



Temperature effects on luminescence centers in natural type IIb diamonds



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ABSTRACT

Blue diamonds are among the rarest and most valuable of naturally occurring gemstones. In this study, 12 rough naturally-sourced type IIb diamonds were subjected to HPHT annealing, three different irradiation energies, and then all were stepwise annealed from 200 °C to 1100 °C and the optical defects were documented by changes in phosphorescence and photoluminescence spectroscopy. Several optical features that are removed from natural type IIb diamonds by HPHT processing, such as 3H, 648.2 nm peak, 776.4 nm peak, and 660 nm band (red) phosphorescence, can be reintroduced into these diamonds with subsequent electron irradiation and annealing at low-to-moderate temperatures. The thermal stability of these centers along with their spatial distribution provided additional insights into their configuration and distinguished them from nitrogen-bearing diamonds.

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1. Introduction

Boron-doped diamond has considerable interest for both the scientific and gem communities. Substitutional boron is a comparatively shallow acceptor in diamond (E_{VBM} [valance band maximum] + 0.37 eV) and much research has been performed on type IIb synthetic diamonds grown by chemical vapor deposition (CVD) or at high-pressure, high-temperature (HPHT) conditions. Boron incorporation into diamond is also important in synthetic diamonds for a wide variety of engineering applications due to its status as the only reliable semi-conducting dopant within diamond.

There are few sources of natural type IIb blue diamonds and they are extremely rare [1,2]. Historically, natural blue diamonds that are known to come from India such as the Hope Diamond and the Wittelsbach-Graff diamond likely were sourced from the Kollur mine near the Krishna river and then distributed from Golconda which is now modern Hyderabad [3]. Most natural type IIb diamonds found today are sourced from the Cullinan mine in South Africa [4]. Besides boron incorporation, there are other causes of blue color in diamond such as hydrogen incorporation [5], very high amounts of silicon doping (for CVD synthetics) [6], or irradiation. This study will focus on blue diamonds with color deriving from boron.

Natural type IIb diamonds are quite rare compared to type Ia (diamonds with aggregated nitrogen) or even type IIa (without detectable nitrogen or boron impurities) diamonds. Therefore, their optical features and effects of treatment and annealing have not been as

well studied. Type IIb diamonds have optical features such as photoluminescence (PL) spectral peaks and phosphorescence that are not present in other diamond [4].

Previously, annealing studies were performed on two HPHT synthetic type IIb diamonds [7] and a CVD synthetic diamond; these also were electron-irradiated and step-wise annealed [8]. To our knowledge, a comparable annealing study has not been performed for natural type IIb diamonds on such a large number of samples.

1.1. Optical centers

As numerous optical centers are affected throughout the annealing range; they will be briefly summarized here for reference. For additional information and example spectra, several reference sources are available (e.g., ref. [9] and ref. [10] and references therein). In FTIR absorption, the principal absorption of uncompensated boron is at 2802 cm^{-1} .

The total boron concentration within diamond (as determined by a different measurement such as SIMS and not included in this study) should not be misinterpreted with the uncompensated boron concentration as determined by FTIR absorption spectroscopy. The uncompensated boron is single, substitutional boron atoms acting as acceptors. Donors within diamonds (such as nitrogen-related defects) can compensate other boron atoms and render that portion of the total boron concentration as optically and/or electrically inactive [4].

As this uncompensated boron concentration, determined by FTIR absorption, for most samples in this study is from an averaging across the entire sample, this method cannot take into account local heterogeneities due to the irradiation dose or local variations in boron

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concentration. Although changes in uncompensated boron concentration are expected with these treatments, those changes could not be reliably detected within the experimental limitations of these samples. Therefore, the spatial distribution of uncompensated boron in relation to other optical features will be addressed in one section and expanded upon in a subsequent study.

The emphasis of this work will focus on the thermal stability of various luminescence features that have not been fully explored previously such as the 648.2 and 776.4 nm centers and the red phosphorescence centered at 660 nm. The thermal properties of other PL features such as 3H, NV⁰, and TR12 have been documented previously [9,10] and will be discussed here as well.

In PL spectra, the GR1 (zero-phonon line [ZPL] at 741.2 nm), is a neutral vacancy (V⁰). The NV⁰ (ZPL at 575 nm) is the neutral nitrogen-vacancy center and NV⁻ (ZPL at 637 nm) is the negatively charged nitrogen-vacancy center. The 3H center (ZPL = 503.5 nm) is ascribed to an interstitial-related defect.

The TR12 (ZPL at 469.9 nm) is a radiation-related feature and tentatively ascribed to a divacancy/di-interstitial defect. The 735.9 nm center is radiation related and ascribed as a self-interstitial defect.

The 3H, TR12 and GR1 centers are also radiation related, but due to the ability of PL spectroscopy to detect optical centers in extremely low amounts, these can be observed in PL spectra of many natural diamonds. However, the 3H and GR1 are typically only observed in UV-Vis-NIR absorption spectra of strongly irradiated diamonds.

The 648.2 and 776.4 nm centers are only observed in PL spectra of type IIb diamond and commonly in spectra of natural type IIb diamonds (the 648.2 nm center is sometimes observed in the PL spectra of nominally type IIa diamonds which have a very low concentration of boron). Both centers have been described as boron-related defects with the 648.2 nm center ascribed as a boron-containing interstitial complex [8] while the 776.4 nm center has correlated to a boron-vacancy related complex [11].

Natural type IIb diamonds commonly show pronounced phosphorescence at room temperature, such as the vibrant red displayed by the Hope Diamond [12]—the phosphorescence may still be observed a full minute after the UV source is turned off. Prior research showed that, regardless of the observed color of phosphorescence, most natural type IIb diamonds have two well-defined phosphorescence bands, centered at 500 and 660 nm. Synthetic type IIb diamonds show phosphorescence bands centered at 500 nm and, less commonly, at 580 nm. The optical center at 648.2 nm has been anecdotally correlated with blue phosphorescence in natural type IIb diamonds while the 776.4 nm peak correlated with red phosphorescence [13].

2. Materials and methods

In this study, twelve naturally sourced type IIb diamonds were chosen (Fig. 1). These type IIb diamonds were HPHT-treated by a third-party company and specific parameters such as time and temperature were kept proprietary; however, we estimate that the temperature and time parameters were likely ~2000 °C for a few minutes. Subsequently, they were split into three groups then electron-irradiated at three different energies (1 MeV, 2 MeV, and 3 MeV). The samples were mounted on a water cooled holder. The irradiation dose for all energies was determined as $1.6 \times 10^{16} \text{ cm}^{-2}$. The irradiation occurred at room temperature, but the samples were simultaneously water cooled. These HPHT-annealed and irradiated diamonds were then subjected to stepwise annealing from 200 °C to 1100 °C. The changes with the treatment and annealing and the thermal stability of these optical centers make up the majority of this article. The changes in features in phosphorescence spectroscopy, and PL spectroscopy were assessed after each annealing step.

The samples were each heated to temperatures of 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100 °C for 1 hour intervals in an alumina tube furnace with flowing 99% Ar/1% H₂ gas. During the heating, the samples

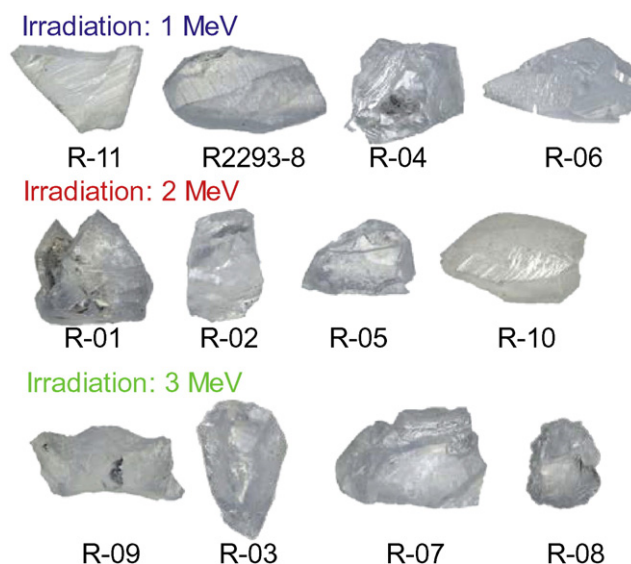


Fig. 1. These 12 naturally sourced rough diamonds were subjected to HPHT annealing, irradiation, and then stepwise heating up to 1100 °C in this study. See Table 1 for additional details; image sizes not to scale.

were contained within an alumina crucible and covered with granules of borax to minimize oxidation. The temperature calibration of the furnace was confirmed by melting salts (NaNO₃ has melting point of 308 °C; it was solid after heating in furnace to 300 °C; liquid at 310 °C. NaCl has melting point of 801 °C; it was solid at 790 °C, liquid at 800 °C).

FTIR absorption spectra were collected from 6000 to 400 cm⁻¹ range using a Thermo Nicolet Nexus 6700 spectrometer furnished with KBr and quartz beam splitters and a DRIFT (diffuse-reflectance infrared Fourier transform) accessory.

PL spectroscopy with 325, 457, 488, 514, 633, and 830 nm laser excitation at liquid nitrogen temperature, were collected on all samples. PL spectra were collected on each diamond in standard (i.e., not confocal) mode at 5× magnification on a pre-identified region of the diamond. To reduce variability between samples due to the non-standard shape of these rough samples and reduce variability within each sample at each experimental stage, this pre-identified region was exposed to the electron beam during the irradiation step and PL spectroscopy was collected from this region after each treatment or annealing experiment.

Using GRAMS software, the spectral peaks observed within the PL spectra were fit to a mixed Gaussian/Lorentzian curve. For each peak in each sample after each annealing step, the fitting determined the peak intensity, full width at half-maximum (FWHM) and peak areas above a baseline. For PL spectroscopy, semi-quantitative data are obtained by ratioing the determined peak area to that of the diamond Raman peak.

The UV-Vis-NIR spectra were collected at liquid nitrogen temperature using a custom-built instrument attached with Avantes AvaSpec-2048 spectrometer (4 channels), and two broad-band light sources (AvaLight-HAL and AvaLight-DH-S). This spectrometer's range is 250–1000 nm, but light source limitations restrict its usage in most circumstances to ~350 to 900 nm. Entrance slit width for each spectrometer of the four channels is 10 μm. Two hundred scans were collected for each sample in order to achieve a good signal-to-noise ratio within this wavelength range. This spectrometer has high resolution to detect the optical defects present within the visible range, but is not quantitative and does not show a proper baseline. Therefore these measurements cannot be used to determine defect concentrations or properly compare the slopes of the UV-Vis spectra caused by differences in the uncompensated boron concentration which creates a slope from the infrared into the visible range.

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