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Gem Diamonds: Causes of Colors

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Diamonds for gem use are colorless in general, but some stones with bright colors are highly valued as fancy color diamonds. The body color of diamond depends on the concentration of nitrogen and the form of aggregation. Structural defects and vacancy bonding may also cause color centers. Furthermore, plastic deformation may bring about color. Recently, artificial coloring to intentionally produce "fancy color" stones has been carried out on a commercial basis. The combined process of electron beam irradiation with annealing and the high-pressure high-temperature (HPHT) process are quite common treatment techniques today. Leading gem laboratories around the world are currently working on these tasks to establish techniques, with a few exceptions, for revealing the origin of the color of the diamond.

1. Introduction

Diamond quality as a gemstone is generally graded by the four Cs. Diamonds of a certain carat with fine cut and clarity grades vary largely in value according to their color.

A perfect diamond is theoretically colorless, transparent and shows no fluorescence to UV light. In nature, however, even an almost perfect crystal is very rare; hence, it is highly evaluated. Commercially available gem diamonds often show a slightly yellow tint that is derived from a nitrogen-related defect. As the yellow tint becomes more intense, the value of a stone is generally lowered, but other colors such as pink, green or blue are valued for the color itself as fancy color diamonds, and there is a market for such diamonds.

As natural color diamonds became highly reputed and popular, new techniques of artificial coloring were developed and new materials flowed into the gem market. While these color-treated stones fill a demand for color diamonds at a lower price, their identification poses a new task for the gem industry.

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2. Importance of Color Origin

A yellow 104.52 ct diamond was on auction at Christie's in Geneva, Switzerland, in May 1971. The stone was famous and was called "Deepdene," but the color was later proved to be artificially irradiation-treated. As the stone was identified as a natural color diamond by noted gem identification authorities in the United States and in Germany before the auction, it was sold for 1.2 million dollars at the auction. After that it was ultimately identified as a treated stone by a third gem identification authority and the entire purchase amount was returned to the winning bidder.(1)

This accident drew attention as a diamond scandal at that time, but similar problems still occur occasionally; here, we can see the importance and difficulty of diamond identification.

3. Natural Diamonds in Various Colors

3.1 *Yellow*

To display a yellow color, diamonds should have some factor that absorbs the blue-violet region of visible light. The diamonds called cape series in the gem industry produce their yellow color via N3 and N2 centers that absorb the blue to violet region in a spectrum. This type of diamond also shows strong absorption bands caused by aggregated nitrogen atoms in the infrared region, and the content of the nitrogen is assumed to be at least 200 ppm. Most of the slight yellow tint seen in gem diamonds originates from this mechanism, and the degree of yellow color is graded as one of the factors of gem diamond grading.

Canary yellow (the color of a pet canary) stones, or those called "true canary," have been traditionally distinguished from cape stones. The canary color belongs to the rare natural type Ib diamond and it is derived from substitutional single nitrogen (C center). Several ppm to several dozens of ppm of these substitutional nitrogen atoms absorb the blue to violet region deeply to produce a color intense enough to be called a fancy color.

Some diamonds of the so-called H-rich type that have high hydrogen content may show a yellow color. These diamonds, similar to the cape series, owe their yellow color to the N3 or N2 center absorbing the blue to violet region in a spectrum. At the same time, there is weak absorption in the yellow to green region; hence, the stones often show a slightly saturated gray-yellow color. Therefore, these stones may be used as starting material for irradiation treatment to alter the stone color.

3.2 *Green*

Some stones may take on a green hue due to the GR1 center that has been produced by natural irradiation. The majority of them exhibit a light color, but the historically famous diamond "Dresden Green" shows a deep green color. Diamonds of this type often show radiation spots on naturals (the unpolished part left on a polished girdle), which are regarded as a trace of their exposure to natural irradiation (Fig. 1). They are assumed to provide incontrovertible evidence of natural α-ray irradiation, and the green spots are known to change to brown after heating at temperatures over 500°C.(2) The observed radiation spots can prove that a stone had been exposed to irradiation in nature; however, they cannot be used as proof to deny any succeeding artificial treatment.

Some diamonds are called "chartreuse," named after the color of the French liqueur. The liqueur has two types depending on the color, yellow and green; likewise, diamonds of this type show a yellow body color with a green overtone. These yellow and green colors are derived from N3 and H3 centers, respectively. The unique hue is due to the H3 center, which produces a green color under a strong fiber-optic light or UV light contained in sunlight.

3.3 *Pink*

Among the fancy colors, pink stones have great rarity and popularity. The presumed cause of the color is exposure to plastic deformation under the ground. A color zone called "pink grain" in gemological terminology can be observed inside the stone. Pink stones with moderate brightness and high saturation are called red diamonds. A pure red diamond with no secondary color is extremely rare.

In the early days, only a small number of light pink diamonds that were of type II called "Golconda pink" were obtained from India or Brazil. The extensive production of pink diamond started after the full-scale operation of Argyle mine, northwest Australia, in 1985, to meet the increasing demand in the gem industry.

3.4 *Brown*

Similar to pink stones, the brown color in diamond is also considered to be derived from exposure to plastic deformation under the ground. The color zone called "brown grain" can be observed in the stone (Fig. 2). In contrast to the rare pink diamond, brown stones are of high yield and have been promoted under commercial names such as "champagne," "cognac" or "coffee." Although the cause of the color is assumed to be plastic deformation, the mechanism under which pink and brown colors are produced differently is still unknown.

Brown color occurs both in type II, which contains hardly any nitrogen, and in type I, which contains more nitrogen, but in terms of quantity, type II brown stones occur at a frequency of one-hundredth that of type I stones. These brown stones are often used as starting material for HPHT treatment as described later, and type II brown diamonds are changed into colorless stones, and type I diamonds are changed into yellow or green stones.

3.5 *Blue*

This color is very popular and rare, next in rank to pink stones. Type IIb diamond contains boron, thereby exhibiting a blue color. The cause of this color is understood on the basis of band theory.(3) Diamond is originally an insulator, but when a boron atom replaces a carbon atom, an electron in the valence band jumps to an acceptor level, while consuming the red and some of the orange to green colors in visible light, hence producing a blue color. Thus, the blue color produced is generally of a light tone and often has a second color of gray. Type II diamonds are electroconductive and show anomalous double refraction under a polariscope due to what is called "tatami-structure" strain.

Some diamonds containing a large amount of hydrogen, so-called H-rich-type diamonds, show a blue color. This blue color is produced by the contained hydrogen absorbing deep red and some of the yellow-green region in the visible-light spectrum.

Other stones exhibit a blue color due to the GR1 center produced by natural irradiation. Most of the stones show radiation spots. A similar blue color can be induced artificially by irradiation with an electron beam. In recent years, pale blue diamonds treated by electron beam irradiation have gained in popularity in the gem market under the commercial name "ice-blue diamond." The lighter the stone color is, the more difficult it is to determine the origin of the irradiated color, whether natural or artificial, and in some cases, the determination is currently not possible.

3.6 *Other colors*

Some diamonds are known to display an orange color through a defect called the 480 nm band. Violet diamonds appeared on the market in 1990, which are a variety of H-rich-type diamonds that contain a large amount of hydrogen.

Another variety of H-rich-type diamond exhibits a color change and it is called the "chameleon" diamond. This stone changes its color from olive green to yellow when it is subjected to gradual heating such as with an alcohol lamp or when it is left in the dark. This color change is reversed in several seconds to several minutes so that you cannot actually enjoy this effect while you wear such a diamond in jewelry.

3.7 *Black and white*

"Black diamond" refers to a diamond that is black in color, but not coal. This material appears black because of numerous inclusions of minute needlelike or tabular crystals such as graphite (Fig. 3). Avant-garde designers started to introduce such black diamonds in the gem market in around 2000 and these stones instantly swept the gem world. The material soon ran short, and then black stones produced by irradiation treatment (the color is actually deep green) or by high-temperature heat treatment (HT) in a reducing atmosphere appeared in the market. Irradiation-treated black diamonds are lower-color-grade stones that have been subjected to high-energy electron beam irradiation or neutron radiation to create a deep blue to green color that originates from GR1. While natural black diamonds have poor luster because the inclusions that cause the black color reach the polished surface, irradiated black stones have a smooth polished surface and thereby have good luster. Heat-treated black stones are made of particularly low clarity single-crystal diamonds or white polycrystalline diamonds that have been heated in a reducing atmosphere to be partly graphitized to produce the black color.

White diamonds are not colorless but are a milky color often expressed as "milky" or "snow." This white color is derived not from optical centers but from light scattered from minute inclusions of submicron size. This type of material is made of H-rich-type Ia B diamond.

4. Artificial Coloration of Diamond

4.1 *Irradiation treatment*

Diamonds are colored by producing lattice defects by irradiating the stones with an electron beam or by neutron radiation, followed by heat treatment to induce new defects or bond defects. The history of this irradiation treatment started several years after the discovery of "radioactivity" in 1896. The most famous event in gemology was the experiment conducted by Crookes in 1905. He buried several pieces of diamond under radium bromide for almost one year and then confirmed that the surface of the stones had changed to green.(4) However, such treatment using a radioactive compound has never been commercialized because the treated diamonds themselves become radioactive. In the 1940s, a new technique using a particle accelerator was developed and put into practical use. In the 1950s, heat treatment after irradiation was revealed to be effective and irradiation-treated diamonds became more marketable.(5) In the late 1950s, neutron irradiation using a reactor started and electron beam irradiation using a linear accelerator was developed in the 1970s. Currently, the primary technique is a combination of electron beam irradiation followed by heat treatment.

4.2 *Identification of irradiation treatment*

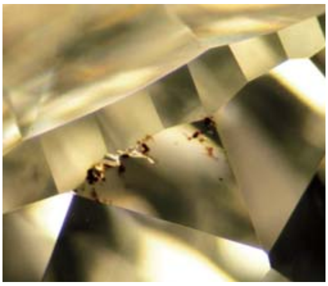
After artificially irradiated color diamonds became commercially available, the determination of color origin became important. Examples of irradiated diamonds are shown in Figs. 4 and 5.

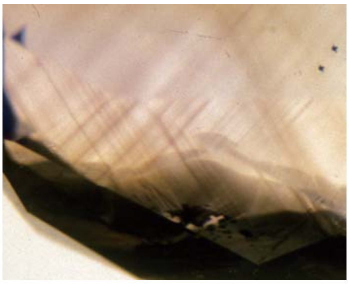
Diamonds treated with radioactive compounds, now hardly seen in the market, are easy to identify because of their residual radioactivity. Diamonds treated with cyclotron, which was often used in the 1940s, show a typical uneven color distribution called an "umbrella mark," which is the identifying feature of the material.(6) Currently, commercial irradiation treatment is mainly performed using an electron beam with a particle accelerator such as a linac. This treatment is generally applied to brilliant-cut stones after they are polished because an electron beam can produce color only on the surface layer. Thus, stones treated by this method show greater color concentration around the culet or girdle, which reveals their artificial color origin.

In 1956, Crowningshield discovered a characteristic absorption at 592 (595) nm in treated diamonds after observing several thousands of yellow to green diamonds.(7) This discovery became an important prescription for gemologists; however, in 1978, Collins confirmed that subsequent annealing at high temperatures caused the 595 nm absorption to vanish without altering the color of the stone.(8) Such irradiated and annealed diamonds were then proved to exhibit H1b or H1c absorption in 1986. Since then, the importance of infrared spectral analysis has been recognized.(9)

4.3 *HPHT process*

The study of diamonds subjected to heat treatment under high pressure has been carried out for many years in order to apply the technique to improve the clarity of diamonds. However, this technique came to be known in the gemological field only after





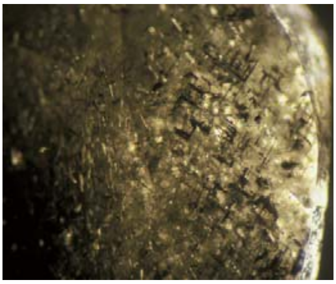
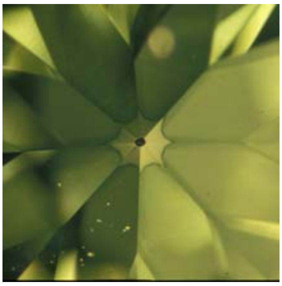


Fig. 1 (left). Radiation spots on a natural green diamond.
Fig. 2 (center). Brown grain in a natural brown diamond.
Fig. 3 (right). Black needle like inclusions in a natural black diamond.



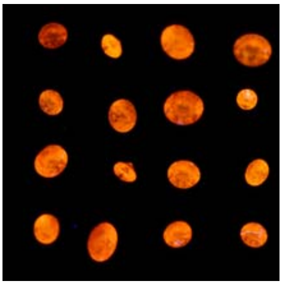
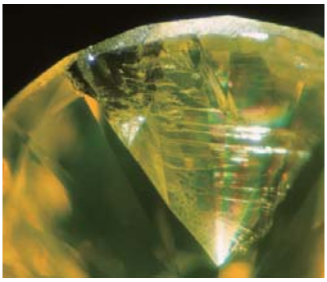
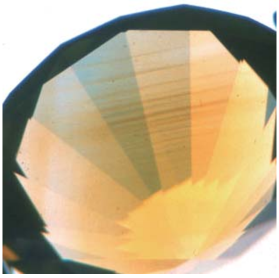


Fig. 4 (left). Umbrella mark seen in a diamond irradiated by a cyclotron.
Fig. 5 (center). Orange UV fluorescence seen in an irradiation treated pink diamond.
Fig. 6 (right). Inscription on a diamond that is HPHT treated by GE.





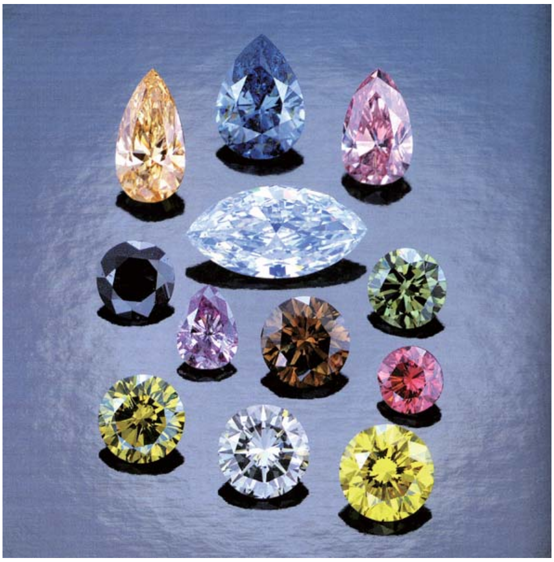


Fig. 7 (upper). Graphitisation on a diamond that is HPHT treated by NOVA.
Fig. 8 (lower). Yellow colour zone in a diamond that is HPHT treated by NOVA.
Fig. 10 (right). Fancy colour diamond Harvey Harris 1990.

Lazar Kaplan International Inc. (LK) released it as their “new treatment technique” in 1999.

A type II diamond showing a brown color due to plastic deformation can be altered into a colorless stone by treatment under HPHT conditions (Fig. 6); thus, its apparent value as a gemstone is raised. Occasionally, some type II brown diamonds change into pink ones. Similarly, some brown to gray diamonds of type IIb may be changed into blue ones by HPHT treatment. In type I brown stones, H3 or H2 centers are formed and the color of the stones changes to yellow or green.(10) In Japan, this type of diamond has been quite popular under the name “apple green” diamond.

4.4 *Identification of HPHT process*

The initial announcement of LK regarding the HPHT process indicated that the new treatment was not detectable, and this disrupted the gem industry. Since then, leading international gem laboratories have been working to discover an identification technique for the new material, and now a technique has almost been established.

The temperature and pressure used for HPHT treatment are generally set in the stability range of graphite so that diamonds treated in this process may show the progression of graphitization in cleavages or on the surface layer. In treated “apple green” diamonds, yellow or green “graining” along octahedral faces, not generally observable in natural diamonds, can be recognized (Figs. 7 and 8).

To detect the HPHT process, photoluminescence analysis using a 514 nm or 488 nm argon ion laser is effective (Fig. 9). In particular, for the diamonds treated to become colorless, it is known that the intensity ratio of the NV center becomes 637 nm > 575 nm.(11) Diamonds treated to give an “apple green” color will show a smaller 535 nm / 575 nm ratio than untreated stones with a similar color.

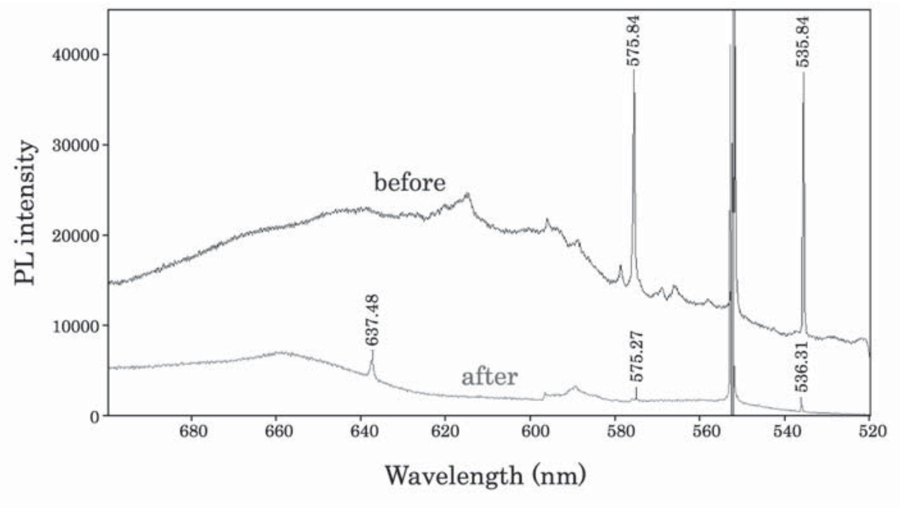


Fig. 9. Photoluminescence spectrum of a brown diamond, measured by 514 nm laser at –150°C before and after HPHT process.

5. Summary

Diamonds for gem use are colorless in general, but some stones with bright colors such as pink, blue or green are highly valued as fancy color diamonds (Fig. 10). Certain colors may appear to be identical to human eyes; however, the cause of the color varies among several different systems, and thus, many factors are complexly mixed to produce the delicate hues. In recent years, artificial coloring to intentionally produce "fancy color" stones that are highly valued in the gem marked has been carried out on a commercial scale, and such materials have been released onto the market. The combined process of electron beam irradiation with annealing and the HPHT process are quite common treatment techniques today. The value of a gemstone is markedly different between natural fancy color diamonds and artificial ones so that appropriate information disclosure is necessary and techniques for distinguishing them are important. Leading gem laboratories around the world are currently working on these tasks to establish techniques, with a few exceptions, that enable us to reveal the origin of the color of a diamond.

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