

REFLECTANCE, LUMINESCENCE AND VIBRATIONAL SPECTROSCOPIES FOR THE CHARACTERIZATION OF GEMMOLOGICAL MATERIALS USED IN WORKS OF ART AND HANDICRAFTS

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The dependence of several properties of natural gemstones - and of their synthetic analogues and simulants - on the wavelengths of absorbed, emitted or scattered light will be reported and discussed. This approach is non-destructive and does not require any treatment of the sample.

FTIR and Raman vibrational spectroscopies are of great help, in particular in provenance studies. Moreover, the micro-Raman technique is invaluable in determining the nature of inclusions.

Photoluminescence spectra are mainly determined by the presence of chemical impurities or defects in the crystal lattice. Such features - whether occurring in nature or intentionally introduced - provide useful information about the natural or synthetic origin of an unknown gemstone and possible treatments that it has undergone.

A comprehensive research project, concerning a low-cost portable apparatus for application of the above-outlined methods to gemmological problems is at present in progress.

Introduction

Most sensitive elemental analysis techniques require treatments or even the destruction of samples, while more classical gemmological methods, such as optical microscopy or refractive index or density measurements, are scarcely applicable to mounted gems, samples of unusual size, or opaque ones.

On the other hand, photoluminescence, FTIR (Fourier Transform Infrared Spectroscopy) and Raman spectroscopies provide information regarding the chemical composition and structure of an unknown gemstone in a fully non-destructive way and, from these, its story from synthesis (or mining) until the final product, passing through possible treatments.

The apparatus were designed for the study of crystalline and amorphous samples of any shape and size and do not require any treatment of the sample.

New results concerning different classes of gemstones are outlined in the following paragraphs.

Amber

Infrared spectroscopy has been always considered a powerful method for the characterization and definition of the geographic provenance of amber [1], which – as an organic material - requires fully non-destructive technique.

Figure 1 shows three spectra of samples belonging to small amber statues coming from an Etruscan necropolis. The presence of a shoulder around 1200 cm^{-1} strongly suggests the Baltic origin of the materials, while the differences observed in the 1600 cm^{-1} region can be attributed to the different state of conservation of the items.

Emerald

The emerald “skeleton” consists of hexagonal silicate rings which are connected to Be atoms in tetrahedral sites and to Al atoms in octahedral sites. Thus, channels are formed where alkali ions and water molecules can locate.

Skeleton bands are included in the $1400\text{--}600\text{ cm}^{-1}$ interval [2]. Bands in the range $800\text{--}600\text{ cm}^{-1}$ are quite stable in frequency, since they belong to the Si-O vibrations in the ring, while bands over 800 cm^{-1} present appreciable shifts since they are related to Si-O- Al , Si-O-Be and Be-O bonds. Consequently, they are affected by the amount and the type of substitution at the Al and Be sites which, in turn, depend on the genesis of mineral or synthetic emeralds [2].

Therefore, a systematic characterization of emeralds ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) is in progress that is aimed at identifying the archaeological gemstone origin. Analyses have been carried out using a number of techniques: particularly useful, among these, is micro-FTIR spectroscopy, often paralleled by Raman which, owing to the crystal symmetry, gives complementary information [3].

Numerous samples have been analysed that come from mines which were presumably cultivated in earlier times. Figure 2 evidences the FTIR spectral features of reference materials from Afghanistan, the Urals, Egypt, Austria and Madagascar (from top to bottom) over 800 cm^{-1} . This collection of data constitutes the starting nucleus of a database to be used for assessing the origin of unknown archaeological objects.

An important role in gemmology is also played nowadays by Raman spectroscopy [4], which give information on the vibrational properties. This technique has been used successfully in the studies of emeralds, since the position and relative intensity of spectral bands are sensitive to substitutions and to water coordination.

The latter topic is omitted here for the sake of brevity, while the Raman results of other gems are reported here as follows.

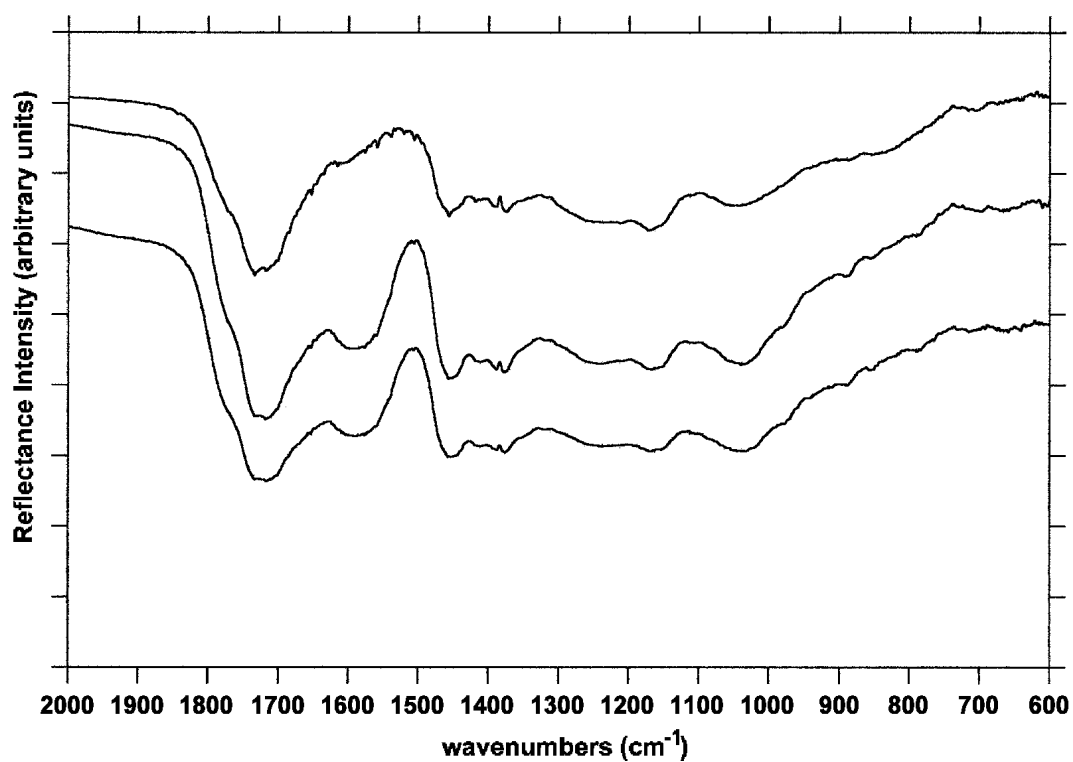


Figure 1: FTIR spectra of different amber samples belonging to Etruscan statues.

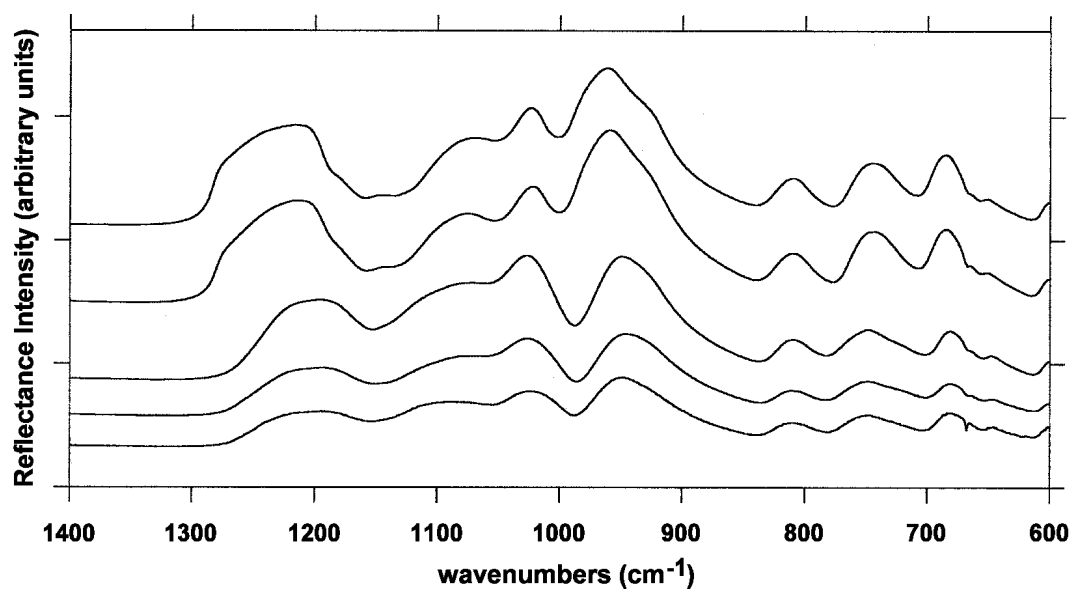


Figure 2: FTIR spectra of emeralds mined in different deposits.

Spinel

In previous papers we reported upon the photoluminescent behaviour of simple and mixed oxides, such as corundum [5] and spinel [6,7], which is mainly determined by the presence of chemical impurities. Spinel was often used as simulants of coloured mineral gemstones even in important pieces of jewellery.

Among other things, the photoluminescence spectroscopy of synthetic "defect spinels" is able to determine, through the "tracing" Cr^{+3} ion, their composition (in particular, the Mg/Al ratio), which is midway between that of a corundum and that of a natural spinel.

The characterization of spinels synthesised in our laboratory [8] or of commercial origin can be also performed by Raman spectroscopy.

Figure 3 shows the Raman spectrum of one of the samples taken from different parts of a "boule" grown by the Verneuil method [8]. The spectra of all the synthetic samples are identical and significantly differ from those reported in the literature [4] for natural spinels. In particular the peak at 866 cm^{-1} seems to be peculiar to synthetic materials, while the other intense peaks lie at a higher frequency (about 12 cm^{-1}) with respect to those of a natural spinel.

These results are ascribed to peculiar features (vacancies) of the defect spinel structure, and are very interesting for gemmological purposes due to the widespread use of Verneuil spinels in the jewellery of the first half of the 20th century [7].

Thorite

In a previous paper [9] we reported on the identification of a superficial inclusion of thorite in a Sri Lanka sapphire by using gamma spectrometry.

However, deeper inclusions are better studied using the micro-Raman technique. In fact, the nature of an unknown inclusion in the same sapphire was determined on the basis of its Raman spectrum, which turned out to be identical to that (Figure 4) of the superficial inclusion.

Diamond

The identification of different classes of natural, synthetic and/or treated diamonds is a topic of growing importance in the gemmological community.

We report here some preliminary results of HPHT (High Pressure High Temperature) treated diamonds from Russia: the FTIR spectra, widely used as a tool for diamond classification, enabled us (Figure 5) to ascribe the three gemstone to the Ia type.

However, photoluminescence measurements using different laser sources (Figure 6) evidenced striking differences within this series of samples, even though, on the basis of currently available information, they should have been subjected to the same treatment.

Only the spectrum of sample HPHT-2 is very similar to the one previously reported [10] for an analogous sample. In particular, this spectrum exhibits the peaks peculiar to the N3 and H3 centres [11].

Deeper insight in these phenomena may be achieved through the variation of the relative band intensities when recording the spectrum of diamonds at different temperatures. Such work is currently in progress.

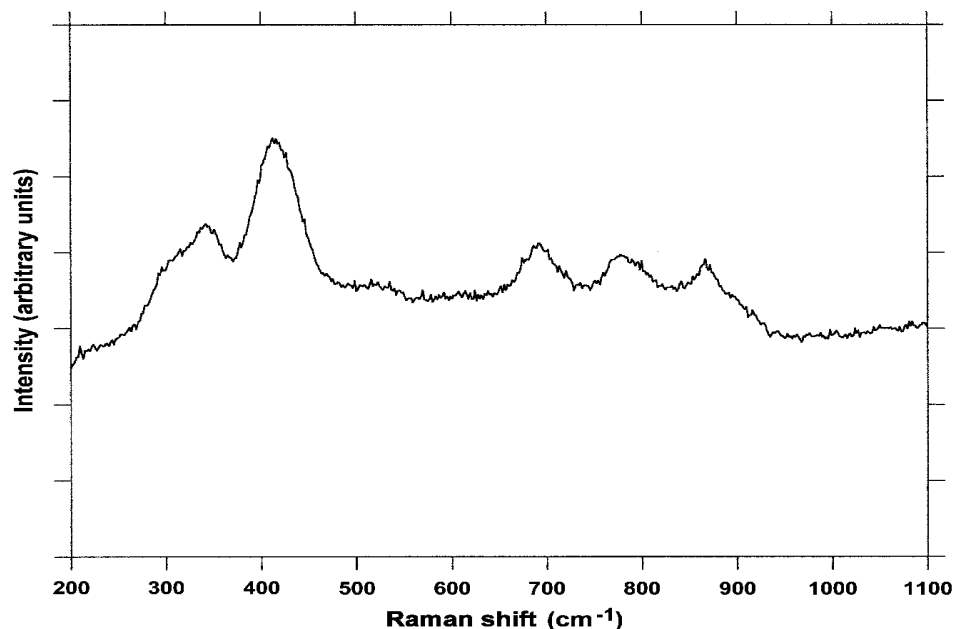


Figure 3: Raman spectrum of a sample of a “Verneuil” synthetic spinel.

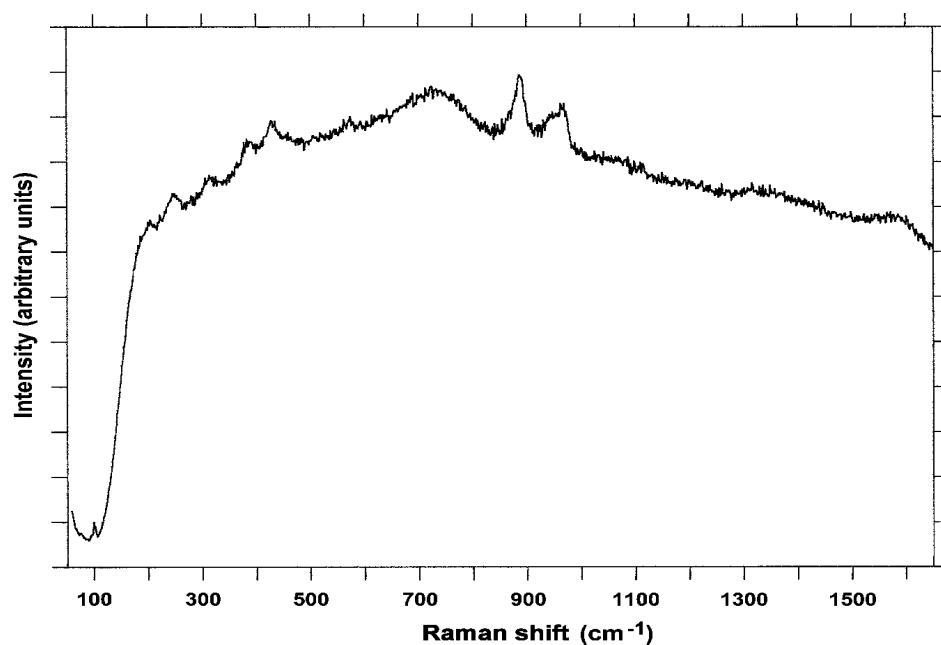


Figure 4: Raman spectrum of thorite.

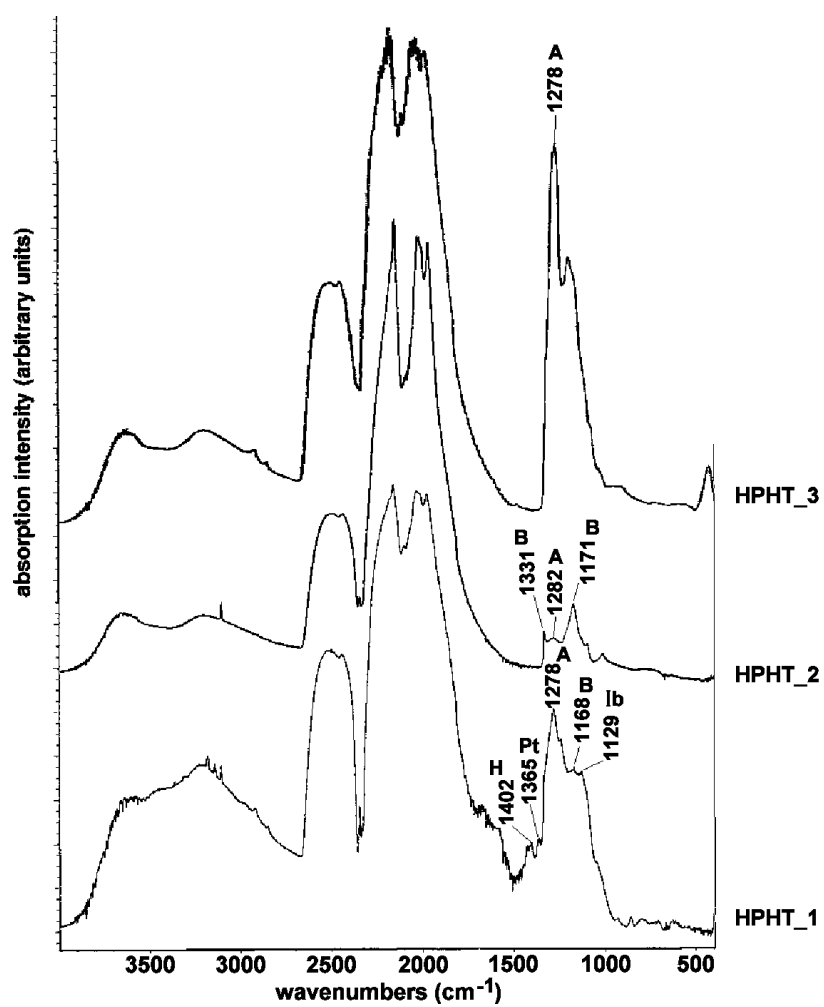


Figure 5: FTIR spectra of three different HPHT treated diamonds.

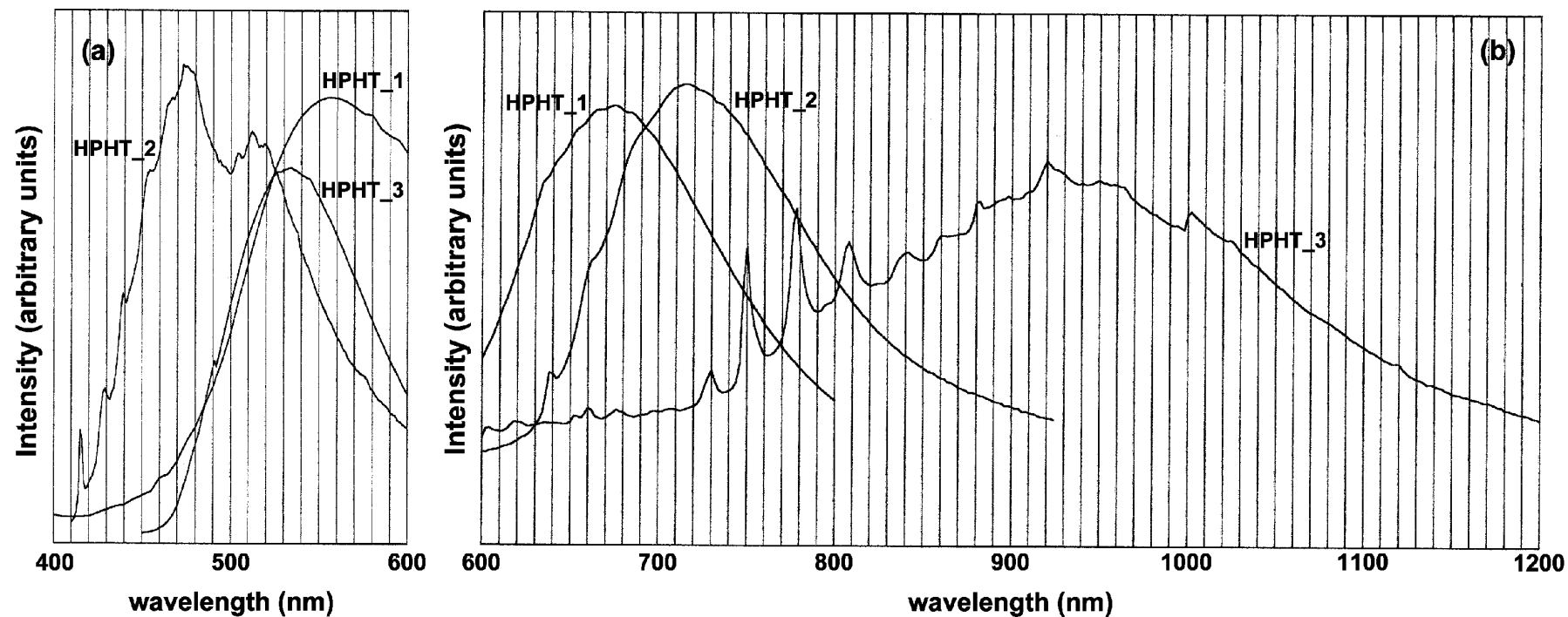


Figure 6: Photoluminescence spectra of three different HPHT-treated diamonds, the FTIR spectra of which are reported in Figure 5.
 (a) as excited by a frequency-doubled Ar laser (244 nm);
 (b) as excited by a frequency-doubled Nd laser (532 nm).

Final remarks

Sophisticated, expensive and heavy types of instrumentation are used in our laboratories to obtain accurate measurements. Nevertheless, a project, dealing with a low-cost portable apparatus for the measurement of optical properties involved in routine gemmological problems is currently in progress.

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