

## Study of the Transformation of Hydrogen-Containing Centers in Diamond at High *PT* Parameters

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The influence of hydrogen is considered in many geological processes, and the special role of hydrogen is emphasized in deep geodynamics in the ascent of mantle plumes [1, 2]. Some models of diamond formation [3, 4] also assume an interaction between the reduced methane–hydrogen fluid and more oxidized rocks. As has been shown by experiments, hydrogen may be a reductant of CO<sub>2</sub> during diamond crystallization as a result of carbonate–silicate interaction [5, 6].

However, keeping the specific features of hydrogen in mind, we have almost no evidence for its influence on the mantle material that would allow us to assess the scale of this phenomenon and the evolution of the process. In other words, no information about the impact of hydrogen on mantle rocks is available to date. However, hydrogen may be incorporated into the diamond lattice with the formation of structural defects that are active in IR absorption (lines 1405 and 3107 cm<sup>-1</sup>) [7, 8]. Hydrogen is the second most abundant impurity, following only nitrogen, in natural diamonds. However, in contrast to nitrogen, investigations of hydrogen in diamonds are extremely rare. Hence, the study of natural and synthetic diamonds that contain hydrogen-related defects and the elucidation of their formation conditions could provide new insights into the influence of deep fluids on mantle material.

This work is aimed at studying the effects of high *PT* annealing on the behavior of hydrogen-containing centers in natural and synthetic diamonds.

In compliance with the problem identified, the preliminary selection of natural diamond samples for annealing experiments was carried out with the application of IR spectroscopy and optic microscopy. We used collections of natural diamonds from the Udachnaya, Mir, and Aikhal kimberlite pipes. The occurrence and

intensity of line 3107 cm<sup>-1</sup>, concentration of nitrogen defects and degree of their aggregation, as well as the absence (or minimal number) of inclusions and fractures that might provoke the failure of samples at high *PT* parameters served as the main criteria for sample selection. As is known, natural diamonds are characterized by a nonuniform distribution of impurities and defects throughout the crystal. Therefore, the exact reproduction of the measurement position over the samples is of principal importance in local research methods (in particular, FTIR microspectroscopy). In this work, the problem has been solved by labeling the crystals with two thin laser-inscribed lines crossing in the center of a sample. Synthetic diamond crystals obtained in the Fe<sub>3</sub>N–C system were also used together with natural crystals. Previously, we established that the diamonds grown in this system are characterized by anomalously high concentrations of nitrogen impurity (2000–3000 ppm) and intensity of line 3107 cm<sup>-1</sup> (50 cm<sup>-1</sup> or more) [9].

The crystals were studied using FTIR spectroscopy, photoluminescence, and electron paramagnetic resonance (EPR). The IR spectra were measured with Bruker IFS-66 and VERTEX 70 FTIR spectrophotometers equipped with Bruker A590 and HYPERION 2000 IR microscopes, respectively. The measurements were carried out locally at several points of the sample with the reference to the laser marks. In all cases, the aperture of the IR microscope was 200 μm. The photoluminescence (PL) spectra were measured at 80 K with a DFS-24 spectrophotometer using DRSh-250 and DRT-220 mercury lamps and a set of color filters as the excitation sources. The EPR spectra were obtained with an E109 (Varian) spectrometer in the X-band of frequency.

The natural diamond crystals selected for annealing experiments may be divided into three main groups (table). The first group comprises diamonds corresponding to type IaB. These crystals are characterized by the maximal degree of aggregation of nitrogen impurity. The IR spectra in the one-phonon region reveal only an absorption band of B defects. Other

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Characteristics of initial diamond crystals and annealing experiments at high *PT* parameters

| Sample                    | Point no. | Nitrogen content, ppm |         |       | $\alpha_{B2i}$ ,<br>cm <sup>-1</sup> | $\alpha_{3107}$ ,<br>cm <sup>-1</sup> | Annealing at a stabilizing pressure of 7 GPa       |
|---------------------------|-----------|-----------------------|---------|-------|--------------------------------------|---------------------------------------|--|
|                           |           | A-form                | B1-form | total |                                      |                                       |  |
| AO1811 IaB, colorless     | 1         | –                     | 304     | 304   | –                                    | 1.4                                   | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |
|                           | 2         | –                     | 285     | 285   | –                                    | 1.3                                   |  |
|                           | 3         | –                     | 260     | 260   | –                                    | 1.2                                   |  |
|                           | 4         | –                     | 230     | 230   | –                                    | 1.0                                   |  |
|                           | 5         | –                     | 280     | 280   | –                                    | 1.3                                   |  |
|                           | 6         | –                     | 310     | 310   | –                                    | 1.4                                   |  |
| AO1915, ~IIa, colorless   | 1         |                       |         | ≤30   | –                                    | 1.0                                   | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |
|                           | 2         |                       |         | ≤30   | –                                    | 0.8                                   |  |
|                           | 3         |                       |         | ≤30   | –                                    | –                                     |  |
|                           | 4         |                       |         | ≤30   | –                                    | –                                     |  |
| AO1939, IaAB, colorless   | 1         | 840                   | 110     | 950   | 2.6                                  | 10.8                                  | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |
|                           | 2         | 823                   | 87      | 910   | 1.5                                  | 18.2                                  |  |
|                           | 3         | 522                   | 28      | 550   | –                                    | 4.1                                   |  |
|                           | 4         | 810                   | 153     | 963   | 2.9                                  | 16                                    |  |
|                           | 5         | 766                   | 124     | 890   | 2.7                                  | 19                                    |  |
|                           | 6         | 472                   | 32      | 504   | –                                    | 0.5                                   |  |
|                           | 7         | 470                   | 31      | 501   | –                                    | 0.5                                   |  |
|                           | 8         | 640                   | 76      | 713   | 1.4                                  | 15                                    |  |
| SL00/132, IaAB, colorless | 1         |                       |         |       | 6.5                                  | 12.9                                  | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |
|                           | 2         |                       |         |       | 7.3                                  | 15.1                                  |  |
|                           | 3         |                       |         |       | 6.2                                  | 13.9                                  |  |
|                           | 4         |                       |         |       | 7.0                                  | 15.8                                  |  |
| SL00/152, IaAB, brown     | 1         | 27                    | 108     | 135   | 3.6                                  | 2.5                                   | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |
|                           | 2         | 37                    | 205     | 242   | 7.9                                  | 3.5                                   |  |
|                           | 3         | 24                    | 50      | 75    | 1.9                                  | 1.7                                   |  |
|                           | 4         | 40                    | 220     | 260   | 8.4                                  | 1.6                                   |  |
|                           | 5         | 28                    | 24      | 52    | 1.1                                  | 1.1                                   |  |
|                           | 6         | 32                    | 196     | 228   | 7.3                                  | 5.5                                   |  |
| G3 IaAB, brown            | 1         | 525                   | 255     | 780   | 8.7                                  | 2.0                                   | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |
|                           | 2         | 287                   | 125     | 412   | 3.6                                  | 2.6                                   |  |
| FN4, IaA                  |           | 2100                  | –       | 2100  | –                                    | 48                                    | 1) 1800°C, 2 h<br>2) 1900°C, 2 h<br>3) 2000°C, 2 h |

Note: Number, type, and color of crystals are indicated in the first column; measurement point numbers are given in the second column. In sample SL00/132, absorption in the one-phonon region exceeds the upper detection limit of the FTIR spectrometer.

aggregate forms of nitrogen, including B' defects, i.e., platelets in (100) planes, are absent. A weak peak 3085 cm<sup>-1</sup> is observed in IR spectra of these crystals along with well-known hydrogen lines. The second group consists of crystals with low nitrogen contents close to type IIa. In this case, absorption in the one-phonon region is very low and the maximal nitrogen content is not higher than 20–30 ppm. Crystals of type

IaAB containing A, B, and B' centers pertain to the third group. The total nitrogen concentration, proportions of A and B centers, and intensity of line 3107 cm<sup>-1</sup> vary within a wide range both from one sample to another and within a crystal. It should be noted that some samples from this group have a brown color that is typical of crystals subjected to plastic deformation. The study of these crystals with luminescence and EPR methods

revealed a number of specific defects related to the plastic deformation, such as the 490.7 nm system in photoluminescence, center  $N_2D$ , and a single line representing an analog of center 490.7 nm in EPR.

For the crystals of different types (table), a series of isochronal (2 h) annealing experiments was carried out at successive temperatures of 1800, 1900, and 2000°C and under a stabilizing pressure of 7 GPa. The annealing was carried out using high-pressure multianvil split-sphere equipment. The experimental technique and calibration data are presented in [10, 11].

Let us consider the results obtained with IR spectroscopy. In natural diamond crystals of types IIa (AO1915), IaB (AO1811), and IaAB without signs of plastic deformation (AO1939, SI00/132), as well as in synthetic diamond sample FN4, no significant variation in the intensity of line 3107  $cm^{-1}$  was found within the entire range of annealing temperatures (1800–2000°C). The strength of absorption bands of nitrogen A and B defects also did not change. The only effect of annealing recorded in IR spectra was a decrease in the intensity of a band corresponding to B' defects in type IaAB crystals. The absence of changes in line 3107  $cm^{-1}$  indicates that the respective hydrogen-containing center is relatively stable. The bond energy of this center may be estimated quantitatively from the empirical rule that connects the activation energy of thermally activated process  $E_A$  with threshold temperature  $T_R$ :

$$E_A(\ominus B) \sim BT_R(K), \quad (1)$$

where coefficient  $B$  in the case of diamond is about  $3 \cdot 10^{-3}$  eV/K [12]. As follows from expression (1), the hydrogen-containing center responsible for line 3107  $cm^{-1}$  has a bond energy of no less than 7 eV.

The results obtained for plastically deformed crystals (SL00/152 and G3) are of special interest. In both samples, the intensity of line 3107  $cm^{-1}$  abruptly decreases after annealing at 1800°C and further decays gradually with increasing annealing temperature (Figs. 1, 2). As in the case of colorless crystals, no substantial variation in the intensity of bands related to nitrogen defects was recorded. The B' defects are annealed under the influence of high  $PT$  treatment. The most prominent decrease in the concentration of these defects is recorded at 2000°C. A weak line 3085  $cm^{-1}$  appeared in IR spectra of sample SL00/152 after annealing at 2000°C. This line was formerly observed only in crystals of type IaB. It is evident that the attenuation of line 3107  $cm^{-1}$  in the course of annealing of plastically deformed crystals is related to the real structural features of crystals of this type, e.g., the high concentration of dislocation defects in sliding planes. These defects are not recorded in IR absorption spectra, but they substantially affect photoluminescence and EPR spectra. The results obtained with these methods are considered below.

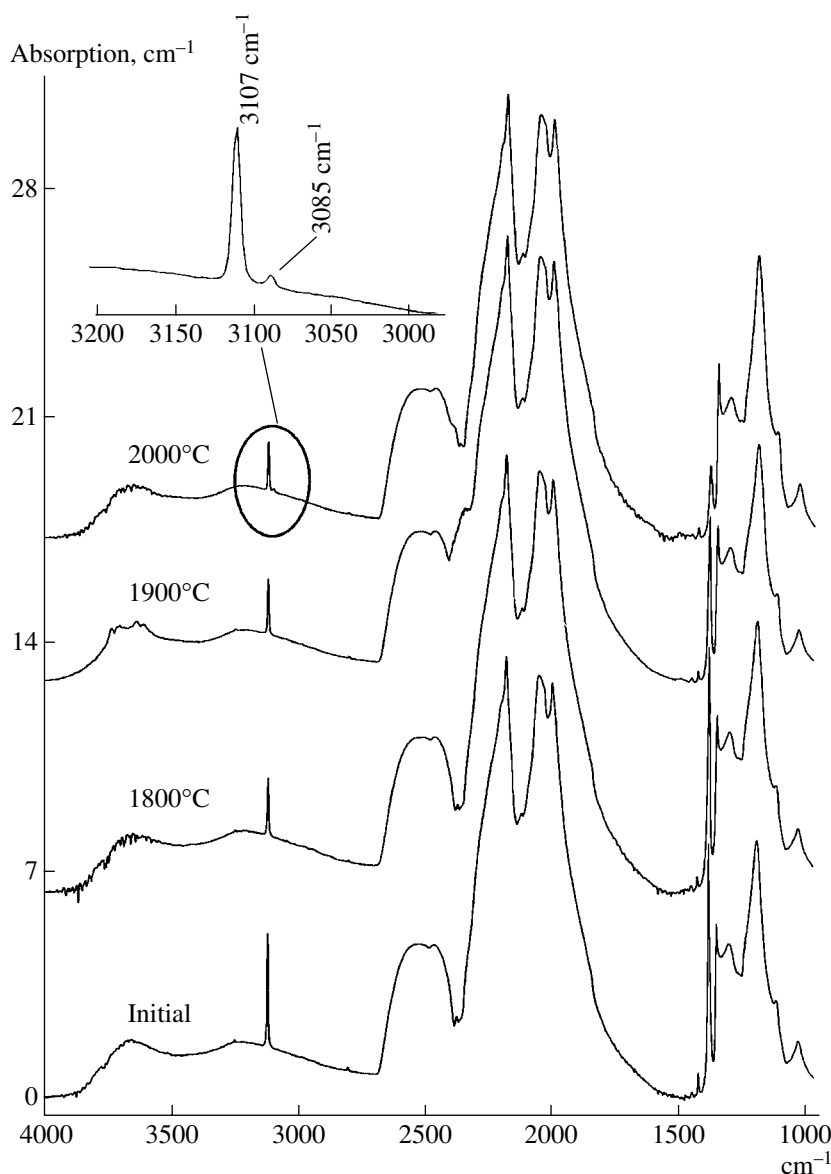
Let us scrutinize line 3085  $cm^{-1}$ . No information on this line has been found in the literature. However, it

was undoubtedly observed in previous investigations (see, for example, [13]). We found no less than 10 crystals of the pure type IaB (without B' defects) among preliminarily selected crystals. Line 3085  $cm^{-1}$  was present in IR spectra in all crystals of this type and was absent in crystals of other types.

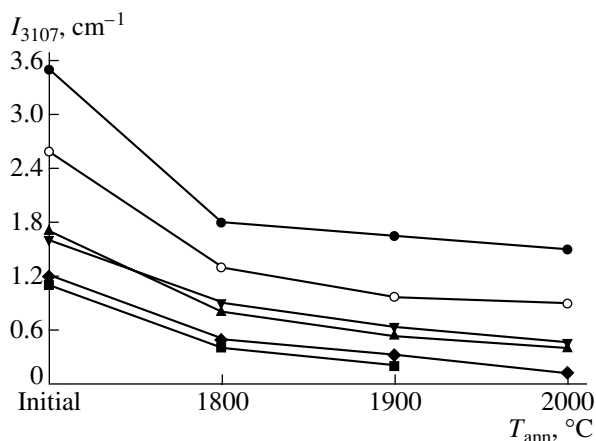
Diamonds containing only B defects are characterized by the following specific feature: B' defects related to platelets in the (100) plane degrade with the formation of dislocation loops and voidites [14]. In sample SL00/152, line 3085  $cm^{-1}$  appeared when B' defects underwent the most intense degradation. All these facts allow us to suggest that line 3085  $cm^{-1}$  is related to the C–H- and N–H-bonds in the structure of dislocation loops and/or voidites.

The study of initial diamond crystals with photoluminescence and EPR techniques revealed a number of impurity-defect centers typical of natural diamond crystals. The main  $N_3V$ -defect, occurring in virtually all samples, is expressed as a system N3 (zero-phonon line, ZPL 415 nm) in PL and P2-center in EPR spectra. The intensity of bands related to this defect depends on crystal type and is the highest in crystals of type IaAB. The brown-colored crystals include a number of specific defects related to the plastic deformation that occur together with center  $N_3V$ , e.g., a system with ZPL 490.7 nm in luminescence spectra and a single line (analog of center 490.7 nm) together with  $N_2D$ -center in EPR spectra. The ND-center is generated from A-center when the dislocation sliding plane passes across this center. In this case,  $N_3V$ -center shows some specific features indicating the presence of high stresses in the crystal lattice. In PL spectra, ZPL 415 nm is rather wide and has a low peak intensity relative to the phonon side-band. In EPR,  $N_3V$ -center appears as a wide band related to the broadening of ultrafine structure lines.

The study of diamond crystals after the annealing has shown that the changes in the impurity-defect structure occur to a variable extent in all crystals, but they are most prominent in the plastically deformed brown crystals. As a result of annealing at 1800°C for 2 h, system N3 in PL spectra is reinforced and an intense band of H3-centers appears, while the intensity of system 490.7 nm decreases. Intense bands of N3- and H3-centers become predominant in PL spectra with an increase in annealing temperature, while system 490.7 nm completely disappears (Fig. 3).  $N_2D$ -centers and an analog of the 490.7 nm line disappear in EPR spectra. A fine spectrum structure of phonon band is established for  $N_3V$ -center in luminescence spectra, whereas the ZPLs become narrower and more intense. In EPR, the intensity of wide line decreases, and a permissible spectrum of three nitrogen atoms appears. As was shown in [15], these effects in type IaB diamonds are caused by lattice distortion near the dislocation core. The annealing at high  $PT$  parameters releases the stresses in the lattice and removes mechanisms that broaden the EPR and PL lines. The centers that controlled the recharging of



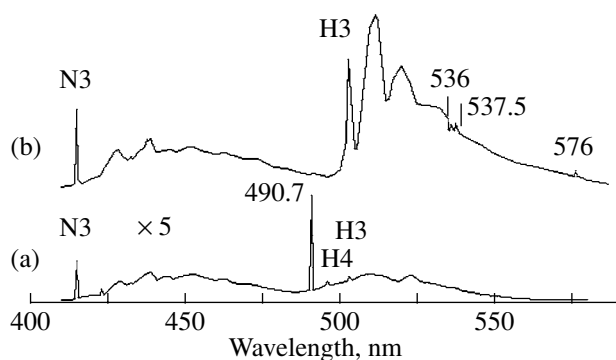
**Fig. 1.** The IR spectra of SL00/152 crystal measured before and after annealing at various temperatures.



**Fig. 2.** Intensity of line  $3107\text{ cm}^{-1}$  as a function of annealing temperature for crystals affected by plastic deformation. Solid symbols correspond to different points in sample SL00/152; open symbols denote the points in sample G3.

nitrogen defects disappear simultaneously with the relaxation of the structure near these defects.

The release of effects of inhomogeneous broadening in type IaAB diamonds indicates a significant relaxation of stresses in the diamond crystal lattice under the influence of high  $PT$  parameters. Hence, upon the annealing of plastically deformed type IaAB diamond crystals within a temperature range of  $1800\text{--}2000^\circ\text{C}$ , the defects caused by plastic deformation are actively transformed with a substantial decrease in crystal lattice distortion. The structure of defects formed in crystals of natural diamond as a result of plastic deformation remains virtually unstudied. Therefore, it is extremely difficult to examine the details of annealing processes. However, the data on the preferentially dislocation character of such defects suggest that the observed changes are related to the thermally activated



**Fig. 3.** Photoluminescence spectra of sample SL00/152 measured (a) before and (b) after annealing at 1900°C for 2 h. Spectra were recorded at 80 K under 365 nm excitation.

mobility of dislocations. In this case, the configuration of dislocations may change and vacancies may be generated by the interaction of dislocations. Consequently, the established weakening of hydrogen line  $3107\text{ cm}^{-1}$  in the course of the annealing of plastically deformed diamond crystals may be caused by the interaction of hydrogen-containing defects with dislocations and/or vacancies.

Thus, we have established that the behavior of line  $3107\text{ cm}^{-1}$  in the process of annealing depends on the impurity-defect structure of crystals. The hydrogen-containing center responsible for the IR absorption line  $3107\text{ cm}^{-1}$  is rather stable and its bond energy is not less than 7 eV. However, this center can interact with dislocations and/or vacancies and produce defects that are inactive in IR-absorption.

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