



# Chameleon diamonds: Thermal processes governing luminescence and a model for the color change

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## ABSTRACT

To date, the eponymous color-changing behavior of chameleon diamonds lacks an explanation in terms of an identified diamond defect structure or process. Well known, however, is that this color-change is driven by the influence of both light and heat. In this paper, we present observations of how luminescence emission in chameleon diamonds responds to temperature changes and optical pumping. Fluorescence, phosphorescence, and thermoluminescence experiments on a suite of natural chameleon diamonds reveal that a specific emission band, peaking near 550 nm, may be stimulated by several different mechanisms. We have observed thermal quenching of the 550 nm emission band with an activation energy of 0.135 eV. The 550 nm band is also observed in phosphorescence and thermoluminescence. Thermoluminescence spectra suggest the presence of low lying acceptor states at 0.7 eV above the valence band. When excited with 270 nm light, we observe emission of light in two broad spectral bands peaking at 500 and 550 nm. We suggest that the 550 nm emission band results from donor–acceptor pair recombination (DAPR) from low lying acceptor states at ca. 0.7 eV above the valence band and donor states approximately 2.5 to 2.7 eV above the valence band. We do not identify the structure of these defects. We propose a speculative model of the physics of the color change from ‘yellow’ to ‘green’ which results from increased broad-band optical absorption in the near-IR to visible due to transitions from the valence band into un-ionized acceptor states available in the ‘green’ state of the chameleon diamond. We report near-IR absorption spectra confirming the increased absorption of light in the near-IR to visible in the ‘green’ when compared to the ‘yellow’ state with a threshold at ca. 0.65 eV, supporting the proposed model.

## 1. Introduction

“Chameleon” diamonds are a distinct breed of naturally-occurring diamond defined by a change in apparent color between green and yellow dependent on ambient conditions [1]. An unperturbed chameleon diamond appears golden yellow to the eye; however exposure to visible/near-visible light drives a photochromic transition towards olive-green (Fig. 1). In the absence of light or upon heating the stone, the color transitions in the opposite direction, suggesting a thermal relaxation from a metastable ‘olive-green’ condition back to the ground ‘yellow’ condition. The diamond will maintain its olive-green color under ambient lighting at room temperature, leading to the green condition being described sometimes as the ‘stable’ condition of a chameleon diamond in spite of the thermal relaxation to yellow (e.g. [1,2]).

The defect structure(s) and processes responsible for creating this color change phenomenon are currently unknown. Both hydrogen and nitrogen impurities are typically found in chameleon diamonds, the

latter predominantly aggregated as “A”-centers (N–N), but also present in single substitutional carbon sites [1–3]. This association has led to the suggestion of N–N–H as the originating defect [4]; this hypothesis is, however, unconfirmed.

Photo-/thermochromism in diamond is often symptomatic of carrier or energy exchange between defect centers (e.g. [5–8]). In these cases, we can gain insights into the electronic structure of the defect(s) responsible for diamond color-change by investigating how the bulk optical properties of diamonds change in response to a variety of external stimuli. Here we present a series of experiments performed on a set of chameleon diamonds, ranging in size from 0.50–6.15 ct, which show a remarkably vivid color-change in response to heat and light. We detail several discrete luminescence behaviors observed when subjecting our samples to a range of optical and thermal excitations. After doing so, we consider how the results of our experiments may be interpreted with a speculative model of electronic processes at defects within the diamond which may explain the observed color changes and luminescence.

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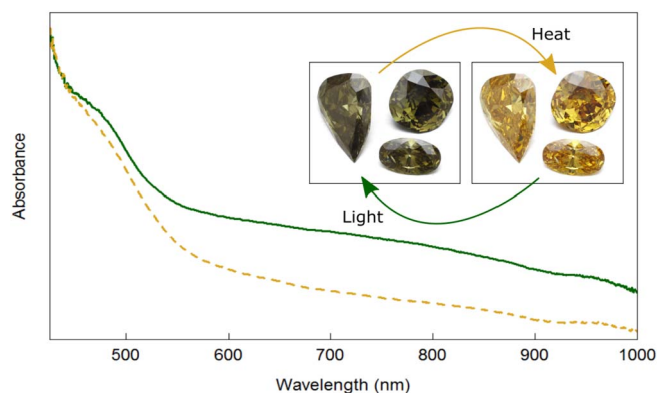


Fig. 1. Three diamonds—samples A5 (1.91 ct oval), A6 (6.15 ct pear) and A7 (4.02 ct round)—demonstrating the characteristic “chameleon” color-change; samples photographed in ambient lighting at room temperature (left) and 473 K (right). Comparing absorbance spectra of diamond A5 at these two temperatures shows that the color change is due to a significant decrease in long-wavelength absorption upon heating.

## 2. Experimental apparatus

Diamond luminescence spectra were recorded with an Ocean Optics USB2000 optical fiber-coupled spectrometer with a spectral resolution of 10 nm and a detection range of 340–1025 nm. All presented spectra are shown with an uncorrected response for the detector and collection optics variations in sensitivity with wavelength. Optical excitation was provided by either (1) discrete-wavelength LEDs or (2) a deuterium/halogen lamp (optically filtered as necessary) depending on the practicalities of each experiment. For spot analyses, an optical fiber probe was employed: a bundle of six 600- $\mu\text{m}$ -diameter fibers guided light from an excitation source to the sample while a seventh fiber, centrally located in the bundle guided light from the sample to the CCD spectrometer [9]. In some experiments the sample was fully illuminated by an undirected light source while the multi-fiber probe remained in use for detection.

A Linkam THMS600 thermal stage and control unit was used to automate temperature control of samples. The stage's native heating element together with an attached vacuum pump siphoning liquid nitrogen allowed manipulation of stage temperatures over the range 83–873 K.

Nitrogen-aggregate concentrations were determined using the infrared absorbance spectra acquired using a Thermo-Fisher Nicolet 6700 FTIR spectrometer with Continuum microscope attachment. Absorbance spectra were normalized to an effective optical path length through the sample using the known intensities of the diamond lattice vibrational bands [10]; the third-order vibrational band at 3640  $\text{cm}^{-1}$  was used for this purpose due to saturation of the second-order structure at 1500–2700  $\text{cm}^{-1}$ . Impurity concentrations were calculated from measured IR absorbance peaks, using fitting routines based on aggregate example spectra and concentration coefficients from Howell et al.'s DiaMap program [11].

The wavelength data presented here has been corrected after calibration of the spectrometer after the experiments using various Hg, Ne, and Ar emission lines. This correction factor varied by  $-5$  to 10 nm, and was less than the spectral resolution of the spectrometer (ca. 10 nm).

In order to investigate the thermal origins of the luminescence observed, thermoluminescence (TL) data were acquired. Samples were primed for TL measurement by cooling to 83 K and exposing the sample for 2 min to optical excitation from a deuterium lamp, with Corning 7–54 glass used to block much of the visible spectrum light. The sample was then left to relax in the dark for 10 min, to minimize contamination of the TL measurement by any luminescence active at this initial temperature. Luminescence intensity was then recorded while the sample was heated at a constant rate of 1 K/s.

The near-IR absorption measurements were performed on a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a quartz beamsplitter and 2  $\text{cm}^{-1}$  resolution. A ca. 0.5 ct chameleon diamond had a large culet facet (ca. 1.3 mm diameter) polished opposite to the table facet. The resulting optical path length through the stone was 2.57 mm. The stone was mounted in a brass ring and heated by connection to a soldering iron with adjustable applied power. The temperature was measured with a hand held optical pyrometer (Fluke 561 IR thermometer). The temperatures recorded were the maximum observed from ca. 6 in., and thus are only approximate. In some experiments the sample was illuminated with a 405 nm laser pointer.

## 3. Samples

12 samples were used for the majority of this study: gemstones cut in a variety of shapes, ranging in size between 0.50 and 6.15 ct. Unfortunately, no sample had an established provenance. 10 chameleon diamond samples were provided for study by anonymous collector (samples A1–A10); the remaining two (S1 and S2) were from the National Gem and Mineral Collection of the Smithsonian Institution. Additional samples at the Gemological Institute of America were studied by near-IR absorption spectroscopy. One of the Smithsonian samples (ca. 0.5 ct) was repolished with a culet facet parallel to the table facet.

All samples were confirmed as “chameleon” diamonds due to a vivid color change between green and yellow states when placed under the influence of light or heat. Some initial observations were made to qualitatively identify the conditions necessary for a color change to take place. Inducing a transition of a ‘green’ chameleon to ‘yellow’ required heating to between 100 and 150  $^{\circ}\text{C}$ ; heating to higher temperatures instilled an increasingly strong gold color in the diamond.

The color-change from yellow to green under optical illumination appears to be wavelength sensitive. No change in color was noted under the influence of red/infrared sources (wavelength  $\lambda > 650$  nm), placing a minimum threshold on the energy required to stimulate this transition. Conversely, green light at 532 nm was sufficient to impart a color change, while a  $\sim 560$  nm source stimulated a very slow change in the color. Based on these visual observations we estimate that light of 550–650 nm, corresponding to photon energy  $\sim 2.25$ –1.9 eV, is the minimum needed to drive the yellow-to-green chameleon photochromism.

FTIR absorbance spectra of samples (A1–8, S11) indicated these diamonds to be type IaA > B, with approximately 40–90 ppm nitrogen. Additionally, a 3107  $\text{cm}^{-1}$  hydrogen-related peak, 1–2  $\text{cm}^{-1}$  in intensity, and a band possibly contributed to by ionized substitutional N at 1332  $\text{cm}^{-1}$  were observed in all samples. Both the IaA > B character and the presence of hydrogen match with previous observations of other chameleon diamonds [1–3].

## 4. Luminescence measurements

### 4.1. Fluorescence under visible/long-wave-UV optical stimulation

When excited by blue or long-wave UV light, all tested chameleon diamonds emitted a yellow fluorescence. The emission spectra of these stones show a band peaking in intensity near 550 nm, matching observations of several diamonds from the Aurora Butterfly collection made by Eaton-Magana et al. [9]. In some samples an additional blue fluorescence component was seen, heterogeneously distributed within the diamond. A series of spectral peaks between 400 and 500 nm leads us to ascribe this fluorescence to emission from N3 center [10].

The limited literature on chameleon diamonds contains a claim of a significant drop in fluorescence intensity in a 22 ct chameleon diamond upon heating [2]. In all chameleon diamonds investigated here, we observed that the 550 nm emission band is highly temperature-sensitive, with output intensity increasing dramatically as a chameleon

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