

Characterization of Various Centers in Synthetic Type Ib Diamond under HPHT Annealing

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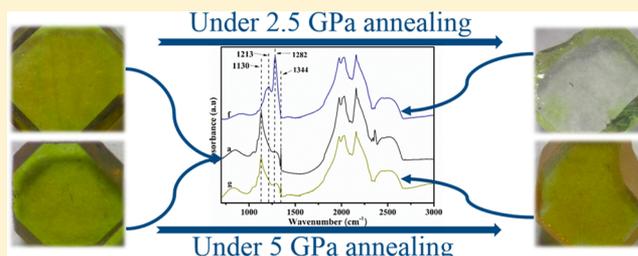
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Supporting Information

ABSTRACT: In this study, type Ib diamond annealing experiments were successfully performed under a pressure of 2.5 GPa and a high temperature range between 1680 and 2060 °C. The color of the diamond changed from yellow to light yellow, and the nitrogen (N) state changed from the isolate C-center to the aggregated A-center as the annealing temperature increased. The NV⁰ center was detected when the annealing temperature was under 1840 °C, and not detected when the temperature reached 1920 °C. The NV⁻ center was more stable than the NV⁰ center at an annealing temperature of 1920 °C. When the annealing temperature reached 1990 °C, the NE8 center appeared in the diamond lattice. When the annealing pressure changed from 2.5 to 5 GPa, high pressure would restrict the formation of A-center N but hardly affected the formation of NV⁻ center in the diamond lattice. This was the first known report on the successful preparation of the type IaA diamond under a lower pressure of 2.5 GPa. Our experiment results could be helpful for further understanding the formation of various centers in the diamond lattice and provided data for distinguishing the annealed synthesized diamond from the natural diamond in the jewelry market.



1. INTRODUCTION

Diamonds are valued gemstones that have attracted attention from many researchers.^{1–7} The diamond annealing experiment is one of the important research topics to date. The annealing method is divided into two categories: low pressure and high temperature (LPHT) and high pressure and high temperature (HPHT). Diamonds annealed by the HPHT method typically occur at close to or within the range of diamond stability region.⁸ The diamond often endures a longer time and a higher temperature in the HPHT annealing experiment than in the LPHT annealing experiment. HPHT annealing offers a more flexible experiment method because of the relatively broad range for adjusting the pressure and the temperature. Type Ia (containing aggregated N) diamonds account for about 98% of natural diamonds. 0.1% of natural diamond belong to type Ib (containing single substitutional N atoms).⁹ One hypothesis suggests that the origin of natural diamonds was the type Ib and then the isolated C-center N aggregated to the pairs of the nearest neighboring substitutional A-center N atoms (type IaA). The state of N could transform from an isolated substitutional N to an aggregated N, according to the annealing treatment process.^{1,10} A synthetic diamond in metal catalyst without the N getter is also a type Ib. The annealing treatment is an effective method for altering type Ib diamonds into type Ia diamonds. Researchers have successfully

transformed the synthetic diamond from type Ib to the type Ia, in accordance with previous HPHT annealing experiments.¹¹ The annealing experiment also could result in significant changes in the natural diamond color, thus improving their grade and quality. The most successful experiment was with Ila-type natural brown diamonds, where the structural defects were removed via plastic flow under the HPHT annealing condition. Type Ila natural brown diamond was transformed from brown to colorless via HPHT annealing.⁹ These HPHT annealing experiments often occurred at a higher pressure ranging between 5 and 9 GPa.^{4,9–17} High pressure, meaning high equipment costs, should be reduced to improve scientific research and commercial treatment.^{8,18} The material properties of the pressure medium (pyrophyllite, dolomite, and graphite) was constrained, where the low pressure and the high temperature annealing experiments at a high-pressure experimental apparatus are precarious and it is difficult to control the annealing condition stability. We performed experiments on diamond annealing under a relatively safe and stable pressure of 2.5 GPa. Also, the pressure of 2.5 GPa approached to the natural diamond annealing pressure.⁸ Unfortunately, the

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complexity of the natural diamond formation process makes the genetic mechanism of natural diamonds unclear and worthy of further in-depth investigation.

Previous literature has stated that the NE8 center in the diamond lattice has more potential applications than the commonly studied NV center and could help design a practical diamond color center-based single-photon source.^{19,20} Previous researchers did not address the effect that the annealing treated process had on generating the NE8 center in the diamond lattice. Our annealing experiments results showed that the NE8 could be created in the diamond lattice under a specific temperature in accordance with the annealing process. Our experiments data could be used to distinguish the HPHT annealing treated diamond from the natural diamond for the research community and the jewelry market. As the HPHT annealing technology progresses, there are many challenges to face in recognition of HPHT treated diamond.^{8,21} The synthetic type Ib diamond is the most common type found, so supplying and enlarging the type Ib diamond annealing database is important. This paper annealed the diamond in a series of temperatures ranging from 1680 to 2060 °C, under pressures of 2.5 and 5 GPa. These experiments condition began when the N state barely changed temperature and ended at the diamond graphitized temperature. We added more complete annealing data for the N state, the NV center, and the nickel (Ni)-related center of the synthesized type Ib diamond when under a pressure of 2.5 GPa. We hope that our current work will be helpful for further research regarding the annealing of the synthetic type Ib diamond and the formation of different centers in the diamond.

2. EXPERIMENTAL DETAILS

The HPHT annealing experiments were performed on a China-type cubic high-pressure apparatus (SPD-6×1200). Seven diamond samples were used for HPHT annealing experiments. The diamonds were obtained in a Ni-based metal alloy system at 5.5 GPa and 1370 °C. The diamond samples were acquired via the temperature gradient growth (TGG) method, and the {100} face of the type Ib diamond seed (about 0.7 mm in size) served as the initial growth plane. The obtained diamond samples were sent to the hot dilute HNO₃, which separated the diamond crystals from the catalyst alloy medium. The diamond samples were subsequently placed in a boiling mixture of H₂SO₄ and HNO₃ to remove the remaining graphite and the metal on the crystal surfaces. Prior to the HPHT annealing experiments, the upper surface and the lower surface of the diamonds were polished. The schematic diagram of the HPHT annealing experiments is shown in Figure 1. The pressure was calibrated by the pressure-induced phase transitions of the Bi, the Tl, and the Ba. A WRe-5%/WRe-26% thermocouple was placed near the diamond sample to measure the

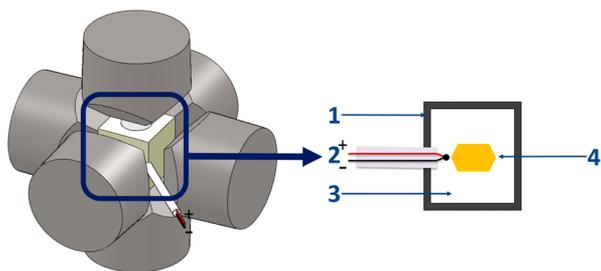


Figure 1. Assembly schematic of the diamond annealing experiment via HPHT: 1. graphite heater; 2. WRe-5%/WRe-26% thermocouple; 3. isolate pillar; 4. diamond sample.

temperature for each experiment. The HPHT annealing temperature ranged between 1680 and 2060 °C.

Following the HPHT annealing experiments, the annealing treated diamond samples were subjected to the polished process once again and boiled in H₂SO₄ to remove the graphite that occurs on the diamond surface during the HPHT annealing experiment. Before the tests, the diamonds were ultrasonically rinsed with a mixture of acetone and alcohol to remove the residual impurities on the diamond surface. The supersonic wave equipment and deionized water were used throughout the cleaning process. An optical microscope was used to observe the morphologies of the diamond samples. Raman spectroscopy was recorded on a Renishaw inVia Raman microscope with backscattering geometry using the 532 nm line of an argon ion laser. The acquisition time for each spectrum was 60 s, monitored with a charge coupled device (CCD) detector system. The infrared absorption spectra was measured with a Vertex80 V Fourier transform infrared (FTIR) spectrometer, with spectral range between 400 and 4000 cm⁻¹ and a spectral resolution of 2 cm⁻¹ in the transmittance mode. The PL spectra were measured with a 532 nm excitation at room temperature and a 325 nm excitation at -120 °C.

3. RESULTS AND DISCUSSION

The conditions and the results of the annealing experiments are summarized in Table 1. The diamonds were examined on

Table 1. Experimental Results of Diamond Samples before and after HPHT Annealing

run	time (min)	pressure (GPa)	temperature (°C)	color (before)	color (after)
E-1	180	2.5	1680	yellow	yellow
E-2	180	2.5	1760	yellow	yellow
E-3	180	2.5	1840	yellow	yellow
E-4	180	2.5	1920	yellow	light yellow
E-5	180	2.5	1990	yellow	light yellow
E-6	180	2.5	2060	yellow	black
E-7	180	5	1990	yellow	yellow

an optical microscope to show the yellow color before the HPHT annealing (Figure 2a–g). The color of the diamond in Figure 2d was different from other optical micrographs, as a result of the distinction between the reflected light and background when an optical microscope photograph was taken. The diamond samples were cub-octahedron shaped and primarily composed of {100} faces. The color did not obviously change below 1840 °C annealing treated (Figure 2c'). The HPHT annealing caused some diamond samples to reduce their initial yellow color. When the annealing temperature reached 1920 and 1990 °C, the diamond samples color changed from yellow to light yellow (Figure 2d'). For the higher temperature of 1990 °C (Figure 2e'), the annealed diamond sample exhibits the light yellow which is more transparent than the sample obtained in Figure 2d'. Figure 2f' shows the black color of the diamond sample after annealing at 2060 °C. When the pressure reached 5.0 GPa and the temperature at 1990 °C (Figure 2g'), the color did not obviously change and was similar to the samples obtained in the E-1 to E-3 experiments.

Raman spectroscopy was used to identify the sp³ diamond structure and sp² graphite structure, as well as other inclusions. Figure 3a shows the typical Raman spectrum of the diamond samples before the annealing experiments. The Raman peak of the diamond before the annealing experiment was located nearly at 1330.5 cm⁻¹ and showed a strong and narrow peak with a linear background. This result demonstrated that the

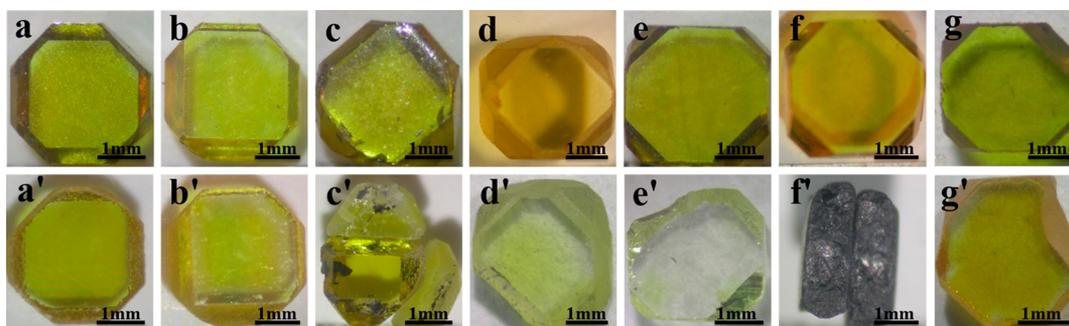


Figure 2. Optical micrographs of the diamond samples before and after annealing experiments. Panels (a)–(g) are before the annealing treatment experiments, and (a')–(g') are following the annealing treatment experiments in E-1 to E-7.

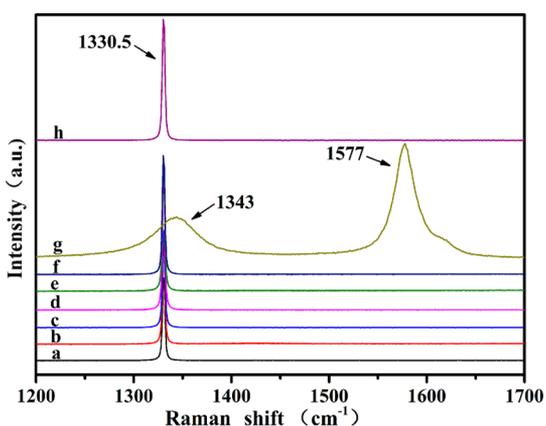


Figure 3. Raman spectra for the diamond sample. (a) Prior to the annealing treatment experiments; (b)–(h) are following the annealing treatment experiments in E-1 to E-7.

diamond samples that were used for the annealing experiments possessed a high-quality sp^3 structure.^{22,23} Figure 3b to Figure 3h depict the Raman spectra of the diamond samples after the annealing experiments (E-1 to E-7). The Raman peaks were located near 1330.5 cm^{-1} in Figure 3b to Figure 3f and Figure 3h. Figure 3g depicts the Raman spectrum of the diamond sample after the $2060\text{ }^\circ\text{C}$ annealing treatment. The former peak at 1343 cm^{-1} was the disordered peak (D peak) and the posterior peak at 1577 cm^{-1} was the graphitic peak (G peak).^{24,25} The spectra of the diamond after the annealing experiments between 1680 and $1990\text{ }^\circ\text{C}$ did not change obviously between Figure 3b to Figure 3f and Figure 3h. The diamond sample transformed into graphitized amorphous carbon when the annealing temperature reached $2060\text{ }^\circ\text{C}$ in E-6 experiment.

FTIR absorption spectroscopy was used to identify the impurity-related defects in diamonds, particularly measurements of the N state. Figure 4a shows the typical IR spectrum of the diamond samples before the annealing experiment. The 1130 cm^{-1} and 1344 cm^{-1} peaks were attributed to the N impurities in the form of the C-center.^{23,26} The 1282 cm^{-1} and the 1213 cm^{-1} peaks that are attributed to the A-center N were not detected.^{27,28} The nitrogen concentration of the diamond samples that were prepared for the annealing experiments ranged between 129 and 201 ppm based on the previously calculated formula.^{23,29,30} Prior to the annealing experiment, the spectra exhibited sharp peaks at 1130 and 1344 cm^{-1} , which were in stark contrast to the extreme weak peaks located at 1282 and 1213 cm^{-1} . This result demonstrated that the diamond samples were a type Ib prior to the annealing

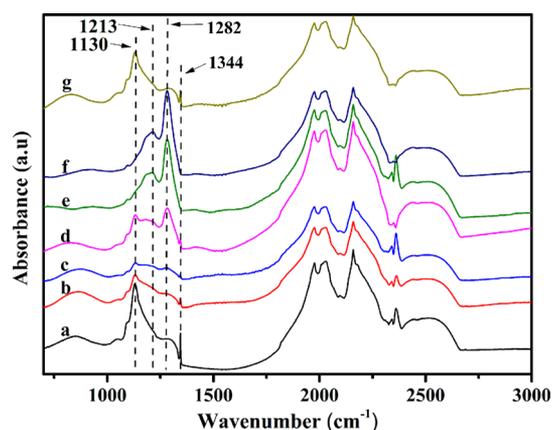


Figure 4. Infrared absorption spectra that were recorded for the diamond samples before and after the annealing experiments. (a) Prior to the annealing treatment experiments; (b)–(f), and (g) are following the annealing treatment experiments in E-1 to E-5, and E-7.

experiment. Following the HPHT annealing experiments, FTIR measurements were taken and between Figure 4b to Figure 4g. Figure 4b shows the IR spectrum of the diamond sample that was annealed at $1680\text{ }^\circ\text{C}$. The peaks at 1130 and 1344 cm^{-1} were weaker than the same peaks in Figure 4a, but the peaks at 1282 and 1213 cm^{-1} were not obvious. The N state was the main C-center and the A-center N only slightly increased. When the temperature reached $1760\text{ }^\circ\text{C}$ (Figure 4c), the peaks intensities at 1130 and 1344 cm^{-1} weakened and the 1282 cm^{-1} peak increased. As the temperature rose to $1840\text{ }^\circ\text{C}$ (Figure 4d), the peak intensities at 1130 and 1282 cm^{-1} were nearly equivalent to each other or the 1282 cm^{-1} peak intensity was slightly stronger than the 1130 cm^{-1} peak. This meant that a large proportion of C-center N transformed into A-center N. When the temperature increased up to 1920 and $1990\text{ }^\circ\text{C}$ (Figure 4e and f), the IR spectra showed that the absorption peaks at 1130 and 1344 cm^{-1} completely disappeared and two strong peaks at 1282 and 1213 cm^{-1} were observed. This result indicated that the concentration of the C-center N was less than 1 ppm , which confirmed a type IaA diamond crystal was successfully produced. Figure 4g shows the IR spectrum of the diamond sample after the 5.5 GPa and $1990\text{ }^\circ\text{C}$ annealing treatment. The spectrum barely changed when compared to Figure 4a. The C-center N state took the dominant role and the A-center N was scarcely detected. Previous annealing research did not emphasize the effect that the pressure had on the N state transitions. This result suggested that the high pressure restricted the vibrations

of the C-center N atoms and hindered the C-center N transformed into the A-center N within the diamond lattice.

We performed the PL measurement to further understand the defects in the diamond lattice caused by the impurity, the plastic deformation, and the vacancy. Figure 5 shows the PL

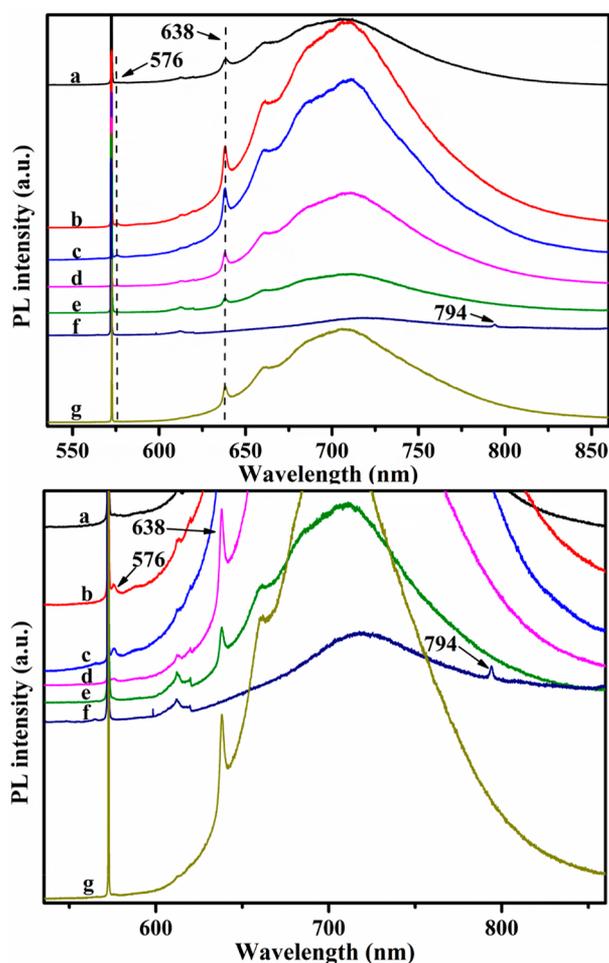


Figure 5. PL spectra of the diamond samples at a 532 nm excitation at room temperature before and after the annealing experiments. (a) Before the annealing treatment experiments; (b)–(f), and (g) are after the annealing treatment experiments in E-1 to E-5, and E-7. (The panel below represents the locally amplified spectra of the original PL spectrogram.)

spectra of the diamond samples excited with a 532 nm laser wavelength at room temperature before (Figure 5a) and after

(Figure 5b to g) the annealing experiments. The peak at 638 nm was ascribed to the negatively charged states of the NV⁻ center,^{31,32} see Figure 5a. There was no peak at 576 nm caused by the neutral charge states of the NV⁰ center.^{33,34} The PL spectra data show that the NV⁰ center was scarcely detected in the type Ib diamond samples, which grew by the {100} face of the seed diamond before the annealing experiments. The PL spectra of the annealing diamond samples are exhibited in Figure 5b to Figure 5g. The weak 576 nm peak is shown between Figure 5b to Figure 5d. This result proved that the NV⁰ center appeared in the diamond lattice after the 1680 °C, the 1760 °C, and the 1840 °C annealing treatments. After the 1840 °C annealing treatment, the intensity of the NV⁰ peak was weaker than the 1680 and the 1760 °C annealing treatments. The NV⁰ and NV⁻ centers vanished when the temperature reached 1920 and 1990 °C (Figure 5d and e). The NV⁻ was more stable than the NV⁰ center below 1920 °C. In addition, the intensity of the NV⁻ center in Figure 5b, Figure 5c and Figure 5d increased slightly. The intensity of the NV⁻ center weakened until it disappeared when the annealing temperature increased. When the temperature reached 1990 °C, both the NV⁻ center and the NV⁰ center disappeared. Figure 5g represents the PL spectrum of the diamond after annealing at 5.0 GPa and 1990 °C. The intensity of the NV⁻ peak in Figure 5g was stronger than that in Figure 5a, meaning the concentration of the NV⁻ center in the diamond lattice increased after the 5.0 GPa and 1990 °C annealing treatment.

The vacancies stabilizing temperature ranges between 550 and 700 °C.^{35–37} As the temperature reached 1680 °C, the vacancies obtained enough kinetic energy to move among the diamond lattice. We suggested that the appearance of the NV⁰ center and the enhancement of the NV⁻ center were caused by the isolated N trapping the residual vacancies in the diamond lattice. The NV center could become mobile and aggregate into larger N complexes when the temperature reached 1840 °C. The intensity of the NV⁰ and NV⁻ peaks was weakened; see Figure 5c. The NV⁰ and NV⁻ centers disappeared when the temperature increased to 1920 and 1990 °C. When the pressure was set to 5 GPa, although the high pressure restricted the vibrations of the C-center N, it did not impede the movement of vacancies in the diamond lattice. The isolated N also could be trapping the residual vacancies in the diamond lattice and then be incorporated into the NV⁻ center.

The diamond samples were synthesized in the Ni-based catalyst alloy, where the Ni atoms are easily incorporated into the diamond lattice to produce a large number of optical centers.^{38,39} The PL peak located at 794 nm (Figure 5f) was attributed to the NE8 center,⁴⁰ which appeared as the diamond

Table 2. Annealing Behavior of Several Centers That Were Detected by IR Absorption and Photoluminescence Spectra^a

pressure (GPa)	temperature (°C)	C center	A center	NV ⁰ center	NV ⁻ center	NE8 center
2.5	0	√	x	x	√	x
2.5	1680	√↓	√↑	√↑	√↑	x
2.5	1760	√↓	√↑	√↑	√↑	x
2.5	1840	√↓	√↑	√↑	√↑	x
2.5	1920	x	√↑	x	√↓	x
2.5	1990	x	√↑	x	x	√
2.5	2060	x	x	x	x	x
5.0	1990	√	x	x	√↑	x

^a“√” indicates the center was detected, “x” indicates the center was undetected, “↑” indicates the intensity of the center that increased after the annealing treatment, and “↓” indicates the intensity of the center that decreased after the annealing treatment.

sample was annealed at 1990 °C and 2.5 GPa. The NE8 center consisted of a nickel atom surrounded by four N atoms in a diamond lattice.⁴⁰ The NE8 center was promising as single photon emitters and was a far more promising source than the more commonly studied NV center. The FTIR and PL spectra data showed that the NE8 center was not generated in the diamond lattice before the C-center N transformed into the A-center N through the annealing treatment. Although the C-center is undetected in Figure 4e, the NE8 center still cannot be found in the diamond lattice. The Ni atom was likely bonded with the vibrated N and then formed the NE8 center in the diamond lattice under that specific condition. We suggested that the NE8 center likely generated at the annealing temperature of 1990 °C, which was close to the diamond graphitization temperature at 2.5 GPa. A summary of the annealing experiments results of the various centers in the diamond lattice is exhibited in Table 2.

Figure 6 shows the PL spectra of the diamond samples before and after the annealing treatment with a 325 nm laser

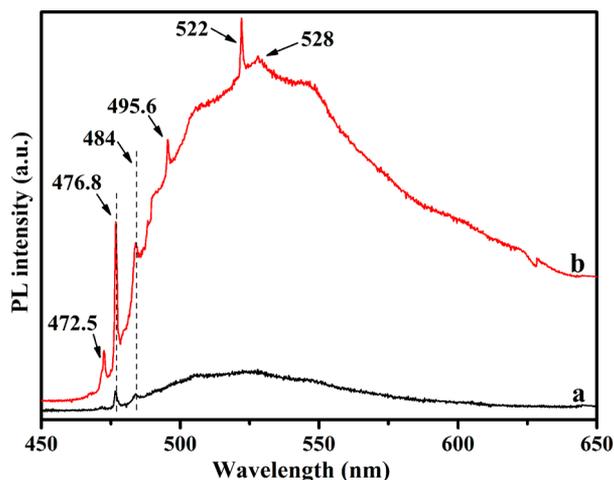


Figure 6. PL spectra of the diamond samples with a 325 nm excitation at -120 °C before and after the annealing experiments. (a) Prior to the annealing treatment experiments, (b) following the annealing treatment experiments in E-5.

wavelength at -120 °C. The peak intensity in Figure 6b is 1000 times stronger than the peak seen in Figure 6a. Figure 6a shows the PL spectrum of the common type Ib diamond before the annealing treatment. The peaks located at 476.8 and 484 nm in Figure 6a were caused by the NE2 center and the Ni-related center.^{4,41} The peaks at 472.5, 476.8, 484, 495.6, and 528 nm in Figure 6b were caused by the NE1 center, NE2 center, Ni-related center, H4 center, and Ni-N-related center.⁴¹ The 522 nm peak could be similar to the 528 nm peak of the Ni-N-related center. These results demonstrated that the isolated N in the synthesized diamond lattice formed the A center or H4 center, and also united with the Ni to form the Ni-N-related center after the annealing experiments. The light yellow diamond sample that was obtained in the E-5 experiment may be attributed to the multiple Ni-related color center or the Ni-N-related center in the diamond lattice. The color centers in the annealing diamond lattice were diverse and complicated. The exact reason for light yellow samples needs further investigation.

4. CONCLUSIONS

Synthetic type Ib diamond annealing experiments were successfully performed under high pressures and high temperature ranges between 1680 and 2060 °C. At 2.5 GPa, the color of the diamonds samples changed from yellow to light yellow as the temperature increased. The N state transformed from the isolated C-center to the aggregated A-center, as a result of the high pressure and high temperature treatment. When the annealing temperatures reached 1920 and 1990 °C, type IaA diamond was successfully prepared. The sp^3 diamond structure did not obviously change after the 1990 °C annealing treatment. When the temperature was increased to 2060 °C, the diamond was transformed to the graphitized amorphous carbon, confirmed by Raman spectra. The PL spectra showed that the NV^0 was undetected in type Ib diamond samples grown by the {100} face of the seed diamond before the annealing experiments and appeared after the 1680, 1760, and 1840 °C annealing treatments. The intensity of the NV^- center was higher in treated diamond after the 1680, 1760, and 1840 °C annealing treatments but was lower after the 1920 °C annealing treatment. The NV^0 center and the NV^- center disappeared at 1920 and 1990 °C. The NE8 center, the H4 center, the Ni-N-related center, and the Ni-related center appeared in the diamond lattice following the 1990 °C annealing treatment. After the 5 GPa annealing experiment, the high pressure restricted the C-center N transformation into A-center N but barely influenced the vacancies and the C-center N combined into the NV^- center.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.8b00145.

Listings of the China-type cubic high-pressure apparatus, the schematic and experimental conditions of annealing diamond samples growth via the TGG method (PDF)

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Notes

The authors declare no competing financial interest.

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