Raman Photoluminescence - An Efficient way to distinguish Natural diamonds and Lab Grown diamonds

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Abstract. The advancements in Science and Technology introduced Lab grown diamonds (LGDs) that meet with diverse applications. The LGD’s possess similar electrical, optical and mechanical characteristics compared to natural diamonds mined from earth. There is a possibility of LGDs infiltration in the Natural diamond pipeline in the jewellery industry. Hence, it becomes crucial to detect LGDs. The present article illustrates the importance of Raman Photoluminescence over absorption spectroscopy and Fluorescence/ Phosphorescence imaging for identification of diamond nature. In the current work, a single Laser source of 532 nm was used to obtain the distinct molecular information of Natural diamonds and Lab Grown diamonds.

Key words: Natural diamonds, Lab grown diamonds, Raman, Photoluminescence, Liquid Nitrogen, Laser.

1. Introduction

At present, the segregation of natural diamonds and Lab grown diamonds (LGD) is a huge challenge to the diamond Industry due to its similar optical, mechanical and electrical properties [1]. The natural diamonds are generally formed at pressures of 5.5 –8.0 GPa (55,000– 80,000 atmospheres) and temperatures of 1000°C – 1400°C at the hottest region of earth called mantel (depths of 140–240 km below earth surface). The oxidation or reduction of methane gas present at mantel, which depends on residence temperature and pressure, results in the growth of diamonds. They are brought to earth due to volcanic eruption [2]. The price of diamond is usually higher due its rarity and multiple processes involved in mining, processing, cutting & polishing and its exceptional diamond characteristics (high hardness, high electrical and thermal conductivity). The diamonds are used in the jewellery due to maximum Lustre (Specular Reflection) and Light Performance (Brilliance, Fire and Scintillation) that enhances its aesthetic look [3]. Additionally it contributes to wide applications such as diamond anvil cells, semiconductor devices, optical components, machine tools and abrasive wheels, etc [4].
Since diamonds are more valuable, that limited its application to be readily accessible. Hence the invention of Lab grown diamonds have reduced the demand of the diamond market. The LGDs are synthesized by High pressure and High Temperature (HPHT) and Chemical vapour deposition (CVD) techniques. The mechanical, electrical and optical characteristics of LGD are similar to natural diamonds except its origin. The LGD can also be manufactured based on the application requirement. The HPHT synthesis consists of reaction chambers where a carbon source such as graphite or diamond powder is placed along with a catalyst to facilitate diamond growth on a diamond seed by temperature gradient at pressures of 5–6 GPa and at temperatures of 1300 °C – 1600°C [5]. CVD diamonds are produced by the ionization of methane gases to produce plasma discharge that deposits on the surface of the substrate, usually Silicon [6]. As technology advances in synthesizing LGD, there is the huge threat in infiltration/undisclosed mix-up of LGD into the Natural diamonds supply chain due its price advantage. The cost of LGD is approx.30-40 % of natural diamonds. In some HPHT diamonds a small magnetic flux due to the impurities added in the molten flux during their growth, fluorescence property, and stress pattern created on diamonds due to prolonged pressure is observed that distinguishes the natural diamonds from HPHT to an extent [7]. In a recent study the magnetic flux was also observed in natural diamonds, due to its formation from the melt containing magnetic materials [8]. And the most recent invention of CVD diamonds produces a similar stress pattern to natural diamonds. Henceforth, it is very crucial for the jewelry industry to confidently detect the LGD from natural diamonds [6]. However, as they are visually identical; the conventional tests are not 100% reliable to separate them. This article gives a glimpse about the equipment/technology available in the market and discusses their shortcomings, which can be overcome by Raman Photoluminescence [9]. The present research paper substantiates the detection of natural diamonds and Lab grown diamonds.

2. Material and Characterization

The Absorbance studies in diamond were carried out using SHIMAZDU- UV Vis spectrophotometer. The Raman Photoluminescence (PL) was analysed using Enspectr Raman-R532. 1.5 L of Liquid Nitrogen was filled in a Cryoseal container (1.75L) was purchased from INOXCVA. The Fluorescence images were carried out using IMAGER.

Totally 250 diamonds were analysed in the present study. Different grades (VVS-GH, VS-EF, SI2-IJ, I1/I2-GH) of natural, HPHT and CVD diamonds of various shapes and sizes were procured from markets across the globe and obtained from the preliminary screening equipment and from external grading. Among them, PL spectra of 50 diamonds have been reported in this work.

3. Results and Discussions

In General, diamonds are classified based on the presence of Nitrogen atoms as per Gemmological Institute of America (GIA) Type classification standards [10]. Figure 1 shows the lattice structure of type classified diamonds. Type I consists of Nitrogen atoms (> 5 ppm) either as aggregates (Type Ia) or isolated form (Type Ib). Type IIa consists of no nitrogen or boron impurities and Type IIb consists of boron impurities. Most natural diamonds fall in Type Ia category and few percent in Type 1b category. CVD diamonds fall in the Type II category. The presence/absence of nitrogen was one of the key factors to segregate diamonds [11]. The equipment faces limitations in identifying 100% diamonds at the first time, it refers to a certain percentage of diamonds to check in some other advanced technology. In some cases, equipment is not viable for detecting all categories of LGDs.
3.1 Absorbance spectroscopy

In UV Vis absorption spectra of diamonds, the presence of aggregated nitrogen atoms (Type 1aA) can be identified by the appearance of 415nm (N3 centre) peak[12]. This majorly distinguishes the natural diamond from LGD. Also, Natural diamonds of Type 1a show 480 nm band, H3 centre and flat absorption bands [13]. These diamonds are categorized as refer, since further screening is required on its authenticity. Figure 2 shows the UV- Vis spectra of natural diamond with N3 centres.

Figure 1. Type Classification of Diamonds
(https://4cs.gia.edu/wp-content/uploads/2014/06/Diamond-Type-Classification)
3.2 Fluorescence and Phosphorescence imaging

The excitation time taken by the molecules of diamond leads to the change in color caused by fluorescence [14]. The Figure 3 shows the fluorescence and phosphorescence imaging of natural diamonds and LGD’s. The natural diamonds give natural ink blue color in short phosphorescence. The HPHT diamonds show a Turquoise green color in long phosphorescence whereas CVD diamonds show colors ranging from brown, green, yellowish orange etc [15]. In some cases the presence of diamond color is distinguishable from the expected fluorescence. Those diamonds are considered as refer, which has to be tested further for its nature of origin.

3.3 Raman Photoluminescence

Photoluminescence analysis in Raman can provides information about the crystal defect, phase solid state structure of a material [16]. The high spectral resolution of Raman spectrometer can be useful in performing photoluminescence spectroscopy of solid state materials. Enspectr Raman (EnSpectr R532®) with 532 nm (green laser) is used for the photoluminescence peak analysis of diamonds. It combines the advantage of a portable probe system with the performance of a highly specified laboratory instrument. The peaks for diamond segregation fall in the excitation wavelength of green laser[17]. Hence it was used for the present study. Spectral peak of diamond is promising for
the segregation of diamonds irrespective of diamond shape, fluorescence, color, carat, cut and clarity. Figure 4 (a,b,c,d) shows the PL spectra of Natural diamond with 4 different clarity and sizes. It was observed that with an excitation laser source of 532 nm, 572 nm was observed in all samples as diamond Peak. Some of the samples showed a peak of 656 nm and 773 nm and some with no distinct peaks that confirmed the origin of natural diamonds irrespective of diamond size, color and clarity [18].

Figure 3. Fluorescence images of Natural, CVD, HPHT and Referral diamonds
Figure 5(a,b) and Figure (c) shows the PL spectra of CVD grown diamonds and HPHT diamonds respectively. The analysis of CVD diamonds showed a significant peak at 737 nm that corresponds to Silicon presence. It might be due to the plasma interaction with the Silicon substrate during their growth [19]. The presence of 596/597 nm was observed for the CVD diamonds with absence of Si peak. The natural diamonds and CVD diamonds are occasionally given High Pressure and High Temperature (annealing treatment) to remove or change its color and obtain a colorless one. Two peaks of 575 nm and 637 nm were prominent for the HPHT treated natural diamonds and CVD [20]. The presence of a peak at 880/883 nm evidently promises to be HPHT diamonds. The peak corresponds to the Nickel presence in the HPHT diamond, which was used as a catalyst in the molten flux during their diamond growth [21].

The samples that were reported as referral from Primary screening equipment were analyzed using Raman. Figure 6 (a) shows the PL spectra of diamonds that have been reported as referral diamonds. Most diamonds exhibited fluorescence that was observed from the hump in the PL spectra. The nature of origin was identified. In some referral diamonds, due to the interference of fluorescence and ro-vibrational hot bands, the peaks were hidden [22]. These diamonds required cooling treatment with liquid nitrogen to arrest the rapid vibrations of molecules that bring out the hidden peaks.

The PL spectra with hidden peaks are shown up only when the diamonds are directly cooled with liquid nitrogen on illumination with laser [23]. As the plunging pressure of Liquid nitrogen over diamond makes them roll over from the point of laser source, a small crucible set up with stainless steel and Teflon cup was designed to hold the diamond intact to the laser source as shown in Figure 7 (b). The liquid nitrogen was poured directly onto the diamond using a PET(Polyethylene Terephthalate) funnel. Figure 7(a) shows the Raman Enspectr with diamond cooling under Liquid Nitrogen.

Figure 6(b) shows the PL spectra of referral diamonds cooled under liquid nitrogen. The referral diamonds R3 and R5 show hidden peaks of 881 nm, which confirms their HPHT origin. The 800 nm peak at R9 shows the presence of Nickel impurities in natural diamonds. It is likely to be natural. Further analysis (Growth Pattern/ absorption spectroscopy) is also required for its confirmation. The presence of 773 nm / 656 nm peaks in R4, R6, R7 confirm its natural origin. The main advantage of using Raman is the flexibility to analyze PL on diamond jewelry irrespective of its size and type. Figure 7(c) shows the PL analysis on the diamond jewelry.
Figure 4. Photoluminescence spectra of Natural diamonds with Grade a) VVSGH; b) VSEF; c) SI2IJ; d) I1/I2 -IJ
Figure 5. Photoluminescence spectra of (a, b) CVD; (c) HPHT diamonds
Figure 6. Photoluminescence Spectra of a) Referral diamonds; b) Referral diamond with Liquid Nitrogen
4. Conclusion

Raman Photoluminescence with laser source 532 nm (green laser) was analysed for natural diamonds and Lab Grown diamonds. The spectral peaks give molecular information on the nature of diamond that forms a basis for effective separation. In addition, analysis was done on Referral diamonds, where the hidden peaks were identified by immersing the diamond in Liquid Nitrogen. Thus, Raman forms an authentic tool for separation of natural diamond and LGD.

References

[1] Brookes C A, Brookes E J 1991 Diamond in perspective : a review of mechanical properties of natural diamond Diamond and Related Materials 1 13–17.
[2] Sorokhtin N O 2019 The Origins of Natural Diamonds Scrivener Publishing, Wiley, ISBN 978-1-119-59344-7.
[3] Shigley J E, Breeding C M 2015 Visible Absorption Spectra Of Colored Diamonds GEMS GEMOL 51(1) 41–43.
[4] Raman C V 1942 The physics of the diamond Curr Sci 11 261-268.
[5] Sivovolenko S, Zhulin S, Zipa K 2013 The Australian Gemmologist 25(2) 82-121.
[6] Eaton-Magaña S, Shigley J E 2016 Observations on CVD-grown synthetic diamonds: a review Gems & Gemology 52(3) 222–245.
[7] Cotter P G, Kohn J A 1954 J. Am. Ceram. Soc. 37 415-20.
[8] Eaton-Magaña S, Shigley J E, Breeding C M 2017 Observations on HPHT-grown synthetic diamonds: a review Gems & Gemology 53 262–284.
[9] Scientific H 2015 Coloured Diamond Defect Identification by Raman Diffusion and Photoluminescence Mineralogy Geology RA15.
[10] Mildren R P 2013 Intrinsic Optical Properties of Diamond Optical Engineering of Diamond (Wiley) 1-34.
[11] Eaton-magaña S, Post J E, Heaney P J, Walters R A, Breeding C M, Butler J E 2007 Fluorescence Spectra of Colored Diamonds Using a Rapid, Mobile Spectrometer Gems & Gemology 43(4) 332-51.
[12] Ramanathan B K G 1946 The absorption of ultraviolet radiation by diamond Proc. Indian Acad. Sci. 24 137.
[13] Eaton-maga S 2020 Naturally Colored Yellow and Orange Gem Diamonds: The Nitrogen Factor Gems & Gemology 56(2) 194-219.
[14] Breeding C M, Eaton-magaña S 2019 Fluorescence of Natural and Synthetic Gem Diamond: Mechanism and Applications In Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.) https://doi.org/10.1002/9780470027318.a9670
[15] Shenderova OA, Shames AI, Nunn NA, Torelli MD, Vlasov I, Zaitsev A 2019 Review Article: Synthesis, properties, and applications of fluorescent diamond particles J. Vac. Sci. Technol. B 37 030802.
[16] Fish M L, Massler O, Reid J A, Macgregor R, Comins J D 1999 The application of photoluminescence and Raman spectroscopy of synthetic diamond Diamond & Related Materials 8 1511–1514.
[17] Nagashima K, Nara M, Matsuda J 2012 Raman spectroscopic study of diamond and graphite in ureilites and the origin of diamonds Meteoritics & Planetary Science 47 1728-1737.
[18] Prawer S, Nemanich R J 2004 Raman spectroscopy of diamond and doped diamond Philos Trans A Math Phys Eng Sci. 362(1824) 2537-65.
[19] Eaton-magaña S, Breeding C M 2016 An Introduction to Photoluminescence Spectroscopy for Diamond and Its Applications in Gemology Gems & Gemology 52(1) 2–17.
[20] Nagashima K, Nara M, And Jun-Ichi M 2012 Raman spectroscopic study of diamond and graphite in ureilites and the origin of diamonds Meteoritics & Planetary Science 47 1728-1737.
[21] Berg D M, Djemour R, Siebentritt L, Susanne S, Perez-Rodriguez A 2012 Raman analysis of monoclinic Cu2SnS3 thin films Appl. Phys. Lett. 100 192103.
[22] Donato M G, Faggio G, Marinelli M, Messina G, Milani E, Paoletti A, Santangelo S 2001 High quality CVD diamond: a Raman scattering and photoluminescence study Eur Phys J B 20 133–139.
[23] Wang W 2004 Identification of CVD Synthetic Gem Diamonds Using Raman Spectroscopy Gems and Gemology 40(2) 2-25.