

Chapter 2

Diamonds Used for HPHT Treatment

Type, color and clarity are three major parameters, which determine suitability of diamond for HPHT treatment. Color is of primary commercial importance. Initial color is the reference point for the evaluation of improvement of the diamond's appearance, increase in its price, and effectiveness of the HPHT treatment procedure.

Clarity is the parameter, which sets the limits of the suitability of diamond for commercial HPHT treatment. Since HPHT annealing is frequently performed at pressures and temperatures close to or within the range of stability of graphite, the inclusions may considerably stimulate graphitization of the surrounded diamond lattice. Moreover, inclusions weaken locally diamond crystal thus resulting in development of cracks. The formation of cracks is especially effective when the pressure applied to the diamond during processing is not uniform. Thus, HPHT treatment may reduce the clarity grade of diamond but rarely increases it. If a diamond has low initial clarity, the HPHT processing may reduce its clarity grade to a level, which would make the treatment unprofitable.

Diamond type is a technological rather than commercial parameter. However, type of the diamond intended for HPHT treatment is a key factor for the technologist when he chooses the treatment conditions with the aim of achievement of desirable final color.

2.1 Types of Diamond

Notion of the diamond type is a corner stone in the understanding of the physics behind HPHT treatment. The types differentiate diamonds with different content of nitrogen and boron—two major impurities, which determine the optical and electrical properties of diamond. For HPHT treatment, the presence of nitrogen and transformation of the nitrogen-related defects are of particular importance. The standard method of recognition of diamond types is IR absorption spectroscopy. Each diamond type has its specific IR absorption spectrum. Boron is

optically active when present in the diamond lattice in the simplest form of single substitutional atoms. It reveals characteristic absorption spectrum in the Vis and IR spectral regions. The optical activity of nitrogen is much more versatile. Nitrogen is optically active when present in form of different point and extended defects of different atomic composition. These nitrogen-related defects induce hundreds of optical centers throughout UV, Vis and IR spectral ranges (Zaitsev 2002). There are four major types of diamond: Ia, Ib, IIa and IIb.

2.1.1 Type I Diamonds

Type I diamonds are the nitrogen-containing ones. They are the most abundant diamonds in nature. Formally, a diamond is of type I when the concentration of nitrogen in it is above the sensitivity limit of conventional IR absorption spectroscopy, what is about 1 ppm. Practically, nitrogen content in natural type I diamonds exceeds 10 ppm and may be as high as 3,000 ppm. Type I diamonds with nitrogen content below 10 ppm are frequently referred to as low-nitrogen type I diamonds.

Subdivisions of type I are type Ia and type Ib. Type Ia diamonds are those containing nitrogen in aggregated forms, when the majority of nitrogen is present in complexes of two and more nitrogen atoms. The major aggregates of nitrogen are A-, B- and B'-defect (Platelets). Type Ib diamonds contain nitrogen predominantly in form of single substitutional nitrogen atoms (C defects) and only minor amount of nitrogen is aggregated. Single substitutional nitrogen atoms are omnipresent impurity in diamond. It is a very rare event that the presence of C defects in a natural diamond could not be detected (Sobolev et al. 1986; Fisher 2012). The highest concentration of single substitutional nitrogen, which can be found in natural type Ib diamonds, may reach a value of 500 ppm. Atomic models of C-, A-, and B defects are shown in Fig. 2.1.

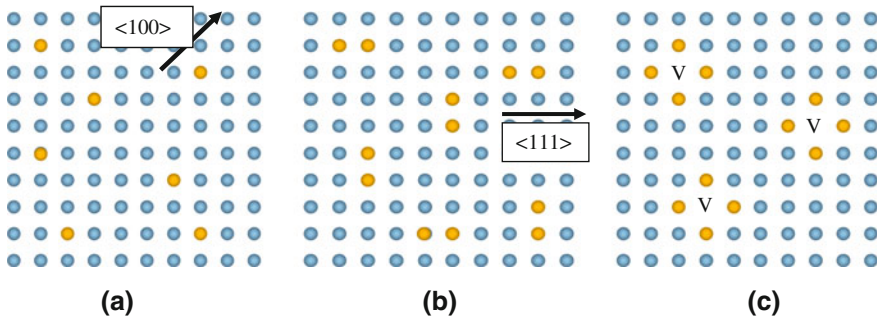
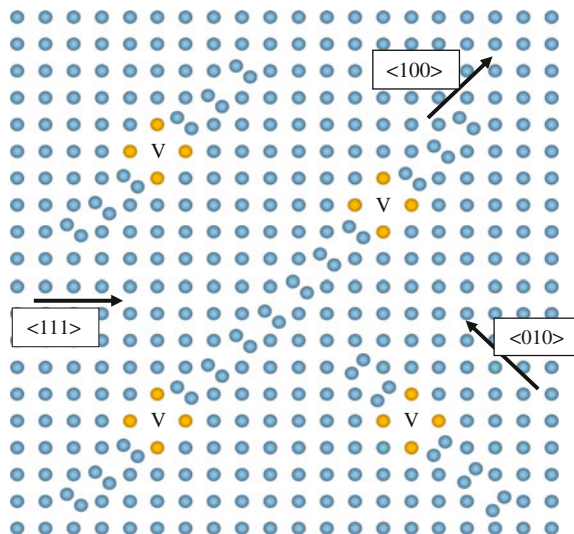


Fig. 2.1 Atomic models of the basic nitrogen defects: **a** single substitutional atoms (C defects), **b** pairs of the nearest substitutional nitrogen atoms (A defects), **c** complexes of four nearest substitutional nitrogen atoms surrounding vacancy (B defects). Blue and yellow circles denote carbon and nitrogen atoms respectively

Atomic structure of A defects is established quite well. It is a pair of neighboring nitrogen atoms in substitutional positions (nitrogen molecule N_2 imbedded into diamond lattice, Fig. 2.1b). The atomic model of B defects is still debated, though the most acknowledged version is a tetrahedron of four neighboring substitutional nitrogen atoms surrounding a vacancy (Fig. 2.1c). The atomic model of the B' defects is even more obscure. The commonly used model of B'-defect is a macroscopic planar segregation of interstitial carbon atoms along cubic (100) crystallographic planes decorated with some nitrogen (Fig. 5). Because of the planar structure, the B'-defects are usually referred to as "Platelets". Typically, Platelets have rectangular shape and their size is in the range of a few tens of nanometers. However, Platelets can be as large as tens of micrometers and then they can be observed in cathodoluminescence (Collins and Woods 1982) and electron microscope (Kiflawi et al. 1998).

There is no any reliably established atomic model of Platelets so far. We use a working model which suggests that the Platelet is a planar aggregation of interstitial carbon atoms around B defect (Fig. 2.2). We assume that B defects serve for intrinsic interstitials as condensation centers. Hence the size of Platelets and the nitrogen content within them depends on the thermodynamic parameters (temperature, pressure), time and concentration of B defects. In theory, one Platelet contains only one B defect. Thus, the larger the Platelet the smaller relative concentration of nitrogen in the Platelet. In diamonds with high concentration of B defects, many small Platelets form and, consequently, relative concentration of nitrogen in them may be rather high (over 10 %) (Goss et al. 2003 and references therein). With time, as the Platelets grow, the relative nitrogen concentration goes down. In diamonds with low concentration of B defects, the Platelets may reach great size still containing only few B defects. Thus, the relative concentration of nitrogen in such Platelets may be close to zero.

Fig. 2.2 Working atomic model of the B'-defect (the Platelet) used in this book: B defects decorated by carbon interstitials. Two (100) nearest planes of 3-coordinated interstitial carbon atoms surround B defect. B defects serve as centers of condensation for interstitial carbon atoms. In diamonds with high concentration of B defects, one platelet may include several B defects over its area. Blue and yellow circles denote carbon and nitrogen atoms respectively



An important issue concerning the process of formation of Platelets is the source of interstitials. Our model of Platelets suggests that the amount of interstitials required to form Platelets is greater than that of B defects. Thus, the release of interstitials during the aggregation of A defects into the B defects is not the only source. The further feasible processes, in which high concentration of interstitials can be generated and which always occur in natural diamonds while in earth, are the plastic deformation and the motion of dislocations.

Additional labeling of type Ia diamonds with letters A, B, C and B' is used to indicate the dominating form of nitrogen defects. For instance, type IaA diamonds contain nitrogen predominantly in the form of A defects. Type IaABb diamonds are these containing comparable concentrations of A-, B- and C defects. Symbols < and > may be used to show the prevailing defects. For instance, type IaA > b describes a diamond with dominating concentration of A defects and a measurable concentration of C defects. For instance, this type is a common result of HPHT treatment applied to originally type Ib diamonds. Some natural diamonds are of this type too. Type IaB > A > b describes a diamond with dominating concentration of B defects, which also contains some A defects and measurable traces of C defects. This type is very common for nitrogen-containing HPHT-treated diamonds, whereas it is very rare for natural untreated diamonds.

Total nitrogen content in natural type Ia diamonds may be very high—up to 10,000 ppm (Sobolev et al. 1986). High-nitrogen diamonds have most nitrogen in the aggregated forms (A-, B- and B'-defects). Concentration of C defects in natural diamonds usually does not exceed 50 ppm and rarely goes above 100 ppm. However, there are reports on natural brown-yellow diamonds containing C defects in concentrations over 500 ppm (Hainschwang et al. 2006a; Vins et al. 2008).

In some natural diamonds, only one form of nitrogen defects can be seen in IR absorption spectra and, on this basis, these diamonds are ascribed to “pure” types IaA, IaB, or Ib. However, even in these diamonds of pure type, trace concentrations of all other nitrogen defects can be detected by more sensitive EPR and/or PL methods. There is no natural diamond, in which all forms of nitrogen defects could not be detected (Sobolev et al. 1986).

The A-, B- and B'-defects do not absorb light in the visible spectral range. Therefore, type Ia diamonds are colorless. In contrast, C defects strongly absorb in the green and blue spectral ranges and, because of this, type Ib diamonds are orangey-yellow in color.

2.1.2 Type II Diamonds

Type II diamonds are those containing no measurable amount of nitrogen. Practically, to be of type II, a diamond has to contain less than 1 ppm nitrogen. Further division of type II into types IIa and type IIb is used to distinguish between diamonds, which do not contain boron (type IIa) and those, which contain boron impurity (type IIb). Boron concentration in natural type IIb diamonds is usually

low and it rarely exceeds 1 ppm. Type IIb diamonds are also the most low-nitrogen natural diamonds with typical nitrogen concentration in the range of 0.01 ppm. Type IIb diamonds show characteristic boron-related broad-range optical absorption starting in IR and spreading through the red towards green spectral range. This absorption makes type IIb diamonds blue.

Type IIa diamonds are nominally impurity-free ones, however, they may contain small but still detectable amount of major nitrogen A-, B- and C defects, as well as their derivatives. These are, for instance, N3, H3 and NV defects (see below), which can be detected using sensitive PL spectroscopy. Their concentration, however, is too low to produce optical absorption in Vis spectral range and to affect the colorless appearance of type IIa diamonds.

2.1.3 Natural Occurrence of Diamond Types

The vast majority of natural diamonds are plastically deformed nitrogen-rich brown diamonds of type Ia. These diamonds contain nitrogen in different forms and belong to the most common mixed type IaABB'. About 98 % of all natural diamonds are of type IaABB'. Of these, about 90 % are high-nitrogen diamonds containing greater than 1,000 ppm nitrogen. Diamonds of pure types are very rare in nature. Natural occurrence of pure type IaA diamonds is less than 0.05 % (Bokiy et al. 1986). No more than 0.2 % of natural diamonds are those of pure type IaB. Type Ia+Ib diamonds with dominating concentration of C defects are also rare and they amount to about 0.8 % of all natural stones. Natural diamonds, which can be ascribed to type Ib are very rare comprising not more than 0.1 % of all natural diamonds. Although being classified as type Ib diamonds, all natural diamonds of this type commonly contain at least A defects in measurable concentrations (Schmetzer 1999a; Collins 2001). In contrast, natural diamonds with measurable content of C defects rarely contain B defects. However, mixed type IaABB' diamonds may contain small amount of C defects. Especially low C defect content is in natural diamonds with dominating B and B' defects.

The A-, B- and C defects are rarely present together in low-nitrogen diamonds of brown to yellow color and in low-nitrogen chameleon diamonds (Hainschwang et al. 2005a). The presence of nitrogen in all aggregated forms is explained by naturally occurring decomposition of B defects by moving dislocations during plastic deformation the diamonds experience in earth (Nadolinny et al. 2009). The diamonds, containing simultaneously A-, B- and C defects in concentrations measurable in IR absorption, are termed as ABC diamonds (Fig. 2.3).

Low-nitrogen diamonds are rare in nature. Type IIa diamonds amount to less than 2 % of all recovered diamonds in major diamond deposits. The relative number of low-nitrogen and type IIa diamonds increases with size. Many large cut diamonds are of type IIa including the biggest and the most famous: Golden Jubilee (545.7 carats), Cullinan I (530.2 carats), Cullinan II (317.4 carats), Centenary (273.8 carats), De Beers Millennium Star (203 carats).

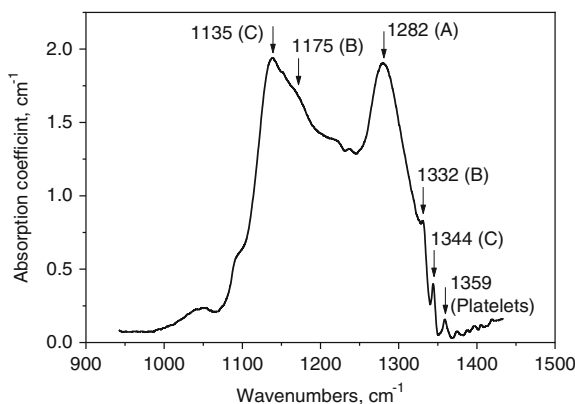


Fig. 2.3 IR absorption spectrum of a natural untreated ABC diamond of fancy *deep brown yellow color*. The spectrum shows the presence of all major nitrogen defects: C, A, B and B'. The spectral position (1359 cm^{-1}) and the spectral width (7 cm^{-1}) of the platelets peak fit well into area of untreated diamonds (see Fig. 6.77). A developed Amber center present in the spectrum confirmed the untreated nature of the stone (not shown)

Type IIb diamonds are extremely rare, comprising less than 0.001 % of all natural diamonds.

2.1.4 Recognition of Diamond Types

A standard way to determine type of a diamond is to measure its IR absorption spectrum. All nitrogen and boron defects defining the diamond type are optically active and their content can be accurately measured via intensity of the corresponding absorptions. Usually IR absorption spectroscopy in the spectral range from 400 to $1,400\text{ cm}^{-1}$ is used to measure the nitrogen concentration of 1 ppm and above. For concentrations below 1 ppm, Vis and UV absorption spectroscopy is employed. A more detailed description of the optical absorptions (optical centers) related to the nitrogen- and boron-containing defects is given below in Chap. 5.

If a natural diamond is colorless, its type can be also recognized by examining it in microscope in polarized light. Most type IIa diamonds possess high dislocation density and show in polarized light characteristic birefringence strain patterns (“tatami” pattern) extending through the whole volume of diamond (Fig. 2.4). In contrast, type Ia diamonds have less dislocations and exhibit banded birefringence strain patterns usually spreading along one dominating direction (Berman 1965; Chalain 2003). However, the nitrogen content influencing the birefringence pattern of diamond is rather high (over 20 ppm). Because of this, the birefringence pattern method is not suitable for differentiation between type IIa and low-nitrogen type Ia diamonds.

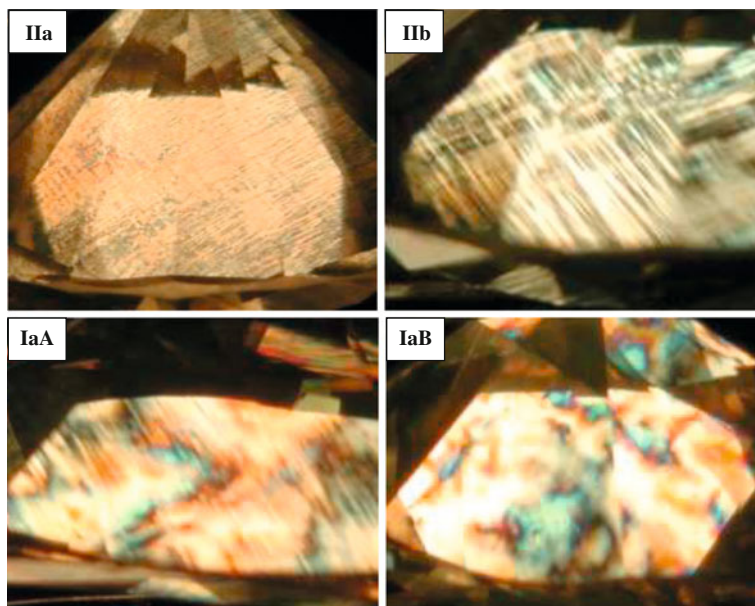
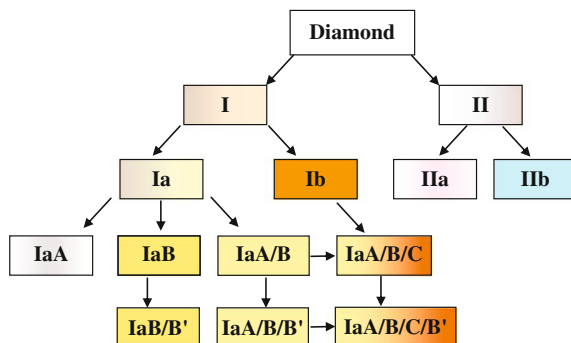


Fig. 2.4 Examples of birefringence patterns of diamonds of different types. Anomalous double refraction pattern called “tatami” is characteristic of natural type II diamonds. “Tatami” is not obvious in type I diamonds (courtesy of D. Simic)

Nitrogen A- and C defects and boron are electrically active in diamond. A- and C defects are both donors and may deliver free electrons in diamond lattice via ionization (Collins et al. 2000). Yet, the ionization energies of A- and C defects are too high (4 and 1.7 eV respectively) to allow them to release free electrons at room temperature. Thus, the nitrogen-containing diamonds of type I are highly insulating at room and even at elevated temperatures. Substitutional boron atoms are acceptors in the diamond lattice and, when ionized, deliver free holes. The ionization energy of boron is 0.38 eV, what is much less than the ionization energy of the nitrogen defects. An appreciable number of boron acceptors are ionized at room temperature and this provides a measurable electrical conductance. This electrical conductance is a unique feature of type IIb diamonds.

The described classification is a physical classification of diamond as a material and it is applicable to diamonds of any nature and origin. It is equally used for classification of natural, synthetic (both HPHT-grown and CVD-grown), untreated and treated diamonds. A scheme of diamond types and their characteristic colors is presented below in Fig. 2.5.

Fig. 2.5 Types of diamond and their characteristic colors



2.2 Colors of Natural Diamonds

The color of any colored diamond results from the presence of defects. Impurity-free, structurally-perfect diamonds are colorless. However, not all defects induce color, but only those optically active in the visible spectral range. For instance, the nitrogen-related A- and B defects are active only in IR and UV spectral ranges and therefore they do not affect the colorless appearance of type Ia diamonds. However, in most natural diamonds, the A- and B defects produce optically active derivatives, like H3, H4 and N3 defects, and then type Ia diamonds acquire yellowish color.

Two major types of optically active defects rendering natural diamond non-colorless are nitrogen-containing defects and aggregation of vacancies. The nitrogen-containing defects are formed of nitrogen captured from the environment during the diamond grow. The vacancies and their aggregates are formed in cause of plastic deformation the diamonds experience in earth. It is a rare event that in nature diamond grows in nitrogen free environment. Also it is a rare event that diamond is surrounded by uniform stable medium during its billion year history in earth. Hence vast majority of natural diamonds contain nitrogen and are plastically deformed. The most common color of these diamonds is unpleasant brown with a tint of yellow. Rare nitrogen-containing but non-deformed diamonds change their hue from colorless to yellow as the nitrogen concentration grows. Very rare nitrogen-free, non-deformed diamonds are perfectly colorless and, because of this, the most valuable gems.

The most common optical centers affecting the color grade of natural diamonds are the Brown absorption continuum (responsible for brown color), the N3 and N2 centers (responsible for yellow color) and the C defect absorption continuum (responsible for orangey-yellow color). Typical UV-Vis absorption spectra of natural diamonds are shown below in Fig. 2.6.

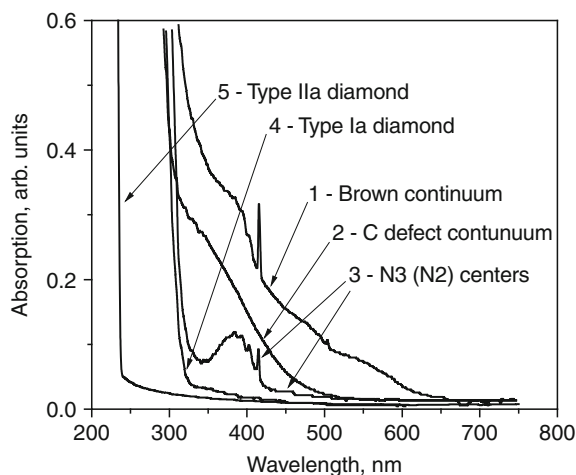


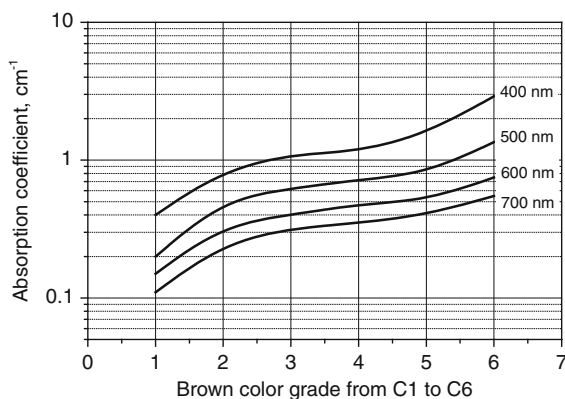
Fig. 2.6 Absorption spectra of diamonds of typical natural colors. *Curve 1* represents *brown color* type IaA/B diamonds. The brown absorption continuum is the major absorption feature responsible for brown coloration. *Curve 2* represents *yellow* type Ib and type Ia+Ib diamonds. The C defect absorption continuum is the major absorption feature determining color. The C defect absorption continuum differs from the brown absorption continuum by much lower absorption in the *yellow* and *red* spectral ranges. *Curve 3* represents type Ia diamonds of *cape yellow color*. The main absorption center of these diamonds is the N3 (N2) center band absorbing in the *blue* and *green* spectral ranges. *Curve 4* represents *non-colored* type Ia diamonds. Traces of the N3 (N2) center band in the spectral range from 350 to 480 nm make most of these diamonds *near-colorless* [based on the data from (De Weerd and Collins 2007)]. *Curve 5* represents *colorless* type IIa diamonds

2.2.1 Brown

Brown is the common color of natural diamonds. Brownish tinge can be recognized in 98 % of all as-mined diamonds. An increased attention to the diamonds of brown color in the last decade is stimulated by the possibility of “improving” their color and converting them into diamonds of bright fancy colors using HPHT treatment. Brown diamonds can be of any type and they are mined from many deposits all over the world. However, the brown color is especially characteristic of natural type IIa diamonds. It has been shown that the presence of nitrogen in A and B aggregates stiffens the diamond lattice against distortion by natural plastic deformation (Nailer et al. 2007). Thus, low-nitrogen diamonds experience stronger plastic deformation than their nitrogen-rich counterparts when under equal mechanical stress.

Brown color of majority of brown diamonds is caused by the absorption continuum, which starts in the near IR spectral range and gradually increases towards shorter wavelengths—so-called the Brown Absorption Continuum (Fig. 2.6). The Brown Absorption Continuum of many brown diamonds has some secondary features like H3 center seen as a band with a maximum at 480 nm and the Pink

Fig. 2.7 Absorption intensity at different wavelengths (as indicated) within Vis spectral range for the brown diamonds, the absorption spectra of which dominate by the Brown Absorption Continuum



Band with a maximum at 550 nm. These features may result in yellow, green and pink modifying colors.

According to the DTC color scale, the intensity of brown color of diamond is characterized by six grades from C1 (the least intense) through C6 (the darkest brown). The brown color is determined visually using master stones of corresponding colors. It can be also evaluated from the measurements of the absorption intensity of the Brown absorption continuum (Fig. 2.7). The brown color scale is not uniform in terms of absorption intensity. The absorption strength of the Brown Absorption Continuum increases only slightly for the grade change from C3 to C4, whereas the absorption increase is considerable when the grade changes from C1 to C3 and from C5 to C6.

Another grade scale of color of brown diamonds uses four categories: Br1 through Br4. An approximate correspondence between the DTC scale and the Br scale is: Br1–C1, Br2–C2 to C3, Br3–C4 to C5, Br4–C6. The Br scale is more uniform as compared with the DTC scale. The Br scale is more convenient for the characterization of rough brown diamonds selected as starting material for HPHT treatment.

Brown diamonds can be grouped into two major categories, which reflect two different types of color distribution: (1) the distribution in form of brown striations (brown graining) and (2) non-graining distribution, which may be either uniform, or in form of irregular patches, or showing some zoning (Fritsch et al. 2005; Massi et al. 2005). The brown graining follows {111} slip planes (Fig. 2.8) and may penetrate though the whole diamond body. These diamonds exhibit strong traces of plastic deformation on the surface like etched pits and grooves. Plastically deformed diamonds, as the most populated category of brown diamonds, can be termed as regular brown diamonds. Diamonds of this category are the most common starting material for commercial HPHT treatment.

Although the brown graining is localized in the deformed areas, the deformation itself is not the primary reason of brown coloration. Because of this, not all plastically deformed diamonds are brown. Artificially induced plastic deformation during non-hydrostatic HPHT treatment at a temperature of 1,600 °C and

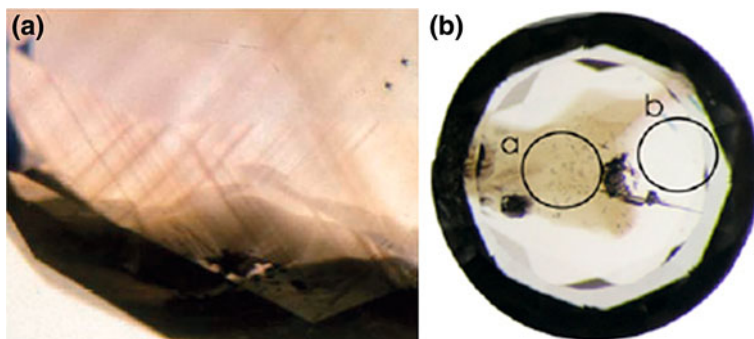


Fig. 2.8 **a** Brown graining in a natural regular brown diamond (Kitawaki 2007). **b** A natural diamond exhibiting *brown coloration* due to high content of CO_2 molecules (Hainschwang et al. 2008) (with permission of the Diamond and Related Materials journal)

a pressure of 6 GPa does not result in brown color (Kanda et al. 2005). Thus, the plastically deformed areas are just the places where the optical centers responsible for the brown coloration are generated. These defects can be vacancy clusters, defects responsible for the Amber Center and dislocations (Fritsch et al. 2005; Hounscome et al. 2006, 2007; Vins et al. 2008). Although all these defects can contribute to the brown graining, the vacancy clusters seem to be the most effective ones (Bangert et al. 2009).

Production of vacancies by plastic deformation and their accumulation into vacancy clusters may begin at a temperature of 1,200 °C, when diamond loses its rigidity and dislocations start to form. Thus, it is assumed that the generation of brown color in natural diamonds may occur in earth at rather low temperatures and the defect structure of such diamonds may reveal characteristic features of low temperature heating. For instance, it can be a trace concentration of single non-aggregated vacancies, which survived the natural heating and which can be detected as a weak GR1 center (see Chap. 5). HPHT treatment removes single vacancies and destroys the GR1 center completely. Consequently, traces of the GR1 center in natural diamonds with brown coloration is an indicator of their pristine state.

In plastically deformed brown type Ia diamonds, no correlation between brown color and nitrogen content has been found (Chapman 2010). However, there is some correlation between internal strain in type Ia diamonds and their brown coloration, the brown color being associated with lower strain fields (Van Royen 2006; Chapman 2010).

Brown color can be artificially induced in diamonds, when they are heated at high pressure at non-hydrostatic conditions resulting in internal strain (Howell 2009). However, the strain alone does not result in brown color. Instead, the brown coloration in the deformed diamonds is distributed rather uniformly throughout the bulk and it does not follow the slip bands or any other crystallographic features. It might be that the concentration of the defects responsible for the brown

coloration in the slip planes is a slow kinetic process occurring after the internal strain has been induced.

Along with the plastically deformed brown diamonds colored by the deformation-induced graining, there are brown diamonds, color of which is caused by micro-inclusions and defects generated by non-deformational mechanisms. These diamonds can be termed as irregular brown diamonds. The defects contributing to brown color of irregular brown diamonds have been identified as C defects in type Ib diamond, micro-inclusions of non-diamond phases, imbedded CO₂ molecules, hydrogen-related defects, some unknown intrinsic defects in type IIa and IaB diamonds (Ewels et al. 2001; Fritsch et al. 2005; Hainschwang et al. 2008; Barnes et al. 2006). Prominent non-graining brown diamonds are CO₂-rich ones (Hainschwang et al. 2008). These diamonds can be recognized by shapeless brown areas (Fig. 2.8b). The nature of the optical centers responsible for brown color of CO₂-rich diamonds has not been established yet. However, it is known that these centers are much more stable than the vacancy clusters in plastically deformed brown diamonds. Due to this high stability, the brown color of CO₂-rich diamonds stands HPHT treatment even when performed at very high temperatures. Because of this, the CO₂-rich brown diamonds are not used for commercial HPHT color enhancement.

2.2.2 Yellow

Two major reasons for yellow color in natural diamonds are the absorption of the N3 and N2 optical centers and the continuous absorption in the visible spectral range due to C defects. The N3 and N2 absorptions cause the color of so-called “cape-yellow” diamonds, which are the most common naturally-colored gem diamonds of pleasant colors (Johnson and Moe 2005) (Fig. 2.9). The cape-yellow diamonds are of type Ia with nitrogen content of at least 200 ppm. A considerable portion of nitrogen in these diamonds is in the form of B defects. The vast majority of light yellow natural diamonds are colored this way. Some cape-yellow diamonds have high content of hydrogen, which provides an additional weak absorption in the yellow to green spectral range. Because of this absorption, the color of the hydrogen-rich yellow diamonds may have an unwanted gray modifier.

The N3 and N2 centers are very temperature stable and therefore cape-yellow color component of natural diamonds cannot be removed or reduced by HPHT treatment. Instead, in some cape-yellow diamonds, HPHT treatment may enhance absorption of the N3 and N2 centers resulting in a deeper yellow color. Whereas the N3/N2 absorptions are in general not affected much by HPHT treatment, the hydrogen-related grayish color can be reduced or even removed by HPHT treatment. Thus, HPHT-treated cape-yellow diamonds are also something to encounter with in the gem diamond market.

The absorption in the Vis spectral range due to C defects causes orangey-yellow or “canary-yellow” color, which can be easily distinguished from the cape-yellow

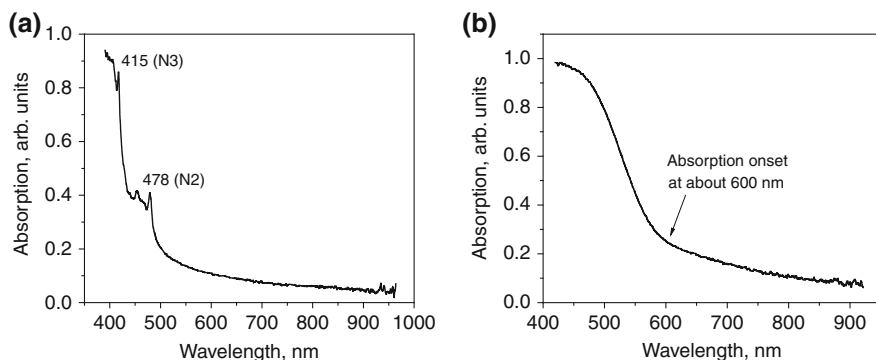


Fig. 2.9 **a** Absorption spectrum of a typical natural *cape-yellow* diamond. Enhanced absorption starting in the *green* spectral range and rapidly increasing towards *blue* and UV spectral range is the cause of the *yellow* coloration. **b** Absorption spectrum of a type Ib diamond exhibiting the absorption continuum due to C defects. C defects absorb light in the *yellow* and *green* spectral ranges stronger than N2 centers in *cape-yellow* diamonds. Due to this difference, type Ib diamonds have an *orange* modifier in their color when compared with the *cape-yellow* diamonds

color. The absorption spectra of *cape-yellow* and *canary-yellow* diamonds are also very different (compare Fig. 2.9a, b). The C defects are very effective in absorption. Just a trace concentration of C defects may affect color grade of natural diamond. A concentration of C defects of 0.1 ppm reduces the color grade of diamond to a level of J. A few ppm C defects is sufficient to cause a fancy yellow color (Collins 2001; Kitawaki 2007). Deep yellow color, characteristic of rare natural type Ib diamonds and most synthetic diamonds, is caused by C defect concentration of 20 ppm and above (Claus 2005). Very deep yellow color of synthetic diamonds is due to high content of C defects in the concentration range of 200 ppm (Collins 2003). Extremely high content of C defects (above 1,000 ppm) causes very deep yellow/brown color (Collins 2001). Although the increase in the intensity of yellow color follows the C defect concentration, it is difficult to accurately link defect concentration to color grade for different diamonds due to the effect of size, shape and cut (Fisher 2012).

Very rarely, natural diamonds with strong absorptions in H3 and H4 centers (see below Chap. 5) acquire orange-yellow color, which may resemble the color of type Ib diamonds (Fig. 2.10a). Some natural yellow diamonds with rather pronounced orange modifier owe their color to a broad absorption band with maximum intensity at a wavelength of 480 nm accompanied by an absorption continuum steadily increasing towards shorter wavelengths (Collins 2001) (Fig. 2.10b). Although the spectral position of the absorption maximum of the 480 nm band coincides with that of the H3/H4 centers, the 480 nm band is a different optical center and it should not be confused with the H3 and H4 centers (Collins 2003).

C defects have moderate temperature stability. Thus, the *canary-yellow* color induced by C defects is easily affected by HPHT treatment. HPHT treatment, when

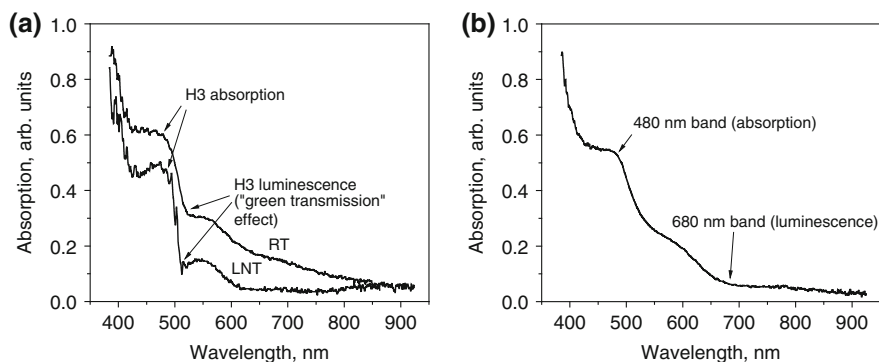


Fig. 2.10 **a** FSI absorption spectra of a natural *orangey-yellow* type IaAB diamond showing naturally present H3 center. The H3 absorption band, when recorded at room temperature, resembles the 480 nm band. Yet the measurement at liquid nitrogen temperature reveals fine structure of the H3 band, what makes it distinguishable from the 480 nm band. In this diamond, the H3 center also exhibits noticeable “green transmission” effect which makes the diamond to look *greener*. **b** FSI absorption spectrum of an *orangey-brownish-yellow* natural diamond with absorption in the 480 nm band recorded at liquid nitrogen temperature. The 480 nm band exhibits no fine spectral structure. Orange tint of the color of this diamond is enhanced by the luminescence band at 680 nm, which is the emission replica of the 480 nm absorption band. This effect is analogous to the “green transmission” effect of the H3 center

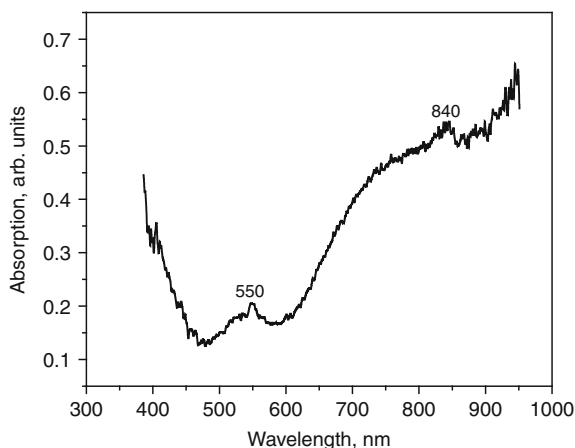
performed at temperatures below 2,000 °C, reduces concentration of C defects and may convert intense canary-yellow color of type Ib diamonds into light yellow, or even make these diamonds near colorless type IaA. However, HPHT treatment performed at high temperature (2,200 °C and above), reversibly produces C defects in type Ia diamonds and may strengthen the yellow color component.

2.2.3 Blue to Violet

Natural boron-containing type IIb diamonds are blue or more typically blue-gray. When viewed in polarized light, natural IIb stones, like other type II diamonds, have characteristic tatami-structure due to low-nitrogen content. Some natural blue diamonds owe their color to high concentration of hydrogen, which absorb in red and yellow-green spectral ranges. Rarely, high-hydrogen diamonds reveal a strong broad-band absorption starting at 600 nm and spreading towards IR spectral range. This absorption may add a greenish tint to the blue and violet color (Darley and King 2007) (Fig. 2.11).

Blue and violet colors cannot be produced by HPHT treatment. However, HPHT treatment can considerably improve the boron-induced blue color of bluish-gray or gray type IIb diamonds via reduction or removal of the gray component.

Fig. 2.11 Absorption spectrum of a high-nitrogen, high-hydrogen type IaAB diamond of fancy *violet gray* color. The *violet* modifier of the color is caused by the transparency windows at a wavelength of 470 nm. The absorption feature at 550 nm, which also adds to the *blue-violet* coloration, is probably due to hydrogen



The bluish color can be also stimulated by natural irradiation, which produces the GR1 center. Electron-irradiated pale-blue diamonds called “ice-blue diamonds” are quite popular in the gem market (Kitawaki 2007).

2.2.4 Green

Many diamonds from some deposits (e.g. from Congo and Canada) have homogeneous surface coloration in blue and green colors because of natural alpha- and/or beta-irradiation. This type of coloration of natural rough diamonds was described in (Orlov 1973). The main reason of the radiation-induced green color is the absorption of GR1 center (Fig. 2.12a). Light green coloration may be observed through the whole diamond body (body distribution of vacancies producing the GR1 center) indicating the action of deeply penetrating beta- and gamma-radiation (Yelissev et al. 2004). Alternatively, green coloration can be concentrated close to the surface as a result of dominating irradiation with alpha-particles, which penetrate into diamond to a depth of a few microns only.

Natural untreated green diamonds have very light color because of weak GR1 absorption. These diamonds often exhibit green to brown irradiation spots (radiohalos, Fig. 2.12b) on naturals (e.g. on unpolished parts of girdle of cut diamonds) (Kitawaki 2007; Hargett 1991). This feature makes the naturally irradiated green diamonds distinguishable from the green diamonds processed by the radiation treatment. However, it is important to understand that the radiohalos are not the ultimate proof of the natural body color of green diamonds. Instead, the diamonds with natural radiohalos can be irradiated with high energy electrons with the aim of improvement of their body color and then the radiohalos can be conveniently used as a “solid” proof that these diamonds are “naturally” irradiated. Moreover, radiohalos can be produced on the diamond surface artificially applying irradiation

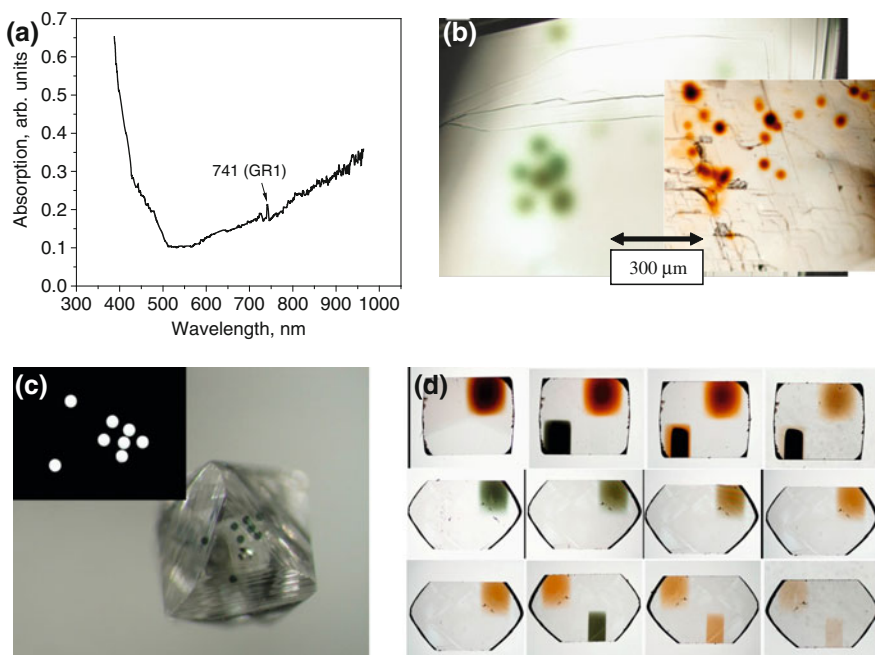
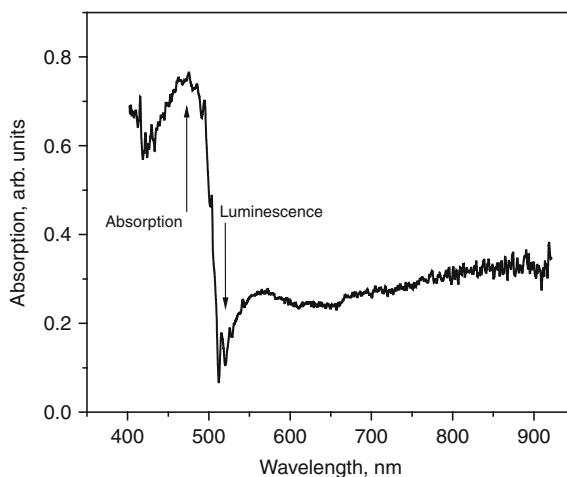


Fig. 2.12 **a** Absorption spectrum of a very *light green* type IaB natural diamond showing weak GR1 center and rather developed H3 center. The *green color* of this diamond is distributed through the whole diamond body. Low intensity of the GR1 center (absorption coefficient is about 0.08 cm^{-1}) suggests its natural origin. **b** Well-shaped, *circular green* and *brown* natural radiohalos on surface of an octahedron from Guaniamo, Venezuela (Nasdala et al. 2012). **c** A little natural diamond octahedron ion-irradiated through a mask (shown in the insert) demonstrating a way of making artificial radiohalos (courtesy of L. Nasdala). **d** *Ion-irradiated spots* on surface of natural diamond plates. These *spots* have been irradiated with different ions, at different energies, with different doses and annealed at different temperatures. Depending on the parameters of the irradiation and annealing, the color of the irradiated areas can be *green*, *orange*, *brown* and *black* (Nasdala et al. 2012)

with light ions (e.g. He or C ions) through a stencil mask (e.g. perforated foil) (Nasdala 2012) (Fig. 2.12c). The color of the artificial radiohalos can be made quite identical to those of natural ones (Fig. 2.12d).

Some natural diamonds exhibit green color when viewed under daylight illumination. This light-induced green color is the result of intense luminescence of H3 optical center excited by blue and UV components of the daylight. Such diamonds are known as “green transmitters”. In perfect low-nitrogen diamonds with little content of A defects, the H3 defects are very effective in green luminescence under daylight excitation. Thus, even being present in small concentrations, the H3 defects may considerably contribute to green color via the characteristic green emission in the spectral range 500–550 nm (Fig. 2.13). The green color of “green transmitters” considerably weakens or completely disappears when diamond is viewed in incandescent light.

Fig. 2.13 FSI absorption spectrum of a natural low-nitrogen type IaAB diamond of fancy *yellowish green* color measured at liquid nitrogen temperature. The dominating *green* color of this diamond results from the H3 center luminescence seen in the absorption spectrum as a “reverse” structured band in the spectral range 500–550 nm. The fine structure of this band corresponds to the vibronic features of the H3 center in luminescence



Some natural yellow-green (yellowish-green) diamonds owe their color to nickel-related optical centers (Wang and Moses 2007). Color of these diamonds resembles the color of synthetic diamonds grown at elevated temperatures in the presence of Ni impurity (Vins 2002). Thus, one may assume that the natural Ni-rich diamonds of greenish color also grew in earth at elevated temperatures exceeding 1,450 °C. Therefore, these stones may exhibit some features characteristic of HPHT-treated diamonds processed at low temperatures of 1,600–1,700 °C.

Green color of natural diamonds induced both by H3 and Ni-related centers can be considerably modified, enhanced or reduced by HPHT treatment. The most characteristic example of this change is the HPHT-induced green transmitters. Whereas the “green transmission” effect is a rare feature of pristine natural diamonds, it is a very common result of HPHT treatment performed at temperatures below 2,000 °C. HPHT-induced “green transmission” effect is particularly pronounced in diamonds with low content of A defects.

2.2.5 *Pink and Red*

Natural diamonds are rarely pink and very rarely purple. It is believed that, like color of most brown diamonds, pink/purple coloration is the result of plastic deformation too. Pink coloration of natural diamonds does not depend on the presence of nitrogen impurity, and these diamonds can be of types I and II (King et al. 2002; Fisher et al. 2009).

Pink coloration, like brown graining, is also restricted to thin bands parallel to octahedral slip planes (pink graining). However, pink color is distributed rather homogeneously within these bands. Nitrogen-containing pink-purple diamonds are

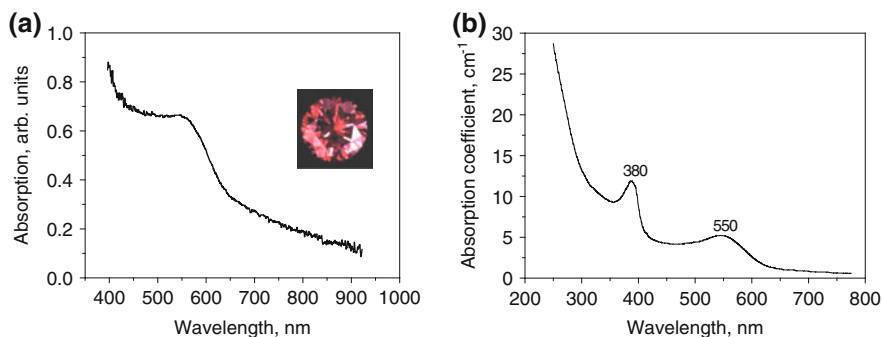


Fig. 2.14 **a** Absorption spectrum of an Argyle low-nitrogen type IaB pink diamond exhibiting a pronounced Pink Band. In this diamond, the Pink Band superimposes with the brown absorption continuum of a moderate strength—a typical absorption spectrum of natural pink diamonds. Insert shows photo of a diamond of this type [re-plotted from Chapman et al. (1996)]. **b** UV/Vis/NIR absorption spectrum showing the dominant absorption bands at 390 and 550 nm typical for natural pink diamonds [re-plotted from (Fisher et al. 2009)]. Two major transparency windows at wavelengths from 400 to 500 nm (*blue color*) and above 600 nm (*red color*) produce *pink color* of this diamond

frequently of dominant type IaA (Titkov et al. 2008). This observation implies that pink-purple diamonds had been brought from the earth interior to the surface at early stages of their formation and the processes of the nitrogen aggregation in these diamonds had not been completed. Such an immature defect structure of many pink/purple natural diamonds poses additional difficulties in detection of HPHT treatment. Indeed, presence of traces of C defects, which are otherwise a strong evidence of HPHT treatment, is not a rare event for untreated type IaA pink/purple diamonds. Therefore, the detection of C defects in these diamonds cannot be considered as a proof of HPHT treatment.

The primary reason of pink color of plastically deformed natural diamonds is a broad absorption band with maximum at about 550 nm—so-called “Pink Band” (Fig. 2.14a). Pink color may be also highlighted by the presence of an absorption band with maximum at 390 nm (Fig. 2.14b). A diamond, the absorption spectrum of which has these two bands of comparable strength, has particularly pleasant pink color. The 390 and 550 nm bands can occur in both type I and type IIa diamonds. However, their strength is usually weaker in nitrogen-free diamonds.

Naturally occurring NV centers (575 and 638 nm centers, see below) may also contribute to red color of untreated natural diamonds. Although it is an extremely rare event that a natural diamond has the 575 nm center strong enough to affect its color (Fritsch 1998; Scarratt 1987), such diamonds are documented in literature. Visible absorption spectra of these diamonds may contain 638 nm (NV⁻ center), H3 and H4 absorptions (Wang et al. 2003).

2.2.6 Gray

Gray color of diamonds is the result of uniform absorption throughout the whole visible spectral range. Since perfectly uniform absorption in a wide spectral range occurs rarely, gray color of natural diamonds is usually accompanied by faint tints of yellow, green, blue or pink. It is believed that the two major sources of gray color are graphitic micro-inclusions and hydrogen (Vins and Kononov 2003). The graphitic inclusions work as light scattering centers causing Rayleigh scattering, rather than light absorbing centers. Because of this scattering, gray diamonds may have translucent appearance. The size of the graphitic micro-inclusions varies and may reach a few micrometers. The big graphitic inclusions can be seen in microscope and identified by their characteristic hexagonal shape. The most probable explanation of the uniform formation of graphite nano-crystals through the body of gray diamonds is that these diamonds grew at the temperature–pressure parameters close to the diamond-graphite phase transition. A less probable mechanism could be the direct incorporation of graphitic inclusions during the diamond growth.

The hydrogen-related defects work like regular absorbing optical color centers. All natural diamonds contain considerable amount of hydrogen, some of which is present in form of optically active defects. In nature, diamonds always grow in the presence of hydrocarbons (mainly methane and the products of its dissociation), carbon oxides, nitrogen hydrides, hydrogen and other gasses (Digonsky and Digonsky 1992). It is also believed that the crystallization of diamond from graphite occurs directly during dissociation of hydrocarbons into carbon and hydrogen irrespective of the growth medium: gaseous, silicate solutions, or metal melts. During the crystallization of carbon, hydrogen may form CH radicals on diamond surface and on the lateral edges of the graphite crystals. It is known that during heating with increasing temperature, hydrocarbons polymerize and experience complex transformations until final graphite phase is formed. During these transformations, hydrogen content reduces. Upon completion of the conversion of hydrocarbons into graphite, hydrogen can localize only on the lateral edges of the graphite crystals. Hence the amount of the remaining hydrogen is determined by the concentration of the graphite crystals and their size: the smaller the graphite crystals the greater amount of hydrogen.

Gray diamonds grew at the conditions of high oversaturation, when the diamond growth medium rapidly cooled down during its travel to the earth surface. Analysis of the impurity-defect structure of gray diamonds suggests that these diamonds experienced rapid annealing, the last period of which was at the conditions close to the graphite-diamond phase equilibrium. Low growth temperature of gray diamonds resulted in the preferential formation of “low-temperature” nitrogen defects: C- and A defects. Thus, natural nitrogen-containing diamonds of gray color are usually of type IaA. The intensity of A center in spectra of these diamonds can be as high as 65 cm^{-1} . Yet some type IaA gray diamonds may exhibit the presence of traces of C defects. In addition to A- and C defect absorptions, all gray diamonds,

irrespective of their type, reveal in their spectra strong hydrogen-related centers, the most intense being the 3,107 and 1,405 cm^{-1} ones.

In type IIb diamonds, gray color may be accompanied by additional brown coloration. Combined effect of the absorption continuum due to boron and the brown absorption continuum due to vacancy clusters may essentially result in gray color. Majority of natural type IIb diamonds have grayish tint because of this effect.

2.3 Color of Diamonds Used for HPHT Treatment

There are four main color-based categories of diamond used for commercial HPHT treatment. The HPHT-induced color changes are very different for diamonds of different categories. The first category comprises type IIa brown diamonds. These diamonds, and especially those of high clarity and light brown color, are suitable for the production of the most perfect high color stones. Brown type IIa diamonds are also used for production of light pink stones, the pink color of which is identical to that of untreated natural pink diamonds. The diamonds of this category are the most valuable starting material for HPHT treatment.

The second category comprises type IaB brown diamonds. The primary aim of HPHT treatment of these diamonds is the production of near colorless stones and, in rare cases, low grade colorless stones. Since HPHT treatment always produces in nitrogen-containing diamonds at least traces of the optical centers active in the visible spectral range, brown type IaB diamonds cannot be converted into colorless stones of high color grade. Another aim of treatment of brown (as well as near-colorless and low color grade) type IaB diamonds is production of pink stones. In this case, the diamonds are subjected to multi-process treatment resulting in the formation of NV^- center of moderate intensity. HPHT annealing of type IaB diamonds does not produce much C defects even at high temperatures. Hence the resulting color of the treated diamonds is not affected by the C defect absorption continuum. The most beautiful pink color is achieved when two major absorption centers N3 and NV^- have comparable intensities. Visible transmission spectrum of these diamonds has two windows at wavelengths around 480 nm (blue) and above 640 nm (red). The combination of these two colors makes diamonds pink.

The third and the most populated category is high clarity type IaAB brown diamonds. Inclusion-free brown diamonds of type Ia are starting material for making beautiful high clarity diamonds of fancy yellow and green-yellow colors. Appearance of some HPHT-treated type Ia diamonds can be very attractive by far exceeding that of any natural untreated stone of this hue. Another aim of treatment of brown type IaAB diamonds is the production of red stones (Imperial Red diamonds). For this purpose, multi-process treatment is applied. The treated red diamonds owe their color to the very strong NV^- center, the absorption of which forms pronounced transmission window in the red spectral range. High-nitrogen diamonds treated in this way may also reveal strong C defect absorption

continuum, which adds to diamond color an orange modifier. In order to achieve a pleasant red color, the diamonds should not contain much nitrogen. High concentration of nitrogen results in too intense optical centers and too deep red color, which could be even modified with unwanted brown tint.

Low clarity type Ia diamonds of any unattractive colors (mostly brown and gray) are the diamonds of the fourth category. The aim of HPHT treatment of these diamonds is the color improvement and obtaining saturated fancy colors, which could hide the included interior.

The four diamond categories mentioned above comprise the diamonds, which are most frequently used for HPHT treatment. However, any natural diamond, regardless its type, color and clarity, can be treated by HPHT annealing with the aim of increasing its commercial value. Even colorless diamonds of the highest color and clarity can be subjected to HPHT treatment with the aim to add them rare fancy colors.

HPHT-Treated Diamonds

Diamonds Forever

Dobrinets, I.A.; Vins, V.G.; Zaitsev, A.M.

2013, XIX, 257 p. 166 illus., 103 illus. in color.,

Hardcover

ISBN: 978-3-642-37489-0