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Raman spectroscopy applied to Gemmology

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Raman spectroscopy has become a routine technique in gemmological laboratories since the late 1990s. It is mostly used for identification of inclusions and this is of interest in determining the geographical origin of a gem by means of specific inclusions or mineral associations. Raman spectroscopy also helps to detect treatment, *e.g.* modification of mineral phases during heating, or the presence of organic impregnation material in open fractures. The identification of macro samples is useful in the small number of cases difficult where it is diffucilt to identify the sample using 'classical gemmology' means, *e.g.* rare gems, exotic simulants, or varieties with unusual appearances. Attention is increasingly paid to the width of the Raman band, which carries information on order-disorder, which is of gemmological relevance because of the state of the crystallinity. For example, synthetic turquoise has a smaller grain size than its natural equivalent, and linewidth increases with the degree of metamictization of zircon. Resonant Raman spectroscopy has proved very useful in identifying pigments in pearls and corals, even in the identification of protected species. This helps, for example, to separate freshwater from saltwater pearls, and to establish whether pearl or coral colour is natural or due to artificial dyes. Finally, laser photo-luminescence spectra of gems obtained on a Raman system are now routinely collected, often at liquid-nitrogen temperature. Originally this was the only way to separate natural colourless diamonds from those turned colourless by high-pressure, high-temperature treatment. Recently, this approach has expanded into the study of Cr^{3+} luminescence in spinel and corundum.

1. Introduction

The purpose of this chapter is to demonstrate the usefulness of Raman spectrometry in the daily operation of a gemmological laboratory. Its prime importance is to establish the identity of a material, which is relevant to all challenges of the gemmologist: determining

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the species of a gem, whether it is of natural origin, synthetic (grown in the laboratory) or treated (for example irradiated and/or heat-treated in the laboratory to enhance its appearance and value). In most cases, these identification tasks are carried out successfully by means of ‘classical gemmology’. This is done using small desk-top instruments such as a good binocular microscope, a refractometer or an ultraviolet lamp (Fritsch & Rondeau, 2009), or more generally, equipment that is not too expensive and could easily fit in the backroom of a jeweller.

However, from the 1990s to date, this approach fell short of identifying some of the more difficult synthetic or treated gems. Hence, the importance of ‘laboratory gemmology’ increased. In other words, more expensive analytical techniques, such as spectrometers or electron microscopes, are required, which are not found in the backroom of a jewellery shop. Raman spectrometry belongs to this approach of gemmology. It became widespread in international gemmological laboratories in the late 1990s, as this corresponds to the advent of smaller, even desk-top, instruments with a new generation of detectors (CCD) of greatly increased sensitivity (Dubessy et al., 2012, this volume).

Developing applications of Raman spectroscopy for use in gemmology is not a recent endeavour. Much pioneering work was done in France in the late 1970s to early 1990s (Dhamelincourt & Schubnel, 1977; Délé-Dubois *et al.*, 1980a, 1980b; Délé-Dubois & Merlin, 1981; Fritsch & Rossman, 1990; Lasnier, 1995a, 1995b). Starting in 1995, reports on the application of Raman spectroscopy to gemmology began to arrive from elsewhere (*e.g.* Hänni *et al.*, 1995). Some of the early results and reference spectra are summarized in a special issue of the *Revue de Gemmologie A.F.G.* (1992) and references therein. This publication also served as one of the earliest databases of Raman spectroscopy spectra for gemmologists, with about 60 species represented. The recent review by Kiefert & Karampelas (2011), for example, makes it possible to measure progress accomplished since then.

This chapter will only deal with applications of Raman spectroscopy to the resolution of actual gemmological challenges encountered in laboratories. It will not concern itself with more academic applications to gems (see for some examples Bersani & Lottici, 2010), disconnected from the everyday concerns of gemmological laboratories. Neither will this work consider the many contributions of Raman spectroscopy to archaeo-gemmology and the identification of historical artefacts. Also, we will not mention a number of potential applications that have been proposed but are never used because other, simpler approaches have been found to be more effective. One example resorts to Raman spectroscopy to elucidate the nature of the remnant molten salts inclusions of ‘flux’ synthetics, grown in molten salts. These gems are otherwise routinely identified, either by microscopy, infrared (IR) spectroscopy, or trace-elements analysis.

In this chapter, we will first present the strength and limitations of Raman spectroscopy applied to gemmology and then the instrumentation. The identification of the species of a gem or its inclusions will be illustrated as it is by far the most common applications. Besides benefits based on determining the position of the lines in the Raman spectrum, some less common applications refer to the width of the Raman bands. They reveal a degree of order-disorder in the material which carries useful gemmological information, *e.g.* if it is well crystallized or not. Resonant Raman spectroscopy has brought seminal contributions to the field of pearls and corals. Finally, we will describe applications using a Raman spectrometer as a luminescence instrument. This aspect is currently extremely important for detecting one kind of treatment in high-quality type IIa (virtually nitrogen-free) diamonds.

2. Raman spectroscopy applied to gems: strength and limitations

2.1. Why Raman spectroscopy is useful for gemmologists

If Raman spectroscopy is so useful in gemmological laboratories today because in some cases, its strength is that it is an enabling technology: results are possible that could not be achieved by previous approaches. The most widespread application is the unambiguous identification of inclusions that do not reach the surface without opening them and thus without damaging the gem. This may prove essential to ascertain the geographical origin of a gem: the presence of pargasite needles together with corroded plagioclase as mineral inclusions in a blue sapphire is taken as good proof that the gem comes from Kashmir (*e.g*. Gübelin & Koivula, 1986; Hänni, 1990). As different mineral inclusions melt at different temperatures, it can also provide useful hints regarding heat-treatment: *e.g.* if diaspore is present in a corundum (*e.g.* in fluid inclusions, as a daughter crystal; Fig. 1), as it decomposes below 1000°C in corundum, it is an indication that the gem has

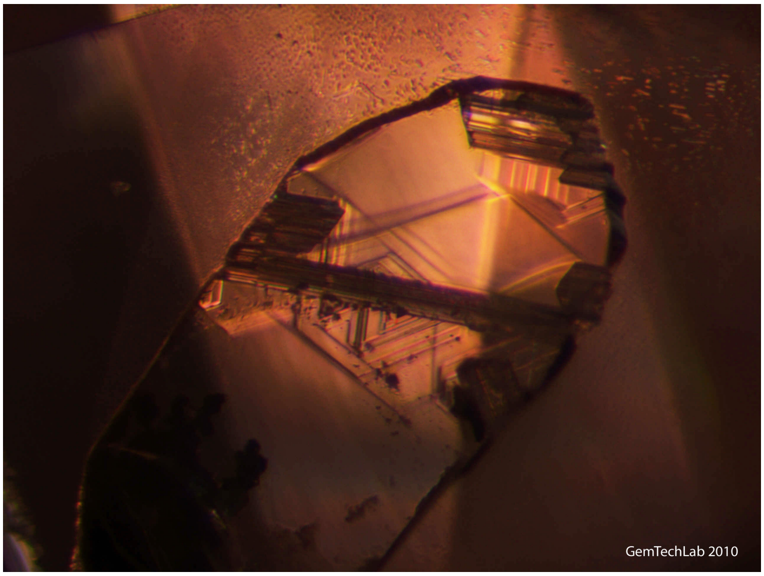

Fig. 1. Crystal identified as diaspore (220 μm long) by Raman spectroscopy inside an orange pink sapphire from Sri Lanka. Photomicrograph by Franck Notari, courtesy of GemTechLab Geneva, Switzerland.

not been heat-treated at the usual treatment temperatures, well above 1500°C. However, not all natural corundums contain diaspore in their inclusions.

The specific advantages of Raman spectroscopy for gemmology are that it is non-destructive, requires no optical contact, necessitates no preparation, and only small amounts of material. Any non-destructive method is relevant to the assessment of the exact nature of gemstones, in particular the most valuable ones, as these must be returned to their owners in their original state. Thus gemmologists are practitioners of many optical methods.

Raman spectroscopy necessitates no sample preparation, whereas some classical gemmological methods do. For example, to measure an index of refraction (RI) one needs an optical contact liquid and a flat, polished surface. In the absence of such a surface, the ‘spot method’ of RI determination is often less precise. Raman spectroscopy is thus well adapted to the identification of rounded or baroque-shaped objects, or pieces of rough, uncut gem materials, for which it produces an unambiguous conclusion. If the lack of direct contact with the material to be analyzed is crucial to identify inclusions, it is also a requisite for less-expected exercises. With the spectacular development of luxury watches, some experts are now confronted to the identification of small faceted gems on the face of a timepiece, protected under a watch glass. The challenge may be to determine whether they are colourless diamonds or sapphires. By focusing on the gem without gathering signal from the window, Raman spectroscopy quickly provides the answer. Diamond has an intense line at 1332 cm^{-1}, often used to calibrate Raman spectrometers, whereas corundum is a poor Raman scatterer with a main peak at $\sim$417 cm^{-1}.

Occasionally, its speed is what brings the gemmologist to the Raman spectrometer, especially in the context of a commercial operation where time is of the essence. To cite but one example drawn from practice, this technique was used to identify a large piece of etched colourless crystal, about 200 g in weight, as quartz in $\sim$30 s, whilst the crystal was presented as a much more valuable truly colourless beryl. Because of the size of the piece and its surface state, it was difficult to quickly obtain a refractive index or density, and the piece being colourless, colour itself or hand-held absorption spectroscopy were of little use. Hence, in identifying rough gems without flat faces, Raman spectroscopy is much faster than any approach, although with much labour and time spent, the determination could have been done through more classical means.

2.2. Instrumentation

Most gemmological laboratories are equipped with relatively simple dispersive instruments, like those described by Dubessy *et al.* (2012, this volume). Though the green Ar^+ laser was the commonly used excitation, many laboratories have now acquired several different lasers ranging from ultraviolet to near-infrared (but not too far from the visible range, to ensure efficient Raman scattering). This is either to avoid luminescence, or to excite certain useful luminescence lines (without the expense of a specific photoluminescence set-up), mostly for the separation of high-pressure high-temperature treated near-colourless diamond from their natural counterpart (see below and Panczer, 2012, this volume). Almost all Raman instruments used in gemmology are equipped with a Raman microprobe, often with a confocal option to increase spatial resolution for an easier determination of inclusions. Fourier-transform Raman spectroscopy instruments are still quite scarce, despite their easy operation, and the virtual absence of luminescence production, because of near-infrared excitation. Small, dedicated Raman spectroscopy instruments designed specifically for gemmologists have been proposed, *e.g.* the SAS2000 Raman PL System (by Adamas, New York, USA), around the year 2000, and two in 2012, the GL GemRaman (from Gemlab, Vancouver, Canada, a subsidiary of the Canadian Institute of Gemmology), and the Gem Ram (by BWTek, Newark, Delaware, USA). The latter instrument is sold with the following amusing advertisement "Novel method for Rapid gemstone Identification". They generally have Peltier-cooled CCD detectors, with standard green and sometimes red lasers at a power of a few hundreds of mW, for a resolution, when mentioned, of $\sim$3 to 4 cm^{-1} according to the producer's documents. None of these dedicated instruments is a microprobe.

2.3. Limitations of Raman spectroscopy

Although Raman spectroscopy is often presented in gemmological circles as a technique that can identify anything, it has several drawbacks which limit its application to gem materials.

2.3.1. Weak 'Raman scatterers'

Some materials simply do not respond well to laser excitation and no Raman signal is observed: they are 'poor Raman scatterers' with weak scattering efficiency and very weak signals. Often, black oxide inclusions give no signal at all. Opal or cubic zirconia give very weak signals, which require long accumulation times to obtain a good signal/noise ratio (*e.g.* $S/N = 10$). In general, weak signals must be addressed with great care to avoid any misinterpretation. This is especially true for micro-inclusions.

2.3.2. Artefacts and non-Raman signal

Depending on the specific instrument used, artefacts and non-Raman signals might be numerous (Fig. 2). They may come from the instrument itself or the immediate environment:

Large emissions in the near-infrared (IR) range with excitation at 1064 nm on FT instruments may completely dominate the signal. They often have the same overall shape, independently of the tested material. Two typical artefact shapes are illustrated in Fig. 2. They fall to zero at both ends of the detection range. In a small number of experiments, cooling the sample with a Peltier device down to $\sim -70^\circ$C weakened this non-Raman signal. The Raman signal appeared progressively superimposed on what was left of that feature. The exact origin of this pattern is unknown. It defies systematic study because its occurrence is random.

Sharp signals may be present in the spectrum and erroneously assigned to Raman lines. The well known green 546 nm mercury emission from nearby fluorescent lighting

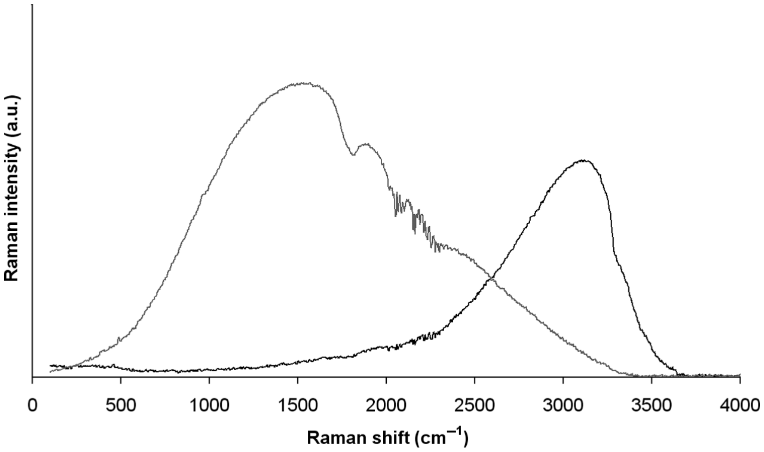

Fig. 2. Two types of instrumental artefacts relatively common in one type of Fourier-Transform Raman spectrometer. These features are obtained while collecting spectra at room temperature on actual gem minerals, with a liquid nitrogen-cooled, high-purity Ge detector. One or the other appears apparently randomly. They often overwhelm the actual Raman signal, even if some very small Raman signals can be seen on both spectra at ~500 cm^{-1}.

superimposes on the Raman spectrum and looks like a Raman scattering peak if the sample is located inside an open chamber. The coating or cement of optical lenses may contribute to Raman signal in some circumstances. For instance, depending on the type of instrument and material probed, this may happen either when a gem material has a very reflective surface, or reversely when it scatters light very efficiently. Such lines will depend on the type of coating or cement: the most intense on one instrument are at 843 and 1294 cm^{-1} for example. In addition to sharp signals, broad Raman signal may originate from the glass of the objectives (Jean Dubessy, pers. comm., 2012). Even 'cosmic radiation' affects all kinds of Raman spectra to various degrees. They come from any radiation resulting from phenomena outside of the normal detected range (*e.g.* X-rays) coming from space but also from the surrounding environment, that can excite the detector (Tarcea & Popp, 2012, this volume). They are usually very sharp, hence rare in FT systems, and most abundant on dispersive machines with cooled CCD detectors. Instruments affected by this type of problem usually have software to eliminate these artefacts, either manually or automatically. 'Parasitic laser lines' may be mistaken for Raman peaks. They are actually other emission lines from the laser. Interference filters may help to eliminate these 'laser lines'. More recently, emission from computer monitors located too near the sample have been recorded as gem Raman spectroscopy signal, before the problem was realized and corrected. When used in luminescence mode at liquid nitrogen temperature with a 514 nm laser, very sharp lines at 584 nm and 611 nm sometimes appear as unusual emissions. They are actually Raman lines of ice and liquid nitrogen, respectively.

2.3.3. Competition with luminescence signals

Luminescence from the gem material itself, and occasionally from its inclusions, may also limit the gemstones that may be identified. Opals often luminesce so strongly, that useful Raman spectra have only been obtained with the 1064 nm excitation (Ostrooumov *et al.*, 1999). The use of the 514 nm Ar^+ excitation or almost any other visible excitation will lead to overwhelming non-Raman signal (Smallwood *et al.*, 1997). A similar situation arises for amber and copal, for which Raman spectra can only be obtained with 1064 nm excitation as well, otherwise blue to green luminescence – common in these gems – overwhelms the Raman signal (Tay *et al.*, 1998). More recently, the luminescence signal was erroneously interpreted as the Raman signature of synthetic tourmaline, as the true Raman signal (which incidentally was no different from that of natural tourmaline) was overwhelmed by luminescence (Williams, 2009).

2.3.4. Sampled volume

One of the main advantages of Raman spectroscopy, its high spatial resolution, turns, on occasions, into a significant limitation. Any user of a Raman microprobe should be aware of the very small volume commonly analyzed by this technique, from hundreds of cubic micrometers for older instruments down to <1 μm in the very latest devices (Dubessy *et al.*, 2012, this volume). Raman microprobes, as they are commonly termed in gemmological laboratories, are generally not designed to give an average measurement of the whole volume of a gemstone. Rather, they give a signal from a small section of this material on which the exciting laser is focused. Great care must therefore be taken to analyse the volume of interest desired, *e.g.* an open fracture filled with polymer. Natural inclusions above or below this fissure might otherwise give signal, which leads to the incorrect conclusion that the fracture is not artificially filled. Another classic scenario is an assembled stone, a doublet or triplet, in which the materials forming the top of the gem (the crown) and the bottom (the pavilion) are different, for example a garnet and glass doublet. This may be hard to see if the assembled stone is in a closed mounting. This gets even worse if the object is further protected, for example analysed behind a piece of protecting glass, as for some historical objects.

2.3.5. Keeping gemmology in mind when interpreting Raman spectra

Finally, we think it is important that the Raman spectroscopy data from gemstones are interpreted by gemmologists, familiar with the pitfalls of this class of materials. An illustration is found in Jenkins & Larsen (2004) in which spectroscopists, unfamiliar with gemmology, identify synthetic sapphires that imitate amethyst (a great classic in gemmology) as ruby. This is because they obtain the same Cr^{3+} emission spectrum on a Raman spectrometer as that for a reference ruby: "Comparison of the spectra of these stones versus that of a known ruby proved that these two amethysts (*sic*) were indeed rubies despite their purple colouring". Not only did they mistake the fluorescence signal with the Raman scattering, but they used terminology in blatant contradiction with the gemmological definition of a ruby, which has to be red. If corundum is purple, it is called a 'purple sapphire'.

In view of all these artefacts, non-Raman signals and other limitations found in the practice of Raman spectroscopy, the user should be encouraged to first obtain a reference spectrum on a sample, always the same, with few Raman lines. This will make some unwelcome signals easier to detect, and will ease the interpretation. In gemmological laboratories, diamond fits the bill perfectly (only one line and one weak second order signal).

3. Determination of the gem species

3.1. Macrosamples

Raman spectroscopy is a powerful technique for identifying mineral species, and hence the nature of gems, either loose stones or mounted in a jewel. This technique has been used since the late 1980s. In practice, one has to acquire the Raman spectrum of the gem and compare this spectrum to a database of reference spectra. This step is and has always been the major difficulty for the species identification. This can be manually done using a printed or an on-line catalogue of reference spectra. A pioneer printed catalogue was the extra volume of the *Revue de Gemmologie A.F.G.* (1992): about 60 main gem species were presented, usually on a 150–1200 cm^{-1} range (restricted spectrum). Since then, several other attempts have been made to realize databases as exhaustive as possible, but most of them are restricted to minerals. Among them, the RRUFF on-line library is one of the most used by the gemmological community. It features, among other things, over 1970 minerals species represented through 2500 samples on which 3500 Raman spectra, sometimes crystallographically oriented. Home-made software for species determination, named '*Crystal Sleuth*', is available (http://rruff.info/about/about_download.php). It is based on the comparison of the sample spectrum with all spectra in the database, and gives a match percentage for each reference spectrum. This statistical approach gives satisfactory results in many cases. However, not all mineral species have been yet documented in this library, but the work is in progress. Of great potential interest to the gemmologist is the database established for phases, gas and ionic species found in fluid inclusions (http://www.dst.unisi.it/geofluids/Raman spectroscopy/spectrum_frame.htm, see paragraph 2.2.1 for further details).

A real difficulty for gemmologists is that these databases only refers to natural species, and not to the numerous artificial products used as gemstone imitations. This underlines the lack of a database specifically dedicated to gemmology: such a database should include all natural materials used as gems, and all synthetic materials used as gem simulants such as cubic zirconium oxide, YAG, or typical lead glasses. Ba-Zr glasses used as peridot simulants (Hainschwang, 2009) are a good example of material absent from all databases, just because this material has been created exclusively for this imitation.

Specific gem materials, especially those that are not considered as minerals, are also lacking. Some of those, their common simulants and other look-alikes, have been investigated: collections of Raman spectra are available for ivory (Edwards *et al.*, 1997 a and b;

Rolandi, 1999), amber (Tay *et al.*, 1998) and tortoise shell (Hainschwang & Leggio, 1996) for example. However, relevant publications are hard to find, or simply forgotten.

Raman spectroscopy is particularly interesting for the determination of a specific mineral composition in a solid solution or in a group. For example, it is quite easy to determine by means of classical gemmology if a gemstone is a garnet, a tourmaline, or a peridot. It is much more difficult to determine its precise composition in terms of pure poles, and this can be achieved by Raman spectroscopy. One such example is the distinction between montebrasite and amblygonite, two mineral names very often confused (Fig. 3). Raman spectroscopy proves that almost all gems of the amblygonite–montebrasite series are montebrasite (Rondeau *et al.*, 2006), although they are still called amblygonite by gemmologists. This is ambiguous as the term amblygonite can be encountered as the group name (including both species) or the species name. However, amblygonite *sensu stricto*, as a mineral species, is not encountered in gem quality.

Numerous spectra available in databases are restricted to the low wavenumbers, typically below 1500 cm^{-1}. This is explained by a certain point of view: many species do not show any signal between 1500 and 4000 cm^{-1}, and systematic exploration of this range used to be time-consuming, especially with single channel detection. Although modern instruments often do not have that drawback, the habit of not exploring this region persists. In addition, many species are nominally anhydrous, and hence there is *a priori* no reason to explore the high-wavenumber region. Conversely, this exploration should be systematic for nominally hydrous species, such as opal (see section 2). However, several nominally anhydrous minerals do show significant Raman signal at ~3000–3500 cm^{-1}, in the so-called 'water region', more correctly the domain of OH-stretching frequencies. This is the case for zircon (Rouillé, 2010; Brian, 2012): all

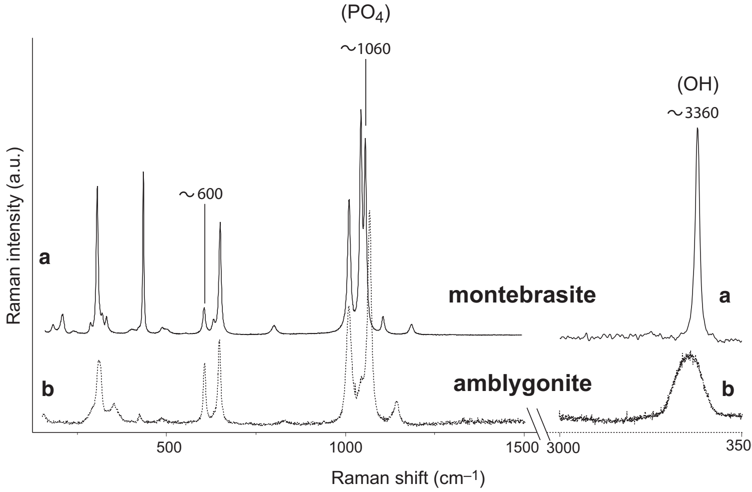

Fig. 3. Typical Raman spectra of virtually pure montebrasite (a, upper) and near-end member composition amblygonite (b, lower), after Rondeau *et al.* (2006).

zircons show a series of numerous, sharp peaks between 2600 and 3600 cm^{-1} under 1064 nm excitation (Fig. 4). Preliminary investigation of this region tends to show that this signal varies slightly with the geographic provenance, reflecting local geological conditions, but on a very restricted set of localities (mostly Cambodia and Burma). This is worth further detailed exploration as this question of geographical origin of gems is of increasing interest for the gem trade. Changing the excitation wavelength shows no signal in this region for the usual 514 nm laser line, and other broad features with any red excitation line. This suggests of course that this signal in the 'water region' is luminescence and not Raman signal. Some peaks of this luminescence system were already identified in the 'restricted' spectrum (Rankin & Edwards, 2003; Wang *et al.*, 2006), and it was stated that they are not due to zircon itself.

Lets not forget that extensive literature exists on water in nominally anhydrous minerals, but mostly using absorption in transmission mode in the mid-IR range (see for example the seminal reference library of George Rossman: http://minerals.gps.caltech.edu, and also Libowitzky & Beran, 2006; Johnson, 2006).

3.2. Microsamples and inclusions

One very interesting use of Raman spectroscopy in gemmology is the possibility of identifying inclusions in gems. The spectrum of the inclusion is compared to those of

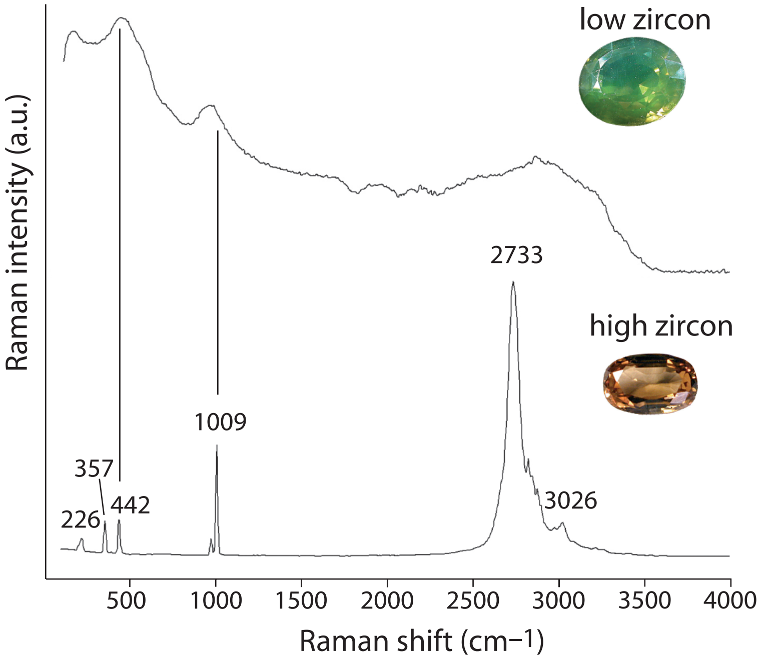

Fig. 4. Fourier-Transform Raman spectrum of low green zircon (upper, fully metamict expanded 100 times) and high zircon (lower, well crystallized).

a database in order to identify the mineral species, exactly in the same manner as previously described for the identification of gems. Very few other techniques (among which is optical microscopy) are able to provide data on non-outcropping inclusions. For example, using Raman microspectrometry, Schmetzer *et al.* (1997) discovered unexpected chrysoberyl inclusions in Chinese hydrothermal synthetic emerald. Often, micro-morphologies of minerals are quite different from their usual macro-morphology, so that inclusions in gems may not be recognized easily through their shape (or colour). For example, a ruby from Madagascar contains a colourless inclusion with a nearly hexagonal outline which is difficult to determine with optical microscopy (Fig. 5). Its Raman spectrum is consistent with pargasite. Raman spectroscopy was the only conclusive technique for this identification. Another good example concerns the tiny, black inclusions in natural diamond. Only Raman spectroscopy gives conclusive data: the spectrum usually displays large bands at 1575 (G band or graphite band) and 1355 cm^{-1} (D band or defect band) proving that they are very small crystallites of graphite (Tuinstra & Koenig, 1970; Chollet & Kajzar, 1997; Beyssac & Lazzeri, 2012, this volume). The Raman intensity of the D band is inversely proportional to the size of the crystallites, which may be helpful in understanding why the black inclusions, often nano-crystallized in black diamond, cannot be resolved optically.

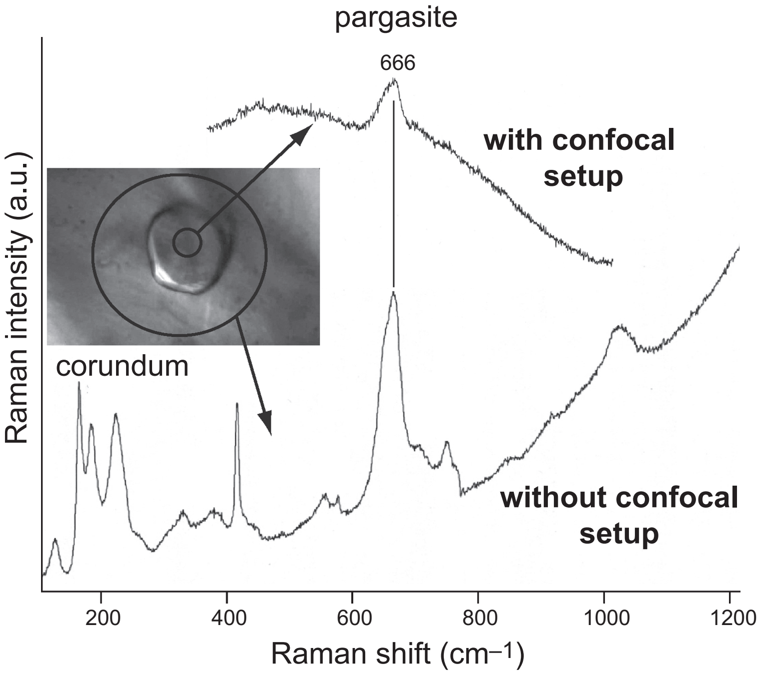

Fig. 5. Colourless, nearly hexagonal inclusion in a ruby from southern Madagascar (middle left). Without confocal, a broad band was detected at ~666 cm^{-1} amongst the corundum spectrum (lower), which is found alone when using a confocal set-up (upper spectrum).

However, in practice, many difficulties can be encountered during the analysis of inclusions in gems. The main concern is the size of the inclusion: the larger, the easier to identify. A confocal-type apparatus is typically able to isolate the signal of a 7 μm wide and 25 μm deep nearly-cylindrical volume, but depending on parameters of both the instrument and the inclusion (type of objective lens, with or without immersion, size of the confocal hole, RI of the inclusion, *etc*.), this volume can go down to ~1 cubic micrometer. So one must determine the minimal volume for unambiguous detection. Also, some host matrices can absorb a part of the Raman light scattered by the inclusion and weaken its signal. Hence, the smallest inclusions are challenging to identify.

3.2.1. Identification of phases in fluid inclusions

Although numerous studies were devoted to the identification of fluid inclusions in minerals, few works focused on those specifically found in gemstones. Indeed, fluid-inclusions identification in gemstones in the gemmological literature often concludes by announcing the presence of a liquid and a vapour phase. When the nature of phases is determined in a potentially gem material (see for example, Giuliani *et al.*, 2003) such data are not used by gemmologists. Gemmologists rarely identify them, for example for geographical origin determination (see for example Rondeau *et al.*, 2008). Gemstone examination must keep the samples intact, and hence not all experiments can be conducted, such as temperature measurements of solid-phase transitions at low temperatures ($<0°C$) and liquid-vapour homogenization at high temperatures ($>100°C$) with the use of a heating-freezing stage, which may lead to damage to the gem. However, the nature of the gas and liquid could easily be determined by Raman spectroscopy at room temperature. There is extensive literature on the use of this technique in mineralogy. A review has been recently published on the determination, by Raman spectroscopy, of natural fluid inclusions in natural minerals (Frezzotti *et al.*, 2012). This review also proposes an on-line database (http://www.dst.unisi.it/geofluids/Raman/spectrum_frame.htm) for the identification of gaseous, fluid and solid phases in fluid (multiphase) inclusions.

The identification of solid phases in multiphase fluid inclusions is sometimes very difficult, especially if salts such as NaCl or KCl, which are not Raman active, are present. We recently encountered an unexpected solid phase in topaz that displays the typical Raman spectrum of sassolite (H_3BO_3; Fig. 6). This identification was consistent with EDS analysis of broken samples, as only oxygen was detected, suggesting the presence of light elements only.

3.2.2. Identification of inclusions due to a treatment

Several treatments of gems induce inclusions that are characteristic of this procedure. For example, fractures in many gems are commonly filled with organic products such as epoxy in emerald (Kammerling *et al.*, 1991; Chalain *et al.*, 1998), and lead glass in corundum (Pardieu, 2005). These substances of a similar refraction index to their matrix make fractures much less visible, artificially increasing the apparent value of

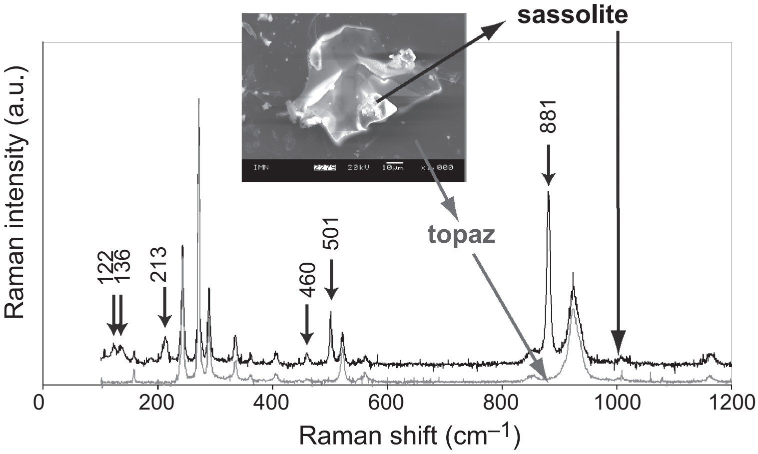

Fig. 6. Back-scattered electron micrograph of a sassolite crystal (H_3BO_3) inside a fluid inclusion and its Raman spectrum.

the gem. The impregnation product can be revealed by optical observation, and in some cases identified by IR spectroscopy. However, some gems contain very little filling substance, and Raman spectroscopy becomes very useful in these cases (Fig. 7).

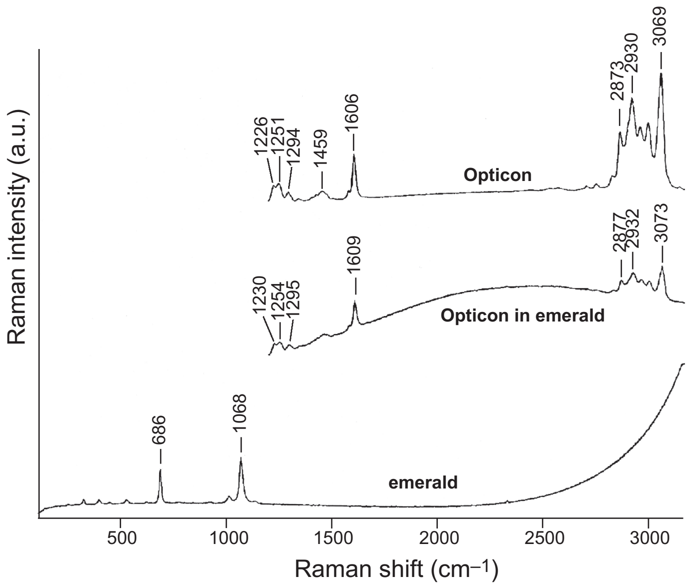

Fig. 7. Raman spectra of the most common impregnation material used for emerald fracture-filling: Opticon^{TM} (a resin, upper), in emerald, and a reference emerald spectrum. All spectra obtained with 514 nm excitation of a Nd-YAG laser with 25 mW power (after Chalain *et al.*, 1998). **Q5**

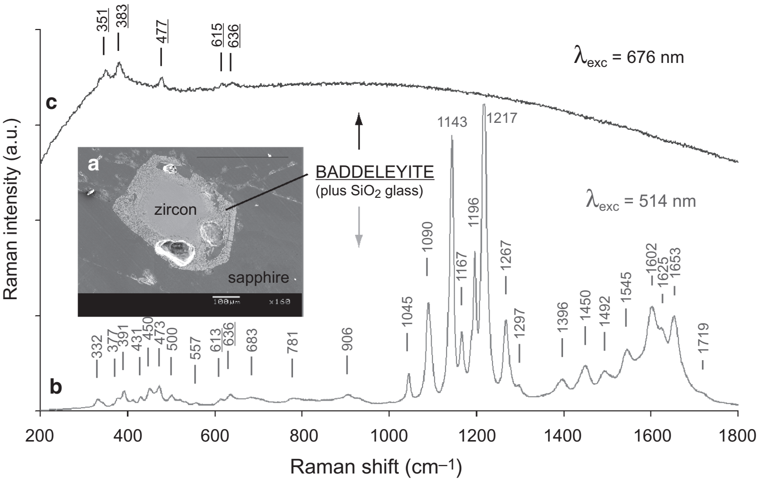

Fig. 8. (***a***) Secondary electron micrograph of a zircon inclusion after heat treatment above 1600°C in a sapphire. The zircon has undergone incongruent melting into a SiO_2 phase (dark grey) and a ZrO_2 phase (light grey – baddeleyite). (***b***) The extremely intense spectrum of the modified zircon inclusion in corundum *via* Raman spectroscopy using 514 nm excitation, shows a weak baddeleyite signal, at ~475 and 385 cm^{-1}. However, the most intense part, with many sharp peaks at 1143 and 1217 cm^{-1} for example, is attributed to luminescence, as it is absent when using 676 nm excitation (***c***). The broad signal at ~380 cm^{-1} seen in (c) may be related to the matrix, made essentially of molten SiO_2.

Some natural sapphires contain zircon inclusions which transform or melt during heat treatment from 1400 up to 1950°C. If treated at <1600°C, the zircon Raman peaks of the zircon inclusions shifted towards higher wavenumbers (Wang *et al.*, 2006). During cooling, these inclusions can transform into droplets of monoclinic zirconium oxide (baddeleyite) in essentially silica glass (Fig. 8), within the original inclusion shape (Lasnier *et al.*, 1996; Rankin & Edwards, 2003). This gives rise to a whitish, opaque inclusion somewhat resembling a ‘golf-’ or ‘snow-ball’. It is very difficult to identify as a modified zircon without the help of Raman spectroscopy. The signal of baddeleyite is very weak with 514 nm excitation, and it is dominated by a very strong luminescence made of many sharp peaks (at 1143 and 1217 cm^{-1}, Fig. 8), which is currently of unknown origin.

3.2.3. Identification of thin films covering gems

Several cases of faceted gems covered by a thin film have been documented. Some carbon-related films (diamond) aim to protect a soft gem from scratching, or aim to imitate diamond itself (see for example Fritsch *et al.*, 1989). Raman spectroscopy is very useful in these cases because the Raman spectrum of diamond is obtained very quickly, and is always different from the spectrum of the gem inside.

Some coloured thin films are deposited on a gem of unattractive colour in order to give it an apparent attractive colour (Shen *et al.*, 2007). The presence of such films can be detected by simple observation under the optical microscope if the film has been partly damaged by wearing. The nature of those films can be identified easily if the material gives a strong signal. However, Raman spectroscopy can be of no help if the film is a weak Raman scatter, such as pink fluorite, iron oxides or silica films deposited on a diamond (Shen *et al.*, 2007).

4. Determination of order-disorder: bandwidth considerations

The spectral bandwith of Raman spectroscopy signals carries information on order-disorder, or the state of crystallinity of the material. The main application for gemmology is to determine the state of crystallinity of a material. Indeed, gems are obviously found as well crystallized minerals, but also disordered ones, as well as glasses and other amorphous materials, such as opals. One of the major surprises discovered by Raman spectroscopy is that the so-called "Verneuil" or "flame-fusion synthetic spinel" is actually a glass (Sidki, 2009). It is well known that this material is not a genuine spinel, as the Mg/Al ratio is different from that of the natural crystals, but the atomic structure was never discussed. The presence of very broad bands (Fig. 9) centred at ~412 cm^{-1} and 697 cm^{-1}, close to those observed in natural spinel (~406 and 667 cm^{-1} in Fig. 9) confirms the amorphous nature of this suppoed synthetic crystal.

Extensive work has been conducted on the Raman spectra of opals. As mentioned above, only 1064 nm Nd-YAG laser excitation can be used, commonly coupled with Fourier-Transform Raman instruments (Smallwood *et al.*, 1997; Smallwood, 2000). Otherwise, intense luminescence, from various sources (Gaillou *et al.*, 2011), dominates the spectrum for all UV and visible excitation wavelengths. The classification of opal varieties was not used in gemmology in the past, as it was based on powder X-ray diffraction, a destructive technique. Raman spectroscopy quickly provides the information without any damage to the gem. The identification of the different opals is based on the

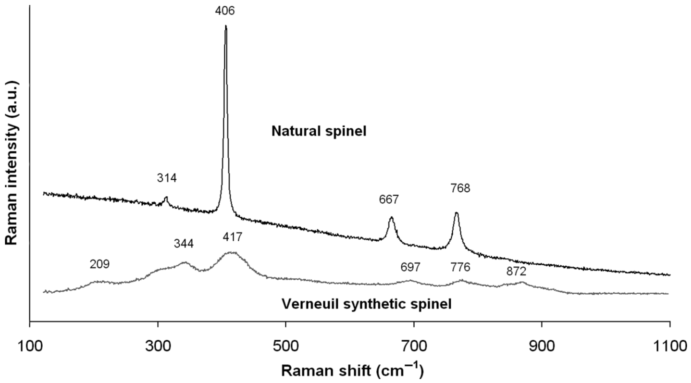

Fig. 9. Raman spectra of well crystallized natural gem spinel (upper) and so-called Verneuil or flame-fusion synthetic spinel (lower).

Raman shift of the O—Si—O bending mode giving rise to the major broad band (Ostrooumov *et al.*, 1999; Smallwood, 2000): ~400 cm^{-1} for opal A (totally amorphous), and ~350 cm^{-1} for opal C-T (poorly crystalline cristobalite with some trydimite-like stacking; Fig. 10). The main O—Si—O bending band is in fact the addition of three bands of varying relative proportions, and the variability in peak position is due to gradual formation of six-membered rings in a disordered SiO_2 matrix (Ivanov *et al.*, 2011). The mineralogical variety of opal is a useful constraint in determining the geographical origin of opal. For example, white gem opal from Australia and Brazil is opal-A, whereas the abundant new white opals from Ethiopia are opal-CT.

While natural opals were studied systematically, a new gem material was discovered through its Raman spectrum. It is a mixture of opal-CT and cristobalite (Gaillou *et al.*, 2004). Relatively sharp bands at ~230 and 420 cm^{-1} betray the presence of well crystallized cristobalite, whereas a weak broad band is related to an opal-CT matrix (again, see Fig. 10). The presence of opal-CT in the middle spectrum of Fig. 10 can be ascertained by, among other arguments, the weak Raman features typical of this material at

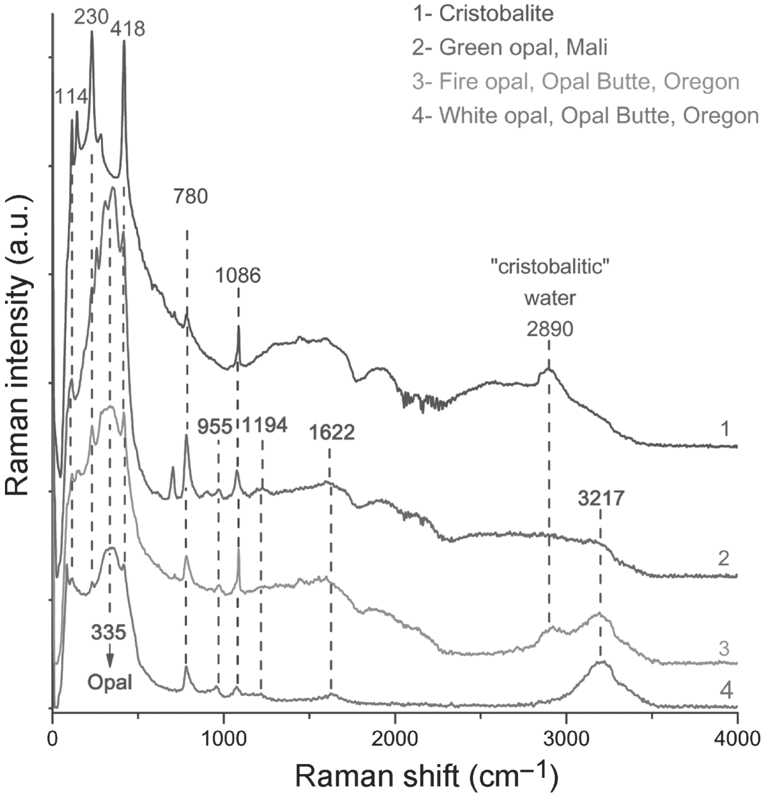

Fig. 10. Fourier-Transform Raman spectra of α-cristobalite (top), and three different opal-CT with α-cristobalite inclusions.

~955, 1194 and 1622 cm^{-1}. This material cannot be identified by classical gemmology, as the refraction index and density of the two mixed phases are quite close, and those of the opal are already somewhat variable. Because it is a mixture of two materials of slightly different refraction index, it always scatters light, affording the stone a milky aspect. This material has since been found to be far more common than anticipated.

Classical gemmologists always made the difference between 'high' (well crystallized) and 'low' zircons which may be totally amorphous gems. All intermediaries are possible. Raman spectroscopy gives insight into the state of metamictization (Nasdala *et al.*, 1995). Here again, it is the determination of the bandwith that brings the information. The position of the band evolves from 1007 cm^{-1} down to <1000 cm^{-1}. Its width evolves from ~5 cm^{-1} in a high zircon to nearly 55 cm^{-1} in a low zircon. Most notable is the very contrasted scattered intensity of the two extremes (Fig. 6).

Similarly, the size of crystals determined using Raman spectroscopy helps to differentiate natural turquoise from its synthetic equivalent. Synthetic turquoise is the laboratory-made equivalent, with the same chemistry and atomic structure as its natural counterpart (see *e.g.* Fritsch & Rondeau, 2009, for more on synthetics). The bands due to phosphate-group vibrations are clearly individualized for natural turquoise, whereas those features are broader and less defined for synthetic specimens (Fig. 11). Indeed, natural specimens contain micron-size, relatively well individualized crystals, and the synthetic material is made of much smaller nano-precipitates. The bands of synthetic turquoise are thus broader and not as high, especially the main phosphate band at ~1050 cm^{-1}. The lesser Raman intensity may result from increased light scattering on smaller crystals.

The distinction of amber from copal (less fossilized material, thus less stable and less valuable) remains unsolved using the usual tools of gemmology. Tay and co-authors (1998) proposed looking at the width of the Raman bands of both compounds. Their preliminary conclusion was that the Raman spectra of copal, in particular bands at

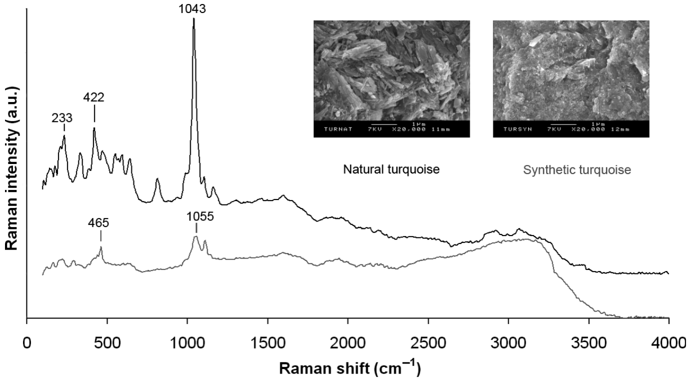

Fig. 11. Raman spectra of natural turquoise (upper spectrum) and its synthetic equivalent (lower spectrum). Secondary electron micrographs show that the grain size is different for both materials: μm-sized for natural turquoise, and much smaller, in the nm range, for the synthetic material.

1640 cm^{-1} (C=C) and 1440 cm^{-1} (CH_3) were generally sharper and better defined than those of true amber. This is tentatively attributed to the degree of polymerization of the original tree resin.

5. Resonant Raman spectroscopy and the identification of some organic colouring agents

5.1 Parrodienes *versus* carotenoids

Raman is also used to study the nature of pigments of some organogenic gems, *i.e.* gems produced through a biological process such as pearls, corals, ivory and amber. Polyenic pigments have been identified in some coloured (natural and cultured) pearls and corals (Merlin & Dele-Dubois, 1986; Urmos *et al.*, 1991; Karampelas *et al.*, 2007). **Q1** Chemically, polyenes are polyunsaturated organic compounds that contain one or more sequences of alternating double and single carbon–carbon bonds (polyenic chain). Polyenic pigments, *i.e.* pigments which contain a polyenic chain, are widespread in nature. The vast majority of these pigments belong to the carotenoid family (a.k.a. carotenoids). Some vegetables and fruits (such as carrots and tomatoes) are the most common examples of carotenoid colouration (Withnall *et al.*, 2003). These pigments have also been identified in other living organisms (*e.g.* bird feathers and human retinas: Veronelli *et al.*, 1995; Ermakov *et al.*, 2005). It was recently found that carotenoids provide important information for biogeological and astrobiological studies (Jehlicka *et al.*, 2009; Vitek *et a*l., 2009, 2010). However, polyenic pigments other than carotenoids have been identified in parrot feathers, bacteria, corals, mollusc shells as well as some natural and cultured pearls (Merlin & Dele-Dubois, 1986; Urmos *et al.*, 1991; Veronelli *et al.*, 1995; Stradi *et al.*, 2001; McGraw & Nogare, 2004; Hedegaard *et al.*, 2006; Rosa-Fraile *et al.*, 2006; Karampelas *et al.*, 2007). These pigments are also known as parrodienes or psittacofulvins or polyacetylenes; they are simple unsubstituted polyenes with various terminal ends. Chemically, carotenoids are polyenes of finite length, with various terminal ends on the chain but those pigments are characterized by four additional methyl groups substituting for hydrogen, making them substituted polyenes.

Raman spectroscopy has been applied to the study of polyenic molecules for >40 years (Rimai *et al.*, 1970; Salares *et al.*, 1977). Compounds with a polyenic chain present strong resonance phenomena, *i.e.* their Raman scattering is enhanced by excitation in the absorption band of the compounds. Thus, these bands are much more intense than those unrelated to the polyenic chain. This strong spectral enhancement is due to the coupling of electronic and vibrational transitions. Molecules with a polyenic chain may thus be detected at very low concentrations ($\sim 10^{-8}$ M in solutions; Hoskins & Alexander, 1977).The chains present two characteristic Raman bands due to strong resonance effect, which occur in the 1100–1200 and 1450–1600 cm^{-1} range. These bands correspond to the carbon–carbon stretching (ν_2) vibration of a C—C single bond (coupled to C—H in-plane bending modes when attached to the polyenic chain), and to carbon–carbon stretching (ν_1) vibration of a C═C double bond in a polyenic chain, respectively (Okamoto *et al.*, 1984). The exact position of these bands is dependent on the length of the chain, *i.e.* the number N of C═C bonds in the chain (Schugerl & Kuzmany, 1981; Schaffer *et al.*, 1991; Barnard & de Waal, 2006).

Differentiation between "simple" (unsubstituted) and substituted polyenes (parrodienes and carotenoids, respectively) can be achieved using Raman spectroscopy (Okamoto *et al.*, 1984; Merlin & Dele-Dubois, 1986; Veronelli *et al.* 1995). The ν_1 vibration is almost at the same position for both types of molecules, at ~1510 cm^{-1}, but not ν_2. For carotenoids which contain methyl groups in their polyenic chain (methylated polyenes), the position of ν_2 is shifted by ~25 cm^{-1}, compared to polyenic molecules without CH_3 substitution (non-methylated) having the same polyenic chain length. For example, for $N = 11$, ν_2 peaks are found at 1157 cm^{-1} for carotenoids (in this case, β-carotene), but only at 1133 cm^{-1} for the corresponding parrodiene. This appears to be caused by the presence of the methyl groups attached to the polyenic chain. Such a small difference in the ν_2 position may be overlooked and sometimes parrodienes are mistakenly reported as carotenoids (Smith *et al.*, 2007; Karampelas & Fritsch, 2007; Leverette *et al.* 2008; Fritsch & Karampelas, 2008).

5.2. Application to pearls and corals

5.2.1 Pearls

Pearls are divided into natural and cultured. Natural pearls are accidentally secreted in a mollusc, whereas cultured pearls are due to a human intervention. In today's pearl market, about 99.8% of the pearls are cultured, and only 0.2% are natural. Natural and cultured pearls, depending on their growth environment, are also divided into freshwater and saltwater. About 95% of the gem-quality pearls found in the market nowadays are freshwater cultured pearls (FWCP). FWCP are cultivated in bivalves from *Hyriopsis sp.* in rivers and lakes of the Far East, mostly China, not far from Shangai.

Figure 12a shows two Raman spectra from 600 to 1600 cm^{-1} of a white FWCP and a natural-colour pink one, using the 514 nm excitation of an Ar$^+$ laser. The vibrations of aragonite (the inorganic part of the pearl) are present in both spectra, *i.e.* the main band at ~1085 cm^{-1} and the doublet at ~702 and 706 cm^{-1} due to the ν_1 symmetric and ν_4 in-plane bending mode of the carbonate ions, respectively (Urmos *et al.*, 1991). The spectrum of the coloured FWCP presents two major additional bands at ~1130 and 1530 cm^{-1}, which are characteristic Raman resonant bands of polyenes (as well as other weak bands at ~1010, 1190 and 1295 cm^{-1}). Figure 12b illustrates the spectra of four different natural-colour FWCPs. In addition to aragonite peaks, all of the coloured pearls also display Raman resonant bands of polyenes. Some slight differences regarding the shape, intensity and exact position of the two most intense polyenic bands are noted from one sample to another. Raman bands at about the same positions are found in all natural-colour FWCPs published to date in various articles, regardless of their specific hue (Karampelas, 2008 and references therein). However, these bands are always in the range of parrodienes, but not of carotenoids.

As stated above, the exact position of these bands is dependent on the chain length. For one isolated parrodiene pigment, the carbon–carbon stretching (ν_1) vibration of a

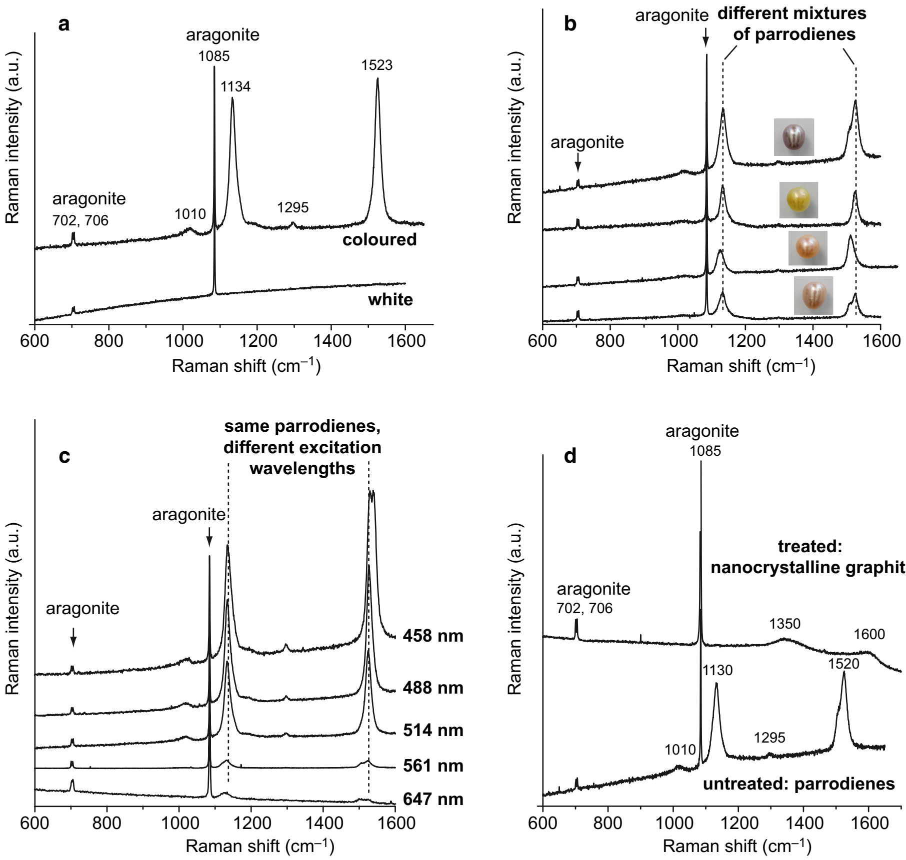

Fig. 12. (***a***) Raman spectrum (excitation: 514 nm) of a white (lower) FWCP and a natural-colour dark grey (upper) FWCP. (***b***) Raman spectra (excitation: 514 nm) of four different natural-colour FWCPs (from bottom to top: pink, orange, yellow, grey-purple). (***c***) Raman spectra at the same position as the same FWCP of natural-colour dark grey, obtained with different excitation wavelengths. (***d***) Raman spectra of two grey freshwater cultured pearls untreated (lower) and treated (upper).

C=C double bond appears at ~1460 cm^{-1} when 17 double carbon–carbon bonds are present in the chain, about 1503 cm^{-1} for 12, 1522 cm^{-1} for ten, and up to 1586 cm^{-1} for only five double carbon–carbon bonds (for more information see Schugerl & Kuzmany, 1981; Schaffer *et al.*, 1991; Barnard & de Waal, 2006; Karampelas *et al.*, 2007). Moreover, acquiring Raman spectra at the same position on the same gem, simply changing excitation wavelength, yields variations in position, shape and relative intensities of the two most intense bands (Fig. 12c). Shorter excitation wavelengths also give Raman resonant peaks at a higher wavenumber position, thus exciting polyenic pigments with shorter polyenic chains. This broad peak due to the ν_1 vibration at

$\sim$1500 cm^{-1} may be fitted as a sum of Raman bands (using constraints, *i.e.* FWHM of all bands is fixed at 10 cm^{-1} and Raman peak position of each polyenic pigment is fixed within 2 cm^{-1}). Each simulated band corresponds to one actual parrodiene (for further details see Karampelas *et al.*, 2007). This reveals up to ten components, thus a mixture of up to ten different parrodiene pigments, depending on the pearl tested. Different colours are explained by different mixtures of parrodiene pigments, and not by one single pigment.

Similar mixtures of parrodiene pigments play a role in the colouration of other pearls. These are much rarer, highly valued natural-colour natural pearls from some molluscs, *e.g.* 'Melo pearls' (from *Melo sp.*), 'Queen conch pearls' (from *Strombus gigas*), 'Quahog pearls' (found in bivalves from the Veneridae family), 'Mytilus pearls' (found in bivalves from the Mytilidae family) and 'Scallop pearls' (found in bivalves from the Pectinidae family). However, it seems that similar colours of pearls from different mollusc families are not caused by the same parrodiene mixtures. For example, the natural pink colour of a FWCP is due to a mixture of polyenes with short chains, whereas the natural pink colour of a queen conch pearl is due to a mixture of polyene with long chains. Thus the latter pearl's main Raman resonant peaks are at higher wavenumbers (for more information, see Karampelas, 2008).

All pearls (natural and cultured) of gem quality consist almost entirely of aragonite. Only some of them may consist of other calcium carbonate polymorphs (such as calcite and vaterite). To the best of our knowledge, only the 'Scallop pearls' consist almost entirely of calcite, with vibrations at $\sim$1085 and 711 cm^{-1} (Karampelas & Hainschwang, 2010). Thus, the presence of calcite Raman bands together with parrodiene resonant Raman bands is a unique characteristic of 'Scallop pearls'.

So far, carotenoids are identified as pigments only for 'Pen pearls' (found in bivalves from the Pinnidae family). Their ν_2 C–C stretching vibration is located at $\sim$1158 cm^{-1} using a 514 nm excitation. It was also found that these pearls contain more than one carotenoid pigment using different excitation wavelengths. 'Pen pearls' consist mostly of calcite, but large parts could be aragonitic. Thus, the presence of carotenoids with calcite is considered to be tell-tale characteristic of 'Pen pearls' (Gauthier *et al.*, 1994; Karampelas *et al.*, 2009a).

As coloured pearls increased in popularity, treated-colour pearls have appeared in the market. Taking into account the observations above, Raman spectroscopy enables their identification. For example, if Raman bands different from those of natural pigments (*i.e.* parrodienes or carotenoids) and calcium carbonates are present in the spectrum of a pearl from the molluscs cited above, it has a treated colour. If a coloured FWCP presents Raman peaks different from those of parrodienes (in addition to the aragonite peaks), it is due to an artificial coloration (Fig. 12d). Among other colouring products, Raman can identify nanocrystallized carbon, which may turn a pearl gray (see Section 2.2).

5.2.2 Corals

Coral is another organogenic gem group of gemmological importance. Corals are marine invertebrates that develop colonies forming calcareous skeletons. Only some skeletons are used as gem material; the major attraction is their pink-to-red colouration. The corals of the *Corallium genera* (Anthozoa class) are by far the most valued in jewellery (Smith *et al.*, 2007). Raman spectroscopy demonstrated these corals to be calcitic, and their natural pink-to-red colours, also to be due to a mixture of parrodienes (Merlin and Dele-Dubois, 1986; Karampelas and Fritsch, 2007). Some pink-to-red corals of the *Stylaster genera* (Hydrozoa class) are also used in jewellery as cheap substitutes for *Corallium* corals. However, *Stylaster* corals are protected by international laws (see Karampelas *et al.*, 2009b and references therein). Odentification of these corals can sometimes be achieved only with a binocular microscope if their characteristic internal structures are well marked and unambiguous (*Stylaster* corals possess pores in circular patterns whereas *Corallium* corals present striations). Their separation can also be performed using Raman spectroscopy, which proves particularly useful when internal structures are not easy to read. Pink-to-red *Stylaster* corals are aragonitic with carotenoid pigmentation (ν_2 vibration at $\sim$1155 cm^{-1} with a 514 nm excitation), whereas pink-to-red *Corallium* corals are calcitic with parrodiene colouration (ν_2 vibration at $\sim$1130 cm^{-1} with a 514 nm excitation; Fig. 13). As for pearls, artificially coloured corals are widespread on the market. Again, the pigments used for treatment give no pigment signal or weaker, different Raman signals from those of parrodienes and carotenoids.

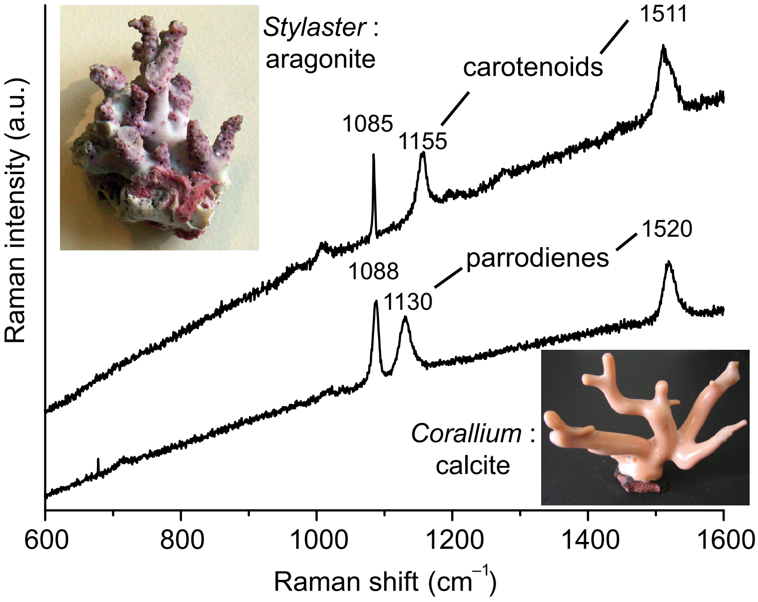

Fig. 13. Raman spectrum and photographs of natural pink corals. Upper: *Stylaster* genus; lower: *Corallium* genus.

6. Raman spectrometers as photoluminescence instruments

6.1. Why do gemmological laboratories use Raman spectrometers for luminescence spectroscopy?

Fluorescence occurs mostly when using UV or visible laser radiations to acquire Raman spectra. Distinct fluorescence generally prohibits the recording of a Raman spectrum. Indeed, using the acquisition times necessary for the detection of Raman signal, the luminescence intensity will probably reach the saturation level of the detector. For gemmological testing, photoluminescence (PL) spectroscopy obtained on a Raman spectroscopy spectrometer has many practical applications (see Panczer, 2012, this volume, for a more general discussion). For diamond, it is equally or probably more important than Raman spectroscopy itself. Indeed, most gemmological laboratories do not have a dedicated classical spectrofluorimeter, but Raman spectroscopy set-up makes it possible to gather only emission spectra, and not excitation or time-resolved data, as on classical luminescence instruments. Nevertheless, the information gleaned is very useful in a rapidly growing number of cases. Indeed, PL is extremely sensitive to low-defect concentrations, and therefore well adapted to separate two gem materials which differ only by subtle variations of low-concentration defects or trace elements.

In contrast to the Raman effect, which is caused by inelastic scattering of the laser light by the crystal lattice, photoluminescence is caused by the absorption of the excitation laser light. By absorption of the laser light, electrons from specific defects move from their ground state to an excited state, and then fall back to their ground state, emitting photons, *i.e.* photoluminescence. These emissions occur at energies that are lower than the energy of the laser, thus generally follow Stokes law. Today, almost exclusively, Raman spectrometers are used to record photoluminescence spectra in gemmological laboratories. This spares the expense of a dedicated spectrometer. The monochromatic laser light does not need a monochromator as with a broadband source, and a greater output power than with a classic excitation lamp is possible for many laser wavelengths used for Raman spectroscopy.

6.2. Instrumentation

Lasers from the UV to the NIR are used; the most common ones are HeCd (325 nm), Ar^+ or diode laser (e.g. 488 nm and 514 nm), frequency-doubled Nd:YAG (532 nm) and diode laser (*e.g.* 532 nm and 785 nm). A large range of laser wavelengths is now available for spectroscopic applications. In consequence, other excitation wavelengths can be found in Raman systems (se also Dubessy *et al.*, 2012, this volume). For PL in gemmology, the use of a Raman microprobe can be useful as many gem materials have an inhomogeneous defect distribution; mapping capabilites using confocal systems can also be useful in certain cases, to demonstrate the defect distribution in a gem material. Neither a microscope nor confocal options are thus necessary for many applications. What is of great importance for PL spectroscopy is the optical resolution and the spectral range covered by the instrument. PL bands can be very sharp in solid gems, the sharpest may have a FWHM of 0.10 nm. This corresponds to a fairly standard

$4\ \mathrm{cm}^{-1}$ resolution at 500 nm. In consequence, a resolution of 0.1 nm or better should be available, and as PL can be detected from the UV to the NIR, the ideal range would from 200 to 1100 nm. In order to best characterize a material by PL spectroscopy it is important to have a range of lasers of different wavelengths available: lasers of different wavelengths may excite completely different defects or trace elements. In the authors' experience this is especially true for diamond: it may happen that only one laser excites a specific defect centre, but then usually with high efficiency. Such a variety of lasers is useful to avoid luminescence in other gem materials, in order to obtain useful Raman spectra.

Photoluminescence spectra are best recorded at low temperature; liquid nitrogen is used most often. This cooling is necessary for diamond, but is rarely performed for other gem materials, even though the technique has a distinct effect on the spectral shape of almost all emissions. Room-temperature PL spectra are often characterized by broad bands. Thus, cooling is necessary to detect the typical PL sharp bands, especially for diamond.

6.3. Applications to gems

6.3.1. Photoluminescence spectroscopy of diamonds

Diamond is the material that is most commonly analysed by PL spectroscopy; no other material shows a greater variety of defect centres detected by this method. In diamond, several hundred emissions are known. However, for many of them the nature of the defect centre is often unknown at atomic scale, or very little has been discovered (Zaitsev, 2001). An example of the complex PL spectra of a chameleon diamond can be seen in Fig. 14. 'Chameleon' diamonds are so called because they exhibit

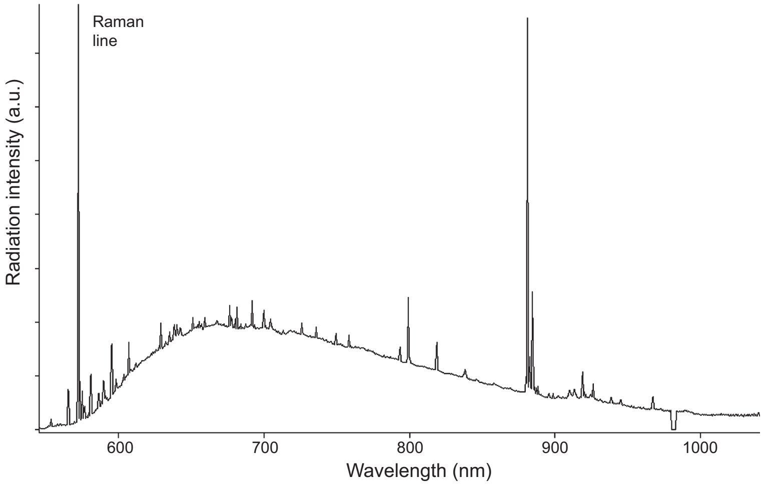

Fig. 14. Photoluminescence spectrum of a chameleon diamond at 77 K using the 532 nm laser excitation and a high resolution (0.07 nm) obtained with an *Echelle* spectrograph.

thermochromic and photochromic colour changes (Liddicoat, 1993). Figure 14 shows the PL spectrum of a chameleon diamond recorded at 77 K on a photoluminescence system using a high-resolution Echelle spectrometer, with an average resolution of 0.07 nm. It exhibits >150 emission bands, from sharp to very sharp (FWHM ranges from 0.15 to 0.40 nm) and weak to very intense, positioned on the top of the very broad band emission from 550 to >1100 nm (T. Hainschwang, unpublished data). Many of the sharp signals have been assigned to nickel defects (Shigley *et al.,* 2004).

The technique of photoluminescence spectroscopy in gemmology was used extensively used for the first time when high-temperature–high-pressure (HPHT)-treated type IIa diamonds appeared on the market in the late 1990s (Smith *et al.,* 2000). Brown diamonds determined as quasi nitrogen-free by IR spectroscopy were found to become near-colourless to colourless by a treatment at temperatures between 2300 and 2500°C and at stabilizing pressures of 65 to 85 kbar for a few minutes. The most promising technique for the identification of such treated diamonds has been found to be PL spectroscopy, as PL spectroscopy permits the detection of extremely low concentrations of defects such as nitrogen-vacancy centres. The detection was originally based on the ratio of the zero-phonon lines (ZPL) of the negatively charged nitrogen-vacancy defect (NV^-, ZPL at 637 nm) and the neutral nitrogen-vacancy defect (NV^0, ZPL at 575 nm) (Fig. 15) when excited by a 514 or 532 nm laser (Chalain *et al.*, 2000), but this criterion alone, although useful, was not sufficient. Several other criteria have been defined since, such as the width of some emission bands (Hänni *et al.*, 2000). Most of these are based on PL spectroscopy, often obtained on Raman spectrometers (Lim *et al.*, 2010). A number of gemmological laboratories have acquired either new or more sophisticated Raman systems for this specific application, equipped with several additional lasers compared to the standard offer.

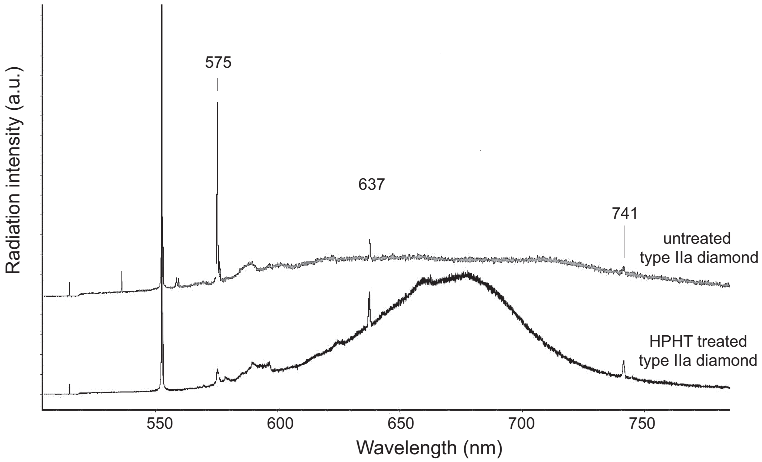

Fig. 15. Photoluminescence spectrum of near-colourless type IIa (nitrogen-free) diamonds at 77 K excited by a 514 nm laser radiation. Images courtesy of Laboratoire Français de Gemmologie (LFG), Paris.

Another important application of PL spectroscopy is the distinction of natural diamonds from synthetic ones. HPHT and CVD (Chemical Vapour Deposition)-grown synthetic diamonds enter more and more into the marketplace, especially for small diamonds (*i.e.* ~0.25 ct or smaller 'melee' diamonds). Mixed within parcels of yellow 'melee', synthetic stones are commonly encountered (Hainschwang & Notari, 2011). The identification of such stones can present a real challenge to most of the classical gemmological techniques. In some cases, the only way to properly identify such synthetics is photoluminescence spectroscopy, on a Raman spectrometer. The small synthetic diamonds encountered in parcels of natural diamonds are usually either grown using a cobalt or nickel catalyst. In particular, the nickel-grown stones are often characterized by extremely low-defect concentrations, and as a result exhibit almost no luminescence. Most of the cobalt-grown diamonds found in melee diamonds were treated by a combined irradiation and HPHT method to enhance their yellow colour. As a consequence, these synthetic diamonds are often dominantly of type IaA instead of Ib, sometimes even with B aggregates present. The PL spectrum of such a HPHT grown, irradiated and HPHT treated ('HIH') diamond can be seen in Fig. 16. The spectrum was recorded on an unusual custom-made high-resolution set-up, using 405 nm laser excitation and an Echelle spectrograph with an average spectral resolution of 0.07 nm. The sample was cooled to 77 K. There are many very weak to very intense, sharp to very sharp emissions, with a FWHM ranging from 0.18 to 0.30 nm. The triplet emissions at 541, 542.8 and 544.3 nm plus 523.6, 521.1 and 519.7 and the doublets at 560.7 and 561.7 plus at 579.1 and 580.4 were attributed to cobalt-related defects (Lawson *et al.*, 1996). The N3 and the H3 centre seen at 415.2 and 503.0 nm were induced by the treatment and the associated nitrogen aggregation. For most of the other lines in Fig. 16, no reference seems to be available. Many probably originate from the radiation of cobalt-related centres, as they have so far been observed only in the spectra of treated cobalt-grown synthetic diamonds.

Besides the determination of treated and synthetic diamonds, one major application of PL spectroscopy in diamond analysis is the characterization of natural diamonds: the extremely high sensitivity to defect centres results in a vast amount of information when recording PL spectra of natural diamonds, especially when using several different lasers for excitation. Even though the cause of many of the emissions may be unknown or highly speculative, the presence (and reaction to treatments) of such emissions yields a very detailed characterization of a natural diamond.

6.3.2. Photoluminescence spectroscopy of other gem materials

Photoluminescence is not a technique frequently used for the analysis of other gemstones, although the authors have found that the potential of the technique is significant. There are some practical applications where PL spectroscopy plays a role in today's gemmological testing procedures, which will be addressed below. They first relate to chromium-bearing gems, then in a lesser number of examples to rare-earth-activated materials, and finally pearls.

Photoluminescence spectroscopy can be used to determine chromium in many gem materials. This type of testing is not quantitative but qualitative only as luminescence

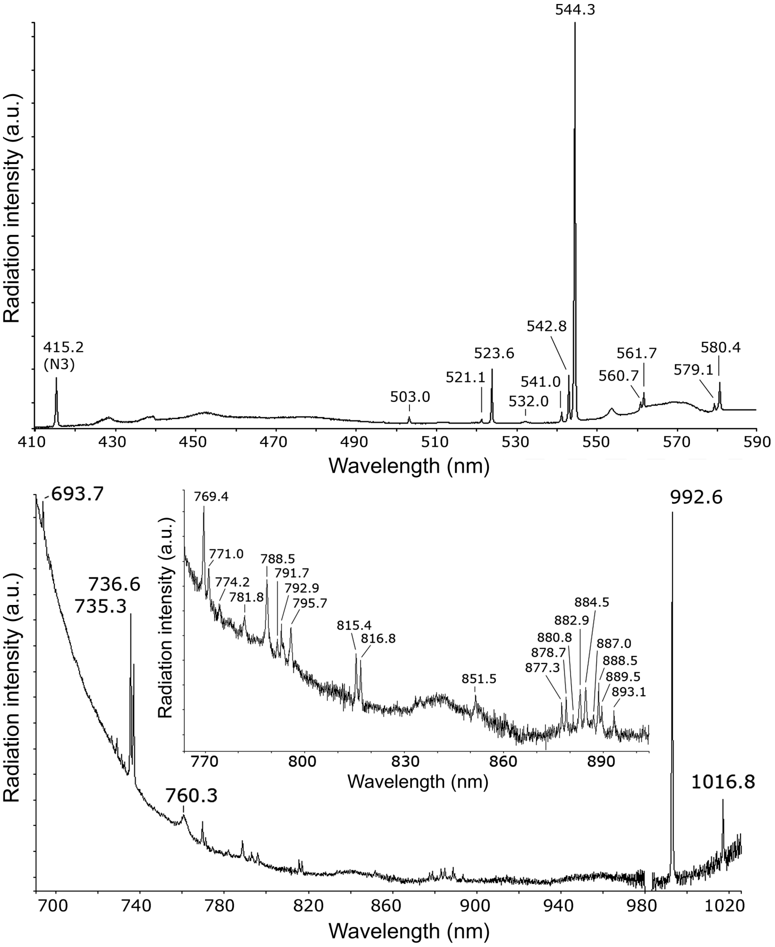

Fig. 16. Photoluminescence spectra excited by the 405 nm laser line of an irradiated HPHT and an untreated, HPHT synthetic diamond grown within a molten cobalt solvent.

intensity depends on many factors, *e.g.* impurities like iron that quench luminescence. Nevertheless, on a given material, the intensity of the Cr^{3+} d–d emission at ~700 nm (doublet at 694 nm for corundum) can give an indication of the Cr^{3+} concentration, especially when the PL analysis is coupled with EDXRF data. The PL spectroscopy can detect Cr^{3+} in extremely low concentrations. In certain materials such as spinel and corundum, the detection limit for Cr^{3+} can be as low as ppb level, or even better. To give an example, a vanadium-coloured, natural colour-change sapphire was tested for chemistry by EDXRF and then ICPMS, but no chromium was detected. Thus, its concentration must be less than 0.7 ppm. On a relatively standard CCD-based Raman system, the simple detection of the Cr^{3+} emission line in this stone took about 1 s.

In 2005, rumours appeared in the market about the heat treatment of red spinel to modify the colour and/or enhance the clarity. These rumours were quickly confirmed and the first results published online in 2009 (Saeseaw *et al.*, 2009). The modifications which take place from ~800°C were found to result in structural disorder and thus in the broadening of the UV-Visible absorption bands, the Raman peaks as well as the Cr^{3+} photoluminescence bands. The Cr^{3+} line at 685.5 nm for a spinel from Vietnam was found by the authors to have a FWHM of 0.88 nm at room temperature. At 77 K the ZPL split into two components at 684.3 and 684.6 nm, and the FWHM was reduced to 0.27 nm (Fig. 17, upper). After heat treatment at 850°C for 56 h, this doublet and

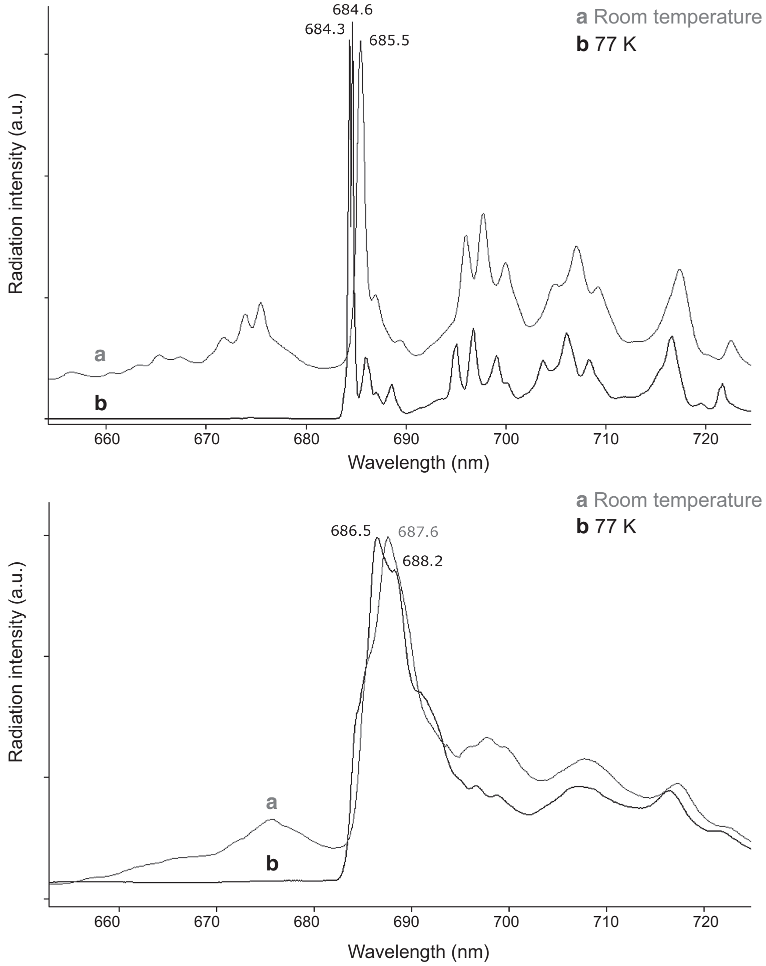

Fig. 17. Photoluminescence spectra recorded at room temperature and at 77 K of a natural unheated spinel from Vietnam (top) and of the same stone after heat treatment at 850°C for 56 h (bottom).

all associated sidebands broadened significantly; the FWHM of the ZPL was determined to be ~5 nm, at room temperature and 77 K (Fig. 17, lower).

Another important gemstone where PL spectroscopy has significant potential is tanzanite. Tanzanite PL spectra are dominated by a relatively broad double emission at 691/709 nm caused by Cr^{3+} and by many weak to very weak, probably rare earth element-related, peaks distributed over the entire range of the spectrum. Detection of the weak features depends highly on the laser wavelength. The dominant 691/709 nm feature was attributed to vanadium (V^{2+}) by some authors (Gaft *et al.,* 2005; see in particular p.106), but, amongst other properties, the behaviour of the feature at low temperature and the fact that several hundred ppm of Cr^{3+} are typically present in tanzanite point towards Cr^{3+}, a geochemically more reasonable assumption.

The emission peaks of zoisite all sharpen very strongly when the spectra are recorded at 77 K. These low-temperature spectra are of great interest and part of a current research project by some of the authors.

Rare earth elements (lanthanides) can be detected efficiently by photoluminescence spectroscopy. The very high resolution achieved by some instruments makes it possible to detect all the lines caused by lanthanide impurities. The sharpness of the lines detected by PL (and also absorption spectroscopy) results from the fact that the 4f electrons of lanthanide ions are shielded by the outer $5s^2$ and $5p^6$ shells. As a consequence they show only weak electron–phonon (=vibronic) coupling. This weak electron-phonon coupling is also the reason why the host lattice affects the positions of the emission (and absorption) bands only slightly (see Campos *et al.*, 2000).

Rare earths in gem materials are better detected by a combination of absorption and photoluminescence spectroscopy; the two methods detect different lines. By use of several lasers, PL spectroscopy can help to identify many more rare earth features than UV-Vis-NIR absorption spectroscopy. In gem materials, lanthanide emissions are typically detected in sphene, zoisite, scheelite, rare-earth doped gem imitations such as yttrium aluminium garnet, and many others.

Zircon exhibits U^{4+}-related absorption bands. Photoluminescence spectroscopy demonstrates that the emissions caused by U^{4+} can be detected efficiently by this method, and that these sharp emission bands often differ from those detected by UV-Vis-NIR absorption spectroscopy.

Photoluminescence spectroscopy of pearls can help to identify the bivalve shellfish species that has produced a pearl. There are differences in the luminescence spectra of freshwater and saltwater pearls; the broad-band emissions allow us to distinguish them in many cases. The presence or absence of porphyrins in pearls is a useful indicator to distinguish pearls produced from various species (Miyoshi *et al.*, 1987). Pearls from *Pteria sp*. contain significant concentrations of porphyrins and as a consequence exhibit luminescence peaks at 618–623, 650–654 and sometimes 683–686 nm. This red luminescence is usually much more distinct in pearls from *Pteria sp.* than in pearls from *Pinctada margaritifera*, which also contain some porphyrins. As pearls are easily damaged by heat, much care is required to not overheat a pearl with the laser, especially when lasers with power of several hundred milliwatts are used. Dark pearls are particularly susceptible to damage by heat during PL measurements because they absorb strongly UV to visible light.

The examples above demonstrate the current development of PL techniques on a Raman spectrometer. The Raman ‘side’ of the instrument gives the nature of the gem species, when other techniques cannot. However, when the species is known, other information on the gem are much easier to acquire through luminescence bands, which are far more intense and thus faster to acquire.

7. Conclusions and perspectives

Raman spectroscopy has become essential to gemmological laboratories, sometimes on its own (*e.g.* the identification of a rare species), and more often in combination with other techniques from classical gemmology and other methods.

However, the databases of Raman spectra available to gemmologists are still not completely satisfactory. They are adequate for all commercial gem species and many collector items, but they are still incomplete with regard to some organic gems, many synthetics or imitations, and a number of inclusion minerals. This work is in progress, but completion would require the construction of a database specific to gemmologists. This goal could be achieved more quickly if a mineralogical database was built which was enlarged to include all gem materials, including those that are not minerals, though this may appear to be a contradiction in terms.

Photoluminescence spectroscopy carried out with a Raman spectrometer is an increasingly useful option in gemmology. Besides the enormous field of applications in diamond analysis, PL spectroscopy has found applications in the testing of some coloured stones and pearls. In the future, its potential for other gem species will certainly be explored. Raman spectrometers already exist, and only cryogenic units working at liquid-nitrogen temperature have to be acquired. The many different laser wavelengths and high resolution and sensitivity of research Raman spectrometers available today, in addition to techniques such as confocal spectroscopy, make the method more interesting than ever before and much research in this domain can be expected.

As they have been used in gemmology for $\sim$20 years, Raman spectrometers for gems have evolved. Some very simple dedicated instruments are aimed at simple species identification. This may announce the arrival of a number of such instruments in jewellery stores, for identification or sorting, although it is probably much too early to tell. Other Raman spectrometers have become more sophisticated. In particular, large gem labs host instruments with several lasers, high resolution, many of them developed for niche applications.

In the past, many instruments or technologies have been touted to gemmologists as the ultimate solution. Looking back at what has subsequently happened, it is reasonable to believe that small dedicated Raman spectroscopy machines may be present in relatively small numbers in the future of gemmology. Research, however, will always be necessary, as gemmologists learn to better exploit the possibilities of this technique.

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