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Spectroscopic and microscopic characterizations of color lamellae in natural pink diamonds

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ABSTRACT

Nineteen natural, untreated, type IaAB pink diamonds from various localities were studied. They display microscopic (~1 μm thick) pink lamellae along {111} in an otherwise colorless diamond. This coloration concentrated in lamellae is commonly referred to as "*graining*". The diamonds were examined using high spatial resolution spectroscopic methods and transmission electron microscopy. TEM revealed that a pink lamella consists of a cluster of paired microtwins created under stress by plastic deformation. Raman line shift and broadening associated with the twinned pink lamellae indicate the presence of residual stress. Ultraviolet–visible absorption spectra from each of the samples showed a broad absorption band centered at ~550 nm, the source of the pink color. Cathodoluminescence spectra of the pink lamellae are different from those of the bulk, colorless diamond matrix. Within the lamellae only, the H3 center is observed along with a less intense N3 center. In some samples, instead of the N3 center a new center with a zero phonon line at 405.5 nm is observed. This previously unreported 405.5 nm center has phonon sidebands qualitatively identical to the N3 center, and may be an N3 center modified by a specific environment. These results suggest that lattice vacancies were created during twinning resulting from plastic deformation, and that impurity centers (such as those containing nitrogen) trap some of the diffusing vacancies. Since the pink lamellae are still under residual stress, new or modified defect centers are created, e.g. H3 and N3. The color center(s) responsible for the pink color (550 nm absorption) was not identified, but likely is only present in diamonds that experienced plastic deformation. Reported annealing of plastically deformed brown diamonds, which results in a residual pink color, suggests that the pink color is stable under these high pressure, high temperature conditions. The reported observations that annealing plastically deformed brown diamonds results in a residual pink color and that the pink color does not anneal out under similar high pressure, high temperature conditions, suggests that the deformation inducing pink color occurs inside the Earth's mantle, whereas brown coloration might be induced during a more recent event such as the ascent of the diamond to the surface in a kimberlitic/lamproitic eruption.

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1. Introduction

Natural pink diamonds are among the rarest and the most expensive colored diamonds, and the origin of their color is still a matter of speculation. Such diamonds are found nowadays most importantly in Argyle, Australia, and to a much lesser extent in only a few deposits that are located in Southern India (Golconda area), Brazil (Minas Gerais), Tanzania (Williamson mine), Indonesia (Borneo), Venezuela and South Africa (Premier/Cullinan mine). The term *pink* refers to colors from reddish purple to orange, and depending on the saturation and tone, terms such as purple–pink, orangey-pink (low saturation, light tone) or purple–red, orangey red (high saturation, dark tone) are used. Brown is a frequent color modifier [1].

Recently, high pressure and high temperature (HPHT) processes have been developed, which can change the color of some natural brown stones to pink [2]. Also synthetically grown diamonds by HPHT or chemical vapor deposition (CVD) processes have produced pink diamonds. The introduction of synthetic and treated pink diamonds to this high value market is itself a primary motivation for understanding the origins of the color in natural, untreated pink diamonds, for example to assist gemological laboratories in differentiating natural from synthetic, or treated, pink diamonds. But beyond any commercial impetus, unraveling the enigma of pink diamonds potentially provides

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Table 1
A tabulation of the main characteristics of the natural pink diamonds used in this study ("V." for "very").

Pink diamonds	Origin	N content	FTIR type	H	Amber center	CL/PL group
168283-15	Unknown	V. high	IaA>B	Medium	AC1 V. weak	Group 2
168283-18	Unknown	V. high	IaA>B	Small	No	Group 2
168283-19	Unknown	V. high	IaA>B	Small	No	Group 2
168283-21	Unknown	V. high	IaA>B	Small	No	Group 2
168298-1	Unknown	V. high	IaA>B	Small	AC2weak	Group 2
168298-2	Unknown	V. high	IaA>B	Medium	AC2 weak	Group 2
168298-3	Unknown	V. high	IaA>B	Small	AC2 weak	Group 2
168298-4	Unknown	V. high	IaA>B	Small	AC2 V. weak	Group 2
168298-5	Unknown	V. high	IaA>B	High	AC2 medium	Group 2
168298-6	Unknown	V. high	IaA>B	Small	AC2 weak	Group 2
168298-7	Unknown	V. high	IaA>B	Medium	AC2 medium	Group 2
168298-8	Unknown	V. high	IaA>B	Medium	AC2 weak	Group 2
B886	South Africa	V. high	IaA=B	Small	AC2 V. weak	Group 2
EG-01	Venezuela	Medium	IaA=B	Small	No	Group 1
JC-1	Australia	High	IaA<B	Medium	No	Group 1
JC-2	Australia	High	IaA<B	Medium	No	Group 1
JC-3	Australia	Low	IaA=B	Low	No	Group 1
JC-4	Australia	Low	IaA=B	Low	No	Group 1
JC-5	Australia	V. low + carbonates	IaA=B	V. low	No	Group 1

fundamental insights into the formation of natural diamonds and into the nature of diamond itself.

Two groups of natural, untreated, pink diamonds are recognized. The first and most common includes either type Ia or type IIa diamonds that exhibit heterogeneous color that is concentrated in the so-called "pink graining", i.e. colored lamellae oriented along the {111} direction, which is also the cleavage direction. The color results from a broad absorption band centered at around 550 to 560 nm [1–11]. The origin of this absorption band is not yet understood, but it has been associated with plastic deformation in the form of glide planes [12]. The second category consists of type IIa pink diamonds that have an even, light pink color, and are represented by the rare "Golconda pink" diamonds, because the historical deposit of Golconda, India, provided most of the large, historical pink diamonds. The color originates from absorption by the NV0 and NV^- centers, with zero phonon lines (ZPL) at 575 and 637 nm respectively, and their associated phonon sidebands [7,13]. The presence of the NV0 center (575 nm) induces a characteristic orange fluorescence. NV centers are also responsible for the color in pink stones grown by CVD or HPHT. In the latter case, synthetic stones are irradiated to form vacancies and subsequently annealed to form NV centers [4,11]. Some anomalous, natural pink diamonds also exist, that do not fit into either of the 2 categories, e.g. the Grand Condé diamond [10].

This study is focused on type Ia diamonds, and the goal was to characterize the pink lamellae in natural samples from various localities. We used high spatial resolution (at the micron scale) spectroscopy and transmission electron microscopy (TEM) methods in order to better understand the origin of the pink color and the nature of the so-called graining.

2. Materials and methods

2.1. Materials

Nineteen rough, gem-quality, natural diamonds, with hues from brownish-pink to pink and pinkish purple, were examined in this study (see Table 1). Some of the samples are from South Africa, Venezuela, and Australia, but for others, the geographic origin is unknown. The diamonds of unknown origin, however, arrived at the Smithsonian Institution's National Museum of Natural History prior to the beginning of the commercial exploitation of the Argyle mine in 1985 [14], and therefore, the Argyle mine can be eliminated as a possible source. Some of the crystals were double-side polished to enable specific measurements, while others were left rough (especially octahedral crystals with natural smooth parallel faces). Most of the diamonds have an irregular morphology indicating intensive dissolution. Polished windows on some of these diamonds revealed that where the pink lamellae intersect the surface, they give rise to "steps" in the surface morphology (Fig. 1). The other crystals have euhedral octahedral shapes with few signs of dissolution.

2.2. Methods

Transmission infrared spectra were acquired using a Bio-Rad Excalibur Series Fourier-Transform infrared (FTIR) spectrometer (4 cm^{-1} resolution) fitted with a UMA-500 microscope; the beam cross section was 250×250 μm. Ultraviolet–visible (UV–vis) absorption spectra in the range 300 to 800 nm were obtained using a UNICAM UV4 spectrophotometer with the VISION V3.40 software. The spectral bandwidth was 1 nm, the sampling 1 nm, and the scanning speed 30 nm/min.

Initial cathodoluminescence (CL) images of the samples were acquired with a luminoscope ELM-3R (20 kV, 20 nA) attached to an Olympus Bx41 microscope; CL panchromatic photos were taken using an Olympus America GKH025664 CCD detector. Additional CL images and spectra were obtained using a Gatan MonoCL3+ spectrometer attached to an FEI Nova NanoSEM 600, a variable pressure ultra-high-resolution scanning

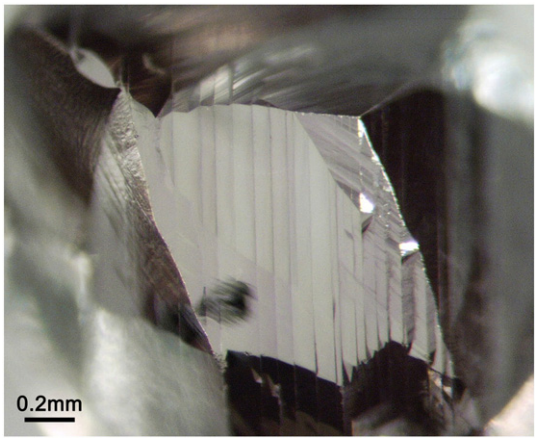

Fig. 1. A transmitted light photograph of a polished surface of sample 168283-15. The pink lamellae ("graining") are approximately normal to the polished surface; the diamond between the lamellae is colorless. Notice the "steps" where the lamellae intersect the top surface.