Specular reflectance infrared spectroscopy – a review and update of a little exploited method for gem identification

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Abstract: Specular reflectance FTIR (Fourier Transform Infrared) spectroscopy is a relatively little-exploited but very efficient technique to identify minerals and other materials that possess a somewhat reflective surface. In the past years the Gemlab and GemTechLab laboratories have used and refined the method for gemmological purposes and developed an extensive database of specular reflectance infrared spectra of minerals, gemstone imitations, organic materials and synthetic gem materials. This paper explains the method, introduces the spectrometer and accessories used and highlights the practical applications and advantages of specular reflectance FTIR spectroscopy in gemmology.

Keywords: intrinsic absorptions, spectral database, specular reflectance FTIR spectroscopy, vibrational spectroscopy

Introduction

Vibrational spectroscopy is very important for gemmological analysis and has been increasingly used in laboratories over the last few decades. The two methods included in the term vibrational spectroscopy are Raman and infrared spectroscopy (Schrader, 1995). Both are based on the interaction of light waves with vibrating molecules or crystal lattices. Raman spectroscopy detects bands due to inelastic scattering of laser light (thus monochromatic light) by vibrating molecules and crystal structure. Upon scattering, Raman bands are detected slightly shifted towards wavelengths of lower energy (higher wavelength, lower wavenumber) (Stokes shift) and with much weaker intensity to higher energy (lower wavelength, higher wavenumber) (Anti-Stokes shift). In infrared spectroscopy the vibrational energy of molecules changes upon absorption of infrared radiation, thus vibrational transitions are detected; in order to be infrared active, a molecule needs to possess a permanent dipole moment (Schrader, 1995).

Infrared and Raman spectroscopy are methods very commonly employed in analytical laboratories (Kiefert *et al.*, 1999). The best-known method of analysing samples with an infrared spectrometer is transmitting the infrared beam directly through the sample and observing the resulting absorption bands (King *et al.*, 2004). The intrinsic absorption bands of most materials (found in the mid infrared from ~ 2000–400, rarely to 200 cm^{-1}) however, are very intense, and cannot be resolved unless samples are thin enough (by polishing into thin films), or powdered and mixed with potassium bromide (KBr) and then pressed into pellets for analysis (Martin *et al.*, 1989). When investigating the infrared spectra of gemstones, however, sectioning or powdering are generally not possible and transmission spectra are performed without special preparation. Although the nature, shape and volume of a gem may allow some latitude, one can generally only observe the near to mid-infrared domain from around 7500 to about 2000 cm^{-1} with a standard Fourier Transform Infrared (FTIR) spectrometer. The features in this domain practically all relate to trace contents or impurities in samples, such as water in beryl (see for example Adamo *et al.*, 2005), and are only of limited use for identifying materials.

A very effective solution for this problem is to use specular reflectance

Materials and methods

For building the Gemlab–Gemtechlab specular reflectance FTIR spectral database and for the research conducted for this paper, a PerkinElmer Spectrum BXll FTIR spectrometer and a Nicolet Nexus FTIR spectrometer, each one equipped with a DTGS (Deuteriated Triglycin Sulphate) detector, were used. One to 100 scans were carried out at room temperature and spectra recorded with a resolution of 4 cm^{-1}. Higher resolutions up to 1 cm^{-1} were also investigated, but found not to be worth the extra time involved since all reflectance bands are far larger than 4 cm^{-1}; the narrowest reflectance band found was 8 cm^{-1} at full width half maximum (FWHM). A PerkinElmer fixed angle specular reflectance accessory and a modified Spectra Tech diffuse reflectance accessory were used to record the specular reflectance infrared spectra *(Figure 1)*. In the PerkinElmer fixed angle accessory the sample is placed with any smooth or near-smooth face on a disc with a central hole to hold the stone which fits into the sample stage *(Figure 1a)*. Small samples need to be fixed with Blu Tack in the centre of the disc. In the Spectra Tech accessory the mirror usually used as 'sample stage' needs to be removed and the stone placed with Blu Tack on the pedestal instead of the mirror; thus the selected sample surface is used instead of the mirror to reflect the infrared beam *(Figure 1b)*. Since both accessories have their advantages and disadvantages, for practical purposes it is good to have both on hand. The fixed angle specular reflectance accessory is low in cost and extremely simple to use; large objects can be analyzed and the time of sample preparation and spectral analysis is very short, since no adjustments whatsoever are necessary. For curved faces, matte surfaces and extremely small facets the accessory is not ideal, although in most instances an interpretable result can be obtained. The best results are obtained from faceted gemstones of 0.10 ct and larger, the larger the reflecting facet the better.

The modified diffuse reflectance accessory is ideal for the analysis of samples with curved and or matte surfaces, but its disadvantages are: the analysis of large stones is not possible due to limited space in the sample chamber, the time of sample preparation is longer, they have to be fixed with Blu Tack, and spectral analysis is more time consuming since the signal strength must be adjusted manually. Therefore the only applications where this more expensive accessory is useful are those rare cases where no acceptable result can be obtained from the fixed angle specular reflectance accessory. Due to the geometry of the diffuse reflectance accessory, very small surfaces and surfaces with little reflectivity can be effectively analyzed.

In order to identify materials automatically, a search database consisting of the spectra of more than 600 mineral species has been built by the Gemlab and Gemtechlab laboratories. The samples used to record the spectra for this database were all selected from the Gemtechlab and Gemlab laboratory reference collections; the stones in these collections have all been precisely identified by various techniques such as chemical analysis, X-ray diffraction, Raman spectrometry, etc. All spectra were recorded in reflectance mode in a range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and normalized to 100% at the wavelength of the most intense reflectance peak. The automatic search database was set up using the Omnic software by Thermo Nicolet, with which recorded spectra can be identified automatically, indicating the match in percent of the sample spectrum with reference spectra.

Due to the intensities of the reflectance bands, atmospheric artefacts can in practice be ignored and thus background spectra do not need to be repeated for gem identification purposes. Another advantage of these band intensities is that for most samples, only a few scans are sufficient to achieve a good signal-to-noise ratio; when a stone has flat facets, then no more than one sample scan is necessary.

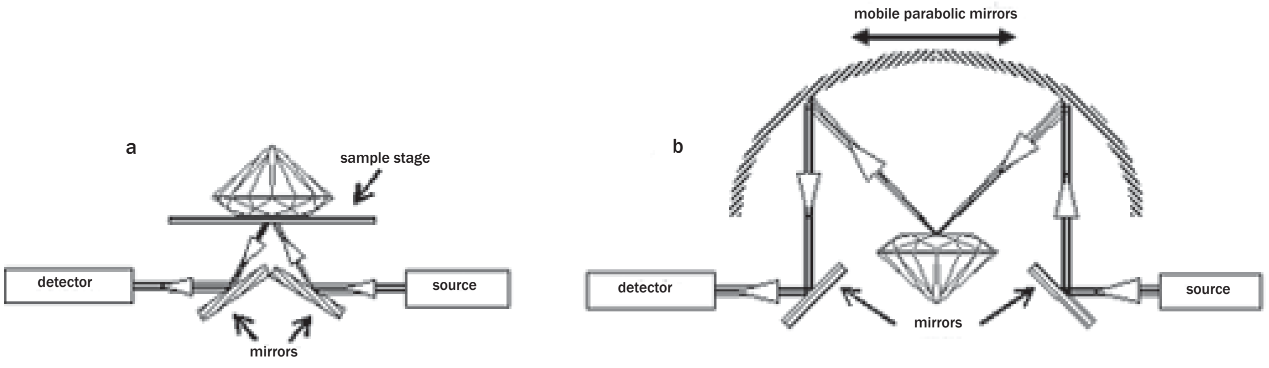

Figure 1: The design and function of the two accessories used to record specular reflectance infrared spectra: (a) fixed angle specular reflectance accessory, (b) modified diffuse reflectance accessory.

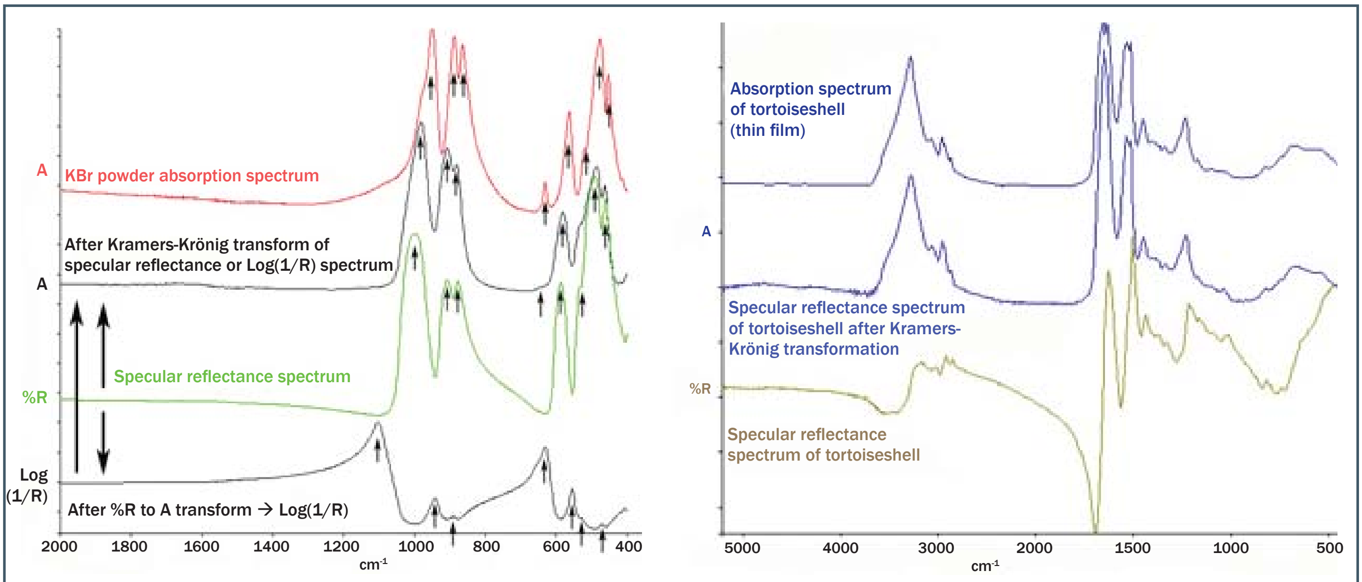

Figure 2: Comparison of specular reflectance versus true absorption spectra for an almandine garnet (left) and for tortoise shell (right, from Hainschwang and Leggio, 2006). The two examples are used to demonstrate the effect of the Kramers-Krönig transform: in the case of tortoiseshell the result is a perfect match with the true absorption spectrum, while in the almandine garnet the transform only had a slight effect on the reflectance spectrum; after the transformation the spectrum still was not a perfect match with the true absorption spectrum. In the garnet graph the bottom trace shows what happens upon %R to A transformation and consequent indexation of the 'absorptions'. Such transformation does not make much sense when determining a mineral from a reflectance spectrum since the unmodified reflectance peaks are much closer to a real absorption spectrum; upon application of the Kramers-Krönig transform to this Log(1/R) spectrum, the resulting spectrum will be the same as the one resulting from the application of the Kramers-Krönig transform to the specular reflectance spectrum. The examples garnet and organic material were chosen for demonstration because of their isotropy.

FTIR spectroscopy: this is a powerful vibrational analysis method to determine intrinsic structural vibrations of materials without destructive sample preparation; the beam is not transmitted through a sample, but reflected off the surface (White, 1974; Martin *et al.*, 1989; Coates, 2000; King *et al.*, 2004). With a comprehensive collection of reference spectra this method allows one to identify all minerals and imitations, most organics, and, in certain cases, even synthetics after only a few seconds analysis time (Martin *et al.*, 1989). The spectral information alone allows identification of the mineralogical group in most instances. Additionally, complexity of a crystal structure and presence of structural OH groups can be determined.

The Gemlab and Gemtechlab gemmological laboratories have refined this method for gemmological applications and have created an extensive database of reference specular reflectance FTIR spectra since 2001.

Characteristics and interpretation of specular reflectance spectra

Specular reflectance spectra resemble true absorption spectra to different degrees. In some gemstones, reflectance bands correspond closely to absorption bands, but in other cases, especially in organic materials, they appear strongly distorted due to abnormal dispersion *(Figure 2)*. This distortion can in most cases be corrected by the application of the Kramers-Krönig transform, which is used to transform specular reflectance spectra into true absorption spectra *(Figure 2)*. However, the applicability of this transform needs to be verified for each material because although the modified spectra of some stones are perfect matches with their true absorption spectra, for others the results are not an improvement on the original reflectance trace *(Figure 2)*. For identification purposes it is thus best to keep the spectra unmodified. So, for most minerals (and consequently for gemstones) the reflectance spectra can practically be regarded and interpreted in the same way as absorption spectra; the most prominent exception is diamond, because diamond is purely covalent and thus does not exhibit distinct FTIR reflectance peaks. For the general case of gemstones, where only infrared light reflected from a mirror-like surface reaches the detector, only structural peaks can be detected. In those minerals where the infrared beam can also be reflected from internal surfaces (such as in foliated minerals like mica), absorptions due to impurities may also be seen in the spectra. These features will then appear as they do in transmittance spectra, that is, they will appear in the opposite direction to that of reflectance peaks caused by structural vibrations. It has been noted in some recent publications that authors have recorded specular reflectance spectra of polished gemstones and shown them upside down, with a Y-scale indexed with 'Log(1/R)'; this happens when a spectrum recorded in reflectance mode is transformed by a spectrometer program

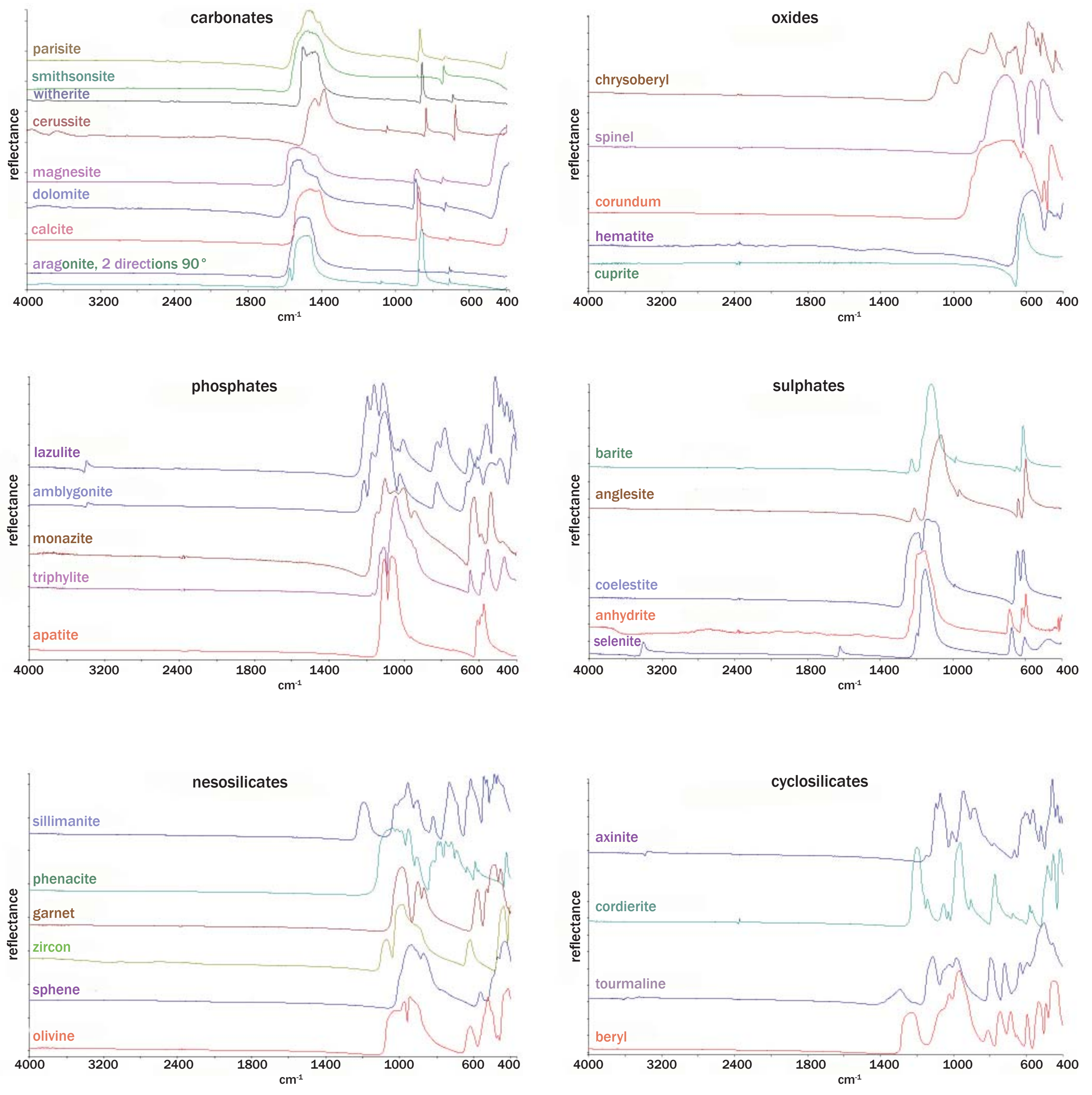

Figure 3: A selection of specular reflectance FTIR spectra of various arbitrarily oriented gemstones and minerals arranged according to their mineralogical groups.

into absorbance, without using the Kramers-Krönig transform. The unusual shape of such transformed spectra and indexing the apparent 'absorption peaks' leads to much confusion and appears not to make much sense for the purpose of gem identification, since the unmodified reflectance spectra are much closer to a real absorption spectrum (*Figure 2,* left graph).

The bands detected in specular reflectance FTIR spectroscopy are very intense and only the peaks due to major compositional components of a material are detected, i.e. vibrations directly associated with the chemical formula of a substance. Because of this sensitivity to chemical composition and to the molecular coordination such a spectrum can be regarded as the fingerprint of a material. From the particular shape of a curve and the presence or absence of certain vibrations, a specular reflectance FTIR spectrum can usually be attributed to a mineralogical group. In *Figure 3* the spectra of gem minerals belonging to some of the more important mineralogical groups are shown and the differences between the groups are quite evident.

In gemstones with a simple structure, such as many of the carbonate and the sulphate minerals, the main vibrations (ν_2, ν_3, ν_4) of the molecular group can

Box A: Notes on spectroscopic terms

- **%Transmittance (%T)**: the ratio, expressed in percent, of the intensity of the light transmitted through a sample to the intensity of light striking a sample, i.e. intensity of emerging light divided by intensity of incident light, × 100.
- **Absorbance**: inversely and logarithmically related to transmittance by the formula A = log(100/%T).
- **%Reflectance (%R)**: the ratio, expressed in percent, of the amount of radiation reflected from a sample surface to the amount of radiation reflected from a standard surface, usually an infrared mirror.
- **Kramers-Krönig transform (KKT)**: transform used to transform specular reflectance spectra into absorption spectra; it is based on the relations between refraction and absorption of electromagnetic waves in a substance.
- **Vibrations in molecules or ions**:

  External vibrations (lattice vibrations/lattice modes) [~600 to 80 cm^{-1}]:

  Translations (T_x, T_y, T_z) and Rotations (R_x, R_y, R_z)

  Internal vibrations (Internal modes) [~ 3800 to 400 cm^{-1}]:

  ν_1 = symmetric stretch (Raman) ν_2 = out of plane bend (b) (IR)

  ν_3 = asymmetric stretch (s) (IR+Raman) ν_4 = in plane bend (IR+Raman)

  Number of vibrations in a non-linear molecule or ion with n atoms = 3n-6 internal vibrations;

  Number of vibrations in a linear molecule or ion with n atoms = 3n-5 internal vibrations.

  Both linear and non-linear molecules or ions possess 6 external vibrations, 3 rotary and 3 translatory.

  Detailed explanations and definitions of terms for vibrational spectroscopy can be found in the Glossary of Terms used in Vibrational Spectroscopy (Bertie, 2002).

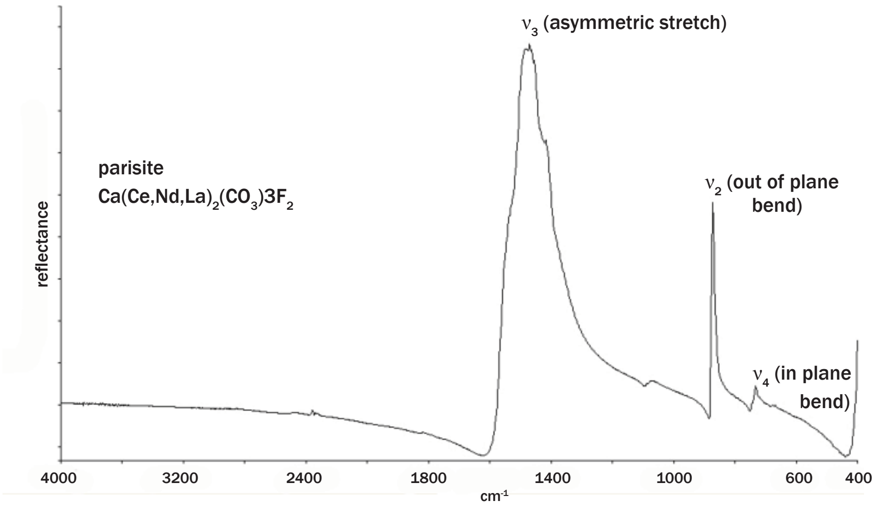

Figure 4: The attributions of the principal reflectance peaks to the corresponding molecular vibrations of the carbonate ion CO_3^{-2} in the specular reflectance spectrum of the rare carbonate parisite.

be directly attributed. For example the carbonate ion CO_3^{-2} in different carbonate minerals (for example calcite, aragonite and dolomite) has its main vibrations at the following positions: ν_2 → 850 – 900 cm^{-1} – ν_3 → 1400 – 1600 cm^{-1} – ν_4 → 680 – 770 cm^{-1} *(Figure 4)* (see, for example, White 1974). For more complex minerals like many of the silicates attribution is more complex and is beyond the scope of this paper.

In anisotropic gem materials (i.e. in all minerals except the ones belonging to the cubic crystal system plus aggregates [for example jadeite, chalcedony, nephrite] 'Mineraloids' [for example obsidian, tektites, opal] and organic materials [for example tortoiseshell, amber, bone]) the orientation of the samples in the specular reflectance accessory can have visible effects on the reflectance spectra due to the anisotropy. Anisotropic materials not only show distinct orientation-dependent variations in the UV and visible part of the electromagnetic spectrum, but also in the infrared region. The spectra of the α, β and γ rays of tanzanite recorded using an infrared polarizer between the infrared beam and the specular reflectance accessory are shown in *Figure 5;* the distinct differences between the individual rays are evident. The effects of this anisotropy are far less distinct without use of a polarizer. Although sample orientation alone will cause certain variations, only in a few materials will they be significant enough to potentially affect the efficiency of the automatic search function. Such minerals with different spectra in different directions therefore need to be recorded in various orientations and several reference spectra saved. In the great majority of gem materials the variations due to anisotropy do not affect the efficiency of the automatic search function, since it is usually only the intensities of the individual peaks that vary, not their positions or wavenumbers.

Practical applications of specular reflectance FTIR spectroscopy

This method has some major applications in gem identification. The specular reflectance spectra are generally characteristic for one single gem species. Therefore, when the matching reference spectra are in a database, any material can be rapidly identified by a technician or gemmologist trained to use the FTIR instrument and the spectrometer software; this is also true for diamond, since all diamond-imitations show reflectance peaks while diamond does not.

Also, even in the absence of a matching reference spectrum, an experienced

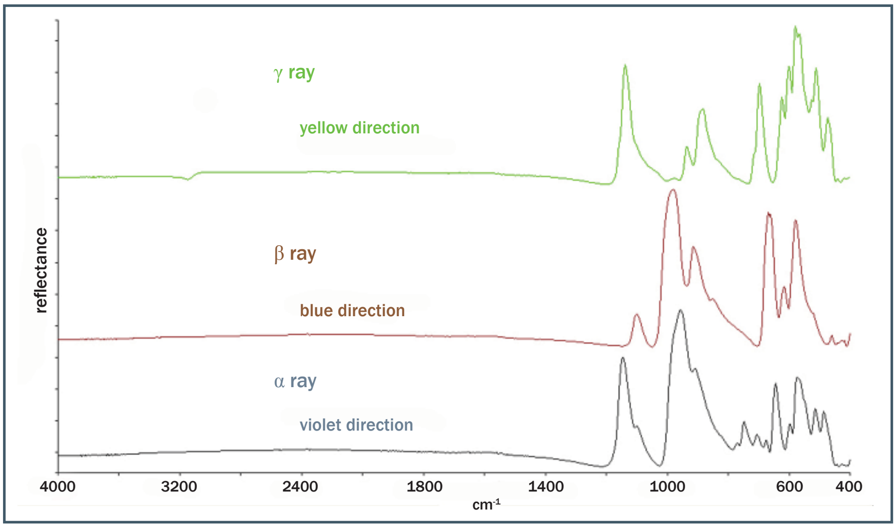

Figure 5: The polarized specular reflectance spectra of the α, β and γ rays of tanzanite. The spectra show very distinct differences due to extreme anisotropy. Arbitrarily oriented tanzanite would result in a spectrum of a combination of the three traces, showing most peaks and varying intensities. The spectra are cut off at 450 cm^{-1} since the infrared polarizing filter used did not transmit below this wavenumber. The colour annotations were added to each trace to show how each ray relates to the pleochroic colours of tanzanite.

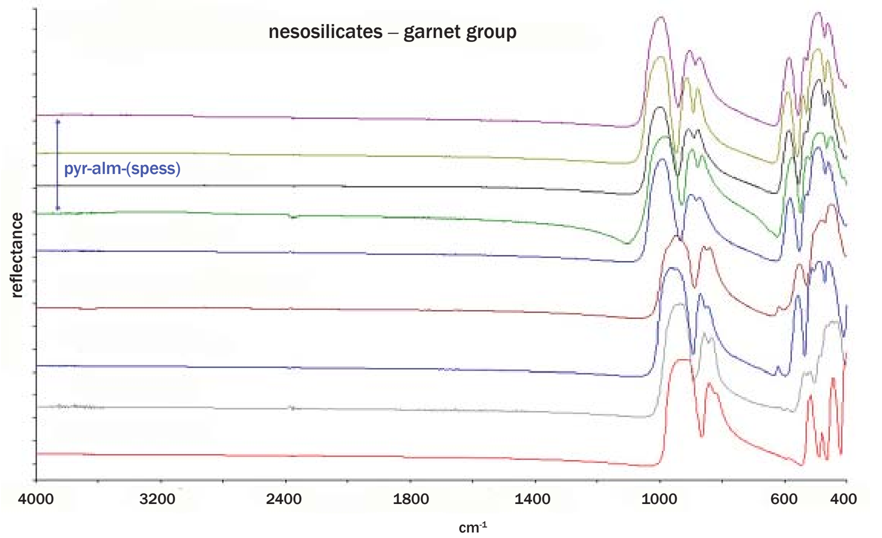

Figure 6: The garnet group shows extensive isomorphous replacement between molecules of almost all of its species. The major components of non-end member garnets can be identified by specular reflectance infrared spectroscopy.

spectroscopist can obtain extensive clues towards identifying a material by relating the major peaks of a spectrum to a mineralogical group and assessing its complexity. Since the method is very sensitive to compositional changes, synthetic gemstones can be differentiated from their natural counterparts when they are not a perfect structural match; so substances like synthetic turquoise, flame fusion synthetic spinel and most synthetic alexandrite can be identified rapidly. The sensitivity to compositional changes even permits in most cases the determination of gems in complex solid solution series such as the garnet group. If properly identified end-member garnets are in the database, at least the major components in a gem garnet under test can be identified *(Figure 6)*.

In many items submitted to laboratories for identification, gemstones are mounted in jewellery and identification by standard gemmological methods or even by many advanced methods like UV-Vis-NIR can be very challenging, time consuming or even impossible. The method described here is the ideal solution for identifying all materials used as gems, and even very small stones in heavy mountings can be identified. Additionally the specular reflectance data can be saved and, together with other gemmological data, used as formal proof in the event of any dispute.

Another application is the identification of very small surface-reaching inclusions in gemstones and grains within rocks; surfaces with a diameter as small as 0.5 mm were sufficient to yield critical data using the modified diffuse reflectance accessory, even when they were curved or matte. Using the fixed angle accessory approximately double the surface diameter was necessary to get good data and surfaces had to be more or less flat and smooth. To avoid interference from the surrounding material on the spot being analysed, Blu Tack was used as a screen because it does not produce artefacts in this analytical method, in contrast to transmittance spectroscopic analysis.

Although all these tasks can also be achieved by Raman spectroscopy, the Raman systems used in gemmological laboratories are generally very costly compared to an infrared spectrometer and to maintain their financial viability, they are normally occupied by tasks other than gem identification. Due to the high intensities of reflectance bands and due to the large FWHM of all bands it is not necessary to use a research-grade FTIR spectrometer for gem identification – a low cost FTIR system with a maximum resolution of 4 cm^{-1} is more than sufficient.

A very important point in day-by-day work is that the time needed for gem identification with this spectroscopic method can be short. Assuming the spectroscopy software is open and the search database ready, by using the fixed angle accessory an experienced operator can take approximately one minute to identify a stone conclusively; this includes sample preparation and data storage. Of course, one should not forget that rapid microscopic observation is always necessary in order to avoid misidentifications of, for example, assembled stones such as doublets or triplets.

Concluding remarks

The advantages of the spectroscopic method of specular reflectance FTIR analysis for gem identification purpose have been presented in this paper. These include high accuracy of gem identification and very short analysis time. Even though the specular reflectance spectra vary somewhat in appearance from true absorption spectra, they are similar enough to obtain most of the information that can be obtained from KBr powder absorption spectra. Compared to the only other spectroscopic method capable of very rapid and precise gem determination — Raman spectroscopy — the instruments necessary for specular reflectance FTIR spectroscopy are relatively low-cost and robust. While the method presented in this paper is limited to the identification of gem materials, the spectrometer used with other accessories has many more applications such as diamond type and treatment determination, determination of foreign substances such as glass, resin and oil in gemstones and is thus an important tool for gemmological laboratories.

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