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Discrimination between natural and HPHT-treated type IIa diamonds using photoluminescence spectroscopy

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ABSTRACT

We have performed low-temperature (8 K) photoluminescence (PL) measurements on 71 natural and 12 high-pressure-and-high-temperature (HPHT)-treated type IIa diamonds. The GR1, NV^0, NV^-, H4, and H3 defect center PL signals are compared. Some distinct differences in the PL lineshape, intensity, and appearance of side-band PL signals are observed. Furthermore, we processed 6 of the natural diamond samples with the HPHT treatment to investigate the effect of the treatment on the PL spectrum. By systematically analyzing the differences in the PL spectra, we developed a scheme to discriminate natural and HPHT-treated diamonds with 99% validity.

1. Introduction

Most natural diamonds have a brown color which is undesirable for gem stones. It is suspected that the brown color is related to plastic deformation and resultant vacancy clusters thus created [1–3]. It has been reported that the color of natural diamonds can be altered by some treatments. The leading examples are the high-pressure and high-temperature (HPHT) treatment [4–7] and ion-beam irradiation [4]. When a diamond is treated at high-pressure and high-temperature conditions (5–7 GPa, 1800–2300 °C), at temperatures higher than the geological forming process [8], the defects in the diamond are rearranged, removed, or created. As a result, the defect energy level in the bandgap changes, which in turn results in the change of the color. Through these treatments, natural diamonds with undesirable colors can be transformed to colorless or at least yellow or green colors [6]. This technological advance poses a serious challenge to the identification of genuine natural colorless diamonds. Since the high values of natural colorless diamonds are not only due to their color but more importantly due to their rarity, it is crucial that artificially modified diamonds be discriminated with high certainty in order to maintain the order in the diamond market. Since the color change in the HPHT treatment does not involve addition or removal of impurities such as nitrogen, traditional IR absorption spectroscopy cannot discriminate between natural and treated type IIa diamonds. We already reported that the photoluminescence (PL) spectroscopy is a more powerful tool to identify defect levels in diamonds since PL can identify different defect levels even among diamonds with similar IR absorption spectra [9]. Several groups [7,10–16] have studied the defect luminescence of diamonds using photoluminescence or cathodoluminescence spectroscopy. However, no reliable criterion to discriminate between natural and HPHT-treated type IIa diamonds has been found yet. In this study, we systematically analyzed PL spectra from many natural and HPHT-treated diamonds to deduce a series of criteria that can identify HPHT-treated diamonds reliably.

The defects in diamonds have many origins: vacancy, substitutional or interstitial impurities, or structural defects such as dislocations or other plastic deformations. At HPHT conditions, some defects may become mobile and may aggregate, dissociate or annihilate. The vacancy (GR1) in the diamond lattice is the simplest defect, and results in a zero phonon line at 740.9 nm [16]. Among the impurities, nitrogen is the most abundant species. A vacancy (V) can become trapped at a single substitutional nitrogen atom (N) and produce an NV center. NV centers can be present in the neutral (NV^0) or negatively charged (NV^-) states, producing ZPLs at 575.0 nm and 638.0 nm, respectively [17]. Vacancies can also form other aggregates with substitutional nitrogen atoms. A vacancy combined with two nearest-neighbor nitrogen atoms to form a neutral $(N–V–N)^0$ complex is called an H3 center and produces a ZPL at 503.2 nm [5]. When a B aggregate of nitrogen (four nitrogen atoms surrounding a vacancy)

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traps a vacancy an H4 center is formed which gives rise to a ZPL at 496.0 nm [5].

2. Experimental

Seventy-one natural diamonds and 12 HPHT-treated diamonds were used in this study. All the samples were type IIa, which means very low nitrogen impurity concentrations [14]. All of them had color grades in the range of D to F (colorless) except for 6 natural diamonds, which had color M and were HPHT-treated later. All colorless diamonds were round brilliants, and the color M diamonds had a cylindrical shape. The spectroscopic measurements were taken from the largest flat facets. The 12 HPHT-treated diamonds were purchased from outside sources, but the details of the treatment are not known. Six color M natural diamonds were measured before and after an HPHT treatment in order to obtain control data. Two of them were treated at approximately 5 GPa and 1600 °C and the other four were treated at approximately 5 GPa and 1800 °C for approximately 3 h. After the treatment, the color of these 6 diamonds did not change much perhaps because the temperatures were not high enough due to the limitation of our equipment. The data from these 6 diamonds before they were HPHT-treated are included in the set of natural diamonds (71 total), and those obtained after they had been treated are also included in the set of HPHT-treated diamonds (18 total).

The photoluminescence spectra were measured in a conventional macro-PL system with samples placed in a closed-cycle He cryostat at 8 K. The 488-nm and 514.5-nm lines of an Ar ion laser, operating at 5 to 20 mW, were used as the excitation source. The luminescence signal was filtered with a long-pass edge filter to eliminate strong laser lines. The signal was dispersed by a Spex 0.55-m spectrometer with a 1200 groove/mm grating blazed at 500 nm and detected with a liquid-nitrogen-cooled charge-coupled-device (CCD) detector array. Both the resolution and the repeatability are approximately 0.06 nm. We devised a special sample holder for round diamonds to hold them in good thermal contact with the cold finger of the cryostat system without interfering with the luminescence measurements.

3. Results and discussion

3.1. Natural and HPHT-treated diamonds

Fig. 1 shows some representative spectra of four colorless natural diamonds and three HPHT-treated diamonds (two colorless and one color M) taken with the 488-nm excitation. Even among diamonds which have the same grades, the spectra exhibit significant variations. The sharp peak at 522 nm is due to the first-order Raman scattering by degenerate zone-center optical phonons (1332.7 cm^{-1}) [18], and there is a band at 545–562 nm due to the second-order Raman scattering, which is not discernible in this scale. The other peaks, indicated by the arrows, are because of the presence of the H4, H3, NV^0 and NV^- defects. Further analysis of these peaks is carried out with PL data using the 514.5-nm excitation.

Fig. 2 shows the GR1 center which gives a doublet of lines at 741.0 nm and 744.6 nm [16,19], which are ascribed to a neutral single vacancy. The small difference in the wavelengths between our measurement and the values in the literature may be due to the difference in the measurement temperatures. Normally, the line at 744.6 nm is much weaker than that at 741.0 nm, as seen in Fig. **2**. The GR1 center signal from natural diamonds tends to be stronger and sharper than that from HPHT-treated diamonds. All the spectra were normalized to the intensity of the Raman signal. Sixty-three out of 71 (89%) natural diamonds showed the GR1 signal whose intensity is at least 0.5% of that of the Raman signal, but 16 of the HPHT-treated diamonds showed no signal and the remaining 2 samples showed only very weak signal (about 0.1% of the intensity of the Raman signal) at 741.0 nm and no signal at 744.6 nm. Since GR1 centers are the simplest form of defects (single vacancy), they are readily removed when a diamond is subject to high pressure and high temperature. However, there is a report that electron beam irradiation on HPHT-treated diamonds re-introduces GR1 centers and restores these PL lines [20]. Therefore, the presence of the GR1 PL lines by itself cannot be a reliable criterion for a natural diamond.

Fig. 3 shows some typical spectra in the wavelength ranges of NV^0 and NV^- centers with the 514.5-nm excitation. The NV^0 and NV^- centers produce ZPLs at 575.0 and 637.0 nm, respectively. The relative intensities of these peaks vary from sample to sample. Neither of the two peaks was observed in some diamonds. It has been suggested that the ratio of 575.0 and 637.0 nm PL intensities (I_{575}/I_{637}) is an indicator of previous HPHT treatments [10,21,22]. A lower ratio was associated with HPHT-treated diamonds. According to Fisher and Spits [10], during the HPHT treatment, the aggregates of nitrogen that are present in natural diamonds dissociate and single nitrogen impurities are produced. These single nitrogen impurities act as deep donors and some electrons from such nitrogen atoms are captured by nearby NV^0 centers to produce NV^- centers. Therefore, it was inferred that the ratio I_{575}/I_{637} should be lower in HPHT-treated samples. However, our data in Fig. 4 suggest that there is no clear correlation between this

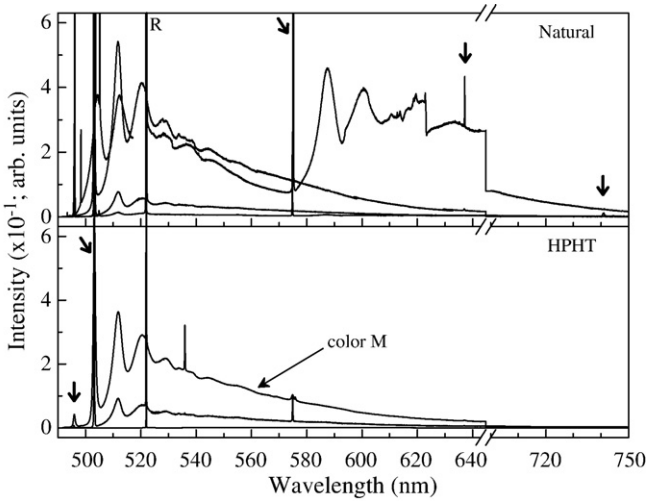

Fig. 1. Typical PL spectra of natural and HPHT-treated diamonds taken with the 488-nm excitation. All diamonds are colorless except for the one indicated. The intensities of all spectra were normalized to the intensity of the first-order Raman signal.

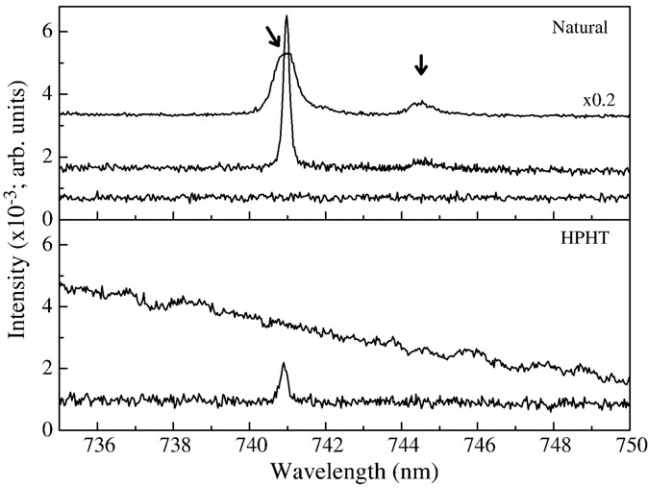

Fig. 2. PL spectra near the GR1 ZPLs from natural diamonds and HPHT-treated diamonds taken with the 514.5-nm excitation.

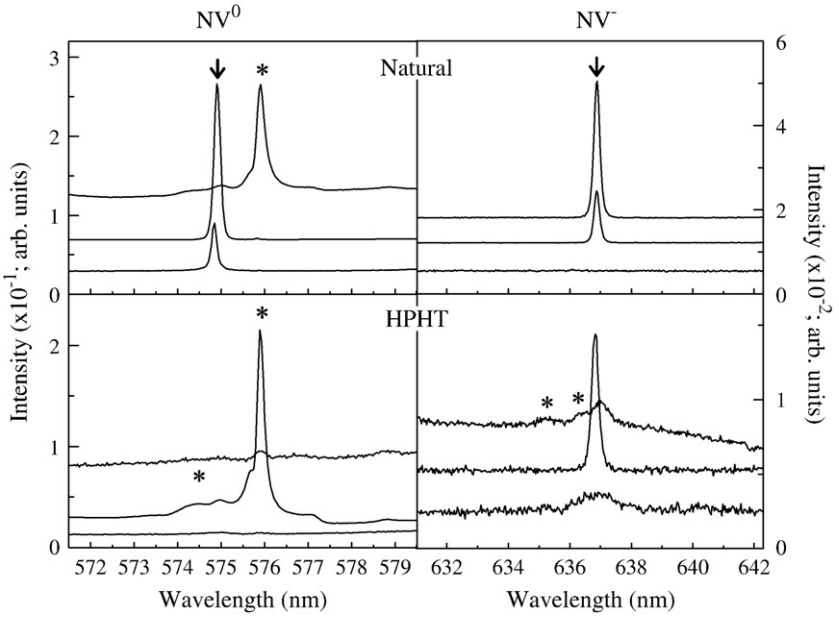

Fig. 3. PL spectra of the wavelength ranges of NV^0 and NV^- from natural and HPHT-treated diamonds. The excitation source is 514.5-nm.

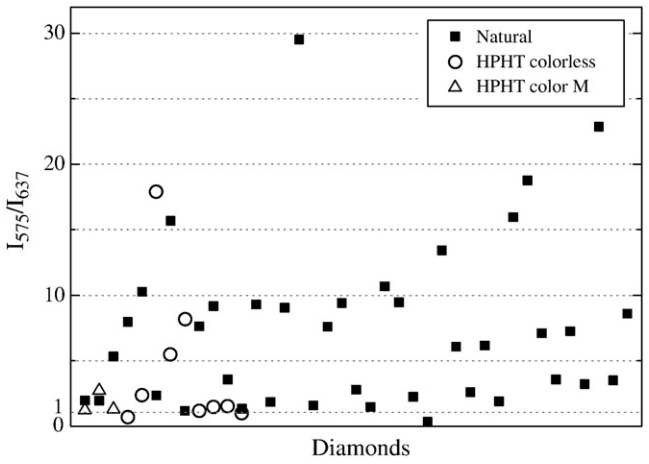

Fig. 4. Distribution of the ratio I_{575}/I_{637} of 39 natural diamonds, 9 HPHT-treated diamonds (colorless), and 3 HPHT-treated diamonds (color M).

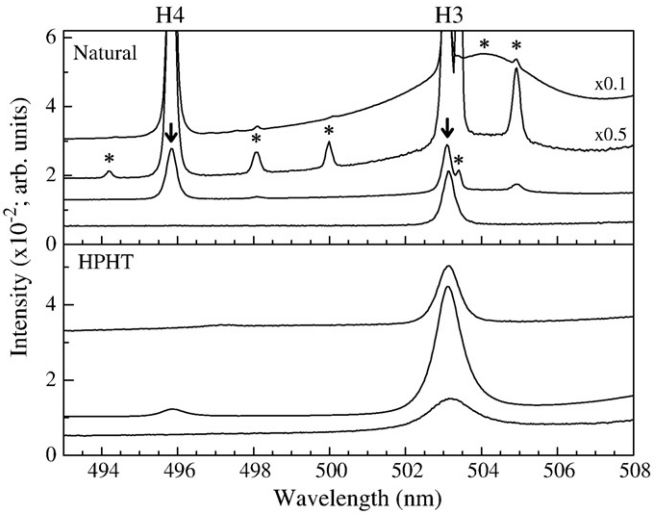

Fig. 5. PL spectra of the wavelength ranges of H4 and H3 from natural and HPHT-treated diamonds taken with the 488-nm excitation.

ratio and the HPHT treatment. Therefore, I_{575}/I_{637} cannot be used as a reliable criterion to identify HPHT-treated diamonds. Some of the diamonds show additional peaks indicated by *, which are fairly weak in most cases. These peaks are thought to be due to various defects, but the exact origins of these peaks are not known. Nevertheless, we found that their presence, in combination with other criteria, can be used in the discrimination procedure as will be shown later. Theses peaks are summarized in Table 1.

Fig. 5 shows some typical spectra of the H3 and H4 centers in natural and HPHT-treated diamonds. The ZPL at 503.1 nm due to H3 centers appears in the spectra of all samples, except one HPHT-treated colorless diamond. The ZPL at 495.8 nm due to H4 centers appears with less frequency: it is observed in 43 out of 71 (61%) natural and in 10 out of 18 (56%) HPHT-treated diamonds.

Several weaker PL peaks, indicated by * in Fig. 5, also appear at 494.3 nm, 498.3 nm, 500.0 nm, 503.5 nm, 504.2 nm, and 504.8 nm in natural diamonds [23]. Sixty-seven of the 71 (94%) natural diamonds (all of which show the H3 center line) and 42 of the 44 (95%) natural

Table 1
Number of samples that showed PL peaks near the NV^0 and NV^- ZPLs.

Wavelength (nm)	574.5	575.0 (NV^0)	575.9	633.9	635.1	636.3	637.0 (NV^-)	Neither 575, 637	Total
Natural	9	58	18	5	0	3	39	13	71
HPHT (colorless)	2	9	3	1	3	7	9	3	12
HPHT (color M)	2	4	4	2	2	2	3	2	6

Table 2
Number of samples that showed PL peaks near the H3 and H4 ZPLs.

Wavelength (nm)	494.3	495.8 (H4)	498.3	500.0	503.1 (H3)	503.5	504.2	504.8	Total
Natural	18	44	29	7	71	50	6	32	71
HPHT (colorless)	0	6	2	0	11	0	0	1	12
HPHT (color M)	0	4	0	0	6	0	0	0	6

diamonds that show the H4 center ZPL, show at least one of these lines. However, most of these weak peaks do not appear in HPHT-treated diamonds. Among the 18 HPHT-treated diamonds, only 1 shows the 498.3-nm and 504.8-nm lines and another show the 498.3-nm line only. These results are summarized in Table 2.

Fig. 6 shows the distribution of the full-width-at-half-maximum (FWHM) of the H3 and H4 center ZPLs. The FWHM was estimated after subtracting the background signal. These PL peaks from most of the natural colorless diamonds are fairly narrow with the FWHM less than 2 meV, whereas those from the natural color M diamonds tend to be broader. The FWHM of those ZPLs in HPHT-treated diamonds shows a wider distribution. Assuming that the HPHT-treated colorless diamonds were processed from natural brown diamonds, the following interpretation may be given. As in our natural color M diamonds, the H3 and H4 center ZPLs of brown diamonds are broad. The broadening is due to inhomogeneous strain as a result of the plastic deformation. It seems that the HPHT treatment does not relieve the inhomogeneous strain and so the broadening remains after the treatment. Comparison of the FWHM of the color M diamonds before and after the treatment supports this explanation. However, the FWHM alone cannot be used as a reliable criterion to discriminate HPHT-treated diamonds because some of the HPHT-treated diamonds do have fairly narrow linewidths of less than 2.0 meV. On the other hand, it seems that the defect centers that give rise to the weaker PL lines are annealed out during the HPHT process, which can be used in the discrimination scheme.

Some of the diamonds show a series of broad luminescence peaks in the range from 580 to 625 nm (Fig. 7). These peaks are present in 48 of the 71 natural diamonds and 17 of the 18 HPHT-treated diamonds. Therefore, these peaks by themselves cannot be used as criteria to identify HPHT-treated diamonds. However, combined with the appearance of other PL peaks, these peaks can contribute to the identification of HPHT-treated diamonds as will be explained in Section 3.3.

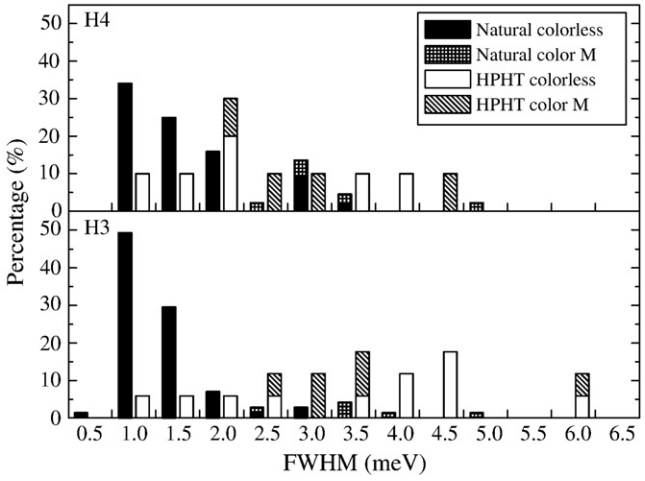

Fig. 6. FWHM of H4 and H3 PL peaks in natural and HPHT-treated diamonds.

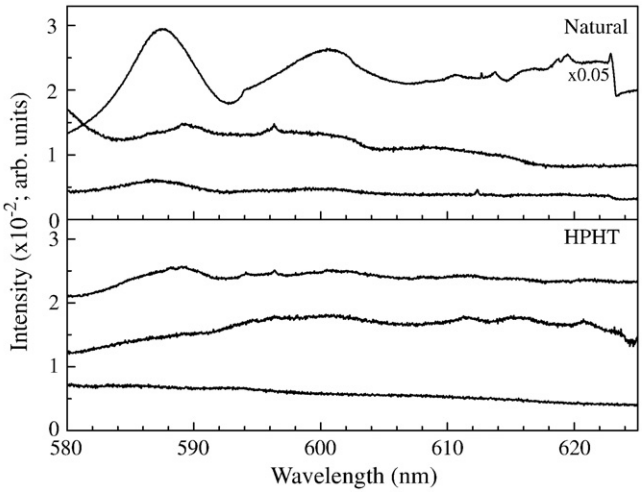

Fig. 7. PL spectra in the range of 580–625 nm. The excitation source is 514.5 nm.

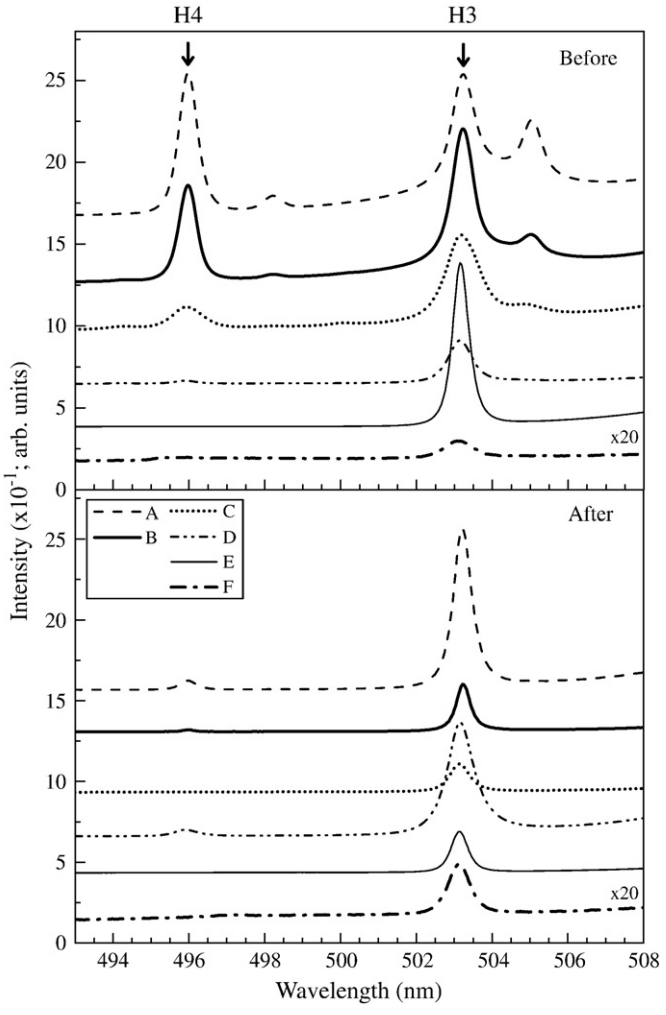

Fig. 8. PL spectra of the H4 and H3 system from natural diamonds before and after HPHT treatments taken with the 488-nm excitation.

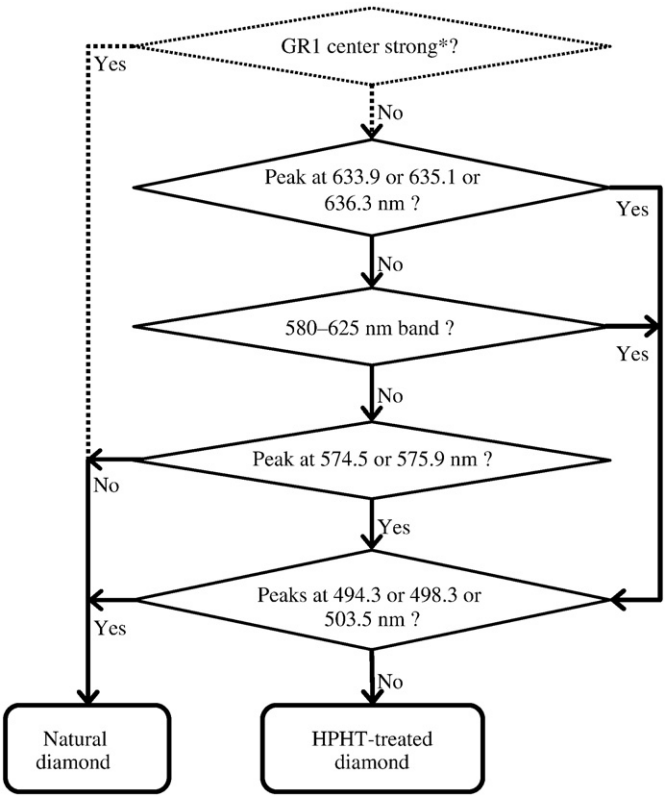

Fig. 9. Flow chart for the discrimination scheme. The first stage, shown by dashed lines, will not apply if an HPHT-treated diamond has been irradiated to reintroduce GR1 centers. *GR1 center line at 741.0 nm whose intensity is at least 0.5% of the Raman signal is classified as 'strong'.

3.2. Photoluminescence spectra from natural brown diamonds before and after HPHT treatment

In order to examine the effect of the HPHT treatment directly, we measured the PL spectra of 6 natural brown diamonds (color M) before and after HPHT treatments. Two samples (A and B) were treated at 5 GPa and 1600 °C and the rest (C, D, E, and F) were treated at 5 GPa and 1800 °C. The color of the diamonds did not change much after the treatment, which implies that the treatment conditions were less than optimal. Nevertheless, we present the comparison of the PL spectra before and after the treatments in order to understand the changes caused by the HPHT process.

In the range near the H3 and H4 center ZPLs, the most obvious change is the suppression of the weaker peaks after the treatment (Fig. 8). Similar effect was seen for the GR1 center luminescence, which disappears completely after the treatment (not shown). Another effect is the reduction of the H4 center luminescence in all but sample D.

3.3. Discrimination scheme

By thoroughly examining the data from all 89 samples, we devised a systematic scheme to discriminate between natural and HPHT-treated type IIa diamonds. The complete set of data is provided as Supplementary Data. When the scheme in Fig. 9 is applied to all 89 diamonds, all but one of the diamonds are correctly identified. Even if we exclude the first step because GR1 centers can be easily re-created after HPHT treatments by e-beam irradiation, all but one diamonds are correctly classified. Only one HPHT-treated diamond is misidentified as natural. The overall statistical validity of the procedure is 99%. Although this method is not perfect, it is by far the best method to discriminate HPHT-treated diamonds from natural diamonds.

4. Summary

Systematic low-temperature PL measurements on natural and HPHT-treated type IIa diamonds show that there are distinct differences in the PL spectra of natural and HPHT-treated diamonds. The chances of finding some of the PL signals from various defect centers are quite different between the two kinds of diamonds. Although these differences are sometimes subtle, we could develop a series of criteria to differentiate HPHT-treated diamonds from natural diamonds. We devised a systematic scheme to discriminate between natural and HPHT-treated type IIa diamonds with 99% validity. This work demonstrates that low-temperature PL measurements can be used as an effective tool in grading and certifying diamonds.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.diamond.2010.06.007.

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[23] It is known that a line at 494.5 nm is observed in ion-implanted natural diamonds and one at 503.4 nm in irradiated diamonds [Ref. 16]. However, our natural diamonds were not previously ion implanted or irradiated.