
AN UPDATE ON SUMITOMO GEM-QUALITY SYNTHETIC DIAMONDS

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Examination of two large (5.06 and 5.09 ct) tabular pieces of Sumitomo synthetic diamond revealed that they were cut from single crystals of predominantly cubic {100} and octahedral {111} morphologies, respectively. These two crystal forms exhibit different patterns of color zoning, internal grain-ing, anomalous birefringence ("strain"), and luminescence. Such differences suggest that both crystal morphology and size can greatly affect the properties observed in a synthetic diamond.

Since GIA first reported on the gemological properties of Sumitomo yellow synthetic diamonds (Shigley et al., 1986), continued developments in high-pressure synthesis techniques have led to the production of larger and better-quality diamond crystals by several companies and research organizations. At present, the high-technology applications that have spurred these improvements consume essentially all single-crystal synthetic diamonds manufactured at Sumitomo Electric Industries. However, the availability of larger crystals, and the fact that there is now a steady commercial production of gem-quality

synthetic diamonds, increase the potential impact this material could have on the gem industry.

In 1990, one of us (JES) visited the Sumitomo research facilities in Itami, Japan, and met with the scientists responsible for Sumitomo's production of single-crystal synthetic diamonds. During this visit, Sumitomo loaned GIA two large (5.06 and 5.09 ct) tabular pieces of synthetic diamond (figure 1), which they reported as having been prepared from 9-ct single crystals, the largest size they had produced thus far. These two pieces, although much larger than the Sumitomo synthetic diamonds we had previously studied, were grown using the same high-temperature/high-pressure flux process (see Shigley et al., 1986, 1987). During our meeting, the Sumitomo representatives stated their continuing company policy of selling only tabular, finished pieces of yellow synthetic diamond and only for industrial applications, not for use in jewelry. The two 5-ct samples they loaned us represent the kind of material they are now beginning to manufacture on a limited basis for high-technology applications such as heat sinks and other electronic components.

Gemological examination of these two samples revealed several features we believe to be characteristic of synthetic diamonds and that can help distinguish them from natural gem diamonds. More importantly, however, this study demonstrates how larger synthetic diamonds have many of the same general

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gemological properties (e.g., ultraviolet luminescence behavior, presence of color zoning) as smaller ones, but the visual patterns of these properties might be significantly different.

INSTRUMENTATION AND METHODS

Our examination was conducted using standard gemological testing equipment as well as other laboratory instrumentation. The former included a binocular gemological microscope, a long-wave (366 nm) and short-wave (254 nm) ultraviolet lamp unit, a Beck prism spectroscope, and a DISCAN digital-scanning diffraction-grating spectroscope. A Pye-Unicam Model 8800 spectrophotometer was used to record visible spectra at liquid-nitrogen temperatures over the range 250–850 nm. A Nicolet Model 60SX Fourier-Transform infrared spectrometer was used to record infrared spectra over the range 400–16,000 cm^{-1} . Observations of cathodoluminescence were made using a Nuclide Model ELM-2B luminoscope. Measurements of interfacial angles on the two samples, to document crystal morphology, were made with a Häber optical goniometer. Qualitative chemical analysis was carried out using a Tracor X-Ray energy-dispersive X-ray fluorescence (EDXRF) system.

DESCRIPTION OF THE SAMPLES

Sample 1 weighs 5.06 ct and measures $11.37 \times 11.12 \times 2.40$ mm. This tabular piece has two large polished surfaces; at right angles to these surfaces, portions of the original, unpolished crystal faces occur around the narrow sides (figure 2). The square shape and the arrangement of the remaining crystal faces suggest that this sample was prepared from a predominantly cube-shaped crystal. The four narrow sides are cube {100} faces (as are the orientations of the two polished surfaces). At the corners there are smaller octahedral {111}, dodecahedral {110}, and trapezohedral ({113}, {115}) faces, all of varying arrangement and relative size (see Rooney, 1992). When examined with reflected light, the original crystal surfaces are smooth to slightly rough. Occasionally, small areas display a subtle dendritic pattern that is an imprint of the solidified flux metal in which the crystals grew (see Shigley et al., 1986; Frank et al., 1990).

The overall color of this sample is brownish yellow. It contains eye-visible areas of brown graining parallel to the cube {100} faces, a central brownish yellow area free of graining, and narrow, very light yellow-to-colorless-to-blue zones beneath the corners

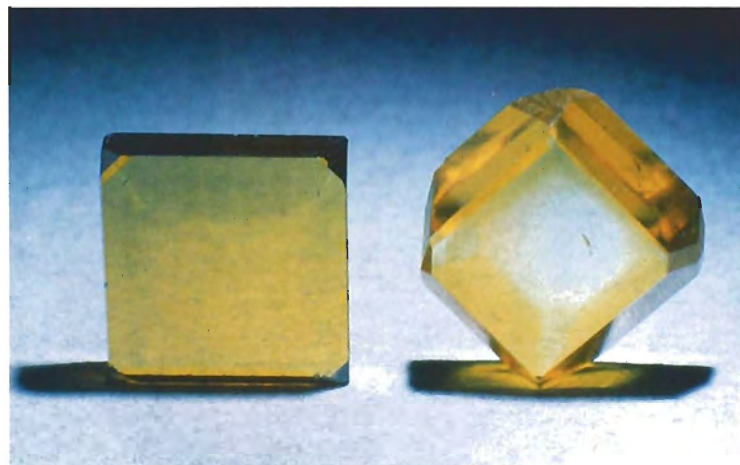
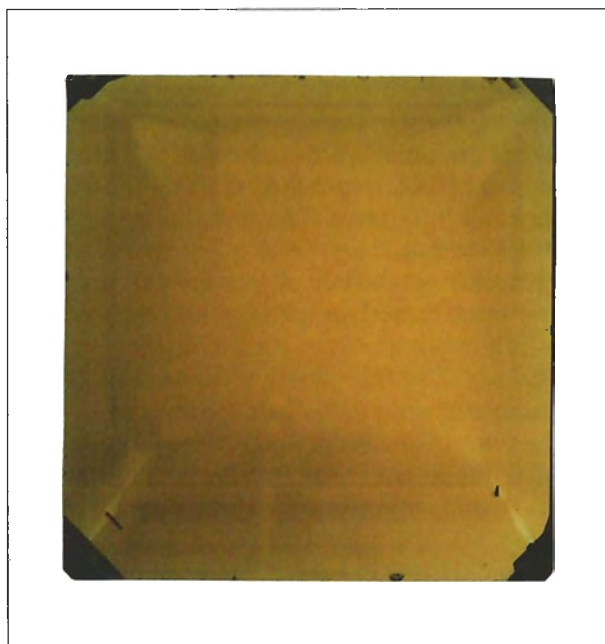


Figure 1. These two polished, tabular samples of Sumitomo synthetic diamond were reportedly prepared from approximately 9-ct crystals. In the text, they are referred to as Sample 1 (5.06 ct, left) and Sample 2 (5.09 ct, right). Photo by Robert Weldon.

Figure 2. Sample 1 exhibits the morphology of a cube-shaped crystal and is predominantly brownish yellow. It contains areas of brown planar graining, as well as zones of darker and lighter brownish yellow and even very small near-colorless zones. Note the two tiny, dark metallic inclusions near the two corners. Photomicrograph by John I. Koivula.



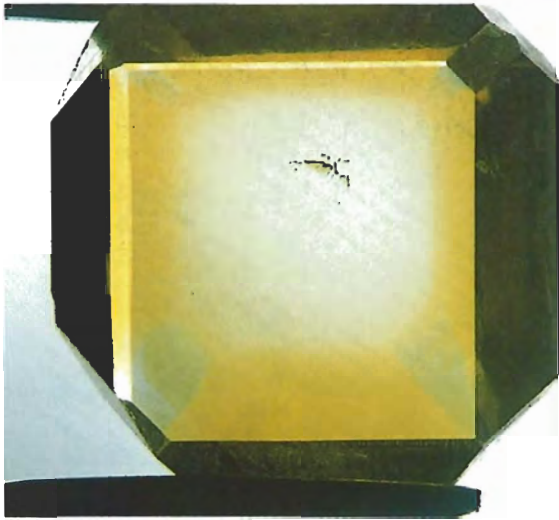


Figure 3. Sample 2 was cut from an octahedral crystal. It displays prominent color zoning, with yellow areas near the outer edges, a colorless area at the center, and narrow blue areas under each of the four corners. These color variations are due to differences in impurity content between the various internal growth sectors in the crystal. In the upper center of the crystal is a small group of metal flux inclusions. Photomicrograph by John I. Koivula.

of the sample (again, see figure 2). Two rounded, elongate, metallic-appearing inclusions (between 0.2 and 0.5 mm long) are also visible 1–2 mm below the surface near the corners of the sample.

Sample 2 weighs 5.09 ct and measures 12.10 × 11.89 × 2.88 mm. It is also tabular with two polished surfaces (figure 3). Along the four narrow sides, which are oriented at a 45° angle to the polished surfaces, there are larger, unpolished octahedral {111} faces and smaller cube {100}, trapezohedral ({113}, {115}), and dodecahedral {110} faces. The morphology of these faces suggests that this sample was prepared from a predominantly octahedron-shaped crystal. Since the most common crystal morphology for synthetic diamonds is a cuboctahedron, the dominant {100} and {111} forms of these two crystals are unusual (for a further discussion, see Frank et al., 1990).

The two polished surfaces on Sample 2 are, like Sample 1, parallel to cube faces. When the rough crystal faces of this sample were examined with a gemological microscope, they appeared to be smooth to slightly undulating. In reflected light, however, the faces did show some distinctive surface markings—a faint dendritic pattern on cube, trapezohedral, and

octahedral faces, and parallel striations on dodecahedral faces. Again, these surface markings are imprints of the solidified flux metal (Frank et al., 1990), and they differ in appearance from the growth markings typically seen on natural diamond crystals.

The most remarkable feature of Sample 2, however, is its striking color zoning (again, see figure 3). There is also a small group of rounded or elongate, crystallographically oriented inclusions with a metallic appearance in the central area.

INTERNAL GROWTH SECTORS

In GIA's original description of yellow gem-quality Sumitomo synthetic diamonds (Shigley et al., 1986), we noted the conspicuous zoning of certain gemological features such as color, reaction to short-wave U.V. radiation, and graining. Rapid crystal growth in the laboratory favors the formation of large cubic {100} (and, to a lesser extent, dodecahedral {110} and trapezohedral {113}, {115}) growth sectors (Woods and Lang, 1975; Burns et al., 1990; Frank et al., 1990). These sectors are not present in natural diamond crystals, which grow only along octahedral {111} planes (i.e., crystal faces). A segregation of impurities (such as nitrogen) during crystallization within and between different growth sectors in synthetic diamond can cause a visible zonation of features such as color and ultraviolet luminescence (Burns et al., 1990; Frank et al., 1990).

Each of the two large Sumitomo samples we examined showed the same internal growth sectors, but these sectors create very different geometric patterns in each diamond because of the differences in sector development and impurity content between sectors. In Sample 1, we observed brown graining within the {100} sectors in planes parallel to the six cube crystal faces (again, see figure 2). Graining in yellow synthetic diamonds is believed to be due to index-of-refraction variations caused by changing nitrogen content (Burns et al., 1990; Frank et al., 1990). The narrow zones under the small faces at the corners lack graining, and point toward the dodecahedral {110} faces. Because of their small size, these narrow {110} sectors may not be easy to observe once the diamond is faceted. Frank et al. (1990, p. 356) provided a photograph of the internal growth-sector arrangement in a De Beers synthetic diamond that is nearly identical to the sector pattern observed in this sample.

In Sample 2, the pattern of internal growth sectors is revealed by color zoning, with only very subtle graining visible between sectors. The narrow

dodecahedral {110} sectors are blue, while the larger octahedral {111} sectors near the edges are yellow. The central section, which contains less nitrogen (as evidenced by its infrared spectrum; see below), is colorless. The near-absence of graining in Sample 2 can be explained by the lack of large cube {100} growth sectors, like those seen in Sample 1, where such graining is best developed (see Shigley et al., 1987).

As these two samples illustrate, the appearance of internal growth sectors can manifest itself in very different ways (zoning of color or graining) depending on the synthetic diamond crystal and its particular growth conditions (see also Burns et al., 1990).

ULTRAVIOLET LUMINESCENCE

Both samples are inert to long-wave U.V. radiation, but fluoresce weak orangy yellow to short-wave U.V. In contrast, natural type Ia diamonds are either inert or fluoresce blue, yellow, or sometimes green to both long- and short-wave U.V. (Liddicoat, 1987, p. 83). There is also some variation in luminescence among natural yellow type Ib diamonds. Our observations on 45 natural-color diamonds of this type revealed that 4 pure Ib and 11 mixed (Ib + IaA) type were inert to long-wave U.V. but luminesced weak to moderate orange to short-wave U.V., while the others were inert or reacted to both long- and short-wave U.V. Therefore, the U.V. luminescence of some natural type Ib diamonds can appear similar to that of these two synthetic samples. Nonetheless, all synthetic diamonds we have tested to date are inert to long-wave and fluoresce to short-wave U.V. Therefore, we continue to believe that this luminescence behavior (but not necessarily the luminescence color) is a good starting point to check for a synthetic diamond.

The short-wave U.V. luminescence pattern in Sample 1 is uneven and duplicates the arrangement of growth sectors: It is weak orangy yellow in the cube sectors and inert in the other sectors.

In Sample 2, the colorless center is inert to short-wave U.V., while the yellow outer areas fluoresce weak yellow in planes that parallel the octahedral crystal faces. Under the corners, a stronger yellow luminescence appears to be banded parallel to the dodecahedral faces. The fluorescent areas (especially those beneath the corner faces) phosphoresce a weak yellowish white that lasts 10–15 seconds. The uneven distribution of ultraviolet luminescence within a stone provides one more way to reveal the presence of both octahedral and cubic internal growth sectors that is typical of the synthetic diamonds we have examined to date.

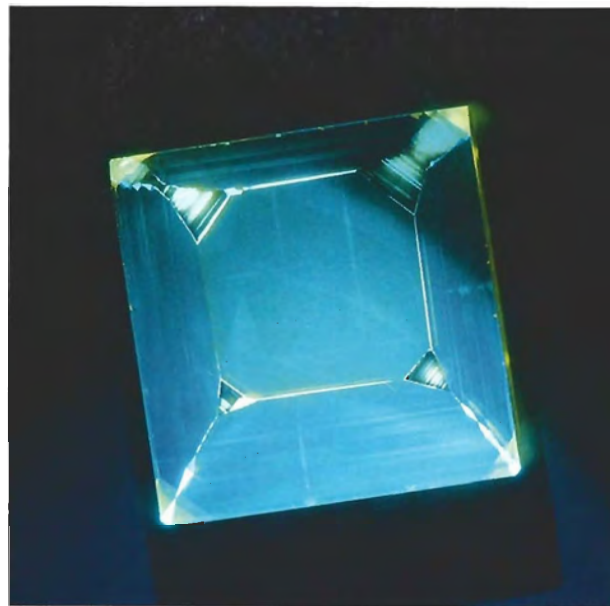


Figure 4. The cathodoluminescence of Sample 1 exhibits a chalky yellow in narrow octahedral growth sectors at the four corners and blue in the large cube sectors around the edges. In both sectors, zoning parallel to the respective crystal faces can be seen. Toward the center, a square, box-like region is also outlined by the bright luminescence. Photo by Maha Smith.

The uneven luminescence patterns are seen more clearly with cathodoluminescence (luminescence to a beam of electrons). As shown in figure 4, the "chalky" yellow cathodoluminescence in Sample 1 is readily visible at the corners, beneath the octahedral and dodecahedral faces. There is also a weak blue luminescence in the larger cube sectors that appears to be banded parallel to the cube faces. Four thin, bright, luminescent bands form a "box" at the center of the crystal. These appear to represent the transition between two growth sectors.

In contrast, the cathodoluminescence of Sample 2 shows the different pattern of the same internal growth sectors. As illustrated in figure 5, the octahedral sectors luminesce yellow, while the smaller cube and other sectors luminesce a weak blue.

Cathodoluminescence may reveal the differing patterns of internal growth sectors in natural and synthetic diamonds (Shigley et al., 1987) more clearly than ultraviolet luminescence. In the future, this method may become a standard technique to distinguish natural from synthetic gem diamonds (Ponahlo, 1992).

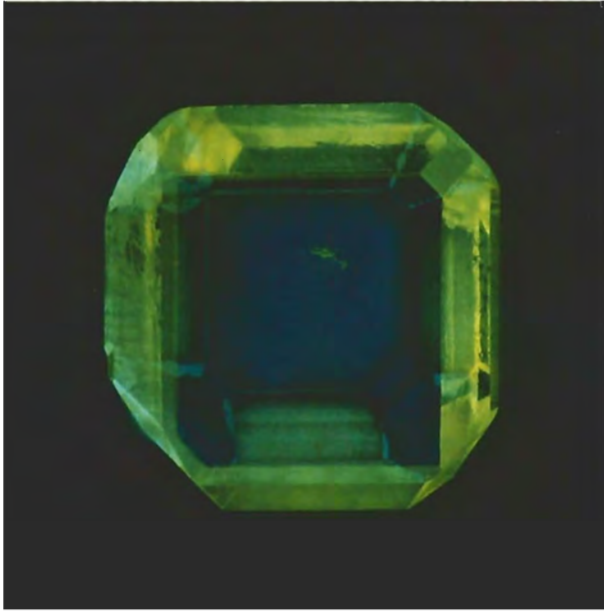


Figure 5. Cathodoluminescence of Sample 2 revealed more intense luminescence in the octahedral sectors (especially the one on the right side of the crystal), with a chalky yellow color that is banded. At the smaller sectors near the corners, and near the center, the sample luminesced a weak blue. Photo by Maha Smith.

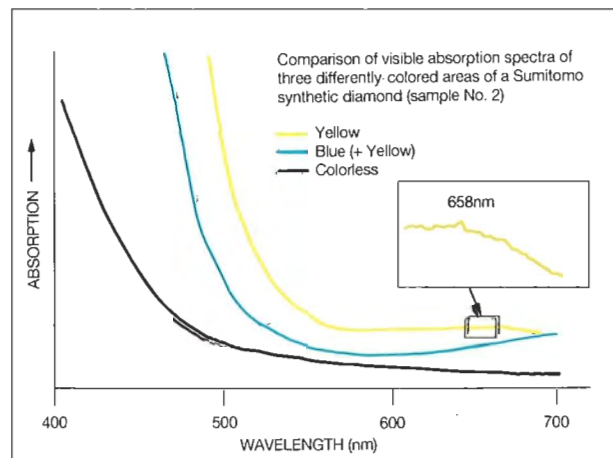
SPECTROSCOPY

All of the yellow synthetic diamonds studied previously were type Ib. Thus, they lacked the sharp absorption bands (the well-known "Cape" lines) present in the visible spectra of almost all type Ia natural yellow diamonds. In general, the visible spectra of Sample 2 exhibited the expected features for a type Ib diamond (with increasing absorption toward the violet). However, the areas of differing color in this sample also displayed differences in their spectra (figure 6). The yellow and colorless areas both showed gradually increasing absorption toward the violet (but less so for the latter), while the blue areas (with some yellow component because they were so small and thus included the surrounding yellow areas) showed a gradually increasing but much weaker absorption toward the red. In addition, a very weak, narrow band at 658 nm was observed in the visible spectrum recorded for the yellow areas of this sample. Collins and Spear (1982) attributed this sharp band (referred to as the zero-phonon line of the 1.883 eV system) to the presence of nickel incorporated into the diamond from the flux metal during crystallization. The visi-

ble spectrum of Sample 1 was the same as that of the yellow areas in Sample 2 and did not show any sharp bands.

The infrared spectra for Sample 1 confirmed that this crystal is a type Ib diamond throughout, but revealed a higher nitrogen concentration in the areas of brown graining. However, the infrared spectra recorded for Sample 2 indicate that the various colored areas each represent a different diamond type (figure 7). The center colorless area is type IIa, the yellow outer areas are type Ib (because of the series of features between 900 and 1600 cm^{-1}), and the blue areas are type IIb (because of the series of features between 2200 and 3000 cm^{-1}), with some amount of intermixed type Ib for the reasons explained above. We previously noted weak type-IIb features in the infrared spectra of the type-Ib greenish yellow De Beers synthetic diamonds (Shigley et al., 1987). The infrared

Figure 6. Visible absorption spectra were recorded for the three areas of different color in Sample 2. The yellow areas show sharply increasing absorption below 500 nm, while the colorless area shows a more gradual increase in absorption, at a region below about 450 nm. Because the blue zone is so narrow, it was impossible to record the spectrum of just the blue area without also recording a contribution from the surrounding yellow areas; however, this spectrum also exhibits gradually increasing absorption toward the red end of the spectrum (plus the absorption below 500 nm due to the yellow areas). The very weak sharp band at 658 nm noted in the spectrum recorded from the yellow area is shown here as an enlarged insert (this band cannot be seen with a hand spectroscope). Spectra were recorded at liquid-nitrogen temperature.



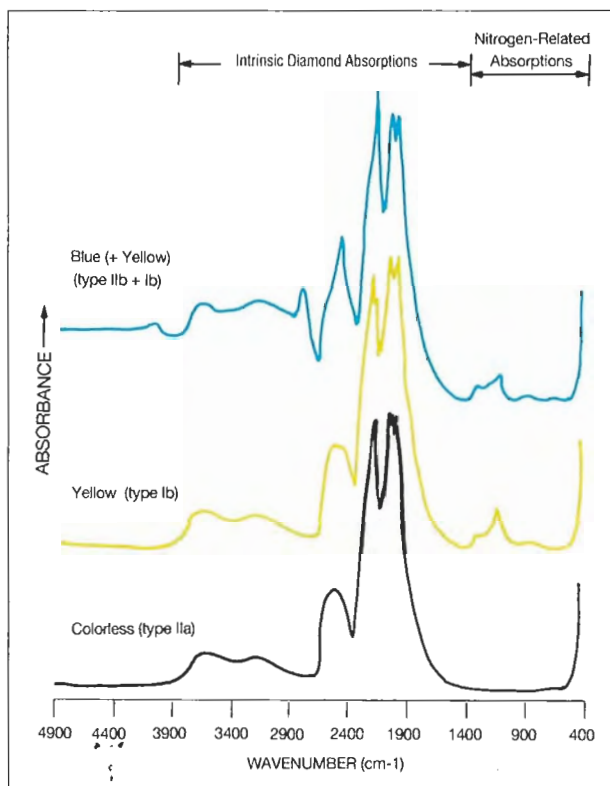


Figure 7. This diagram shows a comparison of the mid-infrared spectra for various color areas of Sample 2. From the top, the spectrum that includes the blue area indicates that it is type IIb with some type-Ib components; the spectrum through the yellow area indicates it is pure type Ib, and the spectrum through the colorless area indicates it is type IIa. Because of the uniform thickness (path length) of the sample, these spectra are scaled correctly one to another relative to their intensity (vertical axis).

spectra in figure 7 again illustrate the very distinctive character of some synthetic diamond crystals. While natural diamonds can be of mixed type (see Fritsch and Scarratt, 1992), we know of no natural diamonds that are a mixed type Ib + IIa + IIb, as is the case for Sample 2.

MICROSCOPY

When viewed between the crossed polarizing filters of the microscope, the two samples display rather weak first-order (black or gray) anomalous birefringence colors ("strain") in a cross-shaped pattern. In Sample 1, black zones extend outward from the center and perpendicular to the four cube faces (figure

8). Near the center of the sample, these zones intersect as a black box-shaped area, the sides of which are oriented parallel to the octahedral faces. Within this box, the birefringence appears to be cross-hatched, and corresponds to the "cluster-type" of mottled birefringence described by Kanda et al. (1990). Around the edges, there is a weak "crystal-type" birefringence pattern parallel to the cube faces (Kanda et al., 1990). The birefringence pattern in Sample 2 is much less regular but, again, appears to form a rough cross that is oriented with respect to the arrangement of growth sectors and external morphology. In general, these birefringence patterns correspond to what has been reported previously in synthetic diamonds (Shigley et al., 1986, 1987; Frank et al., 1990). According to our observations, they differ significantly from those seen in natural diamond crystals, where the planes showing anomalous birefringence are often parallel to the octahedral crystal faces, and the strain is generally more intense.

As mentioned earlier, both samples contain a few rounded, elongate, crystallographically oriented, metallic-looking flux inclusions similar to those seen previously in other synthetic diamonds (figure 9).

Figure 8. This anomalous birefringence ("strain") pattern was seen in Sample 1 with a gemological microscope equipped with crossed polarizing filters. Photomicrograph by John I. Koivula.

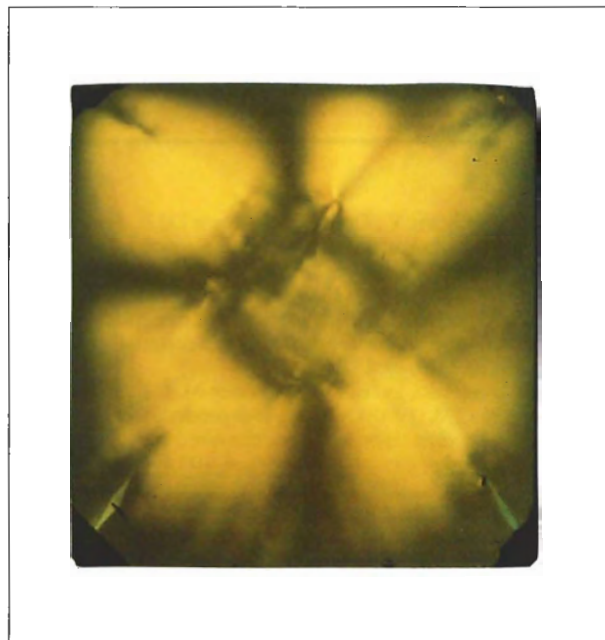




Figure 9. In Sample 1, a narrow, near-colorless-to-blue {110} zone points toward a corner of the sample. Brown graining runs parallel to two sides of the crystal that are cube faces. The elongated flux inclusion appears to be oriented parallel to one of the crystal faces. Photomicrograph by John I. Koivula; magnified 75 ×.

Qualitative chemical analysis of the inclusions in Sample 2 revealed them to be an iron-nickel alloy (with Fe>Ni). Metallic inclusions like these have not been reported in natural diamonds and, when present, are proof that the diamond is synthetic.

DISCUSSION AND CONCLUSION

The two large, 5-ct, samples of Sumitomo synthetic diamond that we examined exhibit different kinds of growth zoning. This zoning is revealed by patterns

of color distribution, luminescence to short-wave U.V. radiation, cathodoluminescence, and internal graining. This combination of features is characteristic of synthetic diamonds grown by the high-pressure flux method, and can help distinguish synthetic from natural gem diamonds of similar size, color, and clarity.

The striking color zoning, luminescence, anomalous birefringence ("strain"), and graining patterns in the two samples illustrate the varied development of internal growth sectors and the uneven distribution of impurities in a synthetic diamond. This uneven distribution of impurities between growth sectors can also lead to the presence of more than one diamond type within a single crystal (as in the case of Sample 2, which contains type Ib, IIa, and IIb diamond) that has never been reported in a natural diamond.

Sample 2 is particularly interesting because it contains a central area that is colorless and outer areas that are yellow. If one attempted to facet a large cut stone from such a crystal, it could show a pattern of gemological features (such as color) that is distinctive of a synthetic diamond, as we have reported previously. However, if one were to facet a smaller stone from just one internal growth sector, this stone might lack the distinctive zonation. Future production of large synthetic diamond crystals with even larger, colorless or colored growth sectors may lead to the possibility of stones cut from just one sector. Such faceted synthetic diamonds might be difficult to identify gemologically, even by advanced techniques such as infrared spectroscopy or cathodoluminescence, when they lack the zonation currently used as the primary indication of their synthetic origin.

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