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Optically stimulated luminescence (OSL) and laser excited photo luminescence of electron beam treated (EBT) diamonds: Radiation sensitization and potential for tissue equivalent dosimetry

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ABSTRACT

We report the first optically stimulated luminescence (OSL; blue light stimulated luminescence (BLSL) and infrared light stimulated luminescence (IRSL)) results on colored diamonds and present experimental evidence that electron beam treatment (EBT) increases the radiation sensitivity of diamonds to a level that makes them suitable for low level radiation dosimetry. A suite of seven samples was examined. These comprise a white, three brown and three yellow diamond pieces. The FT-IR spectra of these diamonds revealed the nature and concentration of nitrogen impurity. The white diamond was kept as a control. The brown and yellow (with varied saturation) diamonds were irradiated by a 1.7 MeV electron beam. These turned blue/dark green; three of them were then heated in vacuum in the temperature range of 850–900 °C for two hours. Heating turned the irradiated diamonds to lemon yellow, pink, and purple colors. The irradiated and unheated blue samples were designated as 2C and 2D.

The control sample, an un-irradiated white type Ia diamond, did not yield any significant IRSL/BLSL with doses up to 100 Gy. The BLSL/IRSL sensitivity of irradiated and heat treated diamonds was very poor, and depended on the heat cycle and hence were not pursued. Sample 2C exhibited significant BLSL and negligible IRSL sensitivity. Sample 2D gave an intense orange red emission under IR excitation as also responded to BLSL. The dose response of the BLSL signal in 2C suggested a minimum detectable dose of ~0.1 Gy and its use as a tissue equivalent dosimeter.

Based on supporting experiments such as laser excited photoluminescence, we suggest that the BLSL process in 2C is primarily driven by carbon vacancies, which release a mobile hole when excited by GR2 band in the blue region. BLSL intensity exhibited a maximum around 285 °C. Given that TL glow peak also occurs near this temperature and that the nitrogen–interstitial carbon (N–Ci) complex also forms at this temperature (as reported in the literature), and it appears that the e–h recombination at sites with N–Ci complex could be involved in BLSL production. Laser excited photoluminescence (PL) at wavelengths 325, 514 and 785 nm and absorption spectra in UV–Visible range gave insights into the contrasting BLSL/IRSL responses of 2C and 2D. These differences were due to differences in nitrogen impurity complexes and the concentration of carbon vacancies produced by EBT in 2C and 2D. In 2D, the presence of Ni as NE8 center (four nitrogens coordinated to Ni) giving 800 nm emission on 785 nm excitation, appeared to suppress BLSL and sensitize IRSL in the orange window.

1. Introduction

Diamond is a covalent crystal with a band gap of 5.47 eV at 300 °K. In its purest form (type IIa), diamond is colorless. Nitrogen is the most common impurity in diamonds and its concentration can be up to few hundreds ppm. In natural type Ia diamonds, the nitrogen impurity exists as a cluster of two nitrogen atoms occupying two adjacent carbon sites (A-cluster) and/or four nitrogen atoms in the neighboring sites associated with a carbon vacancy (B-cluster) and neither of these imparts any color to diamonds. However, isolated nitrogen atoms at substitution sites give yellow color to diamonds. Existence of a single nitrogen at substitution position is common for high pressure–high temperature (HPHT) treated natural diamonds and synthetic diamonds [1,2].

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Ruggedness, robust chemical inertness and tissue equivalence make diamonds good candidates for radiation-detection and -dosimetry (both personal and nuclear accident dosimetry). Earlier attempts to develop Thermoluminescence (TL) methods using diamond films/synthetic diamonds were by [3–12]. Unlike the ionic crystals, radiation induced coloration in semiconductors like diamond is dominated by the electronic structure of carbon vacancy which results in: 1) four electrons distributed over four dangling bonds, 2) a strong affinity to nitrogen impurity, and 3) the electronic excitation of this vacancy leads to a situation that it can be modeled as a V^- bonded to a 'hole', that can be excited to auto ionization states resulting in 'hole' based photo conductivity [13]. In general, diamonds are radiation-hard and the only way in which high energy electromagnetic radiation interacts with diamonds is by photo-electric effect with a low cross section due to low Z of carbon. This was an important reason for developing methods toward the use of diamond as high energy particle detectors in high radiation backgrounds, [14–16].

Irradiation with high energy electrons or heat treatment of diamonds having plastic deformation produces vacancies and imparts blue or green color. Subsequent high temperature heat treatment results in the formation of vacancy–nitrogen complexes and changes the color to pink/lemon yellow. The final color depends on the extent of heat treatment [1,2] and purity of diamond.

Carbon vacancies and interstitials are the primary defects in diamond produced by electron beam treatment (EBT)/neutron irradiation. Stability of these defects depends upon the concentration of isolated nitrogen species. Self interstitials are trapped by nitrogen, which suppresses their recombination with vacancies [17]. The carbon vacancies anneal/transform only above 800 °C and hence do not participate in thermally stimulated relaxation processes up to this temperature. Consequently e-beam treated (i.e. irradiated; EBT) diamonds can be considered as being in a non equilibrium stable structure at room temperature and therefore have a distinctly different radiation (gamma/low energy beta) response compared to an un-irradiated diamond. The interstitial carbons, produced concomitantly along with vacancies, are potentially responsible for increased radiation sensitivity of EBT diamonds. This aspect has not been examined, so far.

The present work deals with BLSL, IRSL and laser excited photo luminescence (PL); using UV (325 nm), visible (514 nm) and IR (785 nm)) studies on e-beam irradiated colored diamonds. The results obtained suggest that e-beam irradiation enhances the BLSL sensitivity; to the extent that 100 mGy dose could be detected, using OSL, and therefore makes them potentially suitable for tissue equivalent radiation dosimetry for therapeutic applications and nuclear radiation accidents dosimetry.

2. Experimental

2.1. Diamonds, e-irradiation, and heat treatment

Seven natural diamond samples in single crystal form were obtained from known trade sources. The diamonds typically were in the range of a few mg. Infrared spectral measurements revealed that all were of type Ia. One of the samples (white, type Ia) was kept as a reference and the others were subjected to electron beam treatment (EBT) using a 2.0 MeV pulsed Industrial Electron Beam Accelerator, ILU-6, at Bhabha Atomic Research Centre, Mumbai, India. The energy of the electron beam was 1.7–2.0 MeV with a flux of 10^{18} e/sq cm, 13–15 mA current and pulse rate of 50 Hz. The exposure dose rate was 30 KGy/s and the samples were irradiated for eight/ten hours imparting about 0.43 MGy of dose. For EBT, the samples were loaded in aluminum trays and were cooled using chilled water. The samples became blue/dark green on EBT. Subsequent to EBT three samples were heated around 900 °C for 1.5 h in vacuum and the samples turned to purple/pink. The coloration of the samples by EBT and its modification by heat treatment are summarized in Table 1. The response of these samples for optical stimulation, to be discussed in this paper, is also given in the last column.

The laboratory dose, for dosimetric measurements, was given using $^{90}Sr/^{90}Y$ beta source. The half lives of ^{90}Sr and ^{90}Y are 27 years and 64 h respectively. The beta particles from this source have a continuous distribution, with the dominant ^{90}Sr component peaking around 0.2 MeV. The energy maximum is at 0.54 MeV with very low intensity. Given that, the laboratory irradiation, in contrast to EBT, does not produce any visible coloration even for very long exposure times; it implies that neither the energy nor the intensity is sufficient to produce carbon vacancies (see the 'Discussion'). The low energy laboratory irradiation merely produces electrons and holes that get trapped at existing defects in the crystal. These trapped e/h participate in OSL and TL of diamonds.

2.2. Optically stimulated luminescence (OSL)

The present study used; i) a Risoe TL/OSL-reader-15, and ii) a Daybreak TL/OSL-reader-2200, both with on plate beta irradiation facility with a $^{90}Sr/^{90}Y$ beta source. The luminescence signal was detected by EMI 9235 QA (bi-alkali type) photomultiplier tubes (PMT). The detection optics comprised a) Schott BG-39 + Hoya U-340 filters for UV emission under blue light stimulation (BLSL); b) Schott BG-39 + Corning Cs 5-58 filters for blue–violet emission under (infrared stimulation (IRSL) and, c) Schott BG-39 + Cs 610 filters in the case of red (or orange) emission under infra red stimulated luminescence; IRSL). In the Risoe System the blue light stimulation was at 470 ± 30 nm and the IR stimulation was at 880 ± 80 nm. The Daybreak TL-OSL-reader had LEDs emitting at ~515 nm and IR excitation was at 880 nm.

It is a common practice in OSL of quartz for geochronology that the starting signal (or residual signal) is zeroed using day light exposure for 1–3 h, before subjecting it to beta dose for investigating its radiation response. In the present experiments also, same protocol was followed. All the diamond samples were examined for their dose responses before and after the day light exposure using Ultra Vitalux 300 W, filtered through a window glass to cut off UV. Typical day light spectrum is in 300–700 nm region with a broad peak around 480 nm. The OSL is a decaying light signal and its yield is measured as counts integrated over one second from t = 0 or the maximum counts at

Table 1
Details of diamond samples investigated, their radiation and heat treatment and color modification thereof.

Sr. no.	Initial color and type of diamond samples and conc of nitrogen in ppm	Treatment		Final color	OSL response
		EBT	Heat		
1	White, type Ia $[N_A]=45,[N_B]=3$	No	No heat	White	Absent
2	Light brown, type Ia $[N_A]=40,[N_B]=30$	8 h	No heat	Blue (2C)	Very good
3	Light brown, type Ia $[N_A]=65,[N_B]=20$	8 h	No heat	Blue (2D)	Moderate
4	Yellow, type Ia $[N_A]=55,[N_B]=6$	10 h	850 °C for 1.5 h in vacuum	Lemon yellow	V. poor
5	Dark yellow, type Ia intense N^+ $[N_A]=10,[N_B]=3$,	10 h	850 °C for 1.5 h in vacuum	Pink	V. poor
6	Light yellow, type Ia $[N_A]=8,[N_B]=5$, intense N^+ intense H_{1a}	10 h	850 °C for 1.5 h in vacuum	Purple	Absent
7	Brown Ia $[N_A]=100,[N_B]=75$	8 h	No heat	Green	Poor