

## On HPHT treatment of brown diamonds

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Transformation of optically active defects after HPHT treatment (1800-2300°C/7 GPa/10 min) was studied in natural type Ia brown diamonds exhibiting traces of strong plastic deformation. Similar studies of colorless diamonds without traces of plastic deformation reported in (Vins, Yelisseyev, 2007) gave the following results:

1. The dissociation of A centers leading to the formation of C centers began at the treatment temperature of 2100°C. The dissociation temperature was higher in the samples with a lower content of nitrogen in the A form.
2. At the treatment temperatures over 2200°C along with A center dissociation, there began A center aggregation leading to the formation of B centers.
3. The absorption at 1365 cm<sup>-1</sup> due to B' defects decreased at all temperatures in diamonds with  $\mu_A$  less than 25 cm<sup>-1</sup>, while in all other diamonds, the absorption due to B' defects increased along with the formation of B defects.
4. The treated samples changed their initial color to yellow due to C center formation. C centers formed as a result of A center dissociation.
5. No changes in the set and concentration of other color centers that had been observed before HPHT treatment (such as, e.g., N3 centers) were seen.

Considerable transformation of structural defects was observed in HPHT treated plastically deformed brown diamonds. Thus, in the samples containing nitrogen impurity predominantly in the A form the following changes were seen:

1. The reduction of brown color was observed.
2. At  $T \geq 1800^\circ\text{C}$ , the absorption due to H3 and H2 centers appeared. The increase of absorption due to H3 and H2 centers caused greenish-yellow and yellow-green color of the diamonds.
3. The absorption due to H3 and H2 centers increased until the treatment temperature reached 2150°C and started to decrease at higher temperatures.
4. At about 2100°C, A centers dissociated to form C centers. Weak absorption due to (N-V) centers appeared, the samples became yellowish-green.

5. The rate of A center dissociation was higher in the initially darker brown samples.
6. At 2200-2300°C, A centers aggregated to form B and sometimes B' defects. The rate of this reaction was higher in the initially darker brown samples.

The diamonds that contain nitrogen impurity predominantly in the B form contain N3 centers as well. B centers form during HPHT treatment of colorless and brown type IaA diamonds at  $T > 2200^\circ\text{C}$ , because A centers aggregate. At this treatment temperature N3 centers were not seen to form.

HPHT treatment of brown type IaB diamonds caused the following changes:

1. After the treatment at 1800°C the brown component of the color reduced, the samples became greenish-yellow due to the formation of H3 centers. N3 absorption did not change.
2. After the treatment at  $T > 1900^\circ\text{C}$ , the absorptions due to H3 and N3 centers increased. This was accompanied by indirect indications of C center formation, such as the absorption at  $\lambda < 520$  nm and a band due to H2 centers. No changes except the decrease of B' absorption were observed in the IR spectra.
3. At temperatures over 2100°C C centers formed intensively. The IR spectra revealed the readily observed peak at 1344 cm<sup>-1</sup> with an intensity of less than 0.4 cm<sup>-1</sup>. The intensity of the main B-related band at 1175 cm<sup>-1</sup> decreased by 10-15%. The increased concentration of C centers gave rise to the strong absorption which completely disguised the absorption due to N3 and H3 centers. H2 absorption increased in intensity. The bright yellowish-green color of the samples was caused by the sum absorption of C, N3, H3 and H2 centers.
4. At the treatment temperatures over 2200°C the absorption intensity of H2 centers began to decrease sharply.
5. No absorption bands due to A centers were observed after the treatments at all temperatures.

It should be pointed out that all diamonds that contained nitrogen predominantly in the B-form (including pure subtype IaB and IaB(B') samples) became yellow-green after HPHT treatment. There

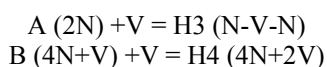
were no cases when such diamonds became colorless after HPHT treatment (as is sometimes reported in the literature).

The changes that took place cannot be understood without understanding the nature of diamond color and what role impurity defects play. Nowadays there exist different points of view on the nature of brown color in plastically deformed diamonds. It was thought for a long time that brown color was associated with dislocations (Sobolev, 1984). However, new suggestions appeared in recent years, which attribute brown color either to vacancy clusters or vacancy discs (Hounscome et al., 2006) or microscopic graphite particles (Kononov, 2006).

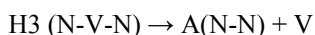
The transformation of optically active defects in type Ia diamonds depends on the temperature of HPHT treatment. Two temperature ranges can be distinguished:

1. The 1800-2100°C range within which defects responsible for the initial brown color are intensively destroyed, free vacancies are generated and captured by nitrogen defects.
2. The 2100-2300°C range, within which thermally activated aggregation and dissociation of main impurity defects go most intensively.

At  $T \geq 1800^\circ\text{C}$  a lot of vacancies are released in type Ia diamonds. They migrate and get trapped at mostly A and B centers. H3 and H4 centers are formed, respectively. These processes can be shown as:

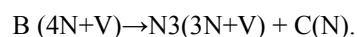


Almost simultaneously with H3 center formation, H2 centers form, which are negatively charged H3 centers. As the treatment temperature grows, the absorption due to H3 and H2 centers increases until the treatment temperature reaches 2150°C. At higher temperatures their concentration decreases. The centers are most likely destroyed to form A centers and vacancies:

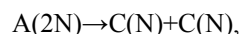


The thermal stability of H4 centers is at about 1600°C. At higher temperatures H4 centers (4 nitrogen atoms and 2 vacancies) are destroyed to produce H3 centers (2 nitrogen atoms and 1 vacancy). Higher stability of H3 centers compared to H4 centers explains why we observe the formation and concentration increase of H3 and H2 centers after HPHT treatment at 1800-2000°C. At these temperatures H3 and H2 centers dominate in visible absorption spectra and cause bright greenish-yellow and yellow-green color and intensive yellow photoluminescence of the diamonds. It should be noted that the intensity of H3 absorption is always higher in darker brown diamonds, other things being equal. When such diamonds are HPHT treated, a larger number of vacancies is released, so it is likely that more vacancies will be trapped at A and B centers and more H3 and H4 centers will form.

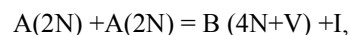
The most interesting thing observed in plastically deformed treated subtype IaB diamonds is a simultaneous increase in concentrations of N3 and C centers. This phenomenon is observed at treatment temperatures below 2100°C, when the dissociation of A centers is almost not noticeable. The following changes, most likely, take place: HPHT treatment destroys the defects associated with brown color; the stress is removed from heavily deformed areas around these defects. Plastic deformation is reduced, dislocations begin to move throughout the crystal destroying complex nitrogen B centers and thus creating simpler nitrogen N3 and C centers. This process can be shown as:



At  $T > 2100^\circ\text{C}$  thermally activated aggregation and dissociation of the main impurity defects go most intensively. Depending on the treatment temperature A centers can either dissociate to form two C centers:



or aggregate to form B centers:



where I is a self-interstitial atom.

The dissociation of A centers is an elementary first order decay reaction, in which the A center dissociation rate is directly proportional to the concentration of A centers:

$$-d[\text{C}_\text{A}]/dt = K[\text{C}_\text{A}],$$

where K is the reaction rate constant, exponentially dependant on the temperature and activation energy ( $E_\text{A}$ ):

$$K = A \exp(-E_\text{A}/kT).$$

More C centers form in diamonds that contain larger numbers of A centers at the same treatment temperatures. The  $E_\text{A}$  value calculated from the experimental results was equal to 6.5 eV.

At  $T > 2200^\circ\text{C}$  the spectra of all studied diamonds showed well-defined absorption lines due to B centers. The A-to-B center transformation is reflected in proportional changes of the corresponding IR absorption bands. It is to be pointed out that at high concentrations of A centers the transformation is accompanied by a small increase of the absorption band due to B' defects and its shift towards longer wavelengths. This is usually associated with an increased concentration and linear size of B' defects. The exact mechanism of A-to-B center transformation is so far not clear, because we can't tell whether A center aggregation is involved or B centers form from single nitrogen atoms (C centers) which form when A centers dissociate. B center formation as well as A center dissociation proceed at high rates in darker

brown diamonds when they are HPHT treated. Accelerated B center formation is most likely due to the presence of free vacancies in the diamond structure which lower the reaction energy threshold. At the treatment temperature of 2200°C, at which B center formation occurs, the majority of defects responsible for brown color are already destroyed, so vacancy sources are almost exhausted. Fewer H3 and H4 centers are formed and the H3 centers that existed before start to dissociate to form A centers and vacancies. Depending on the treatment temperature, A centers can either dissociate to form two C centers or aggregate to form B centers. Judging by the optical spectra, aggregation dominates within the 2200-2300°C range. It continues until vacancy sources are exhausted. A complete disappearance of defects responsible for brown color means a complete depletion of vacancy sources. The initial brown color disappears; the diamond structure and its clarity become more perfect. All H3 centers present in the diamond structure sooner or later dissociate and newly formed A centers aggregate to form B centers. Varying HPHT conditions (P,T and time) it can be possible to transform all intermediate nitrogen centers (A and C centers) and nitrogen-vacancy H3 and H4 centers to B centers. Sometimes the formation of platelets (or B' defects) is observed at certain concentrations of all intermediate centers, along with B center formation. These processes cause initially brown diamonds to become colorless and allow us to obtain samples of pure subtypes IaB and IaB(B'). The approximate conditions of such HPHT treatment are as follows:  $T \geq 2500^\circ\text{C}$ ,  $P \geq 8.5 \text{ GPa}$ ,  $\Delta t \sim 1 \text{ h}$ . The diamonds that underwent such a treatment will not reveal the  $3107 \text{ cm}^{-1}$  line, which is almost always observed in untreated subtype IaB diamonds.

The  $3107 \text{ cm}^{-1}$  absorption line associated with a stretch mode of C-H vibrations shows complex behavior during HPHT treatment. In particular, in subtype IaB diamonds that exhibit a higher concentration of hydrogen defects in comparison with subtype IaA diamonds and the absorption intensity at  $3107 \text{ cm}^{-1}$  in which reaches  $60 \text{ cm}^{-1}$ , the intensity of this line decreases more than 10 times in 80% of diamonds and increases in the remaining 20% of diamonds, though not more than twice (Vins, Yelissev, 2007). If the treatment time is increased, the  $3107 \text{ cm}^{-1}$  line continuously decreases until it completely disappears. Such behavior of the H defect can be explained by the presence of hydrogen sources in the diamond structure. Microscopic graphite inclusions could be such sources. Graphite particles form during diamond crystallization which is considered to involve hydrocarbons. Hydrogen that appears during crystallization could get localized as CH radicals on the diamond surface or on the outer surfaces of microscopic graphite crystals within the diamond. During HPHT treatment C-H bonds are broken in graphite, hydrogen atoms become mobile, diffuse and get localized in the diamond structure forming H defects. If the rate of H defect formation is higher than that of their dissociation, the absorption

intensity of the  $3107 \text{ cm}^{-1}$  line increases. This model seems to take place during HPHT treatment of graphite-containing gray diamonds. These diamonds do not only become colorless but also exhibit an increased concentration of H defects (Vins, 2001; Vins, Kononov 2003).

## References

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