

Non-linear optical properties of coloured diamonds: Observations of frequency up conversion and “whispering gallery-like” modes in photoluminescence

M.D. Sastry^{a,*}, Mahesh Gaonkar^a, Sandesh Mane^a, Seema Athavale^a, K.V.R. Murthy^b, Shripalkumar Desai^a, Hemlata Bagla^c, Jayshree Panjekar^a, K.T. Ramchandran^a

^a Gemmological Institute of India, 503 Sukhsagar Building, N.S.Patkar Marg, Opera House, Mumbai 400 007, India

^b Department of Applied Physics, M.S.University of Baroda, Vadodara 390 001, Gujarat, India

^c Department of Chemistry, K.C. College of Science, University of Mumbai, Mumbai 400 020, India

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Abstract

Four coloured diamonds, 1.7 MeV e-beam irradiated to a dose of 10^{18} e per sqcm and annealed around 900–930 °C, were investigated at room temperature using conventional photoluminescence (PL) and excitation spectra, and PL using 514.5 and 785 nm lasers. Interesting new observations are: (i) excitation spectra reveal energy transfer between NV^0 and NV^- centers (ii) frequency up conversion, blue-green emission on excitation in 740–900 nm range, was observed in blue and lemon yellow samples. This appears to be due to two-photon absorption in GR1 centers and energy transfer to N3/H3 centres. (iii) Excitation with 514 nm line of Ar^+ laser, in pink and purple samples resulted in the appearance of an intense and broad emission at 267 nm with FWHM of 32 nm. This is rather close to 2ν of the exciting line. It is identified as second harmonic generation (SHG) due to a synergistic effect of strain induced birefringence and resonant absorption which facilitated phase matching. The 785 nm excited anti-Stokes PL contained a frequency up converted band in 620 nm region having extensive closely spaced structure like in the case of ‘whispering gallery modes’ due to spheroid inclusions.

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1. Introduction

Diamond, a crystalline form of pure carbon, is a covalent crystal with a band gap of 5.5 eV is implicitly colorless unless it contained impurities or other point defects. It is well documented that nitrogen is the most common impurity present in diamonds and boron to a lesser extent; the extent and the type of these impurity complexes being the deciding factor to classify the type of diamonds [1,2]. Coloured diamonds are known for a long time, e.g. naturally occurring yellow and brown diamonds [3], and the electronic structure and spectroscopy of point defects responsible for the colour were investigated quite extensively over the last four decades [4–6]. Majority of the naturally

occurring impurity complexes are made up of atoms/clusters of nitrogen in which the number of atoms vary from 1 to 4. On the other hand, carbon vacancy with four electrons distributed over four dangling bonds is the primary product of radiation treatment and is at the centre of most of the impurity complexes known to be responsible for coloration of diamond. Majority of these point defects are indeed carbon vacancy decorated with : (i) zero nitrogen (V^0 or GR1), (ii) one nitrogen (NV^0), (iii) two nitrogens (H3) and (iv) three nitrogens (N3). A centre having four nitrogens bonded to two vacancies is called H4 centre. These centers have negatively charged counter parts and contribute to different colours of diamonds. All these centres exhibit zero-phonon lines in optical absorption and luminescence with associated vibronic band extending over a wide wavelength range. These centres exhibit greater photo luminescence yield at room temperature, and long life time for metastable singlet states

* Corresponding author. Tel.: +91 22 6651 9030; fax: +91 22 2367 9189.

E-mail address: gemforum@gmail.com (M.D. Sastry).