CONTRIBUTION TO THE IDENTIFICATION OF TREATED COLORED DIAMONDS: DIAMONDS WITH PECULIAR COLOR-ZONED PAVILIONS

By Emmanuel Fritsch and James E. Shigley

Some treated yellow and blue-to-green diamonds show a peculiar color zoning when viewed through the pavilion. The culet or keel-line area on such stones exhibits a bright yellow or blue color that contrasts with the otherwise lighter (and/or different) body color of the diamond (which does not show any other strong color zoning). Such peculiar color zoning near the culet or keel-line is a strong indication that the stone has been treated by electron irradiation. Although rare, this feature can be useful in identifying irradiated diamonds, especially some green diamonds, for which few criteria are available to separate natural-color from laboratory-treated stones.

To expand the criteria for separating natural from laboratory-treated (i.e., irradiated and, in some cases, annealed) colored diamonds, the GIA Research Department has systematically documented the gemological and spectroscopic properties of more than 1,000 such stones over the last several years. These properties include color and color zonation, ultraviolet- and visible light–excited luminescence, characteristics seen with a microscope, and visible and infrared absorption spectra.

During the course of this study, we have examined a number of colored diamonds that share a peculiar feature: Although their face-up color is either yellow (figure 1) or dark green to blue (figure 2), when viewed perpendicular to the pavilion facets they exhibit a rather striking and unusual color zoning. In these stones, the overall color seen through the pavilion is much lighter than (and/or noticeably different from) the face-up hue, with a narrow area of strong yellow in the yellow stones (figures 3 and 4) or strong blue in the dark green to blue stones (figure 5), that occurs only near the culet or keel-line. In all cases, there is no other strong color zoning in the rest of the stone. We could find no report in the literature of a natural-color diamond with similar zonal coloration; nor have we encountered or heard of such a diamond in the course of our research. Therefore, we suspected that this unusual color zoning might be the result of laboratory treatment.

Our suspicions were further substantiated when we received for examination a similarly color zoned diamond that was known to have been electron irradiated (Saul and Ivin Perlman, pers. comm., 1988). This round brilliant-cut stone, which appeared blue face-up and light brown when viewed through the pavilion (figure 6), was accompanied by a second, untreated, light brown emerald-cut diamond that had been faceted from the same piece of rough. We subsequently submitted the latter stone for electron irradiation. On the basis of the nine stones in which we had observed this peculiar zoning, and the results of our radiation treatment of the 10th, we are able to describe this feature and draw some conclusions regarding its usefulness in separating laboratory-treated from natural-color diamonds.

BACKGROUND

Color zoning is not uncommon in natural-color diamonds. During our study, we have periodically noted diamonds with lighter and darker zones of the same or a different hue where the zones are sometimes separated by graining (which term is used here in accord with the definition provided in Shigley et al., 1987, pp. 203–204). In addition, yellow, brown, pink, and purple stones can show a concentration of color specifically along the graining which may be planar or very irregular (Kane, 1982).

ABOUT THE AUTHORS

Dr. Fritsch is research scientist, and Dr. Shigley is director of research, at the Gemological Institute of America, Santa Monica, California.

Acknowledgments: The authors are grateful to Roger and Richard Krakowsky of JDR Diamonds for the loan of several stones. Saul and Ivin Perlman of S&I Diamonds provided information on colored diamond treatment. John Fuhrbach of Jonz Fine Jewels loaned a diamond for examination. Robert Weldon and John Koivula kindly photographed the stones used in this study. Chuck Fryer provided constructive comments on the manuscript. This research was funded in part by a grant from the Harry Winston Research Foundation.

Gems & Gemology, *Vol. 25, No. 2, pp. 95–101*

Figure 1. These two treated yellow diamonds (samples 2 and 4) show a homogeneous face-up color. Photo by Robert Weldon.

Figure 2. This treated diamond (sample 9) appears bluish green when viewed through the table. Photo by Robert Weldon.

A very different type of color zoning can be seen in some laboratory-treated colored diamonds. One important example is provided by cyclotron-irradiated diamonds, in which some of the color is concentrated along distinct zones that parallel certain facet junctions; in a round brilliant-cut stone, this color zoning is arranged in a "star- or umbrella-shaped" pattern surrounding the culet (Liddicoat, 1987, pp. 181–183). Although diamonds with a pattern of natural color zoning can be irradiated and annealed, this treatment will change only the color of the various zones, not the pattern of color zoning itself.

MATERIALS AND METHODS

All 10 stones were examined thoroughly with a 10× loupe and a gemological microscope, and then tested for their reaction to long- and short-wave ultraviolet radiation. Optical absorption spectra of all 10 diamonds were recorded at low temperature (80°K) with a Pye-Unicam 8800 UV/VIS spectrophotometer. Infrared absorption data were obtained with a Nicolet 60SX Fourier Transform spectrometer covering the energy range from 400 to 25,000 wavenumbers (cm^{-1}; Fritsch and Stockton, 1987). As reported above, the 10th stone was originally received in its natural state. It was first carefully examined and then submitted for electron irradiation through the same commercial diamond treater (Saul Perlman, pers. comm., 1989) who had previously irradiated its treated counterpart. The irradiation was performed in a linear accelerator (Richard Krakowsky, pers. comm., 1989). No further details of this particular procedure are available due to the proprietary nature of the process. The stone was reexamined after this treatment. The results for all 10 stones are reported in table 1 and discussed below.

OBSERVATIONS

Four of the diamonds (samples 1–4) display a yellow (again, see figure 1) or greenish yellow color when viewed face-up through the table. When viewed through the pavilion, all four appear very light yellow, light brownish green, or light brown-

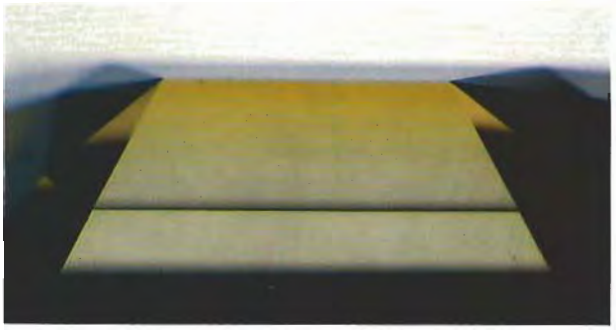

Figure 3. When observed through the pavilion, this treated yellow diamond (sample 2) shows a body color that is much lighter than is evident when the stone is viewed face-up (figure 1), with an obvious zone of a darker, yellow along the keel-line. Photomicrograph by John I. Koivula.

ish yellow except for a darker and much brighter "lemon" yellow area very near the culet (see figures 3 and 4). The remaining six (samples 5–10) are dark green to blue face-up (figure 2), but appear light brown, light to medium brownish green, or light grayish green when viewed through the pavilion, except for a narrow, bright blue zone at the culet (figures 5 and 6). This unusual color zoning was easily observed with the microscope using dif-

Figure 4. When this treated yellow diamond (sample 4) was viewed through the pavilion, it also revealed a lighter overall body color than its appearance face-up (figure 1), with a deep yellow zone at its culet. Photomicrograph by John I. Koivula.

fused transmitted light. It can also be seen with a loupe. In fact, this type of color zoning is first evident to the unaided eye in the dramatic difference in color appearance when the diamond is viewed through the crown and then through the pavilion, for example, as one opens the stone paper.

Figure 5. This treated bluish green diamond (sample 9, see also figure 2) displays a distinct blue zone at the culet. Photomicrograph by John I. Koivula.

Figure 6. This treated blue diamond (sample 5), with a blue culet and light brown body color, is known to be electron irradiated. Photomicrograph by John I. Koivula.

TABLE 1. Physical and optical properties of the 10 "color-zoned" diamonds examined for this study.[a]

Property	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Weight (ct)	2.11	2.18	0.88	1.02	0.87
Cut	Round brilliant	Emerald cut	Round brilliant	Round brilliant	Round brilliant
Face-up color	Yellow	Greenish yellow	Yellow	Greenish yellow	Blue
Color at culet or keel-line	"Lemon" yellow	"Lemon" yellow	"Lemon" yellow	"Lemon" yellow	Blue
Body color (through pavilion)	Very light yellow	Light brownish green	Light brownish yellow	Light brownish yellow	Light brown
Long-wave U.V. luminescence	Moderate yellow	Moderate orangy yellow	Moderate yellow	Weak to mod. orangy yellow	Weak greenish gray
Short-wave U.V. luminescence	Very weak yellow	Very weak yellow	Weak yellow	Very weak orangy yellow	Weak greenish gray
Visible-excited luminescence	Moderate green at culet	Weak green, uneven	Weak to moderate green at culet	Weak green at culet	Weak green
Optical absorption spectrum[b] (nm; band designation, strength of band, sharpness of band)	415 (N3; strong, sharp) 478 (N2; mod., broad) 496 (H3; weak, broad) 503 (H3; weak, sharp)	385 (ND1; mod., medium) 395 (ND1; mod., sharp) 405 (N3; strong, medium) 415 (N3; strong, sharp) 465 (N2; mod., medium) 478 (N2; mod., medium) 496 (H3; mod., medium) 503 (H3; mod., sharp) 563 (weak, sharp) 595 (weak, sharp) 740 (GR1; weak, broad)	415 (N3; strong, sharp) 422 (weak, sharp) 465 (N2; mod., sharp) 478 (N2; mod., sharp) 496 (H4; mod., sharp) 503 (H3; mod., sharp) 595 (weak, sharp)	385 (ND1; mod., sharp) 395 (ND1; mod., sharp) 405 (N3; mod., sharp) 415 (N3; strong, sharp) 454 (weak, broad) 465 (N2; mod., broad) 478 (N2; mod., sharp) 496 (H3; weak, broad) 503 (H3; mod., sharp) 593 (weak, medium) 700 (GR1; weak, broad) 724 (GR1; weak, broad) 742 (GR1; weak, broad)	385 (ND1; mod., broad) 395 (ND1; mod., sharp) 405 (N3; weak, broad) 415 (N3; mod., sharp) 418 (weak, sharp) 428 (GR2-8; weak, sharp) 503 (H3; weak, sharp) 595 (weak, sharp) 620 (GR1; weak, broad) 666 (mod., sharp) 676 (GR1; mod., broad) 700 (GR1; mod., broad) 722 (GR1; mod., sharp) 741 (GR1; strong, sharp)
Near-infrared absorption bands[c]	Weak H1b and H1c	Very weak H1b	Weak H1b and H1c	No H1b and H1c	No H1b and H1c
Diamond type; nitrogen content	Ia; high nitrogen	Ia; high nitrogen	Ia; high nitrogen	Ia; high nitrogen	Ia; moderate nitrogen

[a]Because of the difficulties in photographing the pavilion area, and the fact that the color zone so strongly affects the rest of the stone, the body color in the photomicrographs may not appear as described in this table. For assignments of the absorption bands in the ultraviolet/visible and infrared regions, see Collins (1982) and Woods and Collins (1986).
[b]Optical absorption spectra recorded at low temperature (80°K) with a Pye-Unicam 8800 UV/VIS spectrophotometer.
[c]Infrared spectra recorded with a Nicolet 60 SX Fourier transform spectrometer to determine the diamond type and the presence or absence of the H1b and H1c bands. For the energy positions of the H1b and H1c bands, see the text. When present, the H1b and H1c bands are of weak intensity but are sharp.

Despite the small size of the zone near the culet or keel-line, it influences the color of the remainder of the diamond because of its position directly beneath the table. Such an effect is commonly observed in colored stones, and has been used in faceting to take best advantage of predominantly light-color rough that has some darker areas (see Fryer et al., 1987, p. 107). This bright yellow or blue zone appears to extend about 1 or 2 mm from the culet or keel-line into the stone (when the diamond is viewed parallel to the girdle). Whether this colored zone is only on the surface or actually extends into the culet area is difficult to assess without destructive testing.

In the six diamonds with a blue area at the culet or keel-line, the border separating this zone from the remainder of the diamond appears to be distinct but is not sharp. The border between the two color zones in the four yellow diamonds is slightly less distinct. In both cases, this border appears to be roughly parallel to the table of the stone. No indication of graining could be seen marking the border in either diffused or polarized transmitted light.

In three of the four yellow stones, the small bright yellow area near the culet or keel-line luminesced green when exposed to visible light; the remaining portions of these stones did not luminesce at all. This behavior (referred to as "green transmission") was not noted in the blue-culet diamonds. Green transmission per se is common in both natural and laboratory-treated yellow diamonds; in our experience, it is related to the H3 center (see, e.g., Collins, 1982).

As mentioned above, we knew that one of the blue-culet diamonds (sample 5) had been electron irradiated. The use of electron irradiation for this treatment, where the position of the beam can be focused and thus only a portion of the diamond may be exposed to the radiation, explains why an area of different color may be located only near the culet or keel-line. We suspect that samples 5–9 originally had a light brown or light gray body color and were electron irradiated with a focused

Sample 6	Sample 7	Sample 8	Sample 9	Sample 10[d]
3.31	1.98	1.23	3.06	0.88
Round brilliant	Round brilliant	Round brilliant	Round brilliant	Emerald cut
Dark green	Green-blue	Yellowish green	Bluish green	Greenish blue
Blue	Blue	Blue	Blue	Blue
Light brown	Light grayish green	Light brownish green	Brownish green	Light brown
Inert	Very weak grayish blue	Moderate orangy yellow	Moderate yellowish green	Weak greenish yellow
Inert	Very weak grayish blue	Weak yellowish green	Very weak green	Very weak yellow
None	None	None	None	None
410 (weak, sharp)	(not recorded; GR1 band	405 (N3; mod., sharp)	375 (mod., sharp)	376 (mod., broad)
417 (weak, sharp)	present in FTIR spectrum)	415 (N3; strong, sharp)	385 (ND1; strong, sharp)	385 (ND1; strong, sharp)
428 (GR2-8; mod., sharp)		436 (weak, sharp)	394 (ND1; strong, sharp)	394 (ND1; strong, sharp)
486 (weak, broad)		441 (weak, sharp)	415 (N3; weak, sharp)	416 (N3; weak, sharp)
494 (weak, sharp)		450 (weak, broad)	429 (weak, sharp)	418 (GR2-8; weak, sharp)*
504 (H3; weak, broad)		475 (mod., sharp)	440 (weak, sharp)	428 (GR2-8; weak, sharp)*
514 (weak, broad)		488 (weak, sharp)	480 (weak, broad)	488 (weak, sharp)
620 (GR1; weak, broad)		503 (H3; weak, sharp)	494 (H3; weak, broad)	496 (H3; weak, broad)
666 (mod., sharp)		545 (weak, broad)	503 (H3; weak, broad)	502 (H3; weak, sharp)
670 (GR1; mod., broad)		563 (weak, sharp)	544 (weak, broad)	524 (weak, sharp)*
700 (GR1; mod., broad)		592 (weak, broad)	592 (weak, broad)	554 (weak, broad)*
720 (GR1; mod., broad)		620 (GR1; mod., broad)	620 (GR1; mod., broad)	595 (weak, sharp)*
740 (GR1; strong, sharp)		648 (weak, sharp)	676 (mod., broad)	620 (GR1; mod., broad)*
		666 (weak, sharp)	700 (GR1; mod., broad)	666 (weak, sharp)*
		680 (mod., broad)	722 (GR1; mod., broad)	674 (mod., broad)*
		700 (weak, broad)	741 (GR1; strong, sharp)	695 (mod., broad)*
		722 (GR1; mod., broad)		722 (GR1; strong, broad)*
		741 (GR1; mod., sharp)		741 (GR1; strong, sharp)*
No H1b and H1c	No H1b and H1c	No H1b and H1c	Possible H1b, no H1c	No H1b and H1c
IIa	IIa	Ia; high nitrogen	Ia; high nitrogen	Ia; moderate nitrogen

[d]*Data listed for sample 10 were determined after the diamond had been irradiated. In addition to the change of color, the optical absorption bands marked by an asterisk(*) are the result of treatment.*

beam, giving the culet area an intense blue color. This would be due to the limited penetration depth of the electrons. Samples 1–4, originally with a light yellow body color, were presumably electron irradiated in the same way; the intense blue color produced at the culet in these stones would have been subsequently converted to an intense yellow by heat treatment (Collins, 1982; Collins et al., 1986).

To better ascertain that this type of color zoning is the result of laboratory irradiation, we submitted the natural-color light brown stone cited above (sample 10, cut from the same rough as sample 5) for electron irradiation, as described earlier. Before irradiation, this emerald-cut diamond exhibited a light brown body color due to brown graining; after irradiation, the face-up color is a medium dark greenish blue (figure 7). When the treated stone is viewed perpendicular to the pavilion, however, the light brown body color in the center of the stone is identical to the overall color of the stone before irradiation. Yet the stone has developed a distinct blue color along both the keelline and the edges of the pavilion (figure 8). Although less pronounced than in sample 5 because of differences in facet shape and possibly conditions of irradiation, the color zoning of this second known treated stone is basically the same as that observed in the other blue-culet diamonds. Development of the blue color is due to formation of the radiation-induced GR1 center at 741 nm. This same color center is responsible for the green color of irradiated diamonds (Collins, 1982).

The near-infrared spectra of diamonds in the yellow-to-brown range are known to provide evidence of irradiation and subsequent heat treatment (Woods and Collins, 1986). Near-infrared spectra of three of the four yellow-culet diamonds exhibit H1b (4935 cm^{-1}) and/or H1c (5165 cm^{-1}) bands (see table 1). In our experience, H1b and H1c bands are never found in natural-color yellow diamonds, but they commonly do occur in those yellow diamonds that have been laboratory irradiated and heat treated. Only one isolated example of

Figure 7. Sample 10, which was cut from the same piece of rough as sample 5, was light brown prior to electron irradiation in a linear accelerator (left); after electron irradiation, it appears greenish blue when viewed face-up (right). Photos by Robert Weldon.

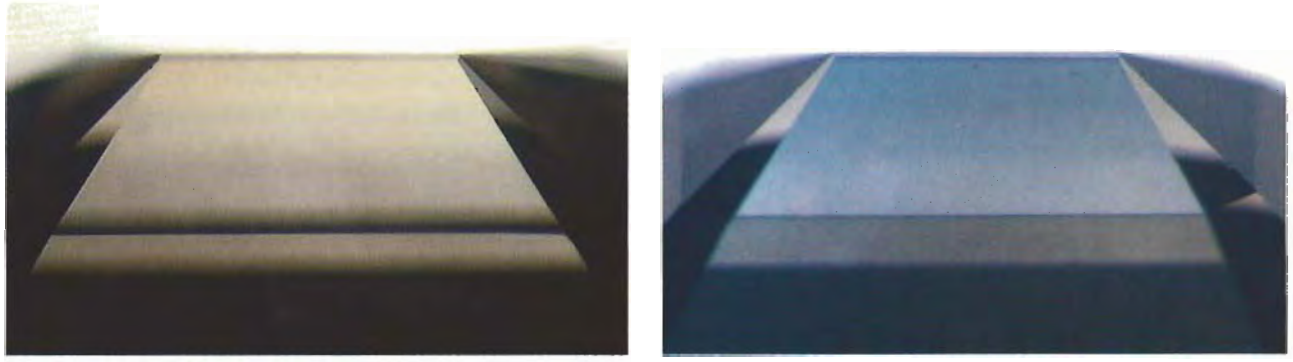

Figure 8. The keel-line of sample 10 before (left) and after (right) electron irradiation illustrates how the blue color produced by this treatment is concentrated in this area of the stone. The blue body color apparent here is the result of reflection from the keel-line within the stone; the overall body color after irradiation was light brown when the stone was viewed perpendicular to the pavilion. Photomicrographs by John I. Koivula.

a natural stone exhibiting H1b and H1c bands has been reported in the literature thus far (Woods and Collins, 1986). Therefore, the presence of the H1b/H1c bands in most of these yellow diamonds is considered further evidence that they were treated. The near-infrared spectra of the blue-culet diamonds revealed no evidence of these absorption bands. This is not particularly surprising since these bands are the result of the heat treatment of laboratory-irradiated type Ia diamonds (Collins et al., 1986), and blue to green diamonds are generally not annealed.

Although treated diamonds with the kind of color zoning described here do not seem to be common, this color-zoning criterion is helpful for stones in the greenish blue to green range, for which the problem of the origin of the body color has not been completely solved (see, e.g., Fritsch et al., 1988).

CONCLUSION

Yellow diamonds that have a darker, brighter "lemon" yellow zone at the culet or keel-line, and dark green to blue diamonds with a bright blue zone in the same area, should be viewed with suspicion if no other strong color zoning is present. We have summarized here the properties of 10 diamonds that display this rather remarkable ap-

pearance. A survey of the information presented in table 1 regarding the dark green-to-blue treated diamonds reveals that there are no features common to all six of these diamonds that are indicative of treatment except for this unusual color zoning. In the case of three of the four yellow stones, the H1b/H1c bands in the near-infrared spectrum confirms that the stones had been treated.

There is no report in the literature of a natural-color diamond with this appearance; nor have we ever encountered or heard of such a stone. We conclude, therefore, that a brightly colored area at the culet or keel-line in a colored diamond of different body color (and no other prominent color zoning) is a strong indication of treatment. Although this type of color zoning may not often be encountered, it does provide an important clue to the origin of color and can be checked easily by the jeweler-gemologist with a loupe or conventional gemological microscope.

REFERENCES

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

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

Fritsch E., Shigley J.E., Stockton C.M., Koivula J.I. (1988) Detection of treatment in two unusual green diamonds. *Gems & Gemology*, Vol. 24, No. 3, pp. 165–168.

Fritsch E., Stockton C.M. (1987) Infrared spectroscopy in gem identification. *Gems & Gemology*, Vol. 23, No. 1, pp. 18–26.

Fryer C.W., Crowningshield R., Hurwit K.N., Kane R.E. (1987) Gem Trade Lab Notes. *Gems & Gemology*, Vol. 23, No. 2, pp. 104–110.

Kane R.E. (1982) Graining in diamond. In D.M. Eash, Ed., *International Gemological Symposium Proceedings 1982*, Gemological Institute of America, Santa Monica, CA, pp. 219–235.

Liddicoat R.T. Jr. (1987) *Handbook of Gem Identification*, 12th ed. Gemological Institute of America, Santa Monica, CA.

Shigley J.E., Fritsch E., Stockton C.M., Koivula J.I., Fryer C.M., Kane R.E., Hargett D.M., Welch C.W. (1987) The gemological properties of the De Beers gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 23, No. 4, pp. 187–206.

Woods G.S., Collins A.T. (1986) New developments in spectroscopic methods for detecting artificially coloured diamonds. *Journal of Gemmology*, Vol. 20, No. 2, pp. 75–82.