MATERIALS ANALYSIS

IDENTIFYING NATURAL GEMS FROM SYNTHETIC AND TREATED COUNTERPARTS USING THE AGILENT CARY 660

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Solution Note

Materials

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Introduction

Gemstones are an important commodity in today's marketplace. Due to the high variety of capabilities, the production of synthetic gemstones is a growing market. A synthetic gemstone shares a natural stone's physical, chemical and often optical qualities, but it is created in a laboratory. Nowadays, synthetic versions of nearly all popular gemstones are available. In many cases synthetic gemstones are difficult to identify. Jewellery that includes quality synthetic gems can be just as beautiful as jewellery made with natural stones. During the last decade, 2000 – 2010, some spin-offs from mainstream materials science have entered the gemstone industry and have brought many new challenges in the field of testing methodologies. This has a special reference to high pressure high temperature (HPHT) / chemical vapour deposition (CVD) synthesis of diamonds, the development of diamond simulants like moissanite, synthetic cubic zirconia, production of black diamonds, beryllium treatment of sapphires for colour enhancement, lead glass filling in rubies etc. In view of these developments, detection of genuine diamonds from a host of look-alikes has become an important issue in the diamond trade. It is important to note that identification of synthetic diamonds is possible only with the help of spectroscopic analyses. Conventional gemmological instruments and methods are not enough to distinguish synthetic diamonds from their natural counterparts.

Fourier Transform Infrared Spectroscopy (FTIR) is a nondestructive method used to analyse gemstones. This technique can produce important information about all kinds of gemstones within a few minutes.

FTIR Spectroscopy can be used for a broad field of applications in the gemstones industry, several examples of which are described in this solution note.

Experimental Setup

Spectrometer

All spectra were measured using the Agilent Cary 660 FTIR spectrometer (Figure 1).

The Cary 660 FTIR is a versatile, high performing spectrometer designed to meet routine spectroscopy and research application needs. It is based on a 38 mm dynamically aligned, 60° mechanical bearing Michelson interferometer and is capable of covering the widest spectral range from 53000 cm^{-1} to 20 cm^{-1}. Due to the large sample compartment, it is compatible with a wide range of accessories that provide extra capabilities.

The Cary 660 FTIR is controlled by Resolution Pro Software, including all the important features for spectral analysis. This spectrometer offers superb performance levels, spectral resolutions and signal-to-noise measurements. It is ideal for a wide range of applications and industries from petro/chemicals to materials/polymers and life sciences.

For these measurements, the Cary 660 FTIR was equipped with Agilent's patent DURAGLOW™ Mid-IR source, Potassium Bromide (KBr) Beamsplitter and a linearised broad band Mercury Cadmium Telluride (MCT) detector. This standard configuration provides a measurement range from 7500 cm^{-1} to 450 cm^{-1}.

Figure1: Agilent's Cary 660 FTIR spectrometer.

Spectra acquisition

All spectra were collected in transmission mode, with a spectral resolution of 4 cm^{-1}. For background, as well as for sample spectra, 128 scans per measurement were taken. The sizes of the gemstones were between 7 mm and 20 mm. All stones were placed into the sample compartment, without further manipulation, using a magnetic holder.

Results and Discussion

Typification of nitrogen substitution in diamonds

Figure 2 shows a comparison of the FTIR spectra of synthetic diamond and natural diamond in the wavenumber range 1650 cm^{-1} to 400 cm^{-1}. In this spectral range, there are absorption bands correlating to nitrogen induced one phonon absorbance. 98 % of all natural diamonds have around 0.1 % nitrogen. These are classified as Type Ia diamond. Within diamond Type Ia, two agglomerate exist - IaA and IaB, as shown in Table 1. Synthetic diamonds exist mostly as Type Ib, containing up to 0.05 % nitrogen. The absorption band at 1282 cm^{-1} is characteristic for diamond Type IaA, the absorption band at 1175 cm^{-1} for diamond Type IaB and the absorption band at 1130 cm^{-1} for diamond Type Ib [1,2,3,4].

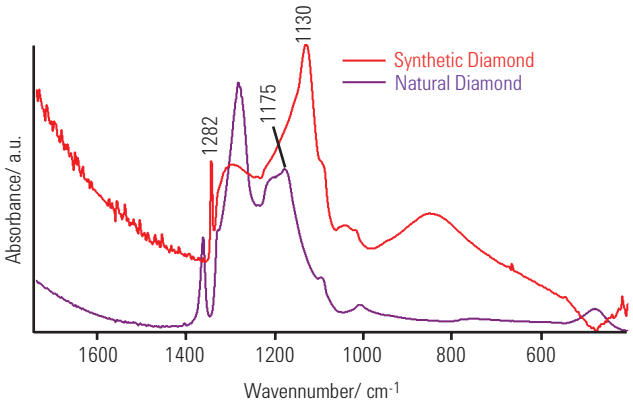

Figure 2: Comparison of FTIR spectra of synthetic Diamond and natural Diamond in the wavenumber range 1650 cm^{-1} to 400 cm^{-1}.

Type IaA diamond	Type IaB diamond	Type Ib diamond
		
1282 cm^{-1}	1175 cm^{-1}	1130 cm^{-1}

Table 1: Classification of diamond Types IaA, IaB and Ib.

The spectrum of synthetic diamond is dominated by the absorption at 1130 cm^{-1}, whereas the spectrum of natural diamond is dominated by the absorbance at 1282 cm^{-1} and 1175 cm^{-1}. This result is in accordance with literature [1,2,3,4,5]. These measurements on diamond, performed without any sample preparation within a few minutes, can easily distinguish synthetic diamond, Type Ib, from natural diamond, Type Ia.

Inclusions in emerald and the analysis of natural and synthetic emerald

The chemical composition of emerald is defined as $Be_3Al_2(SiO_3)_6$. It can have numerous gaps on the surface and different inclusions. If an emerald has no visible inclusions, it is classified as a flawless gemstone. Since emerald can have many gaps, it shows an uneven dye distribution. To improve the appearance, it is an accepted trade practice all over the world that emeralds are oiled or treated in other ways. They are classified as having either none, minor, moderate or highly enhanced modification. X-ray fluorescence is a very expensive technique to analyse emerald. Since inclusions provide an opportunity to distinguish between natural and synthetic emeralds, FTIR spectroscopy is a low cost and very fast method to proof these gemstones.

It was found that the FTIR spectra of natural and hydrothermal synthetic emeralds show different absorption in the spectral range of 2600 cm-$^{-1}$ to 3000 cm^{-1}. Absorption bands at 2830 cm^{-1} and 2745 cm^{-1} have never been detected in natural emeralds [6].

Figure 3 shows a comparison of the FTIR spectra of a hydrothermal synthetic emerald and a natural emerald in the wavenumber range 3400 cm^{-1} to 2400 cm^{-1}. The FTIR spectrum of hydrothermal synthetic emerald shows strong absorption bands at 2745 cm^{-1}, 2830 cm^{-1} and 2870 cm^{-1}.

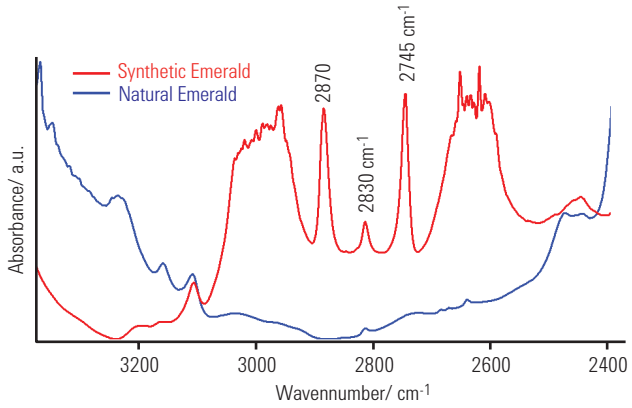

Figure 3: Comparison of FTIR spectra of synthetic emerald and natural emerald in the wavenumber range 3400 cm^{-1} to 2400 cm^{-1}.

This demonstrates that by using FTIR spectra, it is possible within a few minutes, to distinguish between natural and hydrothermal synthetic emeralds.

Identification of resin filled emeralds

As previously written, it is a general trade practice to oil emeralds, with a view to solidify their strength and improve appearance. The use of coloured oil and resins have to be declared whilst trading in the gem market. With the help of FTIR, it is possible to differentiate between peaks for oil and resin.

Figure 4 shows the FTIR spectra of natural and treated emerald. The wavenumber range between 3200 cm^{-1} and 2800 cm^{-1} clearly shows absorption bands that originate from resin. Since oil and resin show absorption in the MID-IR spectrum, FTIR can be used to determine whether emeralds have been treated.

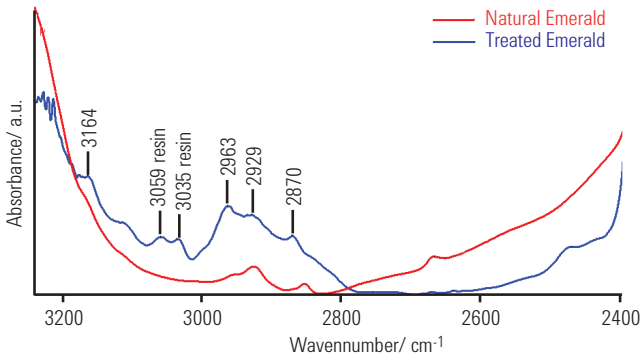

Figure 4: FTIR spectra of natural and treated emeralds in the wavenumber range 3200 cm^{-1} to 2400 cm^{-1}.

Ruby

Ruby is a variety of the mineral species corundum and has been a popular gemstone for centuries. With its characteristic red colour and high hardness, its value is unrivalled by any other gemstones. The red colour in stone is due to the presence of trace elements such as chromium (Cr), iron (Fe) or titanium (Ti). Advances in crystal growth technology have made the creation of synthetic rubies a reality. As a result there exist numerous synthetic and simulated rubies in the gem market which are not easily identified through the use of basic gemmological methods.

Identification of Heat Treated corundum

Corundum has a crystal system of Al_2O_3. It is transparent but can have different colours, depending of impurities. The red modification is called ruby and arises from integrated chromium. Corundum can be heated to improve milkiness and asterism or remove colour and even to alter imperfections [7].

Figure 5 shows the FTIR spectra of heat treated ruby and natural ruby in the spectral range of 3500 cm^{-1} to 2400 cm^{-1}. The spectrum of heated ruby clearly shows an absorption band at 3309 cm^{-1}. This peak was also found in 27 Marosely corundum specimens [8]. Thermal treatment can result in the transformation of diaspore [AlO(OH)] to aluminium oxide [Al_2O_3]. The absorption at 3309 cm^{-1} may be caused from structurally bound OH.

The development of broad absorption from 3000 cm^{-1} extended to 3600 cm^{-1} would be due to the random distribution of unbound hydroxyl groups. FTIR spectroscopy has been found to be invaluable in the detection of heat treatment of rubies and sapphires.

Identification of filling of rubies with foreign substances

Filling is one type of ruby treatment that represents the low or high temperature heat treatment process with a number of additives or fluxes. After solidification these additives or fluxes form glassy substances in fissures and cavities and also on the surface of the treated stone. FTIR spectra for all lead glass filled rubies show three absorption bands at 2250 cm^{-1}, 2600 cm^{-1} and 3500 cm^{-1}. According to Scholze [9], the broad band at 3500 cm^{-1} can be attributed to the absorption of H_2O molecules.

The peaks at 2250 cm^{-1} and 2600 cm^{-1} are related to Si-OH vibrations, as noticed by Efimov et al. [10,11]. In the case of glass filled rubies, a broad absorption centered around 2600 cm^{-1} is a diagnostic signal for identifying fracture filling with glassy substances such as lead glass, bismuth, silica and borax. Nevertheless, FTIR spectra cannot differentiate as to what type of filler is used to enhance the colour. Figure 6 shows the hump at 2600 cm^{-1} which is due to this fracture filling, demonstrating that these bands in the FTIR spectra could become a good indication of glass filling in rubies.

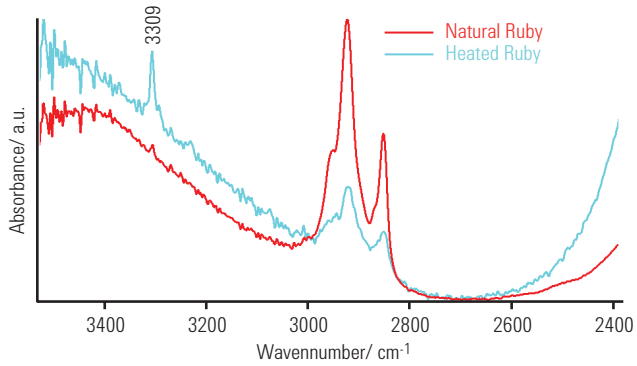

Figure 5: FTIR spectra of natural and treated ruby in the wavenumber range 3500 cm^{-1} to 2400 cm^{-1}.

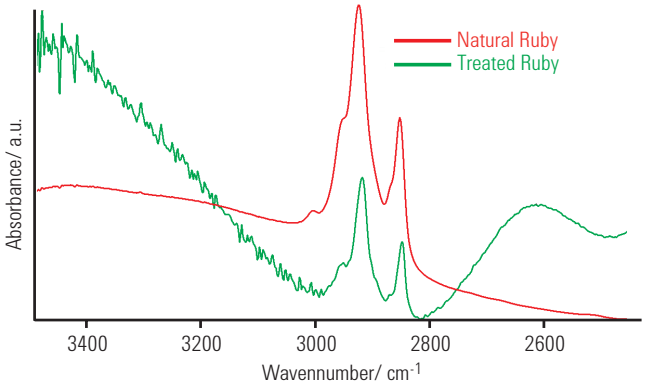

Figure 6: FTIR spectra of natural and treated ruby in the wavenumber range 3500 cm^{-1} to 2400 cm^{-1}.

Conclusion

FTIR spectroscopy is a powerful technique used to analyse all sorts of gemstones. This application note shows that within a few minutes, it is possible to determine whether a gemstone is natural or has been treated. Agilent's Cary 660 FTIR is a versatile instrument as a consequence of its high energy throughput, sensitivity and spectral range. The sample compartment is large and allows for the use of specialist accessories. The gemstones measured for this application note were mounted on a magnetic transmission holder and measured at room temperature.

The analysis of synthetic and natural amethyst for example, is complex. The FTIR spectrum of amethyst is a function of growing conditions like temperature, pressure and growth rate. This is an example where a special sample holder, which can be heated or put under pressure, may be useful. Agilent's Cary 660 offers this possibility.

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