Application Note AN M81

Diamonds – characterized by FTIR Spectroscopy

Diamonds are among the most popular gemstones in the world. Large quantities of diamonds are also used for industrial applications.
The high price for this material motivates people of buying cheaper material that resembles the appearance of a diamond e.g. cubic Zirconia or synthetic Moissanite. The value of a diamond depends on its size and shape, but also on its color. The color of certain types of diamonds can be changed by special treatments (High Pressure High Temperature (HPHT)). FT-IR spectroscopy is an established method to distinguish authentic diamonds from counterfeits, to determine its type (Ia, Ib, ... IIb), and to reveal if a diamond has been treated by HPHT.

Instrumentation

Conventional FT-IR technology for this analysis of gemstones included big research grade spectrometers with a delicate beam condenser and a liquid nitrogen cooled MCT*-Detector.
In contrast, the ALPHA-Drift is a very compact, mobile and robust FT-IR spectrometer. It has proven to be very suitable for the analysis of gemstones.

Figure 1: Bruker Optics ALPHA with diffuse reflection accessory (ALPHA-Drift).

The ALPHA has several inherent advantages:

- Robust instrument, confidence in results
- Small footprint (20 x 30 cm)
- Universal use (mobility)
- Affordable price
- Easy operation, no liquid nitrogen needed
- Full sampling flexibility (solids, powders, liquids, gases)

For the evaluation of diamonds, the "diffuse reflectance" method proved to be a simple and reliable measurement technique. Here, the differently scattered light from the sample is collected over a large solid angle.

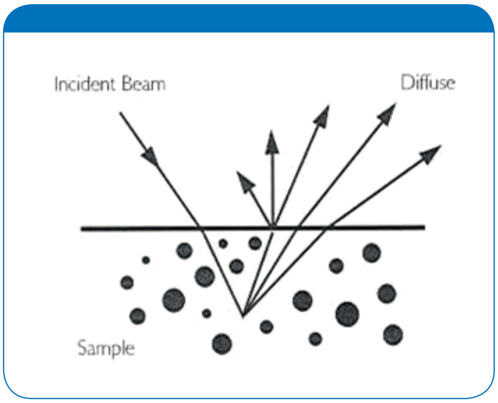

Figure 2: Principle of diffuse reflectance measurement.

Transmission measurements of facetted diamonds using beam condenser are more cumbersome due to the delicate alignment of the condenser itself and the necessity to accurately position the sample. Furthermore, the lower light flux here often requires a more sensitive liquid nitrogen cooled detector.

Measurement procedure

The sampling procedure for the FT-IR analysis of gemstones by the ALPHA-Drift is pretty easy. After the background measurement with the included reference gold, the stone is placed in the sampling cup. Brilliants are generally placed on their flat side in the central position of the sample cup. Stones with lower symmetry (e.g. oval) are orientated with their long axis along the sample holder bar. Rough diamonds with irregular shapes might have to be turned a few times until the measurement results in a high quality spectrum. In order to focus the IR beam on the sample surface, the height of the sampling cup including the stone can be adjusted by a turning knob. The maximal signal intensity indicates the best sample position.
Afterwards, the spectrum of the sample is measured for typically about 30 sec. For data evaluation the acquired spectrum is compared with reference spectra of certain diamond types and/or counterfeits, to determine if the diamond is authentic and to determine its class, respectively.

FT-IR spectra of diamond

Figure 3 shows some typical FT-IR spectra of diamonds. The broad absorption between 1800 cm^{-1} and 2700 cm^{-1} is due to the carbon itself. The sharp absorption band at 3100 cm^{-1} further reflects the hydrogen content, whereas the spectral region between 1500 - 1000 cm^{-1} includes the absorption from the nitrogen.

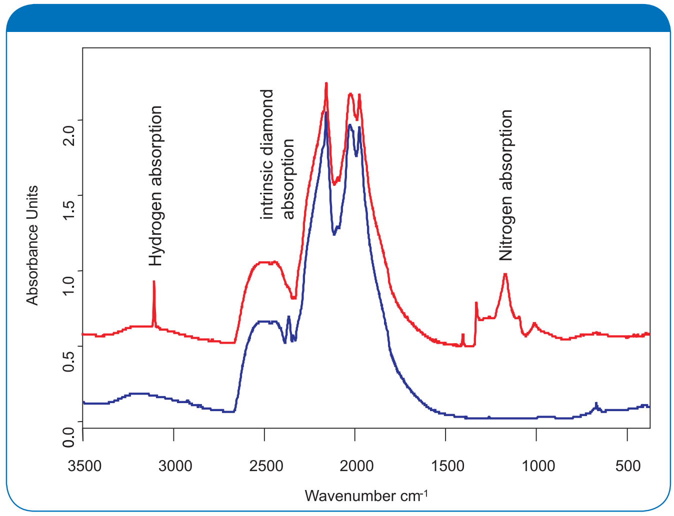

Figure 3: Mid-infrared spectra of diamonds

Diamond or ...?

The most common diamond counterfeits are cubic Zirconia (ZrO_2) and synthetic Moissanite (SiC). While Zirconia is easily detectable by the widely used "thermal pen test" Moissanite could pass as a diamond due to its similar thermal characteristics. Other identification methods rely on a number of consecutive tests that only experienced gemmologists can accomplish.

Figure 4 shows the IR spectra of diamond, Zirconia and Moissanite. The clear differences between these specific spectral patterns are obvious.

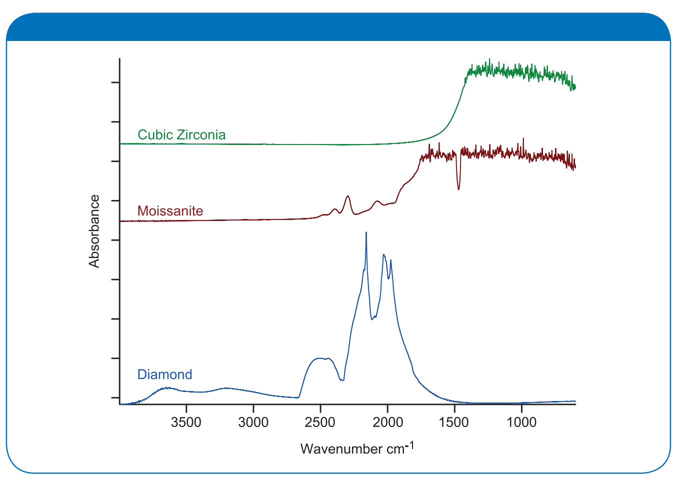

Figure 4: FT-IR spectra of a diamond and different imitations

Which type of diamond?

Generally, diamonds are divided into type I and II where type II contains no measurable traces of nitrogen (N).
The subtypes are:

Type Ia --> Diamond with aggregated N
Type Ib --> Diamond with isolated N (often synthetic)
Type IaA --> Diamond with groups of 2 N's
Type IaB --> Diamond with groups of 4 N's
Type IIa --> Diamond without N or Boron
Type IIb --> Diamond with Boron (blue or grey)

Type IIa and type IaB are of special interest because these diamonds, which are often grey or brown, can be HPHT treated to become colorless or pink. These color changes increase the value of those diamonds significantly.

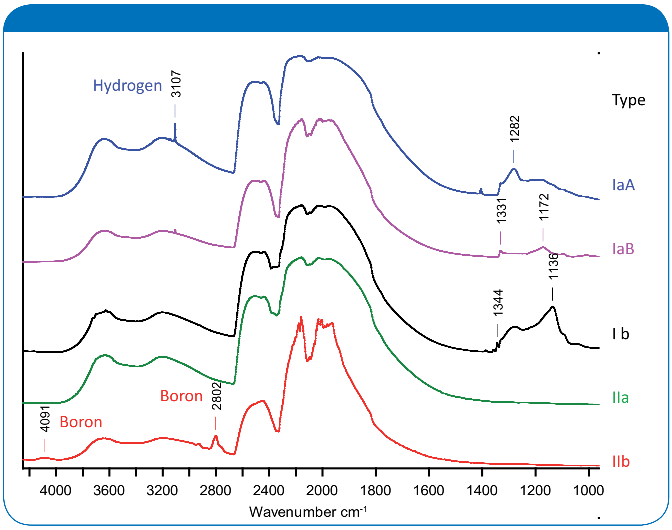

Figure 5: FT-IR spectra of different diamond types

The distinction between type I and II is obvious since only spectra of type I diamonds exhibit the absorption features of nitrogen between 1450 cm^{-1} and 1000 cm^{-1}.
The characteristic differences of type Ib and IaB are given in Figure 5. The peaks at 1136 cm^{-1} and 1344 cm^{-1} are typical for disperse monoatomar nitrogen and hence for type Ib.
The absorbance at 1172 cm^{-1} is considered to be related to the "B-centers" of 4 nitrogen atoms and indicates therefore type IaB [1].

Synthetic diamonds are generally of type Ib and the nitrogen peak at 1344 cm^{-1} is assigned to be indicative for synthetic diamond.

Summary

FT-IR spectroscopy with a very compact and robust instrument as Bruker Optics ALPHA can be a valuable tool in the gemmological laboratory. The "diffuse reflectance" method seems to be the most universal and easiest approach for the analysis of gemstones.

FT-IR spectroscopy can also be used in other fields in gemmology e.g. discriminate synthetic emeralds or lead glass treated rubies from their natural counterparts!

* FT-IR Fourier Transformation Infra-Red
* MCT Mercury Cadmium Telluride; infrared sensitive detector

[1] P. Thongnopkun, S. Ekgasit; FT-IR Spectra of faceted diamonds and diamond simulants; Diamond & Related Materials 14 (2005) 1592 - 1599

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