

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AND ITS GEMOLOGICAL APPLICATIONS

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There are two vibrational spectroscopy techniques successfully used since years in gemology: the Raman and the Fourier Transform Infrared Spectroscopy (FTIR). It is not by a chance they are considered as complementary “sisters” techniques and, therefore, both necessary in the modern gemological laboratory. If Raman spectroscopy, which we have discussed in the issue N° 3 of the magazine, is distinguished by its effectiveness in identification of gems featuring well-defined crystalline structures and is, unfortunately, less suitable for analysis on amorphous and organic materials, FTIR, on the other hand, provides more precise information about the latter and it is also an irreplaceable tool in the analysis of diamonds.

The technique

The operating principle is rather complex and describing it properly goes beyond the scope of this article. It is enough to say that the FTIR it is an absorption technique by which the ability or not of a material to absorb an infrared source is detected and then featured on a spectrum. Compared to classical infrared spectroscopy, the Fourier-Transform technique - which uses the Michelson interferometer - has many advantages including the high power output and the possibility of simultaneously scanning all the frequencies of the infrared source at very fast speed. The Fourier Transform is applied to the interferogram resulting from the scan showing the intensity representation in the time domain. This allows us to obtain the representation of the intensity in the frequency domain, that is, the infrared spectrum. FTIR spectroscopy is one of the most versatile techniques for the analysis of gases, liquid and solid substances. The fields of use are so numerous that manufacturers have inevitably had to opt for configurations with compartments for standard size sampling modules (Figure 1). Variations have been developed in such a number as to allow companies to thrive by producing almost exclusively FTIR modules. In Gemology the most used sampling techniques are the transmission and diffuse reflectance (DRIFT). In the “transmission” technique the gem is positioned between the infrared source and the detector (Figure 2).

The latter will detect the frequencies of the unabsorbed signal and the instrument will provide for the resulting



Fig. 1 Thermo Nicolet 4700 FTIR spectrometer. Note the standard size sampling compartment open featuring a simple transmission setup.

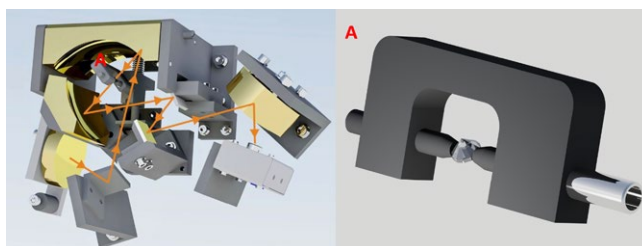


Fig. 2 The transmission sampling setup. On the left the clamp (A) is visible just under the ellipsoid mirror of the optical bench. The Infrared beam path is in orange color. On the right the adjustable clamp for gem positioning.

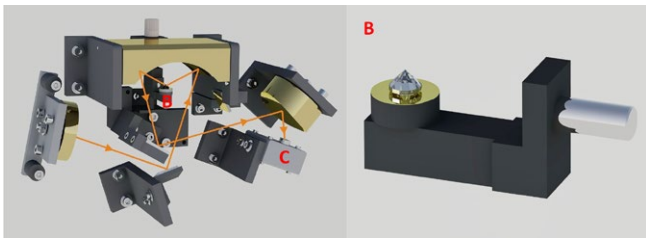


Fig. 3 The DRIFT sampling setup. The stone is positioned table down on the mirror of the sample stage (B). The beam is focused by the ellipsoid through the stone, then reflected by the mirror on the other side of the ellipsoid towards the other mirrors to the detector (C).

absorption spectrum by means of a dedicated software. This is the most commonly used technique in gemology until a few years ago. Unfortunately the sample positioning is not always easy and the correct orientation of the facets can sometimes take time; the beam, in fact must be free to travel through the stone undergoing the least possible deflection. Unfortunately the main purpose of the cut process of a gem is to allow the light to be reflected and refracted as much as possible to enhance its beauty and this certainly does not help our gemologist in adjusting the stone in order to let the beam to be free from deviations. Originally developed for the analysis of powdered substances, the DRIFT technique has recently found effective application in gemology by adopting a reflective sample stage in place of the powder sample container (Figure 3).

In this way the sample stage acts as a reflecting mirror for the infrared source and the DRIFT module basically allows to obtain a transmission scan. The infrared beam passes through the gem and it is then reflected in the direction of the ellipsoid mirror which focuses it on the other mirrors towards the detector. In this way, the effect of beam deflection by the gem facets is drastically attenuated for the benefit of the signal intensity. Another technique widely used in gemology, especially in cases where the infrared radiation is totally absorbed by the sample, is the specular reflectance. The gem is positioned by means of a micrometric lift so that the source beam is reflected from its surface. The resulting spectrum constitutes, similarly to what happens in Raman spectroscopy, a real, unique "fingerprint" for each material analyzed (Figure 4).

Infrared spectrum

In the Figure 5 drawing a typical infrared absorption spectrum can be observed. On the X-axis we can find the frequencies (expressed in wavenumber in cm^{-1}) and on the Y-axis the percentage of transmittance, i.e. the portion of infrared source that is transmitted (thus, not absorbed) from the sample. As far as our gemological studies are concerned,

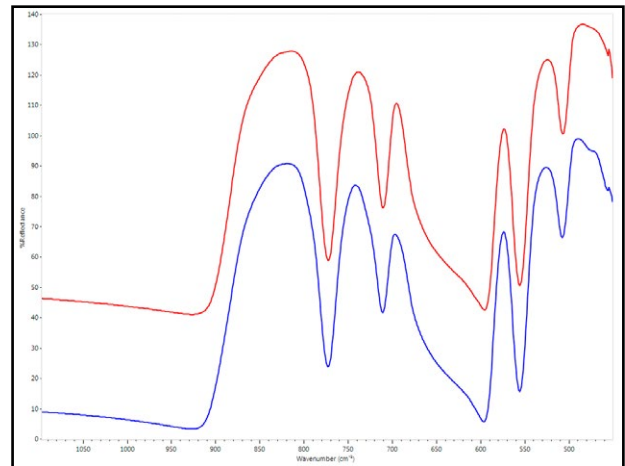


Fig. 4 Fingerprint spectrum of YAG taken with the specular reflectance technique. The red spectrum belongs to the gem under test and the red blue one is the matching reference from the spectral database.

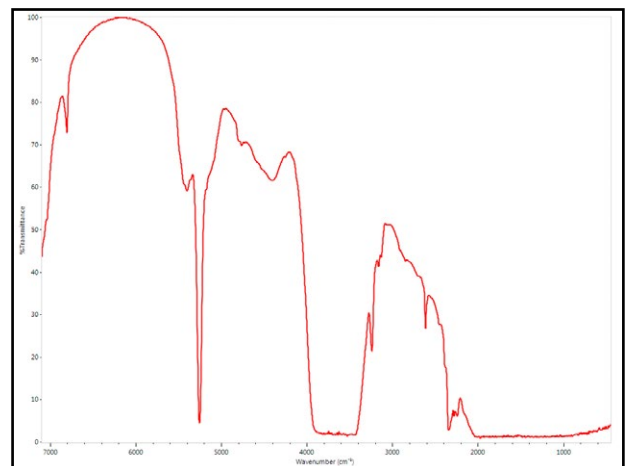


Fig. 5 Transmittance spectrum of Iolite.

it is sufficient here to describe the most relevant areas of the spectrum: the ones of functional groups ($4000\text{-}1300\text{ cm}^{-1}$) which includes bands due stretching of the functional groups themselves, and the fingerprint area, ($1300\text{-}650\text{ cm}^{-1}$) where the characteristic bands of each single molecule can be detected. It is common in gemology to show the spectrum in Absorbance mode, especially for diamonds.

Gemological applications: diamond

The use of FTIR in gemology covers such a large range of applications that we will be forced to mention briefly only some of them. FTIR has been the technique used for the modern classification of diamond types. More precisely, the area between 1332 and 400 cm^{-1} proved to be useful for the analysis of A and B nitrogen aggregates and for single nitrogen (Figure 6). It is therefore possible, through this technique, not only to know exactly the type of diamond but also, by means of specific algorithms, the percentages

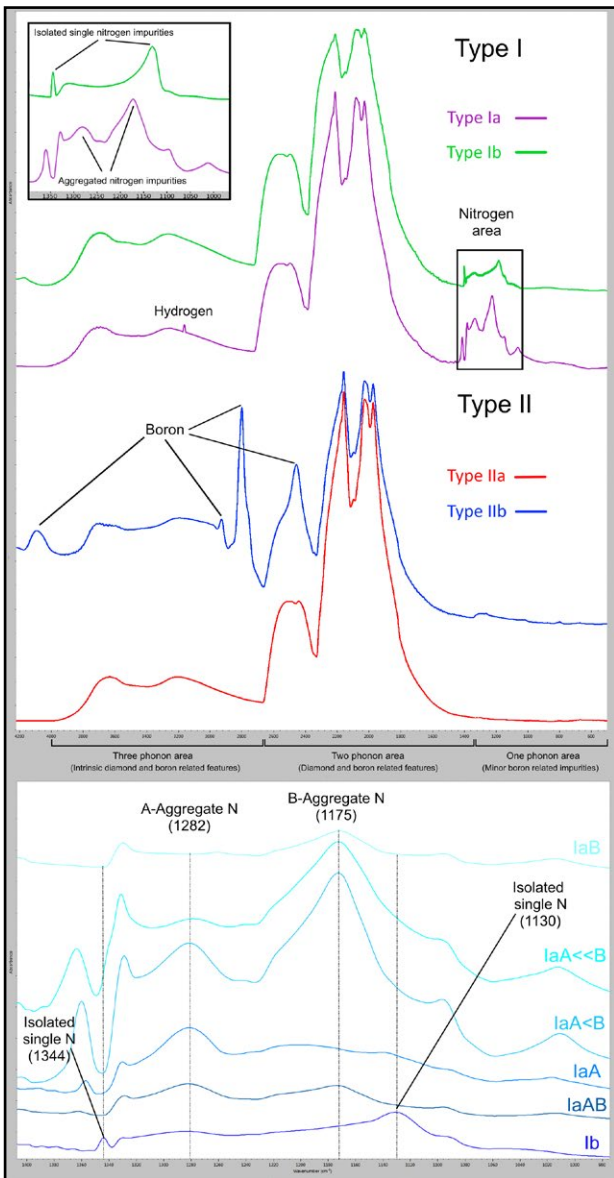


Fig. 6 From top: FTIR spectra of different diamond types. From bottom: zoom of the one phonon area featuring the absorbance bands of A and B nitrogen aggregates and isolated single nitrogen.

of aggregates A and B and of single nitrogen present. The total absence of absorption peaks in this specific area characterizes the diamond as type IIa. Finally, it is also possible to detect boron impurities which characterize the type IIb. There are also a series of additional information highlighted by peaks due to other defects, which allow, for example, the detection of treatment by irradiation, or the presence of hydrogen, or, in some cases, to characterize the synthetic HPHT and CVD diamonds. A classic example is the recent production of HPHT synthetic diamonds. In many cases, the presence of minor traces of boron in a IIa type spectrum is itself indicative of the synthetic origin of the diamond.

Gemological applications: colored gems

Although the specular reflectance technique it is a very useful and effective method for gem identification, the real potentialities of FTIR for one of the most common uses of this spectroscopic technique is the identification of the filler substances in emeralds (Figure 7), whether they are natural organic (traditional oil-based treatments) or synthetic (typically resins). Typically the area where the absorption features of fillers are visible is between 2750 and 3150 cm^{-1} . Specific chemical characteristics also allow the identification of each single method of synthesis of the emeralds themselves (Figure 8). Impregnating substances can be identified also in other gems such as, for example, jade. The presence of water in the FTIR spectrum of natural alexandrite makes it possible to distinguish it from its synthetic counterpart which, being made up to now only by the flux melt and pulling methods, is exempt. Other important applications concern the distinction between amber and copal, or the characterization of synthetic amethyst. Another important field of use is the identification

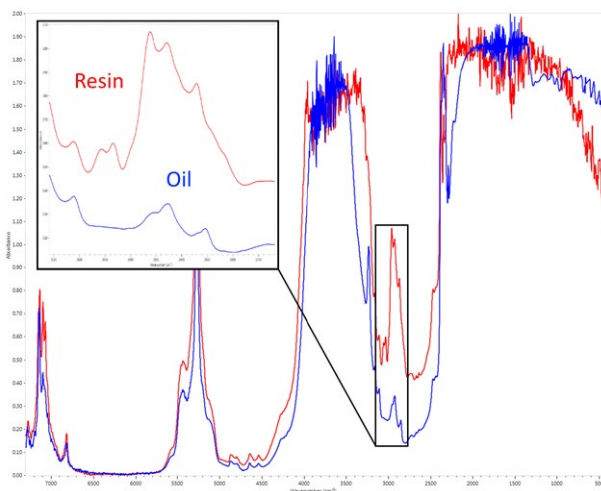


Fig. 7 Fillers in emeralds.

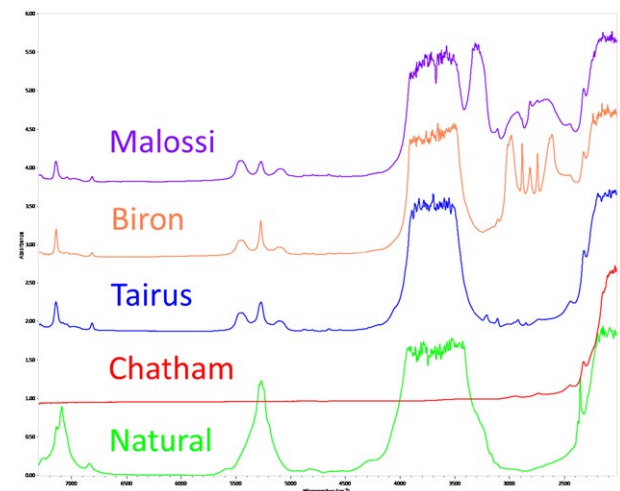


Fig. 8 FTIR spectra of different types of synthetic emeralds vs a natural one.

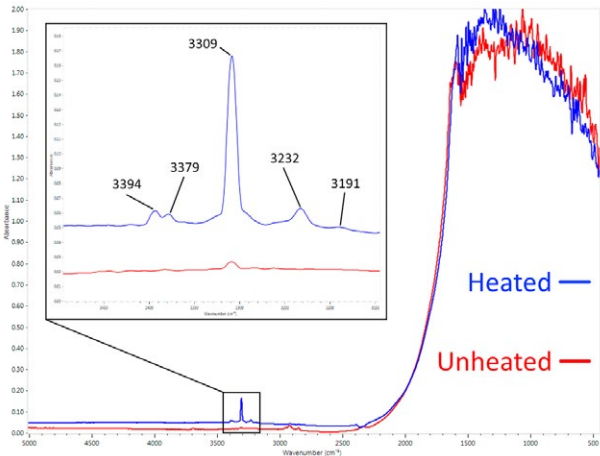


Fig. 9 FTIR spectra of unheated and heated metamorphic sapphires. In the zoomed area the 3309 "series".

of the heat treatments of corundum. In this case, however, the FTIR provides necessary but sometimes not sufficient elements to be evaluated without the aid of other spectroscopic techniques. Corundum heating is performed in controlled atmosphere. The effectiveness of each single process is strictly correlated to the characteristics of the starting material and to the composition of the atmosphere in which this occurs which can be, depending on the case,

reducing (oxygen-poor) or oxidizing (oxygen-rich), in some cases hydrogen is diffused. The process that in many cases leads to a significant improvement in both transparency and color of the starting material, must take into account for multiple parameters and, due to its complexity, will not be examined here in deep. However, it is important to underline that, for the heating of many sapphires of metamorphic origin, a reducing atmosphere is usually preferred and the addition of hydrogen is necessary, both for the reduction of Fe^{3+} to Fe^{2+} and for the association of the proton with O^{2-} which leads the same to become OH^- responsible for the absorption at 3309 cm^{-1} (Figure 9).

The distinct presence of this peak (often identified as a "series" of peaks where the 3309 is the most relevant) in the FTIR spectrum of a metamorphic sapphire is an indicator of possible heat treatment. However, there are metamorphic sapphires that respond better to heating in an oxidizing atmosphere. In this case the FTIR spectrum will not present this characteristic and the identification of the treatment will have to rely on other techniques. In Mozambique rubies, the presence of the peak at 3232 cm^{-1} is nowadays commonly considered a clear indicator of heat

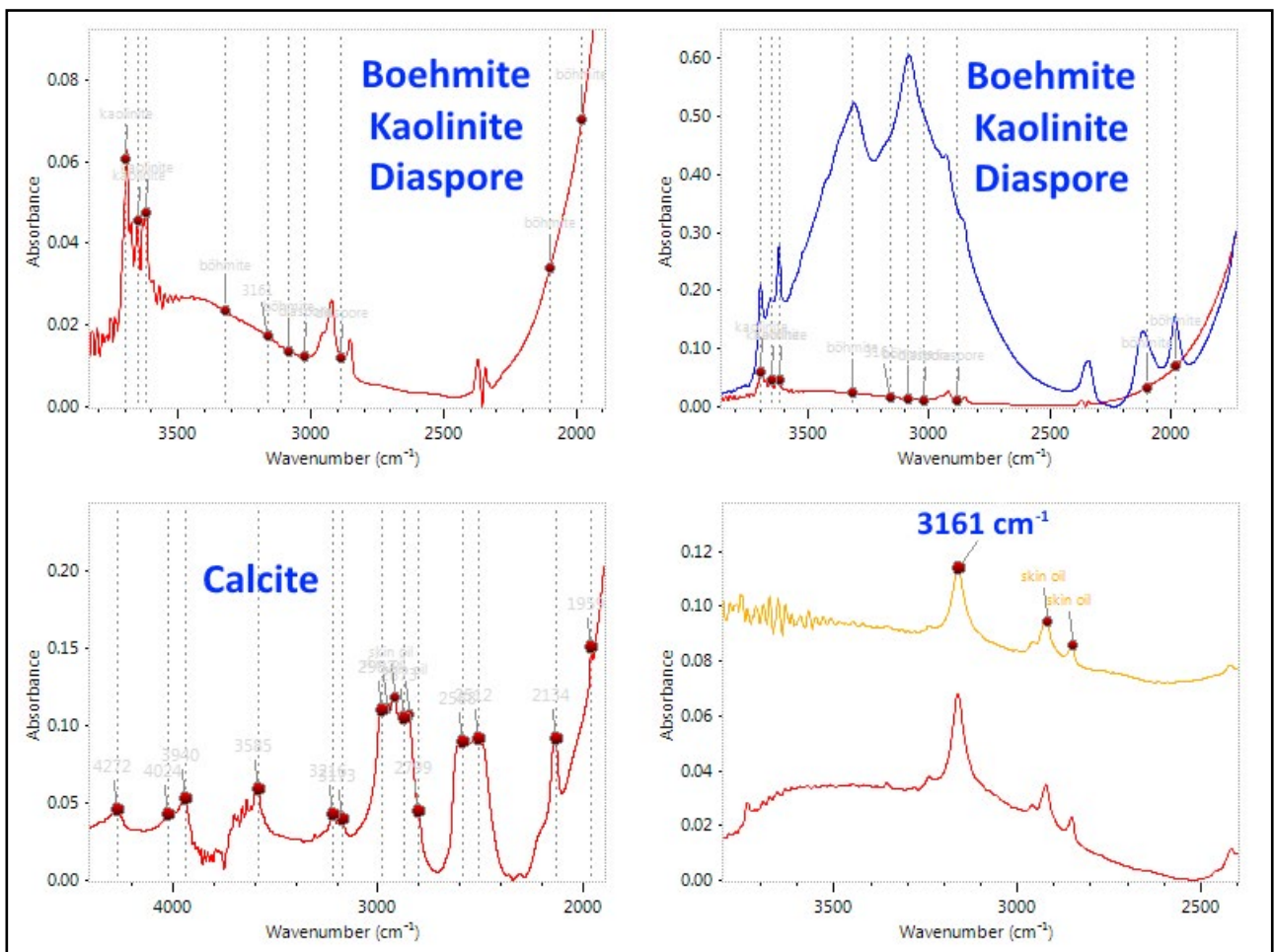


Fig. 10 Absorption features of several inclusions in corundum. When present they are diagnostic of not-heated material. The bottom-right spectra features a specific series which can be found in unheated yellow and blue sapphires; skin oil peaks are also visible.

treatment. In other cases FTIR spectrum can be much more useful and sometimes really diagnostic. Some inclusions are responsible for infrared range specific absorptions: Bohemite, calcite, diopside, gibbsite, kaolinite, these are just some of the “contaminating” minerals that may be found in corundum (Figure 10).

When present, the absorption peaks associated with these minerals constitute a clear proof that the stone has not been heated. Another important feature is the so-called 3160 cm^{-1} center series. If it shows up with significant intensity in the FTIR spectrum of a blue Sri Lanka or Kashmir sapphire or in a yellow one, it's a clear indicator the heat treatment can be excluded. There are many other cases where FTIR spectroscopy provides for very valid diagnostic elements. However, it should be stressed that in the majority of cases these are not sufficient on their own to draw diagnostic conclusions but must be closely related to information obtained through other analysis techniques.

Conclusions

FTIR spectroscopy is one of the pillars of a modern gemological equipment. Its undisputed versatility and extraordinary effectiveness make it a practically irreplaceable as spectroscopic technique today in order to face many of the most current and sensitive gemological problems. Its increasing diffusion in the gemological field will probably force manufacturers in the future to develop real dedicated instrumentation. One of the major limitations of the equipment on the market is the relatively small space available for the materials to be analyzed in the sampling modules. The analysis, in fact, are usually carried out on minimum quantities of substance while, in gemology it is not

uncommon to deal with voluminous stones or, sometimes, with gems mounted in jewelry pieces. Gemology is unfortunately not yet considered statistically relevant to the point of allowing investments in this direction. Hopefully the challenges generated by the latest technological advancements in synthetics and treatments can lead soon to a reversal of such trend.

Previous articles:

Articles by Alberto Scarani and Mikko Åström published on IGR - Rivista Italiana di Gemmologia (Italian Gemological Review) issues:

Nr. 1 (May 2017):

Gemological applications of UV-Vis-NIR spectroscopy

Nr. 2 (September 2017):

Raman spectroscopy: technique and its gemological application

Nr. 3 (January 2018):

Basic elements of photoluminescence spectroscopy in gemology

References

- Infrared and Raman Spectroscopy: Principles and Spectral Interpretation* – Peter Larkin – Elsevier
- Optical Properties of Diamond - A Data Handbook* - Zaitsev, A.M.
- The Distinction of natural and synthetic alexandrite by infrared spectroscopy* – C.M. Stockton and R. E. Kane . *Gems & Gemology*, Spring 1988 – PP. 44-46
- Ruby & Sapphire, a gemologist's guide* – R.W. Hughes, W. Manorktul, B. Hughes
- A question concerning Heat-Treated blue sapphires* – J. I. Koivula and A. Inns – GIA laboratory
- Comments on: "A question concerning Heat-Treated blue sapphires"* – J.L. Emmett
- FTIR in Gem Testing - FTIR Intrigue* – R.W. Hughes, L. Castoro, H.P.K. Nyunt, L. Kiefert
- On the Identification of Various Emerald Filling Substances* – M. L. Johnson, S. Elen, S. Muhlmeister – *Gems & Gemology*, Summer 1999 – PP. 82-107
- Specular reflectance infrared spectroscopy – a review and update of a little exploited method for gem identification* – T. Hainschwang, F. Notari – *The Journal of Gemmology*, 2008, V. 31, No 112, PP. 23-29