

# EPR and luminescence data on the nitrogen aggregation in diamonds from Snap Lake dyke system

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## ABSTRACT

More than 200 samples of diamonds from the Snap Lake dyke system in Canada were studied in details using optical and EPR spectroscopy. About 30% of them were colorless or slightly greenish tinted and were related to IaB type with a high aggregation level of defects: N3 (N<sub>3</sub>V), B nitrogen centers (N<sub>4</sub>V<sup>0</sup>) and clusters of interstitials (B' centers). Traces of heavy plastic deformation in the crystals were found by X-ray techniques. Visual examination of photoluminescence (PL) of another batch of samples shows one type emission: a blue core surrounded by a green shell. As a rule these diamonds were colored in brownish to greenish tints and belong to the IaA type containing predominantly N–N nitrogen aggregates.

Specific features of type IaB diamonds are a dominant broad line in the P2 EPR spectrum and an unusually high concentration of nitrogen in a single substitutional form, N<sub>5</sub><sup>0</sup>. We suggest that this uncommon combination was produced naturally by the destruction of B-centers (N<sub>4</sub>V<sup>0</sup>) during plastic deformation. When IaA and IaB diamonds are heated, movement of dislocations throughout the crystal causes further decomposition of the complicated nitrogen defects (A, B), producing simpler nitrogen forms: P1, P2 and H3 centers. Analysis of light illumination effects on the IaB type diamonds revealed that some of these defects are in different charge states and the color of plastically deformed crystals is believed to be due to the charge transfer between the nitrogen defects and the dislocation core. Results of the current study suggest that a line broadening in P2/N3 and H3 systems and thus unusual ratio between strengths of the zero phonon lines and vibronic bands in PL spectra are related to the lattice distortion because of nearby dislocations. The sharp 1332 cm<sup>-1</sup> IR peak in these samples is due to N<sub>5</sub><sup>+</sup> rather than to B-centers.

The PL 490.7 nm center, most manifesting itself in plastically deformed IaA diamonds, is first shown to be always accompanied by PL blue systems at 406 and 423 nm and to correlate with EPR signal from dangling bonds in the dislocation cores.

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## 1. Introduction

Although most natural diamonds contain dislocations, little is known about the interaction between dislocations and nitrogen centers. The W7 center in IaA brown diamonds (Shcherbakova et al., 1975; Loubser and van Wyk, 1978; Newton and Baker, 1991a,b), with the structure of two nitrogen atoms separated by two carbon atoms, is the only confirmation of dislocation interaction with A-centers well-known as pairs of nearest neighbor substitutional nitrogen atoms. The nitrogen centers in natural IaB diamonds are mainly B-centers, having the structure of four nitrogen atoms in the first coordination sphere of a vacancy, N<sub>4</sub>V<sup>0</sup>. But to date, information about the coloration and possible nature of color centers of plastically deformed diamonds of this type and also about any interaction of dislocations with B-centers is very scanty. Natural Ib diamonds with most nitrogen in dispersed form are

uncommon, and, therefore, no data on the interactions between P1 (N<sub>5</sub><sup>0</sup>) EPR centers and dislocations are available. Previously, we showed that in IaB diamonds with traces of plastic deformation the P2 EPR spectrum related to optical N3 system (a vacancy neighbouring three nitrogen atoms on a (111) plane, N<sub>3</sub>V center) displays a single broad line due to unresolved hyper fine structure (HFS) (Nadolinny et al., 2003).

This communication presents a comprehensive analysis of the EPR and photoluminescence (PL) spectra of IaB and IaA types of Canadian natural diamonds from Snap Lake dyke system with traces of plastic deformation. The influence of HPHT treatment on the transformation of nitrogen defects in these diamonds will be also examined. The outcome of these studies is evidence for the decomposition of aggregated nitrogen defects by plastic deformation and motion of dislocations.

## 2. Experimental

EPR spectra were obtained at 300 and 77 K with an E109 Varian EPR spectrometer operating at X-band. To record and accumulate

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spectra, new software was used, which was adapted to WinEPR and Symfonia programs. The investigation of the influence of photoexcitation on the samples was performed using an optical cavity. IR spectra were taken by an FT-IR Paragon 1000 with resolution  $1\text{ cm}^{-1}$  in the range  $450$  to  $4400\text{ cm}^{-1}$  and an F-IR Bruker JFS-66 spectrometer. The photoluminescence (PL) spectra were obtained at  $77\text{ K}$  with a spectrometer DFS-24 operating in the spectral range  $360$  to  $840\text{ nm}$ . A mercury lamp, fitted with glass filters separating Hg lines  $313$  or  $365\text{ nm}$ , was used to excite photoluminescence. None of the PL spectra obtained has been corrected either for the transfer function of the monochromator or for the spectral response of the detector. The crystals were heated at  $7\text{ GPa}$  and  $1850$ – $2000\text{ }^\circ\text{C}$  for  $12\text{ h}$  using a “split sphere” high pressure apparatus of a BARS type.

### 3. IaB diamonds with the traces of plastic deformation

Sixty diamonds of the IaB type studied here are the natural crystals from the vast deposit on the American continent, discovered in the 90s in the region of Snap Lake, province Slave, Canada (Pokhilenko et al., 2000). The samples selected are free-inclusions and looked colorless or greenish tinted. To select the crystals with B and B' centers, IR spectral examination was carried out. The diamonds from the Canadian deposit contain about 30% such crystals.

Fig. 1a shows typical IR spectra of the IaB diamonds under study. No  $1130\text{ cm}^{-1}$  peak attributable to single substitutional donor nitrogen was revealed using standard procedure of decomposition of the spectra into the nitrogen-related components. In Canadian crystal SL-00/106, IR peaks at  $1175\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  dominate, and also a

small concentration (30–50 atomic ppm) of nitrogen is found in A aggregates. Decomposed spectra of these crystals reveal a small discrepancy in the strength of  $1332\text{ cm}^{-1}$  from B-centers. Recent IR investigations have shown that the  $\text{N}_3^+$  state of isolated substitutional nitrogen makes also contribution to the absorption at  $1332\text{ cm}^{-1}$  (see Lawson et al., 1998).

The IaB diamonds examined have strong blue or whitish-blue glow. Their PL spectra exhibit an intense N3 system with the zero phonon line (ZPL) at  $415\text{ nm}$  (an optical analogue of the P2 center) (Fig. 2a), but the peak intensity of ZPL was observable reduced noticeably as compared to the intensity of the vibronic band. This way, the N3 system differs from that given in the literature. Self-absorption in the ZPL seems an unlikely reason for this. As well-defined phonon structure indicates a stability of a defect structure and its symmetry. The N3 system is found to be accompanied by a group of weak narrow ZPLs at  $407.8$ ,  $409$  and  $411\text{ nm}$ . The  $409\text{ nm}$  line is more intense and always observable. Note that these three lines are observable in the crystals with an uncommon relationship between intensities of ZPL at  $415\text{ nm}$  and phonon side-band.

At room temperature, the EPR spectra of the crystal SL00/106 studied in detail here consist of a single broad line with  $g=2.0031$  and  $\Delta H_{1/2}=11.5\text{ G}$  which as recognized in Shcherbakova et al. (1978) is associated with the P2 center (Fig. 3a). This diamond was exposed at  $77$  and  $300\text{ K}$  to light illumination in the EPR cavity, and the effects observed were analyzed. UV light at  $300\text{ K}$  has no influence on the P2 EPR spectrum. At cooling the sample to  $77\text{ K}$  in the darkness, the broad P2 line intensity decreased drastically (Fig. 4a) and a single narrow line with  $g=2.0027$  and  $\Delta H_{1/2}=1\text{ G}$  appeared. Light excitation with  $\lambda < 380\text{ nm}$  at  $77\text{ K}$  restores the broad line and simultaneously

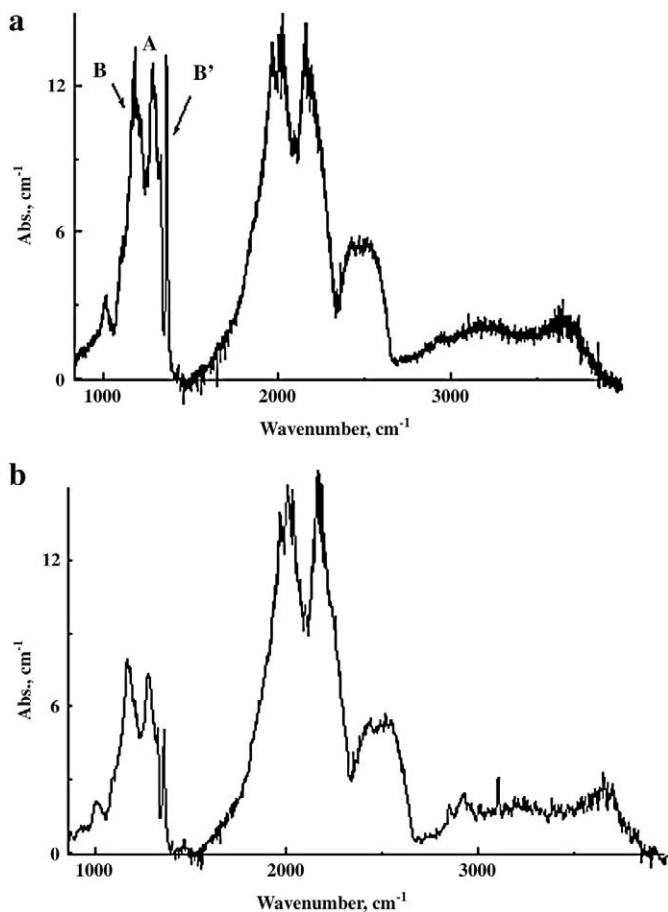


Fig. 1. IR spectra of natural IaB diamond: a – before, and b – after HPHT treatment at  $2000\text{ }^\circ\text{C}$ ,  $7\text{ GPa}$ , for  $12\text{ h}$ .

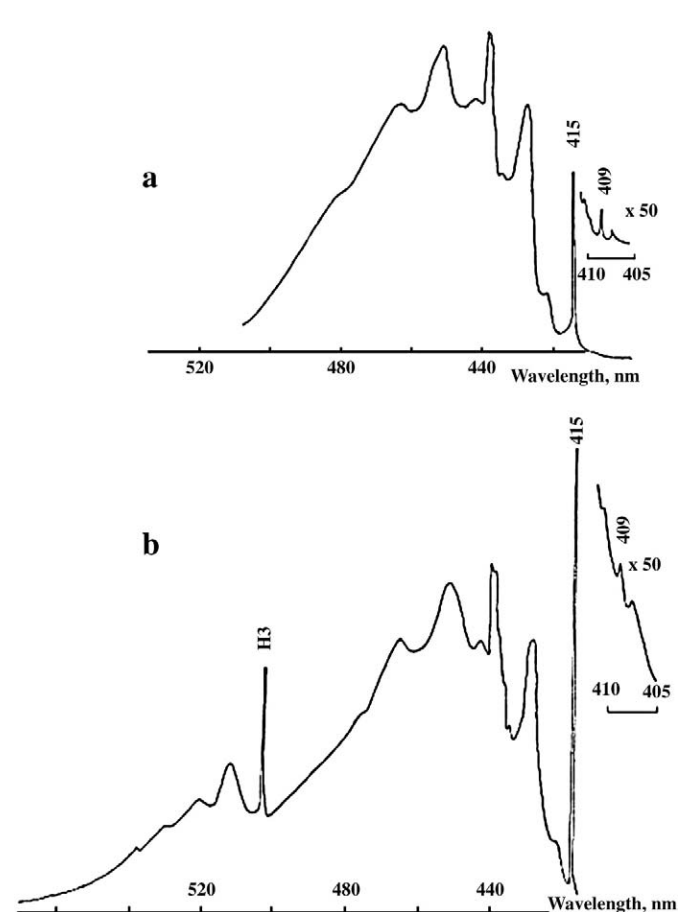


Fig. 2. Photoluminescence of natural IaB diamond: a – before, and b – after HPHT treatment at  $2000\text{ }^\circ\text{C}$ ,  $7\text{ GPa}$ , for  $12\text{ h}$ .

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