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

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In this communication we describe more 200 samples of diamonds from the vast deposit on the American continent, discovered in the 90s in the region of Snap Lake, province Slave, Canada. The samples have no inclusions and looked greenish to brown tinted. Their properties were studied in details using optical and EPR spectroscopy. Two main groups of diamonds were separated: the first of them are related to IaB type with maximum degree of defects aggregation: N3, B nitrogen defects and B' clusters of interstitials, and the second part of specimens has one type emission under visual examination of photoluminescence: green shell and blue core. As a rule these diamonds are the IaA type samples with nitrogen mainly in A-form.

1aB diamonds with the traces of plastic deformation.

The 1aB diamonds studied are 60 crystals. Preliminary IR spectral examination was carried out to select the crystals with B and B' centers. The diamonds from the Canadian deposit contain 30% such crystals.

EPR spectra were obtained with an E109 Varian EPR spectrometer operating at X- band at 300 and 77 K. IR spectra were taken by a FT-IR Paragon 1000 with resolution 1cm⁻¹ in the range 450- 4400 cm⁻¹ and a F-IR Bruker spectrometer. The luminescence spectra were obtained with a spectrometer DFS-24 at 77K. The crystals were annealed using a high pressure apparatus of split sphere type.

In crystal No. SL-00/106, IR 1175 cm⁻¹ and 1360 cm⁻¹ bands dominate, and also a small portion of nitrogen in A-centers (30-50ppm) is observed. Decomposing IR spectra of these crystals shows a small discrepancy in 1332 cm⁻¹ intensity from B-centers. Recent IR investigations have shown that the N⁺ nitrogen state has also absorption at 1332 cm⁻¹.

The 1aB diamonds examined have strong blue or whitish-blue glow. Their PL spectra exhibit an intense system at 415 nm (see Fig.1, top), but the peak intensity of the zero-phonon line (ZPL) appeared reduced as compared to the intensity of the side-band This distinguishes the system shown from that known in the literature and no self-absorption in the ZPL is likely. A well-defined phonon structure is easily observable indicating a consistency of the defect structure and determining its symmetry. The N3 system is accompanied by a group of weak narrow zero phonon lines at 407.8, 409 and 411 nm: 409 was always observed and sometimes additional lines at the other two wavelengths.



Fig. 1. PL spectra of 1aB diamond before (top) and after (bottom) HPHT treatment.

At room temperature, the EPR spectra of the crystals studied consist of only a broad line with g = 2,0031 and $\Delta H_{1/2}$ = 11.5 Gauss (see Fig.2, top), which is due to P2 center (Nadolinny et al, 2004). The diamonds were optically illuminated in the EPR cavity at 77 and 300 K. At room temperature, illumination of the crystals has no influence on the P2 EPR spectrum. Cooling the sample to 77 K causes the broad P2 line to disappear. Light excitation with $\lambda < 380$ nm at 77 K causes the broad P2 line to restore, and an additional P1 EPR spectrum and a single narrow line with g = 2.0027 and $\Delta H_{1/2} = 1$ Gauss to appear. The line width of the P1 spectrum is estimated as $\Delta H_{1/2} = 2.5$ Gauss. The estimation indicates a P1 content in the crystal SL00/106 of 6 ppm, which is not typical of IaB diamonds.

The dynamics of the photo-excited P2 EPR spectrum was studied. UV excitation showed slow decreasing EPR spectra in the dark. Light of $\lambda >$ 400 nm at 77 K produces a decrease of the P2 EPR spectrum to the level observed after crystal cooling. Under these conditions the P1 EPR spectrum disappeared and the



narrow line was restored to the intensity it had in the dark after crystal cooling. All changes observed are reversible on UV excitation followed by red illumination. The spectrum left after the red illumination consists of poorly resolved P2 EPR lines. The broad line can be simulated by increasing the line width of the resolved P2 EPR spectrum to 2.5 Gauss.

HPHT annealing the diamonds studied was carried out in two stages: 1) at 7 GPa, 1850° C for 12 h and 2) at 7 GPa, 2000° C for 12 h. The first annealing stage reduced photo-excitation effect on the EPR spectra and a weak P1 signal was detectable at room temperature in the absence of excitation. The second annealing at 2000° C causes the broad P2 line to disappear and a single narrow EPR line and simultaneously an intense P1 center and P2 center with resolved HFS to become observable (see Fig.2, bottom). The line width of an individual line for the both centers is 0.46 Gauss.





In PL spectra the second annealing stage results in some increase in intensity of the blue band as a whole and removal of the broadening effect of 415 nm ZPL, its peak intensity being enhanced markedly (Fig. 1, bottom). Simultaneously there were observed a decreased 409 nm line and an appearance of a rather intense H3 system (see Fig. 1, bottom). The latter is likely to be responsible for the greenish color of the annealed crystal.

Very dramatic changes can be seen in the IR spectra after the second annealing stage, the intensities of all optical systems were found to be decreased by a factor of 2-3.



1aA type diamonds with the traces of a plastic deformation

To investigate HTHP treatment in diamonds with traces of plastic deformation a set of brown crystals from the Canadian deposit was selected. Their IR spectra present 1282, 1175 and 1130 cm⁻¹ bands. EPR spectra show the P1 center, the separated W7 nitrogen pairs (Scherbakova et al, 1975) and a single line with g = 2.0027 and ΔH = 1 Gauss from dangling bonds in the core of dislocations. The crystals selected show a rather intense green glow, the 490.7 nm system (phonon energies of 68, 93, 114, 158, 165 meV) being dominant in PL spectra. As a rule, it was accompanied by the H3 and H4 systems of a different strength. A detailed examination of the blue spectral region allows us to define weak systems at 406 and 423 nm. In the cases where these systems were not masked by the usually more intense 415 nm center their phonon structure was carefully analyzed (406 nm - 46, 82, 93, 160 meV; 423 nm - 40, 65, 93, 128, 165 meV) (see Fig. 3).



Fig.3. PL spectrum of 1aA crystal with 490.7 nm system.

Our observations show that the 423 and 406 nm systems always accompany 490.7 nm, however no correlation between their intensities was established. Investigations of the optical and EPR spectra in parallel have shown that the 490.7 nm center has an analogue in the EPR single narrow line with g = 2.0027.

P,T treatment of these 1aA diamonds was performed at 7 GPa at 1850° C for 12 h. In the crystals treated, the W7 center and the single line from dangling bonds in the EPR spectra and also the 490.7, 406, 423 nm and H4 optical systems disappeared. The color of P,T treated diamonds changed to green. The intensity of the green glow was enhanced considerably (in some cases by more than two orders). The strongly broadened 503 ZPL is noteworthy.

The existence of an ionized nitrogen pair in the structure of the W7 center indicates electron transfer from this center to an electron acceptor. In these crystals possible acceptors are dangling bonds in the core of dislocations. The creation of such donor-acceptor pairs with different distances between components implies the existence of a continuous system of electronic states with large dipole moments. This allows us to postulate that the brown color of the

diamonds under study is due to bands of charge transfer in such donor–acceptor pairs. The result of interaction between the main form of nitrogen defects in these crystals (A-centers) and dislocations is the disruption of A centers by shifting carbon layers and creation of such centers as W7, H3.

Discussion

1aB type diamonds contain the nitrogen impurity mainly in B and P2 forms. These centers are forms of high nitrogen aggregation in the diamond. An unusually high P1 content for this type of diamonds is the surprising thing in the diamonds we have studied, as well as that all P1 centers are in the ionized state N⁺. The ratio obtained between P1, A- and B-centers doesn't agree with the kinetics of the transformation of nitrogen defects. The production of P1 centers in this type of the diamond suggests the possibility of of complicated nitrogen disruption defects. Dissociation of the complex nitrogen defects on annealing higher than 2300° C is a well-established experimental fact, but our effects occur in temperature range $1850 - 2000^{\circ}$ C. Under these conditions a known interaction between interstitial carbon atoms and nitrogen defect occurs where the interstitial carbon atom substitutes nitrogen in the regular lattice position, but this mechanism does not account for all effects observable in EPR and optics. We postulate that a plastic deformation of the diamonds can be such a possible mechanism for disruption of complicated nitrogen defects.

During plastic deformation, as is well known for the W7 center in 1aA diamonds (Scherbakova et al, 1975), one of nitrogen atoms in the B-center structure seems shifted by sliding carbon layers along a {111} plane and in a [110] direction. The observed P1 and P2 centers show quite a large separation between these centers. In addition to the possible displacement of P1 and P2 centers located on opposite sides of the sliding plane, at high temperature they may also diffuse along the directions of the stress gradient away from one another along the sliding plane. In other words, under these conditions the P1 and P2 centers don't revert back to B-centers. This mechanism can account for a different P2 content in the 1aB natural diamonds. The appearance of the N^+ nitrogen charge state in these crystals is due to close location of dislocations whose dangling bonds in the core are electron acceptors. The observed disappearance of the broad P2 EPR line with a decrease in temperature to 77 K is associated with the charge-transfer process between P2 centers and DB of dislocation on the assumption that the location of the energy level for one of these two centers changes. Because the structure and symmetry of the P2 center is seen to be invariable, as shown by lack of change in the optical spectrum, such an effect may be due to a change in the energy level at the dislocation. Usually as the temperature decreased the energy level is lowered. In our case this means that on decreasing the temperature the electron transfer from P2 centers to DBs of dislocations occurs creating diamagnetic $(P2)^+$



and DB states. At low temperature UV light excites

the electrons from DB to the conduction band and then they are captured by N^+ and $(P2)^+$ electron traps. This allows the P1 and P2 centers to be observed in EPR spectra. Red illumination released the electron traps, turning the electrons back to the DB levels and P1 and P2 centers return to diamagnetic N^+ and $(P2)^+$ states. That these effects are absent after annealing out the dislocations supports this model.

Removing dislocations from the crystal allows both these centers to be observed at room temperature without any additional excitation. The P1 and P2 EPR line widths are evidences that a broadening of the EPR lines in the crystals examined is due to the lattice stress in vicinity of the dislocation core. The same reason may explain the ZPL behavior of the 415 nm PL system. The major portion of the P2 centers observed are assumed to be located close to the dislocation core. The 409 nm PL system is due to the negative charge state of the P2 center and increasing intensity of the 415 nm and 409 nm PL bands on red illumination corresponds to the process of electron removal from P1 centers and its capture by (P2)⁺.

All experimental data obtained here support the hypothesis of the disruption of the B-center by the plastic deformation. It is very interesting, that the 1aB crystals studied have no brown color. Apparently the brown color is an inherent characteristic of the 1aA diamonds with traces of plastic deformation. Because the nitrogen centers are donors of electrons, it seems likely the brown color is due to the charge transfer band from nitrogen centers to DB in the dislocation core. For 1aA diamonds an energy level of the A center is positioned higher than that for DB and here the electron transfer is effected from the A center and its derivative defects to DB. For the 1aB diamonds the energy levels in the P2 and B-centers are located lower than those for DB and the color of the 1aB crystals depends on P1 and A-center contents.

The decrease in the content of A, B and B' defects in the P,T treated 1aB crystals with a trace of plastic deformation is a very interesting and very important result. It means that on removing dislocations they disrupt the complicated forms of nitrogen aggregation to make the simpler defects such as P1, P2, H3. These results may explain the failure of many experiments attempting to change the color of diamonds with the traces of plastic deformation by P,T treatment.

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