

Significance of Spectroscopic Methods for the Identification Defects in Diamonds

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Defects in the diamond lattice are the potential source of the information about genetic history of a diamond. On the other hand, the major treatments used to improve the color of natural diamonds create and destroy defects in the diamond lattice. For commercial reasons it is important to detect a diamond treatments. This Poster focuses on the characteristics of defects in type IaAB and type IIa natural brown diamonds and high-pressure, high-temperature (HPHT) treated diamonds as studied by infrared absorption spectroscopy (IRS) and low temperature laser induced photoluminescence spectroscopy (PLS) excited by 514.5 nm Ar⁺ laser.

Brown is the most common color among mined diamonds. In many cases brown color in natural diamonds is attributed to plastic deformation and can be altered by HPHT treatment. The color resulting after treatment depends on the impurity-defects in the diamond lattice and the conditions of treatment.

IRS is the first step in spectroscopic identification defects in a diamond. Type IaAB diamonds contains nitrogen-impurity in the form of A-, and B-aggregates with the main absorption peaks at 1282 and 1172 cm^{-1} , respectively. Frequently type IaAB diamonds contains B' defects (platelets) which have absorption peaks from 1358 to 1380 cm^{-1} . Type IaAB diamonds are divided in regular (relatively high content of B' defects) and irregular (low content of B' defects) types. Single substitutional nitrogen atoms (C center) is the dominating defect in type Ib diamonds also present in type IaAB natural diamonds after HPHT-treatment. C center has the principal peak at 1130 cm^{-1}

and an additional sharp peak at 1344 cm^{-1} . Natural diamonds which do not show specific IR optical absorption due to nitrogen-, boron- or hydrogen-related defects in the one-phonon region are defined as type IIa. Hydrogen is also a common impurity in diamonds and shows the principal peaks at 3107 and 1405 cm^{-1} . Most diamonds are inhomogeneous, have growth zones with various compositions of impurities, and, thus, present mixed types.

In nature, annealing typically occurs at modest temperatures compared to those used in laboratory HPHT treatments. The relatively low temperatures allied with geological time scales ensure that in nature the forward nitrogen aggregation reaction dominates. HPHT treatments altering brown coloration of diamonds are carried out over much shorter time scales, and significantly higher temperatures are required to achieve the desired reaction. The higher temperature also substantially raises the probability of the reverse aggregation reaction (breaking up nitrogen aggregates) and the creation new defects (both intrinsic and impurity related). The next transformation of the defects occur in natural brown type IaAB diamonds during HPHT treatment to produce yellow, greenish-yellow or green colors:

A, B centers, H3, 535.8, 612.5 nm, (N-V)^o defects → A, B, C, N3 centers, H3, H4, 535.8, 612.5 nm, (N-V)^o, (N-V)⁻ defects → A, B, C, N3 centers, 535.8 nm, (N-V)^o, (N-V)⁻, H3, H2 defects.

PLS is very sensitive technique for identification defects in the diamond lattice, the intense laser beams can excite defects which have extremely low concentration in diamonds. The combination of defects is

observed in natural diamonds differ to those in HPHT-treated diamonds. The most significant features in the PLS of natural brown type IaAB diamonds are the strong lines at 535.8, 576, 612.5 nm and relatively weak lines at 558 and 741.5 (GR1 center) nm. The 558 nm line is suggested to be associated with amorphous diamond-like carbon (Zaitsev, 2001) and very often presents in natural brown diamonds. The strong 637 nm line, and the less intensive lines at 535.8, 575 nm are observed in PL spectra of HPHT-treated type IaAB diamonds.

The 535.8, 574.8, 637, and 741.5 nm lines are observed in PLS of brown type IIa natural diamonds. HPHT treatment transforms these diamonds into colorless, nearly-colorless, or more rarely into light pink or blue color. During HPHT treatment at temperature ranging from 1500 to 2000 °C, plastic deformation in type IIa brown diamonds are decreased, accompanying by significant reduction of dislocation density, and, as a result, discoloration of type IIa diamonds is occurred. Dislocation movement within the crystal lattice started at temperature exceeding 1500 °C, and this caused the formation of vacancies and interstitials, their concentration were always higher in diamond exhibiting greater dislocation density (Vins, 2002). Different concentration of vacancies and interstitials after HPHT treatment can explain various results which appear in PL spectra of HPHT-treated type IIa diamonds. PLS reveals the presence 575 and 637 nm lines in most, but not all, HPHT-treated stones. When those centers are present, the ratio of the 575/637 nm PL intensities should be less than 1 for HPHT-treated type IIa diamonds. The total absence of luminescence may be another important indicator of HPHT treatment (Fisher & Spits, 2000).

We shall consider of the main defects is observed in PL spectra natural and treated diamonds. **The (N-V)⁰** (574.8 nm line) **and (N-V)⁻** (637 nm line) **centers** are photochromic nitrogen-vacancy centers in diamonds. They are connected and their intensities depend on any irradiation and HPHT treatment conditions. Electron and

neutron irradiation reduced and suppressed (respectively) the intensity of the 637 nm line, while simultaneously the 574.8 nm line intensity increases with neutron irradiation. The (N-V)⁰ and (N-V)⁻ centers anneal out in irradiated stones at approximately 1400 and 1500 °C, respectively, but in non-irradiated HPHT-treated diamonds these centers can be survive to about 2000 and 2200 °C, respectively (Zaitsev, 2001). The lineshape of the 637 nm line depends on crystal morphology of diamond, showing larger FWHM as the morphology become more cubic.

The GR1 center (740.8 and 744.5 nm lines, more often observed 741.5 nm line) is intrinsic lattice defect unrelated to impurities and is attributed to the neutral single vacancy (V⁰). This is the main feature of irradiated diamond of any type. GR1 center disappears after heating at about 800 °C. However, the GR1 center may alive to temperature as high as 900 °C in relatively pure (types IIa, IIb) diamonds and as high as 1000 °C in diamonds irradiated with heavy high-energy ions (Zaitsev, 2001). The GR1 center, if it presents, is a reliable feature to identify that the diamond has not been heated over 1000 °C.

The 535.8 nm defect is not well studied. It is observed in natural brown diamonds and irradiated with subsequent annealing diamonds (Field, 1992). Kanda and Watanabe (2006) have reported that the luminescence peak at 535.8 nm in type IIa synthetic diamonds disappears after irradiation and appears after annealing at 500 °C. Our research show consistent data: the 535.8 nm narrow line has strong intensity in both natural brown diamonds and type IaAB HPHT-treated diamonds, it has significantly less intensity in type IIa HPHT-treated stones and almost absent in irradiated and annealed (up to 1250 °C) type IaAB diamonds. Based on these results, we suggest that 535.8 nm is not a radiation center. It appears during relatively low temperatures annealing and presents in diamonds after HPHT annealing at temperatures up to 2000 °C.

An origin of the **612.5 nm defect** and its behavior during treatments are not clear enough. The 612.5 nm line presents in PL spectra of type Ia brown natural diamond (Zaitsev, 2001) and attributes to a Ni-containing defect by Lindblom et al., (2005). We observed the 612.5 nm defect in PL spectra of nearly-colorless and brown type IaAB (irregular) natural diamonds containing hydrogen. The intensity of the 612.5 nm narrow line correlates to the B' defects and B-aggregates ratio, the intensity is strong when the ratio is $B'/B < 1$. The intensity decreases when the concentration of B' defects increases. In all of these samples, we also observed tension fractures, graphitization of mineral inclusions, graphite inclusions, and graining. The 612.5 nm defect remains stable in type IaAB (irregular) diamonds after irradiation and annealing at temperature up to 1250 °C, but it has not been observed in diamonds after HPHT treatment (2000 °C, 6.5 GPa, 10-30 minutes) (Hainschwang et al., 2005; our data). Thus, this defect anneals out at temperatures ranging from 1250 to 2000 °C, but precise annealing temperature of this defect is unknown.

The 603.2, 640.6, and 700.6 nm defects are naturally occurring in type Ia (Cape) yellow diamonds and diamonds of a mixed cubo-octahedral habit (Field, 1992). These lines were attributed to Ni-containing defects in high-nitrogen synthetic diamonds grown in Ni-containing melt after annealing at temperatures above 1700 °C (Yeliseyev et al., 2002). The 603.5, 641, and 700.3 nm centers are observed in natural diamonds from the Argyle mine (Australia) and were tentatively attributed to some interstitial-type Ni-related defects by Iakoubovskii & Adriaenssens (2002). Lang et al., (2004) are described the 603.5, 640, 700.5, and 787 nm defects as (Ni-N-V) defects associated with cuboid growth sectors in natural diamonds. All these attributions do not contradict each other and even more likely, these centers are some complicated (Ni-N-V) complex in natural diamonds related to cuboid growth sectors. We observed these lines in PL spectra of some yellow and brown natural type IaAB

diamonds containing hydrogen and irradiated and annealing type IaAB yellow diamonds containing hydrogen.

In summary, the important defects in natural and HPHT-treated diamonds can be observed with IRS and PLS. Knowledge of the origin and the behavior of the defects in natural diamonds can indicate the temperature and chemical conditions which a diamond subjected at a long time in the earth's crust. HPHT treatment of natural diamonds produces a wide variety of results depending of initial characteristics of stones and the form of treatment. Specific combinations of defects support the identification diamond origin. Some defects are still not understood and more research is necessary before the physical processes taking place during treatment can be fully explained.

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