Gemstone Analysis by Spectroscopy

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Introduction

The most common species and varieties that are associated with the term "gemstone" are diamond, sapphire and ruby (corundum color varieties), emerald and aquamarine (beryl color varieties), and tourmaline, as depicted in Fig. 1; for most people the topic stops here. It is only little known that there are many more mineral species — far more than 100 — which are being used as gemstones. Common minerals like quartz but also very rare ones like väyrynenite ($MnBe[PO_4][OH,F]$) or poudretteite ($KNa_2B_3Si_{12}O_{30}$) appear on the list of gemstones. Hence the first challenge that is encountered in this specific discipline of science is the proper identification of a gem material. This is complicated further by the fact that there is a large range of synthetic and imitation that need to be distinguished from the natural gemstones. Historically, this basic identification work has been established by the relatively time consuming combination of a range of rather simple instruments, including binocular microscope, refractometer, polariscope, dichroscope, long and shortwave fluorescent lamp, and hand-held spectroscope. Today the basic identification of a gemstone at a properly equipped laboratory is typically made through a combination of microscopy plus infrared or Raman spectroscopy; this way the identification of a gemstone often takes only seconds. What is truly complex and time consuming — or even impossible — is the identification of the treatments of gem materials: many gemstones are treated in order to modify their color, eg, by dying, heat treatment, irradiation by electrons, neutrons or gamma rays, high pressure high temperature (HPHT) treatment or combinations of them, or to enhance their apparent transparency, eg, by fissure filling or polymer impregnation. On some occasions, there is an easy solution for the identification of certain treatments, but in many cases a combination of spectroscopic techniques needs to be used to identify them. Furthermore, some laboratories offer the determination of the country of origin of gems species, that is, ruby, sapphire, emerald, alexandrite, Paraiba tourmaline, and spinel. This task is often particularly challenging and typically requires a combination of microscopy with various spectroscopic techniques plus chemical analysis. It is hence obvious that spectroscopy has become an essential part of gem testing.

Instrumentation

The most common and important spectroscopic instruments used in gem testing are UV–Vis–NIR, Fourier transform infrared (FTIR), and Raman/photoluminescence (PL) spectrometers.

There are basically two types of UV–Vis–NIR spectrometer systems in the market used for gem testing: (1) the classical scanning-type spectrometers where the monochromator is before the sample, hence where monochromatic light is passed wavelength by wavelength through the sample, and where the detection is typically done via a photomultiplier tube, with typically a combination of deuterium and halogen light sources to cover the UV, Vis, and NIR. (2) The more recent Charge-coupled device (CCD) type spectrometer where the monochromator is found after the sample, hence all the broad band light (deuterium/halogen, xenon halogen, LED, etc.) is passed through the sample at the same time, and where the detection is generally done via a CCD detector. These instruments have advantages and disadvantages, the most obvious being the following: in a scanning-type spectrometer, it is much more difficult to get the light through a facetted gemstone than in a CCD-type spectrometer, and while in a properly designed CCD-type system — for example, with an integrating sphere as sample chamber — a spectrum can be easily and rapidly recorded for samples of virtually any size and shape, in a classical scanning-type spectrometer this is fiddly, time consuming, and for really small samples practically impossible. Also, it is much easier and rapid to record spectra of samples of practically any size that need to be cooled: particularly diamond needs to be cooled in liquid nitrogen in order to detect weak absorption lines. Also polarized UV–Vis–NIR spectra are much easier to record with the CCD-type spectrometer system.

Fig. 1 A suite of very fine gemstones as received at a gem testing laboratory for analysis (left to right): red diamond, unheated ruby from Myanmar, emerald from Colombia with diamonds, and blue sapphire from Kashmir/India. Photos by T. Hainschwang.

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The scanning-type spectrometer has the advantage that luminescence is virtually not excited through the monochromatic light, while the intense broad band light that is being passed through a gemstone in the CCD-type spectrometer will excite luminescence in any distinctly fluorescent gemstone, and this fluorescence will be seen in the final spectrum. Also, using a scanning-type system the true absorption coefficient value can be determined or at least estimated by the pathlength the light travels through a gemstone, while this is difficult or impossible with the CCD-type spectrometer system, at least when using an integrating sphere as sampling chamber.

Infrared spectroscopy is practically only performed using FTIR spectrometers, typically with a deuterated triglycine sulfate detector that is generally thermoelectrically cooled. The more sensitive and faster mercury cadmium telluride is also used, but must be cooled by liquid nitrogen. For cut and uncut gems, infrared spectroscopy is either performed with the beam transmitted through the stones using either a beam condenser or a diffuse reflectance accessory used as a beam condenser, or with the beam reflected off the surface.

Raman spectroscopy is performed either by Fourier transform (FT-) Raman spectrometers or more commonly by dispersive Raman spectrometers, with or without a microscope. Dispersive Raman spectrometers use either thermoelectrically cooled CCD (range 200 to ~1100 nm) or scientific complementary metal-oxide semiconductor (sCMOS) (range 400 to ~1100 nm) and hence permit the use of laser excitations from the UV to the NIR. The most common ones in use are 325, 488, 514, 532, and 785 nm. Since a few years, a large range of laser wavelengths is available for spectroscopic applications and in consequence other excitation wavelengths can be found in Raman systems.

PL is generally recorded using a dispersive laser Raman spectrometer. Lasers from the UV to the NIR are used, with or without microscope. 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, with Full width at half maximum (FWHM) measured as narrow as 0.07 nm in the spectra of some Chemical vapor deposition (CVD) diamond. In consequence, a resolution of 0.1 nm or better should be available, and since PL can be detected from the UV to the NIR the ideal spectral range would be of 200–1100 nm. In order to characterize a material by PL spectroscopy, it is important to have lasers of different wavelengths available: lasers of different wavelengths do excite completely different defects in certain materials. PL spectra are best recorded with the sample at low temperature (77 K or less), especially diamond.

Applications

Raman Spectroscopy

This vibrational technique is mainly used to identify the different mineral species since each mineral species has a characteristic Raman spectrum (Fig. 2). It is in use in gem testing laboratories since the late 1990s. Micro Raman spectroscopy is the preferred method for very small samples and the only method to identify mineral inclusions within gemstones. While this technique permits the identification of different species, in most cases it does not permit to distinguish natural from synthetic gemstones. The technique can also be used to verify the crystalline quality of a material since the Raman bands broaden distinctly in defective lattices. Good examples for this include diamond and zircon: diamond can be very rich in defects and impurities and therefore can show broadened Raman lines, while some zircons lose their crystallinity and become metamict because of their uranium and thorium content, and hence show strongly broadened Raman spectra. Another gem where Raman line broadening can be observed is spinel, where it is caused by heat treatment at >800°C because of lattice disorder caused by the treatment.

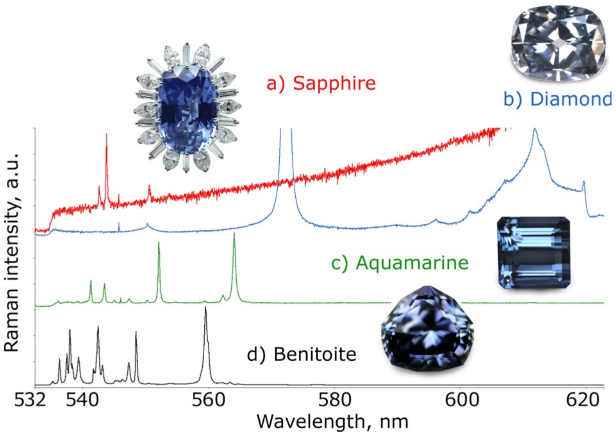

Fig. 2 Raman spectra of various blue gemstones (recorded using a 532 nm laser). The spectral differences easily distinguish the stones shown. Photos by T. Hainschwang.

In gem testing, there are some specific scenarios where Raman is very useful, one being the identification of inclusions in gemstones in order to help in the determination of the country of origin, and the other one being the identification of porphyrin and other pigments in pearls. Another useful application of this technique is the distinction of Musgravite and Taaffeite which is not possible by any other simple means.

Infrared Spectroscopy

Infrared spectroscopy is the other vibrational technique besides Raman spectroscopy; it has been in use in the some gem testing labs since the mid 1980s. It must be divided into the two techniques: specular reflectance infrared spectroscopy and transmission infrared spectroscopy. Specular reflectance is a very rapid and practical method to identify the different gem species similar to Raman spectroscopy (Fig. 3). In contrary to Raman spectroscopy, it cannot be used for the identification of inclusions, but is more efficient than Raman spectroscopy for the identification of facetted samples. Also, while a good Raman system needs high resolution capacities, reflectance infrared spectroscopy does not need high resolution since the observed bands are never very narrow. The specular reflectance spectra do not need the entire spectral range available on the average FTIR spectrometer, but a limited range from 4000 to 400 cm^{-1} is sufficient since intrinsic lattice bands are found from 1800 to 400 cm^{-1} only. With a proper spectral database

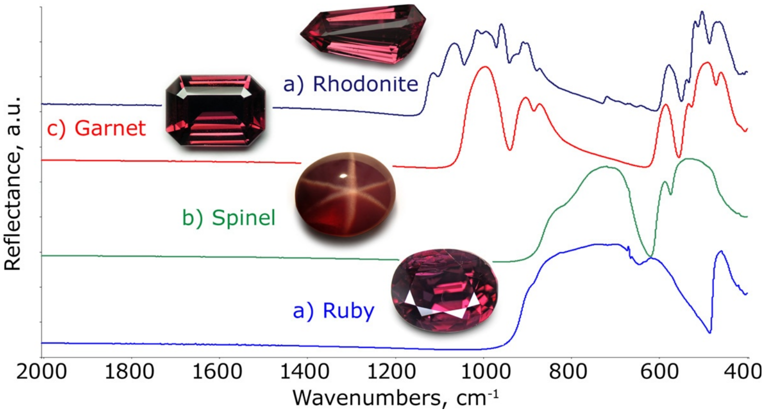

Fig. 3 The specular reflectance infrared spectra of various red gemstones. The reflectance peaks clearly and easily identify each of different gems shown. Photos by T. Hainschwang.

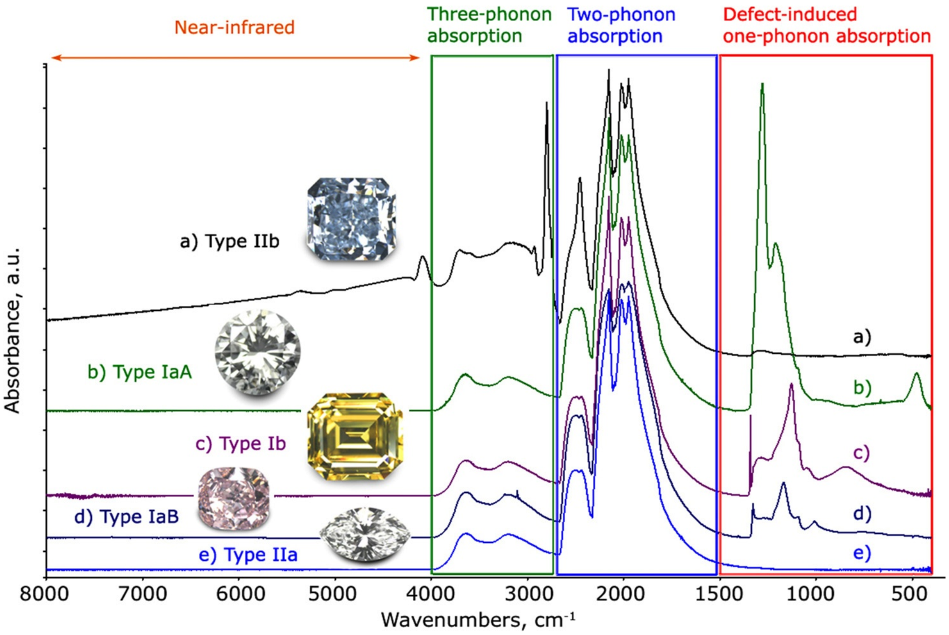

Fig. 4 The transmission infrared spectra of diamonds of the pure poles of the different types. This technique is used to classify diamonds based on the presence/absence of nitrogen or boron. Type Ib diamonds contain isolated substitutional nitrogen, type IaA diamonds contain dinitrogen aggregates, type IaB diamonds contain aggregated nitrogen consisting of four nitrogen atoms surrounding a vacancy, IIa diamonds are practically nitrogen free, and IIb diamond are nitrogen free but contain isolated substitutional boron atoms. Photos by T. Hainschwang.

this technique tends to be the preferred method for gem identification at many laboratories.

Besides gem identification, this method helps identifying certain treatments such as polymer impregnation of turquoise and also certain synthetics such as synthetic spinel.

Transmission infrared spectroscopy is performed with the same instrument, but in contrast to the specular reflectance technique the impurity-related absorptions from 8500 to about 2000 cm^{-1} will be detectable but the intrinsic bands caused by the lattice absorptions can generally not be resolved since they are too strong. Infrared spectroscopy is one of the most important techniques for the analysis of diamond. It is used to identify the diamond type, based on the presence or absence of nitrogen or boron impurities and the nitrogen aggregation state. Essentially nitrogen-free diamonds show only the intrinsic diamond absorption bands from 4000 to 1500 cm^{-1}, nitrogen induces characteristic absorption bands in the one-phonon domain from 1500 to 400 cm^{-1}, boron induces one-phonon absorption plus several other absorptions over the entire infrared spectrum (Fig. 4). Hydrogen defects cause distinct and sharp absorptions, the best known one being at 3107 cm^{-1}. Irradiation and annealing induces several absorptions in the infrared, the most cited ones being the so-called H1a, H1b, and H1c defects at 1450, 4932, and 5160 cm^{-1}, respectively. Another application is the observation of the so-called platelet peak centered at 1358–1380 cm^{-1}: in HPHT-treated type I diamonds, this peak is unusually weak and broadened. There is much more in infrared spectroscopy of diamonds, but going into these details would go far beyond the scope of this text.

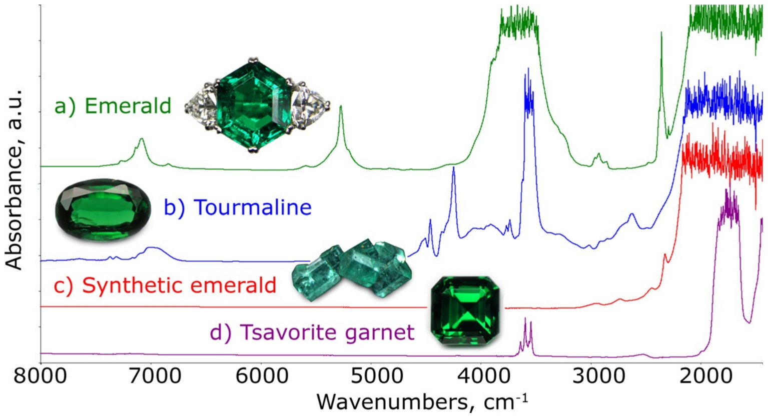

Fig. 5 The infrared spectra of various green gems, the infrared radiation having been transmitted directly through the samples. The presence/absence and position of the OH-related absorptions and of the absorptions of other organic molecules is distinct from gem species to gem species. Photos by T. Hainschwang.

Transmission infrared spectroscopy of by far most other gem materials is mainly used to identify OH-related absorption and the presence of any organic compounds. The analysis of the OH-related absorptions helps distinguishing certain natural and synthetic gemstones (Fig. 5). The most obvious examples for this are flux grown emeralds and alexandrites synthesized by anhydrous methods that do not exhibit any noticeable OH-related absorption, with their natural counterparts exhibiting distinct OH-related absorption. Even synthetic gems grown by hydrothermal methods can often be distinguished via infrared spectroscopy since there are noticeable differences in the OH absorptions between the natural and the synthetic gems; this is true for most beryls as well as quartz; for hydrothermally grown synthetic corundum, the situation is quite easy since natural corundum does not show OH absorption except when OH containing alumina phases such as boehmite (γ-AlO[OH]) or diaspore (α-AlO[OH]) are present.

For corundum the infrared spectra can give valuable clues for the heat treatment; the presence of absorptions from hydrated alumina phases in a sapphire or ruby is proof that the stone has not been heated at high temperature since these phases start to dehydrate below 400°C. A small absorption at 3160 cm^{-1}, possibly an Mg^{2+}–OH impurity, present in the spectra of corundum indicates lack of heat treatment.

Several other hydrogen-related absorptions are important for the analysis of corundum, especially the one at 3309 cm^{-1}, likely related to Fe, Ti–OH^{-} impurity. This line is typically very weak or absent in the spectra of metamorphic blue sapphires, but characteristic when they have been heat treated in a reducing atmosphere. In the spectra of magmatic sapphires, a distinct 3309 cm^{-1} line is present naturally and it depends on the heating conditions if it is present after heat treatment or not.

The 3309 cm^{-1} line and associated bands are also characteristic for flame fusion synthetic corundum: their spectra usually show distinct 3309 cm^{-1} and/or important 3231 cm^{-1} absorption.

Another long known absorption of importance for corundum is a band at 3060 cm^{-1} since it is a good indicator that a corundum has been treated by beryllium diffusion; it has been published in 2011 only.

The other important application of infrared spectroscopy is the identification of oil, wax, resin, and other polymers that are used to fill the fissures and/or pores of gem materials. This is of particular importance for emerald, jadeite, and turquoise, but can be an issue for other gem materials such as ruby and aquamarine, since any gemstone can be fissure filled by such substances in order to make them less apparent. Luckily, the spectra of jadeite and emerald show a transmission window in the domain of 3100–2800 cm^{-1} where the most important CH absorptions of the used substances can be found.

PL Spectroscopy

This electronic spectroscopy technique is extensively used for diamond analysis since the late 1990s. It was found to be the only really useful technique to determine whether type IIa (practically nitrogen free), IIb (nitrogen free but boron containing), and low nitrogen IaB diamonds have been HPHT treated or not. HPHT treatment at temperatures between 2300 and 2500°C at stabilizing pressures of 6.5–8.5 GPa for a few minutes of such brown diamonds changes their color to either colorless or pink (IIa or low nitrogen IaB) and to gray or blue for type IIb samples.

PL spectroscopy permits the detection of extremely low concentrations of defects such as nitrogen-vacancy or vacancy centers and the detection of this HPHT treatment is based on a range of PL features mostly from simple vacancy and nitrogen-vacancy defects (eg, V^0, NV^0, NV^-, etc.).

It became quickly apparent that the unrivaled sensitivity for the detection of defects in diamond by PL spectroscopy is of great importance in the analysis of diamond in general. Since lasers of different wavelengths often excite totally different defects — especially in diamond — it is inevitable to use a range of lasers. Today many hundreds of PL lines are known in natural and synthetic diamonds and it is of great importance to know them and to be aware how they behave upon treatment by irradiation, annealing, and HPHT. Even though the cause of many of the emissions found may be unknown or highly speculative, the mere presence (and reaction to treatments) of such emissions allow a very detailed characterization of a

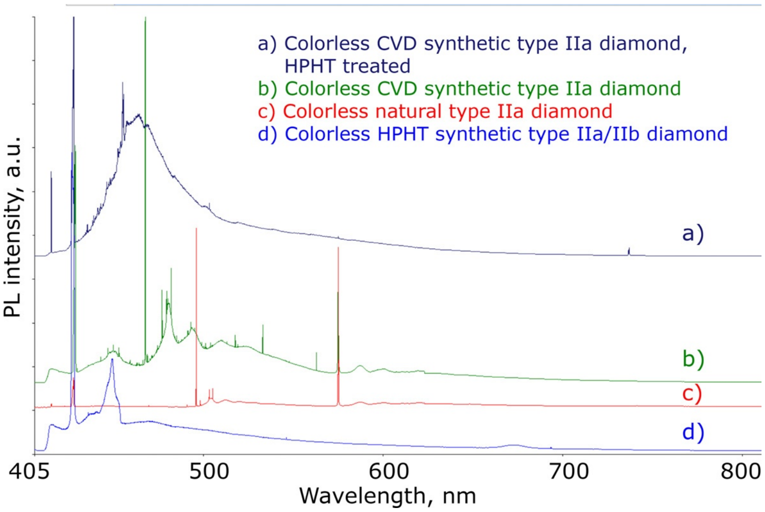

Fig. 6 The photoluminescence spectra recorded from four type IIa diamonds, excited by 405 nm laser and cooled to 77 K. The spectra are showing the diamond Raman features and many bands and peaks from different defects present in the lattice of these stones, and based on these peaks synthetic diamond can be distinguished from natural ones and HPHT-treated diamond can be distinguished from untreated stones.

diamond. Hence PL spectroscopy is used to distinguish natural and synthetic diamonds and it helps determine whether the color of a diamond is of natural origin or not (Fig. 6). While for most synthetic diamonds there are imaging methods that identify them as synthetic, especially in certain small-sized samples PL spectroscopy may be the only reliable way of identification. The growth media for both HPHT and CVD synthetic diamonds are responsible for the presence of defects that are often unknown in natural diamonds, while the far more complex growth media of natural diamonds are responsible that such stones often contain much higher defect concentrations than synthetic diamonds. Of the many defects known in natural diamonds only some are known in synthetic diamond.

PL is not a technique that is very frequently used for the analysis of other gemstones. Some practical applications where PL spectroscopy plays a role in today's gemmological testing procedures for gem materials other than diamond will be addressed here.

PL spectroscopy can be used to determine chromium in many gem materials. This type of testing is not quantitative but only qualitative since luminescence intensity depends on many factors, such as, eg, impurities that quench luminescence like iron. Nevertheless, on a given material the intensity of the Cr^{3+} emission can give an idea on the Cr^{3+} concentration, especially when the analysis is accompanied by chemical data. PL spectroscopy can detect Cr^{3+} in extremely low concentrations. In certain materials, such as spinel and corundum the detection limit for Cr^{3+} must be in the low Parts per billion (PPB) level or even better. With the best PL spectrometers the acquisition time per scan can be very long (up to an hour or more), so there is almost no limit to the detection of an emission.

Heat treated spinel can be identified by PL spectroscopy through a strongly broadened Cr^{3+} PL band that appears in the spectra of spinel heated at $\geq 800°C$. The Zero-phonon line (ZPL) at 685.5 nm for spinel broadens from approximately <1 nm FWHM to ± 5 nm.

Beside chromium, rare earth elements can be efficiently detected by PL spectroscopy. The very high resolution that can be achieved by certain instruments permit the detection of all 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. In consequence they show only weak electron–phonon (=vibronic) coupling. This weak electron–phonon coupling is also the reason why the emission (and absorption) positions experience only little influence from the host lattice. By the 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, scheelite, zoisite (together with a relatively broad double emission at 691/709 nm caused by Cr^{3+}), rare earth doped gem imitations such as yttrium aluminum garnet, and others.

Uranium-related luminescence is also of interest for gem testing. Zircon exhibits U^{4+} related luminescence bands and that these sharp emission bands often differ from the ones detected by UV–vis–NIR absorption spectroscopy. The uranyl ion $[UO_2]^{2+}$ causes strong yellowish green luminescence in some opals and also in red beryl from Utah (Fig. 7).

PL spectroscopy of pearls can help identifying the bivalve shellfish species that has produced a pearl. There are differences in the luminescence spectra of freshwater and saltwater pearls. The presence or absence of porphyrin in pearls is a useful indicator to distinguish pearls produced from various species. Pearls from *Pteria* sp. are the most common ones that contain significant concentrations of porphyrin and in consequence exhibit 618–623, 650–654, and sometimes 683–686 nm luminescence peaks. This red luminescence is usually much more distinct in pearls from *Pteria* sp. than in pearls from Pinctada margaritifera, that also contain some porphyrin.

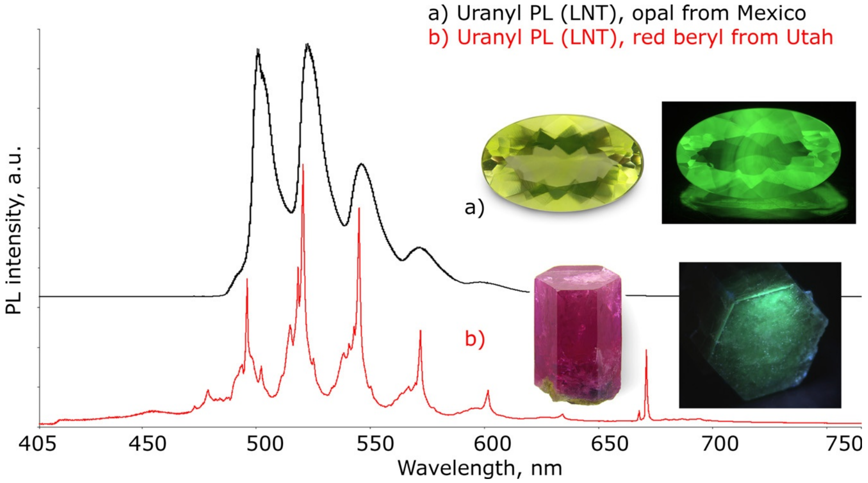

Fig. 7 The photoluminescence spectra recorded from an opal from Mexico and a red beryl from Utah (USA), excited by 405 nm laser and cooled to 77 K. The spectra are showing that both gems contain uranyl ions $[UO_2]^{2+}$, responsible for the green luminescence shown in the images. Photos by T. Hainschwang (beryl luminescence) and F. Notari (Beryl, opal, and opal luminescence).

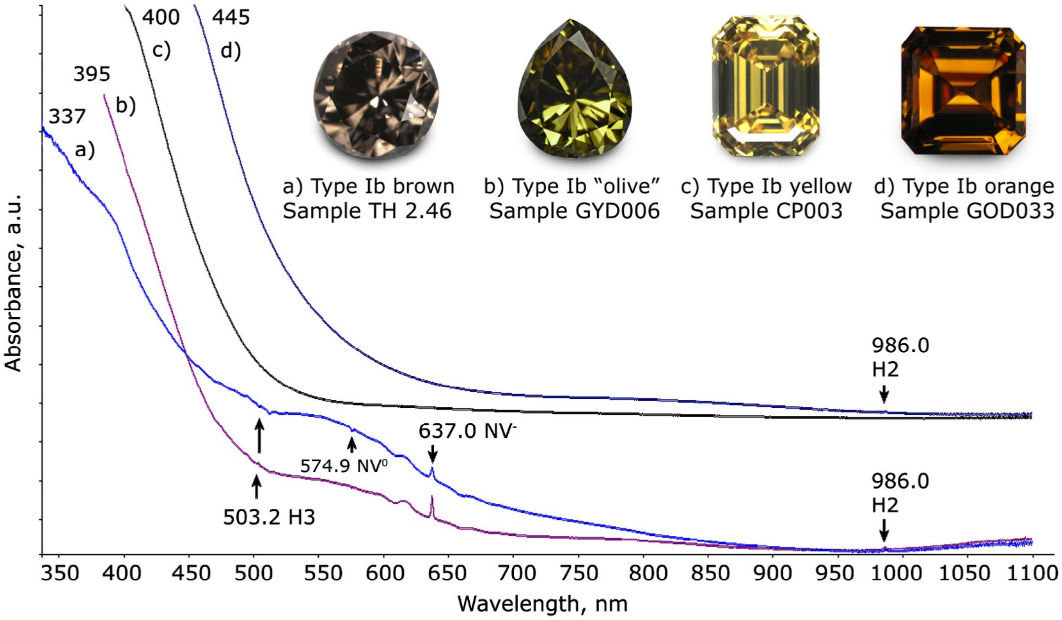

Fig. 8 The low temperature spectra of type Ib diamonds of the different colors. A range of different defects are responsible for the various absorptions that result in the observed colors of the diamonds. Photos by T. Hainschwang.

UV–Vis–NIR Spectroscopy

This electronic spectroscopy technique has been available in gem laboratories since the 1980's, but at the time only in very few laboratories. Until the late 1990s, the only systems in use were scanning-type spectrometers, from then on both scanning-type and CCD-type spectrometers have been in use. This technique is very important for the analysis of many gem materials and can be an essential part in order to identify the authenticity and origin of color of colored diamonds or the geological context and possibly country of origin of sapphires, rubies, and emeralds.

For diamonds the spectra are typically recorded at liquid nitrogen temperature (77 K) in order to sharpen all absorption features and make even the weakest peaks visible (Fig. 8). Important clues for the identification of irradiated, irradiated and annealed, and HPHT-treated colored diamonds as well as synthetic colored diamonds can be obtained by low temperature UV–Vis–NIR spectroscopy. Since detailing the many different features that exist for diamonds would go far beyond the scope of this article, only some important examples will be given. Irradiation — naturally or artificially — induces vacancy defects in diamond; the neutral and negatively charged vacancies give rise to absorption at 741/744 nm (GR1, V^0) and

393 nm (ND1, V^-), respectively. When irradiated stones are annealed, some features appear that are very indicative for the irradiation/annealing treatment, such as the 594 nm absorption and various nitrogen-vacancy defects such as H3, H2, NV^-, and NV^0. The spectra of HPHT-treated type I diamonds often exhibit distinct H2 centers at 986 nm, and compared to H2 that is naturally present, these bands have a larger FWHM. Yellow to orange synthetic diamonds are often identified through various nickel or cobalt-related absorptions.

In the spectra of blue sapphires, the position of the absorption edge in the UV, plus the presence or absence and the shape and intensity of the Fe and Fe–Ti related absorptions can give valuable clues to their formation and can help distinguish them from synthetic, heat treated, and diffused samples. The characteristic bands that may be observed in the spectra of blue sapphires are a shoulder at ~330 nm (Fe^{3+} pairs), the 377 absorption (Fe^{3+} pairs), the 388 nm absorption (single Fe^{3+} ions/O^{2-}), the 450 nm band (Fe^{3+} pairs), a very broad band in the visible range ($Fe^{2+}/Ti^{4+}/3O^{2-}$ molecular orbitals), and a very broad band in the NIR range (Fe^{2+}/Fe^{3+} pairs). Blue sapphires from a magmatic geological context show spectra with the broad band absorption due to the Fe^{2+}/Fe^{3+} pair that is far stronger than the one by the $Fe^{2+}/Ti^{4+}/3O^{2-}$ molecular orbitals, while in metamorphic sapphires the opposite is true. Flame fusion synthetic sapphires are characterized and identified by absent or very weak Fe^{3+} absorptions. In emerald, there are two basic types of spectra, one is characterized by Cr^{3+} and/or V^{3+} absorptions only, and one is characterized by Cr^{3+} and/or V^{3+} plus Fe^{3+} (370 nm band) and Fe^{2+} (broad NIR band). Fe-related absorptions are very uncommon in emeralds from certain deposits such as the ones in Colombia, but always present in the spectra of stones from other deposits such as Kafubu in Zambia. Flux grown synthetic emeralds can be identified based on their UV–Vis–NIR spectrum because of their lack of OH-related absorptions in the NIR, some hydrothermal synthetics can also be identified. Dyed gemstones can generally be identified via this technique, polymer impregnated dyed green jadeite being one of the most common examples where UV–Vis–NIR spectroscopy is used to identify the treatment; instead of the characteristic Cr^{3+} spectrum with a Fe-related absorption at 437 nm, such dyed green jadeite generally exhibits only broad bands very different to the Cr^{3+} absorptions.

Another application of this technique is the distinction of copper-bearing, vanadium-bearing, and iron-colored green to blue tourmaline; the copper-bearing — so-called “Paraiba” — tourmalines exhibit spectra with strong Cu^{2+}-related broad bands at 670 and 900 nm, very different to the strong iron (Fe^{2+})-related band at ~720 nm, or the vanadium (V^{3+})-related bands at ~440 and 600 nm seen in other tourmalines.

Conclusions

Not too long ago gem testing used to be a field that was dominated by relatively simple optical testing methods, and only in the 1980s and 1990s gem testing laboratories started to work with spectrometers. With the many new developments in the gem world such as plenty of new treatments, new synthetic materials and new sapphire, ruby, and emerald deposits, the tasks of a gem testing laboratory have become far more difficult than in earlier days. Without the aid of the different advanced methods available today, it would be virtually impossible to offer any type of reliable gem testing. While the microscope remains to be the most important of all instruments, and while the other optical tools such as the refractometer have their place in some labs, it is obvious that UV–Vis–NIR, FTIR, Raman, and PL spectrometers have become indispensable and fundamentally important analytical equipment in modern laboratories.

Without these modern analysis methods incorporated, laboratory gemology could have never developed into a serious field of science.

See also: Chemical Applications of EPR; Geology and Mineralogy Applications of Atomic Spectroscopy; Infrared and Raman Spectroscopy of Minerals and Inorganic Materials; IR and Raman Spectroscopies of Inorganic, Coordination and Organometallic Compounds; Luminescence Spectroscopy, Inorganic Condensed Matter Applications; NMR Spectroscopy, ^{29}Si; Raman Spectrometers; Structural Chemistry Using NMR Spectroscopy, Inorganic Molecules; UV-Visible Absorption and Circular Dichroism Spectroscopy, Inorganic Chemistry Applications; UV–Visible Absorption Spectrometers; UV–Visible Fluorescence Spectrometers; X-Ray Diffraction, Studies of Inorganic Compounds and Minerals; X-Ray Fluorescence Spectrometers.

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