

Raman and Photoluminescence Spectroscopy in Gem Identification

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Extended Abstract

Raman spectroscopy is particularly useful for rapid identification of gemstones. Searchable data-bases such as in the RRUFF project [1] contain a large number of reference spectra and are in public domain; the data-bases can be modified and expanded to the user's requirements.

Raman Applications: Fig 1 demonstrates the quick identification of Zektzerite which is an extremely rare mineral; there are few gem quality specimen known and they could easily be mistaken for other gem materials.

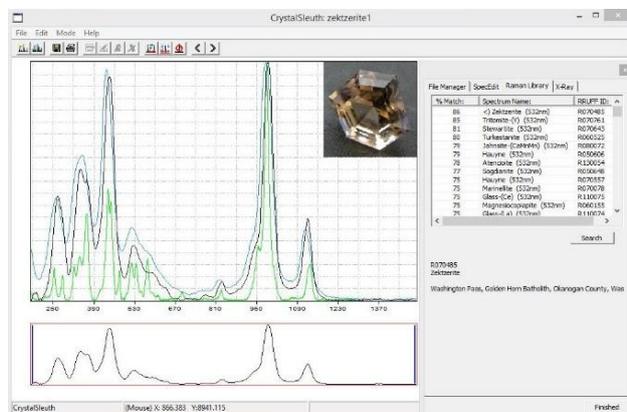


Figure 1 Zektzerite confirmed with RRUFF database

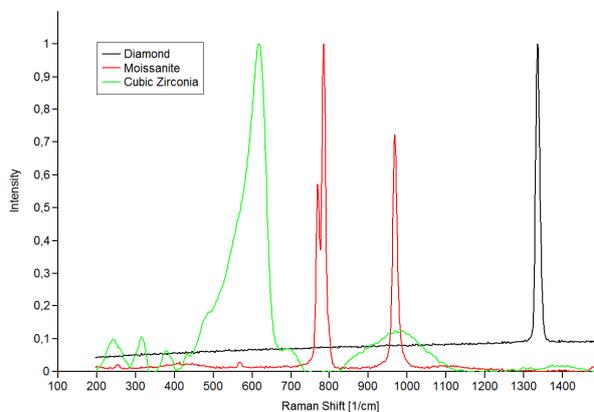


Figure 2 Separation of diamond from simulants

Gemmologists often have difficulty to identify gemstones set in finished jewellery. A Raman spectrometer can quickly separate gems with overlapping refractive indices.

The measurement of refractive index (RI) with a gemmological refractometer requires a flat polished surface; if the RI of a gemstone is above the limit other time consuming gem testing tools and methods have to be used.

The quick separation of diamond from its most popular imitations such as Cubic Zirconia and moissanite is illustrated in Fig.2.

Garnet varieties cover the full colour spectrum and due to their similarity are difficult to identify; Raman based spectral measurements can give a precise and relatively inexpensive solution for these problems [2].

The detection of treatments in gemstones is often challenging; for example in Fig 3 the use of extended Raman spectroscopy can detect polymer treatment in jadeite.

Fluorescence Problems: As seen in Fig 4 the strongly fluorescent flux grown sapphire crystal (Chatham) shows a dramatic signal improvement in Raman mode after insertion of a band pass dielectric filter (GL Gem Raman Band Pass Filter - GLBPF); these filters are not in-expensive and have to be specified for each application.

Combined with the TEC option exposure time was increased to 5,000 ms and the sample could be matched with an entry in the RRUFF database.

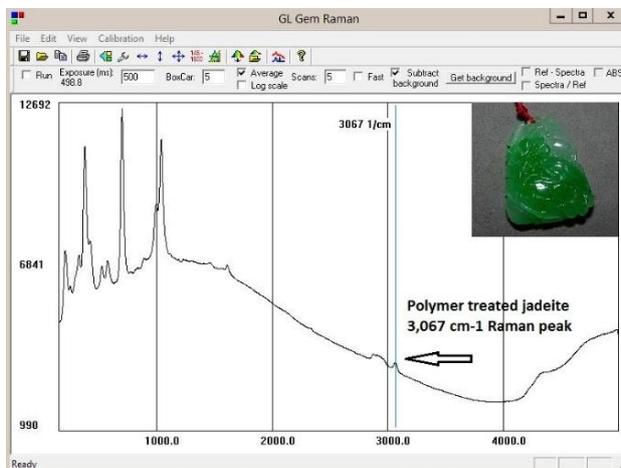


Figure 3 Raman spectrum of polymer treated jadeite

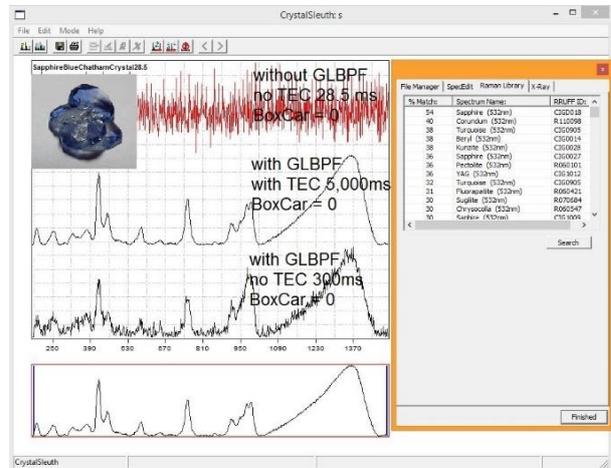


Figure 4 Suppression of fluorescence with GLBPF

Photoluminescence (PL): In some cases luminescence features are so intense that one can no longer see the Raman peaks associated with the atomic vibrations of the mineral. Luminescence spectroscopy is used to measure the energy levels of luminescence centers [3].

PL Applications: The GL Gem Raman PL532 TEC is a dual purpose Raman spectrometer with an adjustable 532 nm laser source (200 mW) and is suitable for PL studies in the range from 530 – 750 nm.

After reducing the laser output to approximately 30% of full power photoluminescence patterns become visible.

In Fig 5 a synthetic red flux grown spinel is quickly separated from natural red spinel; to arrive at the same conclusion the use of a microscope and other gem testing tools would have been necessary.

In a similar manner emerald types (whether natural or synthetic, also geological provenance) can be determined by observing chromium PL peak locations.

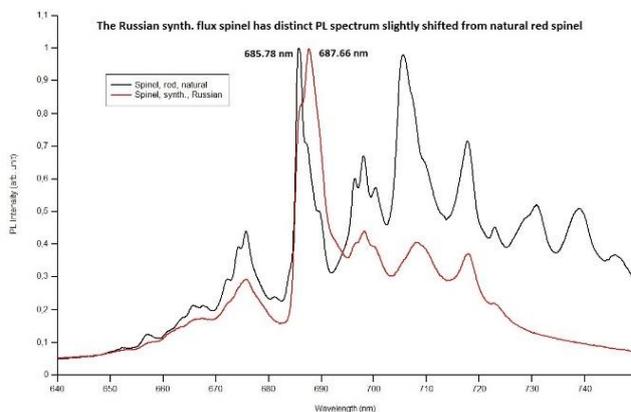


Figure 5 Separation of syn. and natural red spinel (685 nm)

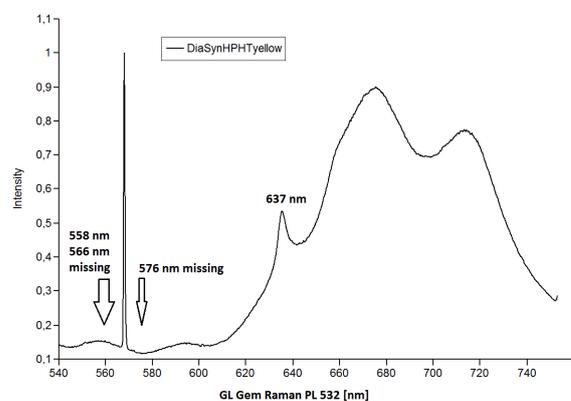


Figure 6 Synthetic HPHT treated diamond

Current Challenges: Synthetic materials, treatments, imitations and fakes are problems facing not only dealers, buyers and collectors but the entire jewellery industry. With the advent of small synthetic diamonds mixed in parcels with natural diamonds scientists are urgently working on methods and instrumentation to properly identify synthetic and treated diamonds.

One area of great interest are photoluminescence studies for diamond type screening and detecting HPHT treatments [4]. However, this method should be supported with other instrumentation and not be used alone.

Fig 6 illustrates a synthetic HPHT treated diamond with a nitrogen-vacancy defect at 637 nm; it also shows the suppression of the 558, 566 and 576 nm bands which usually indicate an untreated diamond if the 637 nm peak is missing as well. Strong silicon-vacancy peak at about 737 nm may indicate CVD (chemical vapor deposition) grown synthetic diamond.

Crystallographic defects causing the above mentioned PL peaks for natural untreated diamonds are not fully understood.

Conclusion: Several economically priced Raman spectrometer systems are now available and allow for rapid identification of gems and minerals. In general polished surfaces of gemstones produce good Raman scattering with high percentage matches in the RRUFF data-bases. For rough surfaces spectrometers with thermo-electric cooling (TEC) allow for low signal detection at exposure times of 1,000 ms and higher.

For the detection of synthetic diamonds and HPHT (high pressure high temperature) treatments the PL option of the Raman spectrometer is of particular value. With experience it may even provide a semi-quantitative estimate of trace elements such as chromium.

The analysis of Gr1 and SiV centers in CVD-grown yellow diamonds and the comparison with existing published data indicate that other impurities like Xe, Ni or Cr may produce other colours as well; more research is required. [5]

Acknowledgement: Raman and PL spectra were obtained with a GL Gem Raman PL532 TEC (175 – 5,470 cm⁻¹) system from Gemlab Research & Technology; spectra were edited in Spekwin32 [6]. Sample gemstones courtesy Canadian Institute of Gemmology.

References: [1] RRUFF Project at www.rruff.info [2] Roman Serov, Yuri Shelementiev and Alevtina Mashkina (2012) GIT 2012 Proceedings, 214 - 216 [3] Renata Jasinevicius (2009) Characterization of vibrational and electronic features in the Raman spectra of gemstones (MS thesis, unpublished), 15 ff [4] Inga A. Dobrinets, Victor G. Vins, Alexander M. Zaitsev (2013) HPHT-treated Diamonds, 10 [5] Contributions to Gemology #14 (2014) New Generation of Synthetic Diamonds Reaches the Market, 41 – 55 [6] F. Menges "Spekwin32 - optical spectroscopy software", Version 1.71.5.1, 2012, <http://www.efemm2.de/spekwin>