

# Raman Diffusion and Photoluminescence Analysis for Coloured Diamond Investigation

Laser Raman microspectroscopy is a standard analytical technique in many gemmological laboratories. Such spectrometers can also be used to investigate luminescence emissions.

## Introduction

The set of analyzed diamonds consists of gemstones naturally coloured or colour enhanced by means of a specific treatment (heating, irradiation...). The aim of the following investigation is to determine if the photoluminescence (PL) generated by a UV excitation of these diamonds leads to significant differences depending on the technique used to colour the gemstones. Indeed, routine characterizations based on photoluminescence analysis already allow us to determine if the diamond is originally colourless or undergone a decolourisation treatment (High Pressure High Temperature – HPHT- treatment) [1].

Photoluminescence analyses may also help to confirm that the colour of a diamond has been enhanced by an appropriate processing. The study initiated here tries to evidence the treatments (irradiation, annealing [3]) that the diamond could have undergone to look more intensely coloured.

## Experimental and technical aspects

### 1. Experimental Set-Up

The **LabRAM HR UV-Vis** is an integrated and compact 800mm focal length Raman system equipped with an internal He-Ne laser of 17mW at 632.8nm. An external entry is also available to provide the system - in the present case - with the 325nm line of an Helium-Cadmium laser.

The spectral range investigated in those experiments covers a wide domain from 388nm to 780nm to collect both Raman diffusion and Photoluminescence emission.

### 2. Measurement Conditions

Measurements were undertaken at room temperature and at  $-100^{\circ}\text{C}$  for each diamond. Indeed, luminescence bands are significantly sharpened when cooling at  $-100^{\circ}\text{C}$ . Therefore the structure of the luminescence emission and its intensity are easier to determine and tendencies can be pointed out that can be assigned to colour centers in diamond crystallographic structure.

The colour centers in the diamond structure are due to vacancies and Nitrogen atoms and are classified under diamond type (Ib, IaA, IaB) and defect centers (N3, H3, H4, N-V) [2]. The samples are easily cooled down thanks to a temperature-monitored stage.

## Results

PL spectra of native brown and yellow diamonds were recorded and compared to PL spectra of corresponding colour-enhanced diamonds. PL spectra of artificial violet and green diamonds were also investigated.

### 1. Temperature effect on photoluminescence (PL) spectra

The first spectrum reported Figure 1 includes the Diamond Raman band located at 340nm ( $1332\text{ cm}^{-1}$ ) and luminescence bands between 400nm and 650nm.

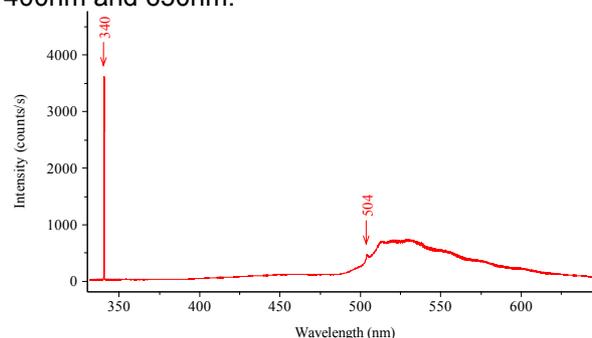


Figure 1: Full spectrum of the natural brown diamond.

We can clearly see in Figure 2 that lowering the temperature permits to sharpen and intensify luminescence emission.

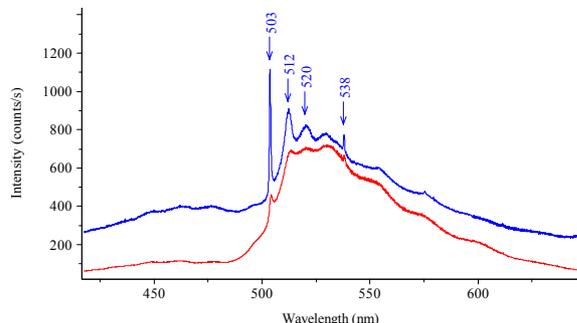


Figure 2: Photoluminescence bands of the natural brown diamond at room temperature (a) and at -100°C (b).

### 2. Untreated / treated & annealed brown diamond

The photoluminescence spectrum of the treated and annealed brown diamond shows new bands at 415nm, 496nm and 503nm that are assigned respectively to N3, H3 and H4 systems. Those systems may be generated by the treatment and annealing of the natural brown diamond. In the range 400nm-450nm, the spectrum is modified with a new peak at 415nm.

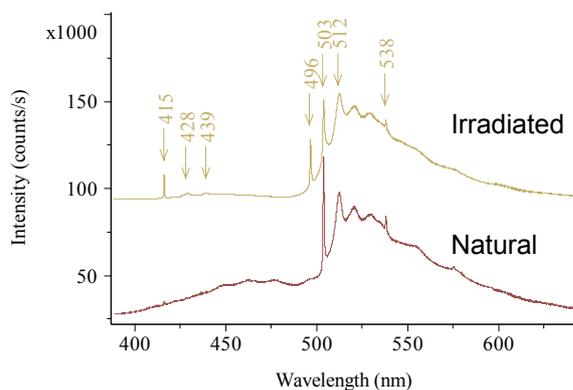


Figure 3: Spectra of the natural and treated brown diamonds at -100°C.

So, the photoluminescence, emitted around 400-450nm, is able to give a characteristic signature of the specific treatment to turn the diamond browner.

### 3. Untreated / irradiated & annealed yellow diamonds

Usually native yellow diamonds owe their colour to the presence of the N3 system. And so we observe that the luminescence emission spectrum of the native yellow diamond exhibits a band at 415nm characteristic of the N3 system.

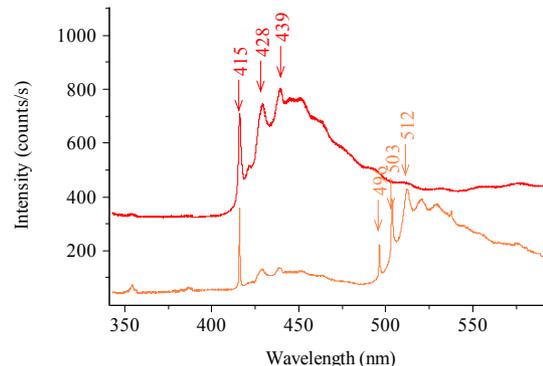


Figure 4: Photoluminescence bands of the natural and irradiated yellow diamonds at -100°C.

The PL emission spectrum of the irradiated and annealed yellow diamond displays other features at 496nm (H3) and at 503nm (H4). With these latter PL bands, the specific treatment to enhance the colouration of a yellow diamond is proved to be identifiable thanks to a Raman spectrometer.

### 4. Treated green diamond

The treated green gemstone exhibits features relative to H3, N3 systems.

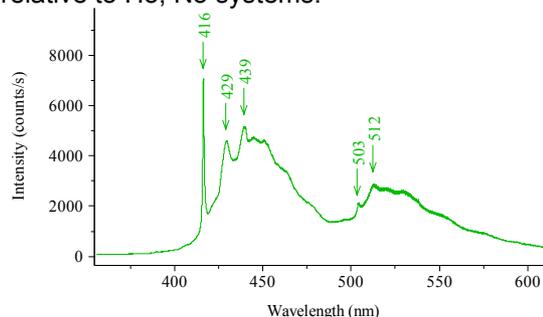


Figure 6: Photoluminescence bands of the treated green diamond at room temperature.

### 5. Irradiated violet diamond

The irradiated violet diamond PL spectrum exhibits very particular features at high wavelengths. These are characteristic of N-V centers [2].

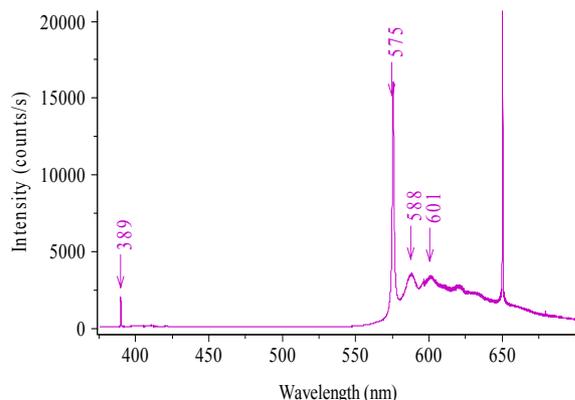


Figure 5: Photoluminescence bands of the irradiated violet diamond at -100°C.

### Conclusion

The colour enhancement treatment on native brown and yellow diamonds can be highlighted by Photo luminescence analyses performed with the Raman spectrometer LabRAM HR. The PL signature of green and violet diamonds has also been recorded. The defect centres responsible of the colour of the diamonds have all been detected and assigned. This proves the Raman spectrometer to be a very good tool to investigate the fine defects in the Diamond structure by Photoluminescence analysis.

### References

- 1- *Spectroscopic evidence of the GE POL HPHT-Treated Natural Type IIa Diamonds.* David Fisher and Raymond A. Spits, Gem & Gemology. pp 42-49, Spring 2000.
- 2- *GE POL Diamonds: Before and After.* Christopher O. Smith, George Bosshart, Johann Ponahlo, Vera M.F. Hammer, Helmut Klapper and Karl Schmetzer. Gem & Gemology. pp 192-205, Fall 2000.
- 3- *Des Diamants Bien Traités,* Emmanuel Fritsch, James Shigley, Pour la Science (French edition of Scientific American) pp 78-83, special issue April-June 2002.