

# Using phosphorescence as a fingerprint for the Hope and other blue diamonds

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## ABSTRACT

Sixty-seven natural blue diamonds, including the two largest such gemstones known (the Hope and the Blue Heart), were probed by ultraviolet radiation, and their luminescence was analyzed using a novel spectrometer system. Prior to this study, the fiery red phosphorescence of the Hope Diamond was regarded as quite rare compared to greenish-blue phosphorescence. However, our results demonstrated that virtually all blue diamonds phosphoresce at 660 nm (orange-red) but that this emission often is obscured by a concomitant luminescence at 500 nm (green-blue). Although both bands were nearly always present, the relative intensities of these emissions and their decay kinetics varied dramatically. Consequently, phosphorescence analysis provides a method to discriminate among individual blue diamonds. Treated and synthetic blue diamonds showed behavior distinct from natural stones. Temperature-dependent phosphorescence revealed that the 660 nm emission has an activation energy of 0.4 eV, close to the 0.37 eV acceptor energy for boron, suggesting that the phosphorescence is caused by donor-acceptor pair recombination.

**Keywords:** phosphorescence, type-IIb diamond, donor-acceptor pair recombination, fingerprinting.

## INTRODUCTION

Blue diamonds are among the rarest and most valuable of all gems, and the Hope Diamond is the most famous member of this exceptional group. At 45.52 carats (ct), the Hope is the largest deep-blue diamond known, and its turbulent history can be traced back nearly four centuries through one English and three French kings. Today, the Hope Diamond is the focal point of the Harry Winston Gallery in the United States National Gem Collection. There, it attracts millions of visitors each year, exceeding in popularity any other object in the vast repository of the Smithsonian Institution. In fact, it is likely that more people view the Hope Diamond than any other museum piece in the world.

Most visitors, however, do not have an opportunity to observe the fiery red, long-lasting phosphorescence of the Hope after exposure to ultraviolet (UV) radiation (Fig. 1). This behavior was believed to be so rare that other blue diamonds with red phosphorescence have been represented as coming from the same parent diamond as the Hope (Fritsch and Scarratt, 1992). Little scientific research exists on the phosphorescence properties of natural blue diamonds, and much is qualitative; often

only visual observations are provided (e.g., King et al., 1998, 2003), or studies have focused on the dependence of luminescence on temperature (e.g., Halperin and Chen, 1966). This previous work has suggested that the majority of blue diamonds phosphoresce chalky blue to green.

In this study, we investigated the luminescence properties of three synthetic, one treated, and 67 natural blue diamonds, including the Hope, the Blue Heart (at 30.62 ct, the second largest deep-blue diamond), and a number of diamonds selected from the Aurora Butterfly and the Aurora Heart collections of colored diamonds. The blue color in diamonds generally arises from the incorporation of boron at trace (ppb to ppm) levels and relatively low concentrations of nitrogen impurities (below detection using infrared [IR] spectroscopy). Since natural blue diamonds are quite rare, most research on the optical properties of boron-containing diamonds has been conducted on synthetic stones (Zaitsev, 2001). The simultaneous presence of such a large number of rare diamonds in one location provided an extraordinary, and perhaps unique, opportunity to explore the properties of blue diamonds.

In addition to providing insights into the cause of luminescence in blue diamonds, this study also has suggested a simple and robust method for characterizing individual specimens. A method capable of fingerprinting blue diamonds, whether loose or mounted in jewelry,



**Figure 1.** The 45.52 ct Hope Diamond (top) is the most famous example of a blue diamond showing red phosphorescence. Blue diamonds show several phosphorescence colors, including pink to blue (such as 0.52 ct oval and 0.56 ct heart). Photos are by Chip Clark, John Nels Hatleberg, Sood Oil (Judy) Chia, and Kyaw Soe Moe. Horizontal dimensions of the stones (from top to bottom) are 25.60 mm, 4.01 mm, and 6.25 mm.

can provide valuable applications for the gem industry. As examples, blue diamonds that have been stolen, submitted for jewelry repair, or cut into smaller stones require identification techniques that are quantitative, nondestructive, and portable for use in a variety of locations. Perhaps just as important, the need to distinguish natural blue diamonds from gems that have been treated or synthesized has acquired greater urgency as high-pressure, high-temperature (HPHT) treatments increase in sophistication, and as a range of new techniques to fabricate colored diamonds are showing reproducible success.

## MATERIALS AND METHODS

Most of the diamonds used in this study were graded by gemological laboratories and are known to be natural and untreated. The three

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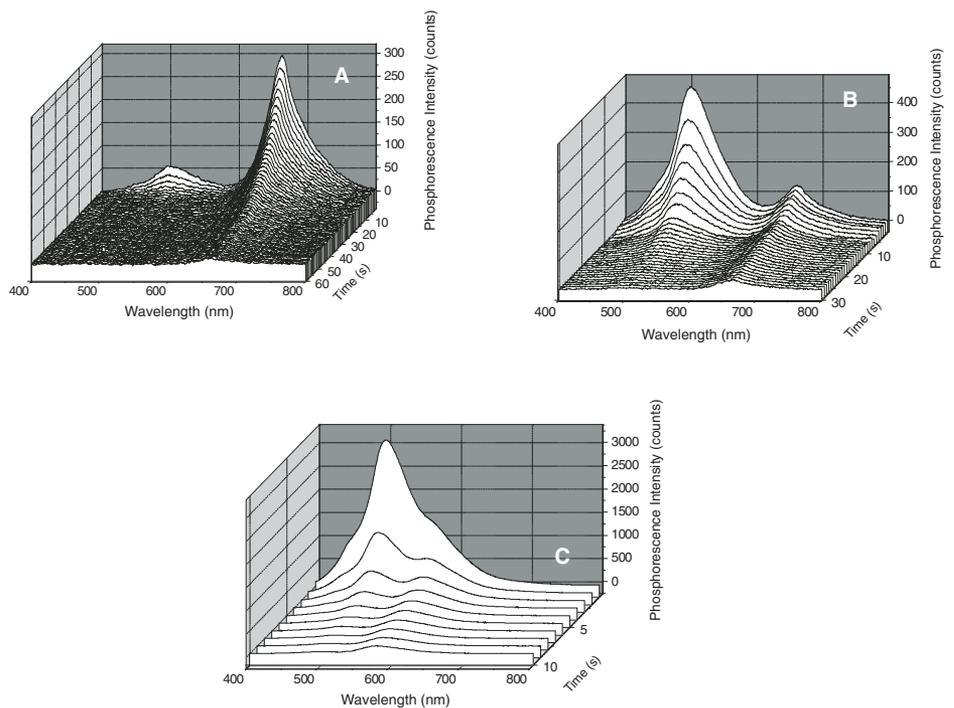
dark blue, boron-doped synthetic diamonds examined in this study were grown at HPHT conditions. The Aurora Butterfly is a collection of 240 loose colored diamonds (total weight of 166.94 ct) that were on temporary display at the Smithsonian Institution. Because most diamonds that were color-graded as gray gave similar phosphorescence results, they were grouped with the blue diamonds in this study.

Phosphorescence at room temperature was excited by broadband UV radiation (215–400 nm) that was delivered by a portable desktop instrument that included a deuterium lamp coupled to a fiber-optic assembly and a high-sensitivity spectrometer that recorded the spectra. The Ocean Optics USB 2000 spectrometer measures wavelengths from 340 to 1020 nm and has a 200  $\mu\text{m}$  slit width that provides a 10 nm full width at half-maximum (FWHM) resolution. The calibration was confirmed using the 435.8 and 546.1 nm mercury lines. Due to equipment limitations, we measured the phosphorescence beginning  $\sim 1$  s after the light source was extinguished in most experiments. In addition, the phosphorescence spectra of a rough natural blue diamond were measured at 10  $^{\circ}\text{C}$  temperature intervals ranging from 25  $^{\circ}\text{C}$  to 155  $^{\circ}\text{C}$  in air. The temperature of the diamond was maintained at a constant level as the phosphorescence decay was recorded following UV excitation.

Two natural blue diamonds and two boron-doped HPHT synthetic diamonds were characterized by steady-state and time-resolved laser-induced photoluminescence (PL) spectroscopy. The steady-state PL measurements were performed using the 325 nm line of a He-Cd laser. The diamond samples were positioned (table-side-up) on a helium-cooled cold finger (temperature  $\sim 5$  K), and the measurements were recorded using photon counting and a Spex 1404 (0.85 m double monochromator) fitted with an 1800 grooves  $\text{mm}^{-1}$  grating blazed at 350 nm. The pulsed PL measurements were performed at room temperature using 355 nm light from a Q-switched Nd:YAG laser, a 0.22 m double monochromator, GaAs photomultiplier and time-correlated photon counting. Additionally, Fourier-transform infrared (FTIR) spectra were collected on 20 diamonds using a Thermo-Nicolet Nexus 670.

## RESULTS

Our investigations revealed that red phosphorescence is, in fact, a hallmark of most blue diamonds, but the color is often masked by a companion luminescence in the green-blue region of the visible spectrum. Of the 67 natural blue diamonds examined in this study, 62 exhibited two phosphorescence peaks. One peak had a maximum at  $\sim 500$  nm (greenish blue), and the other had a peak in the red portion of the spectrum at  $\sim 660$  nm (orange-red; Fig. 2A).



**Figure 2.** Phosphorescence spectra for Hope Diamond (A), a gray-blue diamond from Aurora Butterfly collection, B29 (B), and a dark-blue synthetic diamond, HPHT-C, (C). In A, large peak at 660 nm accounts for observed strong red phosphorescence. Peak at 500 nm plays a lesser role for this particular blue diamond. Half-life,  $\tau$ , for 660 nm peak is 9.2 s, and it is 1.8 s for the 500 nm peak. In B,  $\tau$  is 12.7 s for 660 nm peak and 2.5 s for 500 nm peak. In C,  $\tau$  is 0.82 s for 500 nm peak and 1.4 s for 575 nm peak. For all samples, diamond was illuminated for 20 s. Data were taken at 1 s integration times.

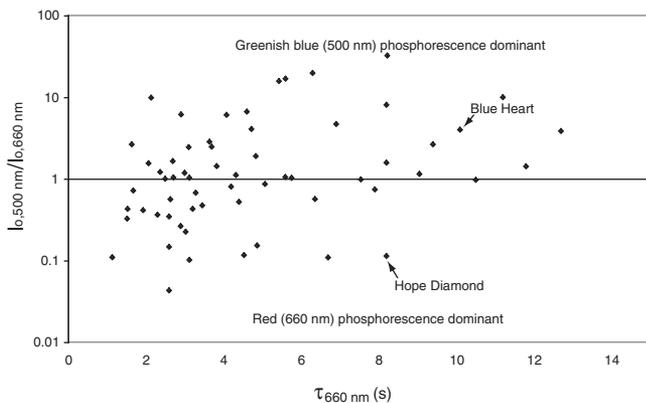
The variations in peak positions for these two peaks among different samples were  $\pm 3$  nm. All 20 blue diamonds showing the 500 and 660 nm peaks that were tested by FTIR spectroscopy were type-IIb diamonds (i.e., measurable boron and low nitrogen).

Visual examination of the color change during the phosphorescence decay of the Hope Diamond revealed a distinct reddening with increasing time. The spectra shown in Figure 2A confirm and quantify this observation. Although both the 500 and 660 nm peaks were detectable at the onset of phosphorescence, it can be seen in Figure 2A that the 500 nm peak decayed much more rapidly than the 660 nm band, resulting in a relative intensifying of the red color. Contrasting behavior is illustrated by the phosphorescence spectrum in Figure 2B. To the eye, this diamond phosphoresced blue-green to white, as the initial intensity of the 500 nm peak was greater than that of the 660 nm band. A secondary peak at  $\sim 440$  nm also is evident as a shoulder on the 500 nm band. When the 500 nm emission predominated, as was the case for the majority of the natural diamonds examined, the initial phosphorescence appeared to the eye as greenish blue. In the less common cases in which the 660 nm emission was stronger (as with the Hope Diamond), the phosphorescence appeared to be orangey red to

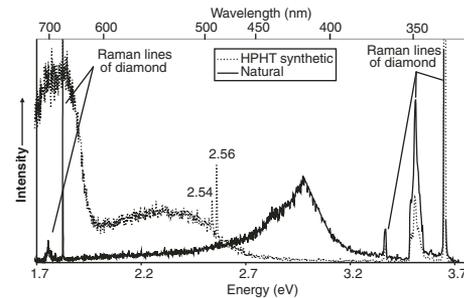
the eye. Thus, the variation in the relative intensities of these two emission bands accounts for the wide variation in phosphorescence observed in blue diamonds. In some diamonds, the observed phosphorescence changed from greenish blue to red at longer decay times.

The decay of the phosphorescence was characterized in terms of half-lives (i.e., the time for the initial intensity to diminish by 50%). The measured half-lives for the 500 nm peaks ranged from 0.5 to 6 s; but for each diamond, the 660 nm peak always exhibited a longer half-life, with values ranging from 3 to 30 s. The spectral line-shapes and widths did not differ significantly among the diamonds studied. When illuminated by short-wave UV radiation (254 nm) rather than the broad UV source used in most of the experiments, the diamonds emitted at both 500 nm and 660 nm. Using a long-wave UV source (351 nm), however, only the 660 nm peak was observed. No correlation between the intensity of the blue body color and the measured phosphorescence half-lives or intensities was detected.

When the ratios of the peak intensities of the 500 and 660 nm bands, as excited by the broad UV source, are plotted against the half-life of the 660 nm peak for each specimen, virtually every diamond exhibits a unique combination of parameters (Fig. 3). The scatter in Figure 3 suggests that easily measurable phosphorescence



**Figure 3. Ratios of initial intensities of 500 nm and 660 nm bands are plotted against measured half-lives of 660 nm emission for natural gray-to-blue diamonds. For y-axis values greater than 1, greenish-blue band dominates, and, conversely, for values less than 1, red band dominates. For diamonds that had ratios of ~1, observed phosphorescence would appear whitish.**



**Figure 4. Photoluminescence at 5 K from a boron-doped synthetic diamond and a natural blue diamond using a 325 nm (3.82 eV) laser and an 1800 grooves mm<sup>-1</sup> grating blazed at 350 nm. In addition to luminescence bands, there are also first- and second-order, one-, two-, and three-phonon Raman bands of diamond. Sharp peaks at 2.54 and 2.56 eV in synthetic diamond are likely related to nickel incorporation during growth (Zaitsev, 2001). Data are shown on a linear scale. HPHT—high-pressure, high-temperature.**

properties might provide a useful tool for characterizing and distinguishing individual blue diamonds. Moreover, the spectrometer used in our study was relatively inexpensive, easy to use, and highly portable.

In contrast with natural blue diamonds, the three boron-doped synthetic diamonds exhibited a phosphorescence band at 500 nm but not at 660 nm. In one deep-blue synthetic diamond, an additional peak at ~575 nm was apparent (Fig. 2C). The intensities of the emissions in these synthetic stones were the highest of any diamonds studied, but the half-lives of the 500 nm peak were comparable to those of natural stones. Additionally, we examined a natural gray diamond that had been treated by HPHT-annealing to turn it blue. Like the synthetic stones, this diamond phosphoresced only at 500 nm. It was the only blue/gray diamond of natural origin to phosphoresce at 500 nm and *not* at 660 nm; this result recently was confirmed by visual observation on a similarly treated stone (Breeding et al., 2006). These results suggest that phosphorescence spectroscopy might be an effective tool for discriminating synthetic and HPHT-treated diamonds from natural blue diamonds.

Five of the 67 natural blue diamonds showed different luminescence behaviors from the majority. Two showed no phosphorescence, and three diamonds exhibited yellow fluorescence and green phosphorescence. The latter three stones proved to be type Ia, not boron-containing type-IIb diamonds, and FTIR spectra indicated a high amount of nitrogen and hydrogen (see Fritsch and Scarratt, 1992). All other blue diamonds showed negligible fluorescence. Our study suggests, then, that all natural type-IIb diamonds yield phosphorescence spectra with 500 and 660 nm peaks, and, conversely, that the absence of such phosphorescence features strongly indicates that the diamond is not type IIb.

Representative data of the steady-state PL experiments performed on a few natural and synthetic diamonds are shown in Figure 4. The synthetic diamonds show similar characteristics to previous PL experiments on synthetic stones

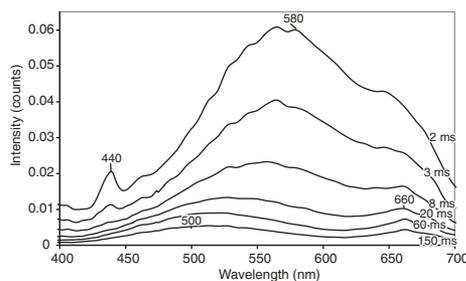
(see, e.g., Klein et al., 1995). There are two broad peaks centered at 1.85 eV (670 nm) and 2.3 eV (540 nm). The natural blue diamond has a single luminescence peak with maximum at ~3.0 eV (413 nm).

Time-resolved PL spectroscopy revealed how the emission spectra evolved as a function of time. Despite the fact that the 500 and 660 nm peaks in phosphorescence spectra of natural blue diamonds were not observed in steady-state laser-excited PL measurements, both peaks, as well as bands at 440 and 580 nm, were visible in pulsed PL spectra (Fig. 5). At the later times, the intensities of the 440 and the 580 nm peaks weakened significantly, such that by 20 ms, only the phosphorescence at the 500 and 660 nm peaks was observed. Boron-doped synthetic diamonds exhibited a significantly different behavior; the 575 nm peak in the synthetic diamond persisted sufficiently to be observable in the phosphorescence spectra (Fig. 2C), but the 660 nm luminescence was short-lived and decayed at much shorter time scales. Although the 660 nm band is clearly seen in steady-state PL for synthetic diamonds (Klein et al., 1995), it was not detectable in pulsed spectra after 1 ms.

In order to monitor the thermal response of the phosphorescence, emission spectra were recorded for a natural blue diamond at 10 °C intervals between 35 °C and 155 °C (Fig. 6A). The resulting Arrhenius plot in Figure 6B (log intensity versus inverse temperature) reveals exponential behavior for both bands. A fit of the data using  $I(T) \propto \{1 + A[\exp(-E_i/kT)]\}^{-1}$  yields a thermal activation energy,  $E_i$ , of ~0.4 eV for the 660 nm peak, close to the 0.37 eV binding energy of the neutral boron acceptor (where  $I$  is the measured integrated intensity,  $T$  is temperature,  $A$  is the Arrhenius constant, and  $k$  is the Boltzmann constant). Similar calculations for the 500 nm band indicate an activation energy of 0.8 eV.

## DISCUSSION

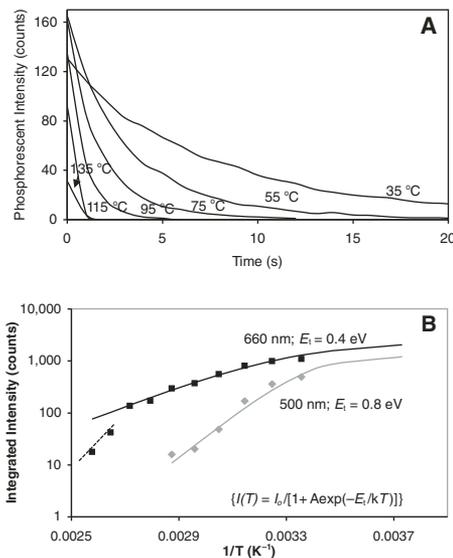
What is the origin of the phosphorescence in blue diamonds? The variability in the intensities and decay times of the 500 and 660 nm peaks



**Figure 5. Photoluminescence (PL) decay (pulsed spectra) of natural blue diamond was excited by a 355 nm laser at room temperature in time range of 2–150 ms. At shorter delay times (e.g., 5 μs, not shown), dominant feature is a broad peak centered at ~580 nm. In this time frame shown, peak appears to shift to 500 nm. Shift is only a consequence of fact that 580 nm peak decays at a faster rate than other emissions, which leaves only 500 nm and 660 nm peaks at later times; 440 nm emission is seen to decay on milli-second time scales.**

implies some differences in the concentrations of the impurities and other defects that create the excited states. We have insufficient evidence to completely describe the defect states, impurities, or energy-transfer mechanisms responsible for the observed phosphorescence in this work. Nevertheless, our results do constrain the possible mechanisms.

Donor-acceptor pair recombination (DAPR) is reviewed in depth by Dean et al. (1965), and it supposes that holes bound to acceptors recombine with electrons that are bound to donors and emit light with an energy that is approximately equal to the difference in energy level between the donor and acceptor. Numerous authors have provided compelling evidence that DAPR is the mechanism responsible for a



**Figure 6. Phosphorescence intensity for a natural blue diamond versus temperature. (A) Heating diamond reduces phosphorescence of broad band centered at ~660 nm. (B) Integrated intensity of the phosphorescence decay for the 660 nm band shown in A, along with similar data for 500 nm band, is plotted against inverse temperature on semilogarithmic coordinates. Thermal activation energies,  $E_a$ , are approximated as ~0.4 eV and 0.8 eV for 660 nm and 500 nm bands, respectively.**

variety of bands observed in phosphorescence and laser-induced PL in boron-doped synthetic diamonds produced by chemical vapor deposition (Dischler et al., 1994) and HPHT conditions (Klein et al., 1995; Watanabe et al., 1997) in which boron acts as the acceptor. To our knowledge, this is the first analogous study on natural blue diamonds, and it demonstrates that the same DAPR mechanism is active.

The temperature dependence of DAPR is a function of the rate-limiting step, either the emission itself or the formation of the neutral donor-acceptor pair; in the latter case, the thermal ionization of the weaker of the donor or acceptor will be the rate-limiting step. The observation that the 660 nm band yields an activation energy of ~0.4 eV (Fig. 6B), close to the 0.37 eV acceptor energy of boron, strongly suggests that this band is caused by DAPR and is consistent with prior research (Watanabe et al., 1997). The band at 500 nm is also likely boron-related (Watanabe et al., 1997; Won et al., 1996), but the high activation energy of 0.8 eV (for reference, the band gap of diamond is 5.5 eV) suggests that thermal activation of boron is not the rate-limiting step. At long time scales (order of seconds), the DAPR mechanism between distant neutral donors and neutral boron acceptors is likely (Watanabe et al., 1997).

An examination of the luminescence spectra taken under steady-state conditions (Fig. 4),

intermediate time scales (order of milliseconds; Fig. 5), and long time scales (order of seconds; Fig. 2) shows that the dominant peaks change with time. For example, in natural diamonds, the band centered at 660 nm is not observed in steady-state PL spectra (e.g., Fig. 4), it is seen to develop over time scales of milliseconds as more dominant peaks decay in pulsed spectra (Fig. 5), and it appears visually as phosphorescence (Fig. 2). Conversely, a similar peak at 670 nm is observed in synthetic diamonds under steady-state PL conditions (Fig. 4), where it decays on the microsecond to millisecond time scale, and it is not observed by phosphorescence (Fig. 2C). This difference in peak decay times between natural and synthetic diamonds is likely due to differences in the concentrations and arrangement of donors and acceptors in the crystal (e.g., short-range ordering over laboratory versus geologic time scales), and the resulting separation distance (Watanabe et al., 1997).

In addition, a band at ~575 nm is observed in synthetic diamonds (Fig. 1C) by phosphorescence spectroscopy, as has been noted by other researchers (Klein et al., 1995; Watanabe et al., 1997). A similar band is seen in natural diamonds at ~580 nm at shorter times scales (Fig. 5). The peaks at ~660 and ~580 nm in natural diamonds, which may be observed at different time scales, might have an identical origin as the peaks observed in their synthetic counterparts, and similar values for FWHM are consistent with that fact.

Although the 660 nm emission is caused by DAPR, the specific form of the donor is unknown. Due to the energy of the observed luminescence, the donor energy associated with a DAPR mechanism with boron as an acceptor is constrained to the approximate range of 2.6–3.3 eV (see, e.g., Klein et al., 1995; Watanabe et al., 1997). The donor energy of substitutional nitrogen is 1.7 eV, which is located too high in the band gap to be accountable, and the nitrogen A aggregate has a donor energy of 4 eV, which is too low in the band gap. However, prior research has indicated that substitutional nitrogen may undergo strong lattice relaxation, with corresponding energy of ~1 eV, which would bring its recombination energy much closer to the experimental range (Nazare et al., 1995). It is likely that the variation in initial intensities and the half-lives for the 500 and 660 nm peaks is caused by variations in the boron-to-nitrogen ratios present in each diamond. Measurement of these concentrations will be the focus of future research.

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