



Luminescence Studies of Gemstones and Diamonds

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Abstract— A brief account of the luminescence studies of gemstones ruby, chryso beryl and diamond are given. The luminescence of ruby primarily arises due to trivalent chromium impurity, where as the nitrogen-vacancy complex are the main centres of luminescence in diamond. In the case of diamond surface fluorescence mapping under deep UV excitation is invaluable in detecting the lab grown diamonds.

1. INTRODUCTION

Some of the minerals like Corundum, chryso beryl, beryllium alumino silicate (emerald) and also Diamond exhibit exceptional optical properties[1] and in some cases attractive colours; in India these were recognized quite early since the days of Indus valley civilization. In more recent times there has been a lot of scientific interest in colours and colour modifications in Gem minerals and in Diamonds. Science of gem stones deals with their identification by non destructive means and understanding of origin of colour and excellent optical properties[1]. Optical methods have long been used to obtain properties like 'Refractive Index' which still remains an important parameter as a preliminary test to identify the gemstone/mineral. The spectroscopic studies of gem grade minerals are essentially directed towards some of these features in identifying and understanding the spectral properties of chromophores, either chemical impurities and/or radiation induced point defects, in solids. In this context a variety of spectroscopic methods are used to address the problems of the Gem stone identification and identification of origin of colours and colour modification treatments. The methods frequently used in Gem testing labs are the following: (i) Electronic absorption in UV-Visible-NIR range. (ii) UV-Vis excited luminescence, (iii) Vibrational spectra – Absorption in the Infra red range (iv) Vibrational spectra using Light Scattering (Raman spectroscopy) (v) Surface Fluorescence mapping Under deep UV excitation. The present paper deals with the luminescence studies in rubies, sapphires, emeralds and diamonds. Special mention may be made of fluorescence mapping using deep UV excitation (around 205 nm) corresponding to the band gap of diamond. Under such an excitation inter band excitation takes place creating a e-h pair and most of the absorption and subsequent emission being restricted to the surface. This makes surface mapping possible and thereby elucidating the growth patterns. This is invaluable in the diagnostics for the detection of synthetic diamonds. In this introductory presentation on the Luminescence methods in Gemmology, we give a brief account of optical spectroscopic methods which mainly deal with identification of corundum based gem stones (rubies,

sapphire) and diamonds including the electronic absorption and luminescence of chromophore centres. In gem testing infrared absorption and Raman scattering methods are main work horses and they will be brought in as and when necessary to give a complete picture.

2. EXPERIMENTAL

The standard gemological testing methods include measurement of specific gravity, refractive index, dichroism and visual appearance under 10 x/ 20x microscope. These methods give reasonable information at the first level; do not, however, give unambiguous information by themselves in most of the cases. More often, it is advisable to use these results in conjunction with spectroscopic information by the methods mentioned above. The absorption experiments in UV-Visible-NIR region are conducted using a Cary 5000 spectro photometer and Luminescence studies are done using Cary Eclipse Fluorimeter. The laser excited Raman studies are done using a RENISHAW Invia Raman microscope coupled with 325,532 and 785 nm lasers. Experimentally the laser excited fluorescence and Raman scattering are nearly identical, except that in the case of Raman scattering one has to use a sharp cut off filter to suppress Rayleigh component. Furthermore, the Photo Luminescence (PL) observed during Raman measurements are excitation dependent and the PL-Excitation (PLE) spectrum cannot be obtained as PL is observed at fixed laser wavelengths. The microscope and the reflection geometry used in Raman microscope make the confocal geometry possible and also the study of inclusions such as CO₂ in sapphires. The surface fluorescence mapping is done using the Diamond View (DV) apparatus supplied by DeBeers. This has the provision for surface excitation by 205nm and digitally photographing the surface emission in both fluorescence and phosphorescence modes.

3. GEMSTONE INVESTIGATIONS

3.1 Ruby Cr³⁺ Doped Al₂O₃

Aluminium Oxide, Corundum in mineralogical and gemological literature, has a remarkable lattice structure

and played important role in the early spectroscopic investigations of transition metal ions in solids and has direct relevance to gemology. Aluminium oxide lattice with no impurities is colour less(white sapphire) and trivalent Cr impurity imparts pink colour, trivalent iron imparts yellow colour and $Fe^{2+} - Ti^{4+}$ coupled impurity complex an intense blue colour. Pink/red coloured corundum is called Ruby, yellow one is called 'Yellow Sapphire' and the blue one is called 'blue sapphire'. Among these ruby exhibits interesting luminescence properties whereas the electronic spectra of yellow and blue sapphires are more interesting in absorption. As this presentation is focused more on luminescence, the electronic spectra of only ruby and related beryls, are presented; in both cases the chromophore, trivalent Cr at Al site, is subjected to distorted octahedral symmetry due to six oxygen ligands. The crystal structure of Al_2O_3 , the local symmetry/coordination around Cr^{3+} substituting at Al^{3+} sites is shown in figure 1(a-c). Cr^{3+} with electronic configuration of $3d^3$, has the lowest free ion electronic state 4F ; with the seven fold orbital degeneracy being lifted by the octahedral crystal field. The crystal field levels have been well worked out by Tanabe and Sugano[1,3]. Figure 2 shows the Tanabe-Sugano diagram for Cr^{3+} subjected to octahedral crystal field with a trigonal distortion superposed as in Corundum. B and C are Racah parameters as defined in Ballhausen's book[3].

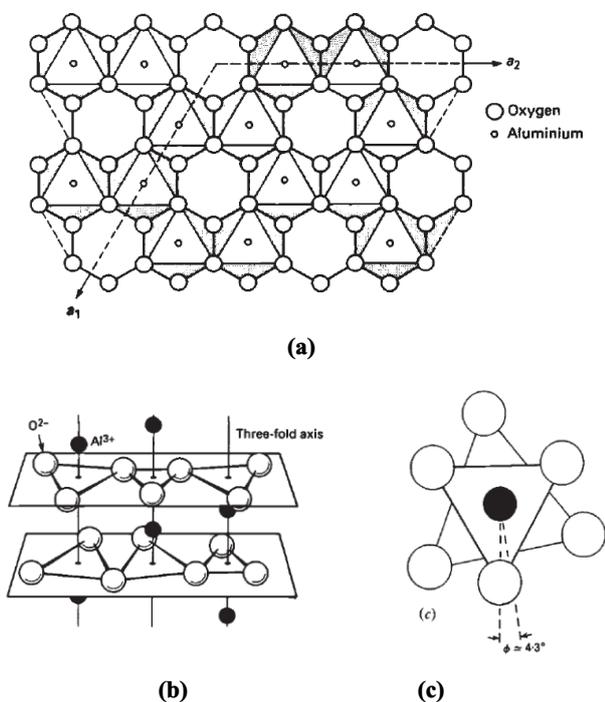


Fig. 1: The corundum crystal structure (a) projected down the c axis showing layers of edge-shared $[AlO_6]$ octahedra with one octahedron vacant for every two Al^{3+} ions;(b) section perpendicular to the c axis showing pairs of Al^{3+} ions in face-shared $[AlO_6]$ octahedra; (c) configuration of the trigonally distorted $[AlO_6]$ octahedra with point symmetry C_3 projected onto the (0001) plane [ref 1, p152].

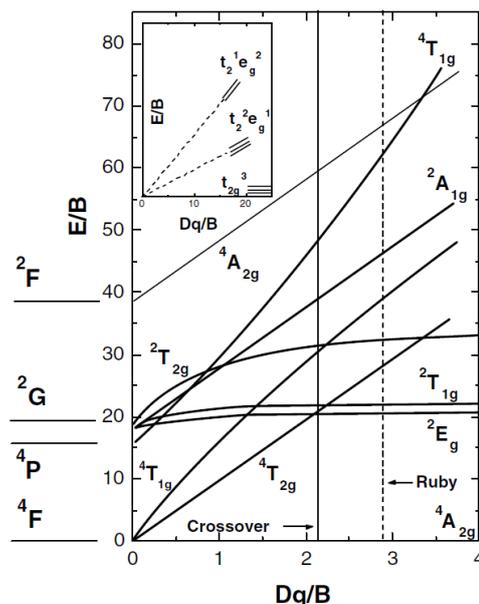


Fig. 2: Tanabe-Sugano diagram for the crystal field splitting of Cr^{3+} in octahedral symmetry. For the case of Ruby Dq/B is around 2.8. (ref 2 p213)

The electronic states of Cr^{3+} subjected to crystal field are shown in figure 2. The main absorptions to excited to $^4T_{1g}$ and $^4T_{2g}$ and to other doublet states will all relax to populate the 2E_g state coming out of 2G . The absorption and fluorescence emission spectra for Ruby are shown in figure 3. The emission from 2E_g to the ground $^4A_{2g}$ is the famous R1, R2 lines of ruby which are the laser lines of RUBY LASER, the first solid state laser.

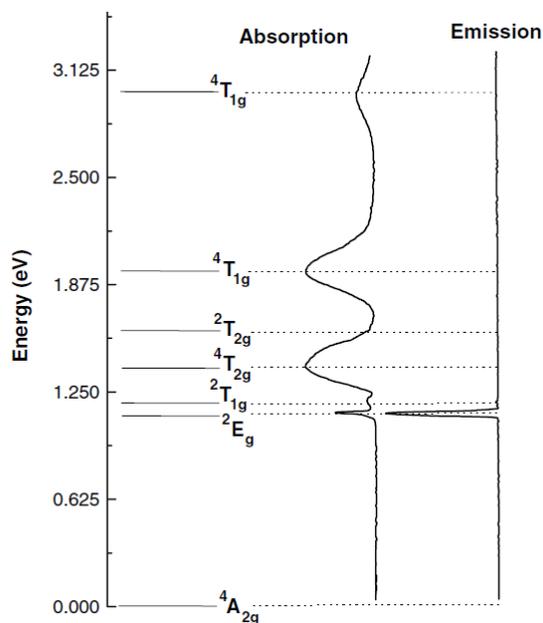


Fig. 3: The absorption and emission spectra of ruby ($Al_2O_3:Cr^{3+}$). On the left-hand side, the energy levels of Cr^{3+} in Al_2O_3 are shown for assignment of the observed optical bands [2, p 215].

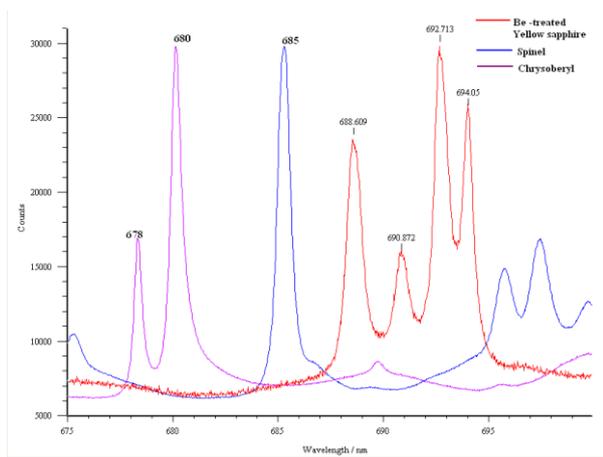


Fig. 4: PL spectra of Be treated yellow sapphire, spinel and chrysoberyl

The doublet structure of R-line emission is shown in figure 4, arising from residual Cr impurity present in yellow sapphire. It is interesting to note that R1, R2 emission in chryso beryl, beryllium aluminate, shifts to 680 nm. This suggests that Cr(Al) – O bond in chryso beryl is more ionic than in corundum. This tendency can be used to detect Be treated corundum by examining its luminescence spectrum, as illustrated in figure 4.

As mentioned above the experimental setup for Raman and Luminescence are identical and using microscope it is possible to examine the inclusions in natural minerals for their identification and also luminescence emissions there of. Figures 5 and 6 show the Raman spectra of Zircon, apatite and carbon di oxide inclusions in sapphires.

3.2 Diamonds

Diamond and graphite are two common allotropes of crystalline carbon and they can be transformed from one to the other by changing conditions of pressure and temperature. Both in diamond and graphite the carbon – carbon bonds are strong and can only be broken at high temperature. In fact, diamond in isolation can be converted to graphite only at temperature above 1800 K. High pressures and high temperatures (HPHT) are needed to convert graphite into diamond; rather for growing diamond crystals from graphite dissolved in molten iron. A number of successful attempts to

synthesize diamonds through this HPHT process using tungsten carbide anvils have been reported. Furthermore, the use of Chemical Vapour Deposition (CVD) route in which diamond films are deposited epitaxially on suitable substrates by dissociating carbonaceous gases such as methane by subjecting them to microwave heating (generating microwave induced plasma) or by thermally dissociating them using hot filament []. All bulk properties of natural and synthetic diamonds are identical; they can be distinguished only by studying the nature of point defects in the diamond samples and their absorption and emission characteristics. The fluorescence emission from the more commonly occurring point defects, Carbon Vacancy ‘V’ and its complexes with various nitrogen aggregates are shown in figures 7-9. An important luminescence characteristic is the surface fluorescence

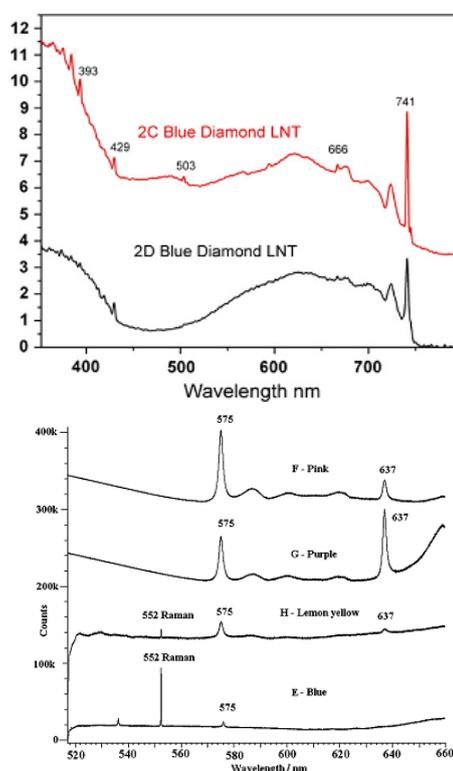


Fig. 7: The absorption spectrum of Carbon Vacancy, 741 nm-zero phonon line with vibronic structure (Left) and the PL of NV (575nm emission) and NV- (637nm) emissions under 514 nm laser excitation.(Right)

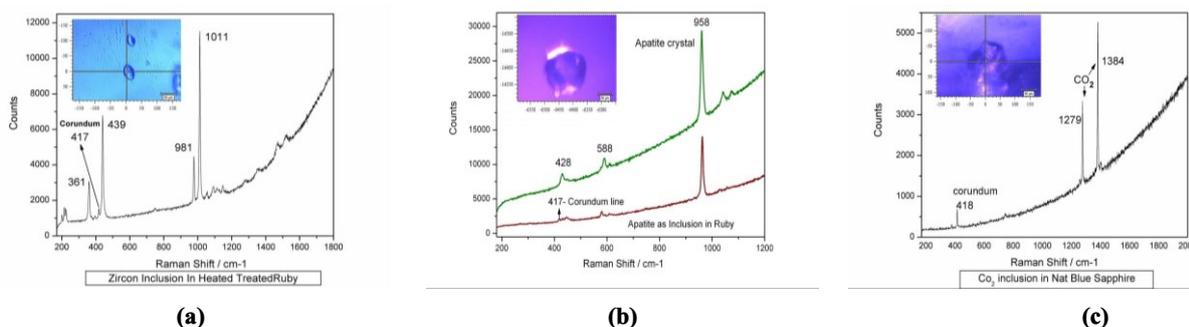


Fig. 5: Raman Spectra of inclusions in Sapphire lattice : A- Zircon, B- Calcite and C- carbon dioxide.

Table 1: Electronic absorption and Fluorescence Emission spectral data of common colour centres in diamonds. (V represents carbon vacancy and N represents nitrogen except in ND1)

Point Defects	Site Symmetry	ZPL* (nm)	Spectral Region (nm)		Reference
			Absorption	Fluorescence emission	
ND1 (V ⁻)	C _{3V}	396	320-400	390-450	4
N3 (N ₃ V)	C _{3V}	415	360-420	415-550	4,9
H3 (N ₂ V)	C _{2V}	503	400-508	500-600	5,8,9
NV ⁰	C _{3V}	575	500-580	580-650	8,9
NV ⁻	C _{3V}	637	600-640	640-700	8,9
V ⁰	Td	741	540-740	740-900	4,5,9

* Zero phonon line

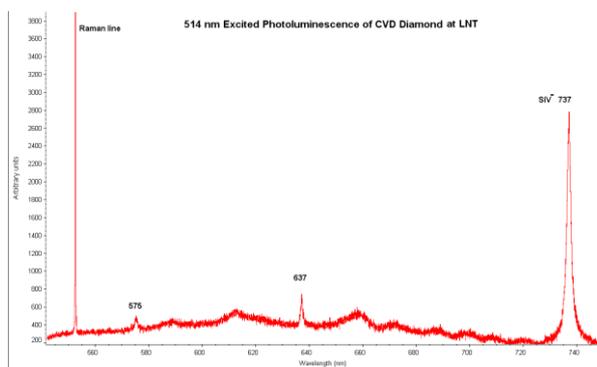


Fig. 8: 514 nm laser excited PL of a CVD synthetic diamond at 77 K. The emission due to Si-V at 737 nm can be seen. This is absent in most natural diamonds.

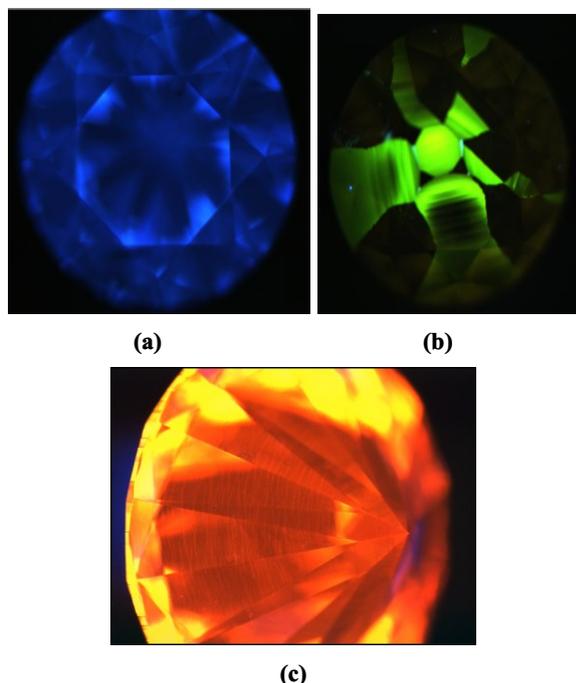


Fig. 9: Surface Fluorescence imaging under deep UV excitation (a) Natural (b) HPHT synthetic and CVD synthetic

mapping under inter band excitation. These are commonly used for identification of naturally grown diamonds and

also lab grown diamonds under high pressure high temperature (HPHT) and Chemical Vapour Deposition (CVD) routes and also treated synthetics. The well established nitrogen –Vacancy complexes and their spectral properties are listed in Table-I.

Under inter-band excitation in natural diamonds the emission corresponds to what is known as A- band in blue, due to donor- acceptor recombination. As the surface fluorescence dominates in inter-band excitation it reflects the growth patterns due to large dislocations. In HPHT growth the growth is cuboidal in contrast to octahedral growth in nature, is easily seen in HPHT grown crystals. The CVD diamonds are grown by epitaxial growth in which the layered dislocations reflect as striations in the surface fluorescence. These are shown in figures 9(a-d)

4. SUMMARY

This brief presentation gives an account of luminescence studies in gemstones and diamonds. It may be stressed that photo luminescence of diamond is not only an important diagnostic tool in diamond testing but also is playing an increasingly important role in developing and investigations of single photon emitters.

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