the ultraviolet, it defines a region of transmission around 560 nm in the yellow-green.

The 700-nm broad band may be a vibronic structure associated with the 793-nm band (C. Welbourn and P. Spear, pers. comm., 1993, based on their examination of our spectra). The 793-nm band has been reported in type-Ib synthetic diamonds grown in nickel and subsequently annealed at 1700°C (Lawson and Kanda, 1993a, 1993b). The well-known greenish color in low-nitrogen, non-HPHT-treated synthetic diamonds (typical of certain types of diamond grit) is due to a broad, nickel-related absorption with an apparent maximum and superimposed sharp peak at 885 nm (Collins, 1990). This feature is very different from the broad band with an apparent maximum at 700 nm seen in the HPHT-treated Russian material. It has never before been described as a cause of a greenish component in yellow synthetic diamonds.

The presence of sharp bands, some of which can be seen with the handheld spectroscope, is one of the new and important characteristics of the Russian production. Most of the absorption features described here, although essentially new to gemology, are not unknown to science.

The series of six absorption bands (from 617 to 658 nm, with the strongest at 658 nm) seen in the as-grown samples was first reported by Davies (1977), but at the time it was wrongly attributed to radiation damage. Collins and Spear (1982) discovered that this series, like the 494-nm band, was caused by Ni-related defects. Collins et al. (1990) later demonstrated that these defects occur only in the octahedral growth sectors of synthetic diamonds, where the nitrogen concentration is relatively high (100 to 300 ppm).

The group of four bands from 671 to 732 nm in some as-grown samples, and the series of sharp bands identified between 460 and 670 nm in our HPHT-treated samples, were first reported by Collins and Stanley (1985) in synthetic diamonds heated in the range 1700°–1900°C. At the time, it

was hypothesized that they represented intermediate states of nitrogen aggregation. Only recently, Lawson and Kanda (1992, 1993a, 1993b) demonstrated that these bands are produced exclusively in diamonds grown using nickel or nickel-containing alloys and, therefore, are presumably all nickel-related defects. Similar results were obtained simultaneously, but independently, by Nadolinny and Yelissev (1992). It is interesting that Lawson and Kanda (1993a, 1993b) also describe yellow-to-green synthetic diamonds. Their green samples contain low concentrations of nitrogen, with nickel dominantly in a positive charge state, whereas their yellow samples contain more nitrogen, with nickel apparently dominant in a negative charge state. Therefore, Lawson and Kanda believe that many of the features observed in Russian synthetic diamonds are due to color centers involving not only nickel, but also nitrogen, presumably as dispersed atoms and A aggregates (see table 3).

Thus far, nickel-related absorption bands have been reported exclusively in synthetic diamonds (Collins and Spear, 1982; Lawson and Kanda, 1993b), so their presence can be considered proof of synthetic origin. They are particularly useful to the gemologist, since those located in the visible spectrum can be seen with a handheld spectroscope if the stone is cooled by a spray refrigerant. For example, the detection of the sharp band at about 658 nm helps identify a yellow diamond as synthetic.

We do not believe that any of the absorption bands we observed in the Russian samples described here are a result of radiation treatment.

*Infrared Absorption.* These Russian samples are the first gem-quality synthetic yellow diamonds we have examined that show a mixture of type-Ib with type-IaA diamond, although the occurrence of both type-Ib (dispersed) and type-IaA (aggregated) nitrogen has been reported in small, nongem diamonds grown for research purposes that were synthesized at relatively high temperatures (Kanda et al., 1990; Vins et al., 1991; Kanda and Yamaoka, 1993). All other gem-quality synthetic yellow diamonds we have examined have been pure type Ib.

The infrared spectra indicate that almost all of the dispersed nitrogen present in the as-grown crystals aggregates during HPHT-treatment to form exclusively A aggregates (pairs of nitrogen atoms). The conversion of type-Ib dispersed nitrogen to A aggregates was first reported by Chrenko and others (1977; see also Evans, 1992). Changes similar to

those reported here have also been described by Lawson and Kanda (1993a, 1993b). To the best of our knowledge, this is the first report of the formation of A aggregates in as-grown crystals. The feature at 1050 cm<sup>-1</sup>, rarely seen in natural diamonds, has been attributed by the same authors (1993b) to a defect related to a positively charged nitrogen ion.

Natural diamonds with strong infrared absorption due to type-IaB nitrogen often have the familiar 415-nm "N3" band in their visible spectrum. However, we did not observe this band in any of the Russian samples, even those with the strongest type-IaB character.

**Comparison to Natural Diamonds.** As with other productions of synthetic diamonds, these Russian samples exhibit several features by which they can be distinguished from natural diamonds of similar color. Specifically, the patterns of color zoning and graining—characteristic of synthetic diamonds—have not been seen in natural diamonds. Metallic inclusions, too, are distinctive of synthetic diamonds (Shigley et al., 1986, 1987). Although both metallic sulfide minerals and metallic iron have been reported in natural diamonds (Sobolev et al., 1981), these inclusions are neither Ni-containing nor Ni-rich, as is the case with the Russian synthetic diamonds examined here. GIA researchers have never encountered an Fe-rich metallic inclusion in a faceted gem-quality natural diamond.

Although metallic inclusions are of diagnostic value, the presence of tiny pinpoint inclusions should not be used as an indication of synthesis because they can occur in both natural and synthetic diamonds with similar appearance.

When comparing the color and absorption spectra of these synthetic and similar natural diamonds, it helps to distinguish between yellow and greenish yellow samples. Most natural yellow diamonds are type-Ia, with blue, yellow, or green U.V. fluorescence (long-wave > short-wave) and an absorption spectrum with a 415-nm and other sharp bands of the "Cape series" (Collins, 1982; Liddicoat, 1987). Type-Ib natural yellow diamonds (sometimes referred to as "canary" diamonds) invariably display some type-Ia character in their infrared spectra, fluoresce yellow or orange-yellow to U.V. radiation (in some cases, with short-wave > long-wave), and have an optical absorption spectrum that lacks sharp absorption bands (Collins, 1982).

The green coloration in greenish yellow type-Ia natural diamonds has several possible causes. These

include the broad absorption centered about 620 nm due to the GR1 band, which is produced by exposure to radiation either in nature or in the laboratory. Alternatively, natural yellow diamonds with strong H3 (503 nm) and H4 (496 nm) spectral bands may exhibit a greenish color as a result of these two color centers luminescing to visible light. Often, the color in yellow to greenish yellow diamonds is concentrated along graining planes that luminesce green (or blue) to visible light. Again, the greenish hue of two of the HPHT-treated samples is not due to either GR1 absorption or green luminescence to visible light.

The Russian synthetic diamonds are either type Ib+IaA (and sometimes a little IaB) or nearly pure type IaA. They exhibit yellow to greenish yellow U.V. luminescence, but with a zonation different from that of their natural counterparts. Their absorption spectra contain sharp bands in wavelength positions that are different than those seen in natural diamonds. These sharp bands, due to Ni, are sometimes visible with a handheld spectroscope. For the most part, they are located where few if any bands are seen in the spectra of natural yellow diamonds (except the bands at 496, 503, and 594 nm seen in some natural- and treated-color yellow diamonds).

**Effects of HPHT Treatment.** The yellow to greenish yellow treated synthetic diamonds described here are the first HPHT-treated synthetic diamonds we have examined. The possibility of treatment could increase the challenge that identifying synthetic diamonds poses for gemologists. In the present case, HPHT treatment appears to have affected the color, the U.V. luminescence, and the visible absorption spectra. Fortunately, HPHT treatment also gives rise to other diagnostic gemological properties; for example, some additional sharp bands are visible at low temperature with the handheld spectroscope. Moreover, it does not alter either the graining or the zoning of color and U.V. luminescence, which patterns remain the same as those seen in the as-grown samples. Finally, it is important to note that we have seen no evidence to date that HPHT treatment can produce a near-colorless synthetic diamond from type-Ib starting material.

## CONCLUSION

The gemological properties of these Russian samples, grown by the BARS technique, expand the

documented criteria for identifying gem-quality synthetic yellow diamonds. In these Russian samples, we observed the characteristic metallic inclusions as well as zoned U.V. luminescence, uneven color, and/or graining patterns related to the arrangements of internal growth sectors.

These Russian synthetic diamonds also exhibited some properties that we had not seen before in other synthetic diamonds. First and foremost, all but one fluoresced to long-wave U.V. radiation, and the HPHT-treated stones fluoresced stronger to long-wave U.V. radiation than to short-wave U.V. (as is typical of fluorescing natural diamonds). One of the as-grown samples, and all three HPHT-treated samples, showed yellow phosphorescence. As a result, U.V. luminescence (i.e., short wave > long wave) can no longer be considered diagnostic for synthetic yellow diamonds. However, the presence of sharp absorption bands between about 460 and 560 nm, and about 637 and 658 nm, are distinctive of Russian synthetic diamonds. Many of these bands can be seen with a handheld spectroscope. The sharp bands, in some cases quite numerous, in the visible absorption spectrum are due to the fact that nickel can enter the crystal structure of dia-

mond and there give rise to one or more color centers. Heat treatment of these yellow synthetic diamonds at high pressure can produce a greenish yellow color.

There is one final point of interest: the significant variation in gemological properties from one sample to the next. Even considering that only 10 stones were studied, this variability was greater than what we have observed in other yellow synthetic diamonds. Several factors may be responsible. The small chamber in the BARS apparatus means that only a few good-quality synthetic diamond crystals (perhaps just one) can be grown at a time (as opposed to batch growth, which is possible with the "belt" apparatus). Each synthetic diamond crystal is, therefore, grown under slightly differing conditions of temperature, pressure, time, system chemistry, and so on. The concentrations of nitrogen and nickel are also likely to vary between crystals. Variability in the conditions of HPHT treatment will also affect the different gemological properties. Thus, gemologists are warned that it may be a challenge to establish simple identification criteria for gem-quality Russian synthetic diamonds that will be valid in all cases.

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