Application Note: 51124

Analysis of Rubies and Sapphires by FT-IR Spectroscopy

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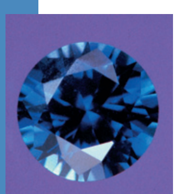
Key Words

- Gemstones
- Simulants
- Synthetics
- Treatment Detection

Introduction

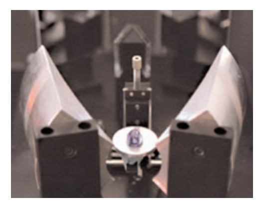
Two of the most desired gemstones, ruby and sapphire, are both gem varieties of the corundum group and have the same chemical structure (Aluminum Oxide). FT-IR spectroscopy can confirm that a stone is corundum and not a simulant, however, the infrared spectra of ruby and sapphire are virtually identical. In fact, synthetic sapphire is colorless and is often used as a window material in near infrared and visible optics because of its unique spectral properties.

Today, red stones are usually classified as ruby, while the other remaining colors are classified as sapphires even though the name "sapphire" was originally reserved for blue stones. The color differences are created by the presence of trace amounts of metal ions that cannot be detected by infrared spectroscopy. For ruby, the red color comes from chrome and iron. For sapphire, the blue color comes from titanium and iron. Pink, green, and yellow stones contain different states of chrome or iron. As with many natural materials, corundum is not particularly rare and colored forms of low-quality stones are readily available. To the contrary, high-quality natural gemstones are rare and very valuable, particularly when the stone has a non-traditional color.



Recently, a beryllium treatment process has been reported that can greatly enhance the colors of these poor-quality stones. This high-temperature treatment diffuses beryllium atoms into the corundum crystal and greatly improves the appearance of the stone. Most natural rubies and sapphires have a small peak in the infrared spectrum near 3310 cm^{-1} that corresponds to the O-H stretching mode of water. While FT-IR spectroscopy cannot detect the presence of the beryllium atoms, the high temperature of the treatment usually eliminates the water that is trapped in most natural stones and consequently, this peak loss can be measured.

In this application note, we will describe a simple method to verify the presence of trapped water in a ruby or sapphire. As with all naturally created stones, it is possible to find ones that contain low levels of residual water. FT-IR provides a rapid, non-destructive technique to identify stones that might require further investigation.



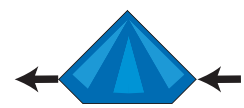


Figure 1: Thermo Scientific Nicolet 6700 FT-IR spectrometer and 4X Beam Condenser

Experimental

All spectra from this work were acquired using a Thermo Scientific Nicolet™ 6700 FT-IR spectrometer with a 4X Beam Condenser accessory. The spectrometer was equipped with a high sensitivity MCT detector and extended range KBr beamsplitter. The 32 scans were acquired at 4 cm^{-1} resolution for a measurement time of 20 seconds. Figure 1 shows the spectrometer and accessory as well as a schematic of the light passing through the stone.

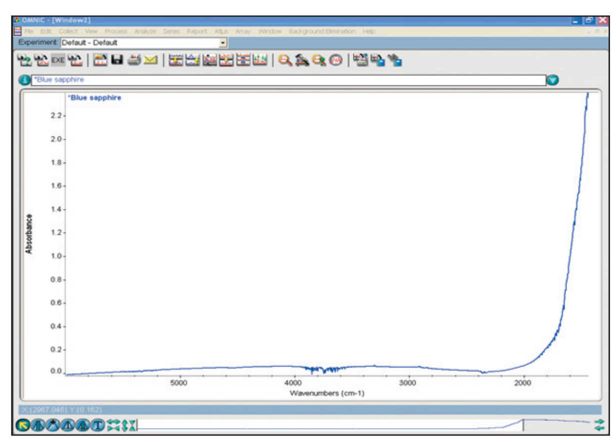


Figure 2: Infrared spectrum from a blue sapphire

The spectrum of a sapphire in Figure 2 shows the strong absorption from the Al-O bonds below 1500 cm^{-1} and a lack of major other features in the spectrum. The unique spectrum of corundum makes it very easy to differentiate ruby and sapphire from most of the simulants or other similarly colored gemstones.

The peak to be used in this analysis is barely visible in the 3300 cm^{-1} region of this spectrum. Figure 3 shows the scale expanded spectra from several stones. On this scale, the peak of interest is clearly visible in three of the four spectra.

The lack of an OH peak in the spectrum of the small pink sapphire suggests that this might be a treated stone. While a visual confirmation is straightforward, this is an excellent application for an automated analysis technique. A Classical Least Squares (CLS) analysis method was created to verify if the peak is present and to determine the magnitude. A CLS method minimizes the difference between a sample spectrum and a set of reference spectra containing the components to be analyzed. In this case, we use a curve fitting technique to create a standard from this single component analytical method. Figure 4 shows the expanded spectrum from a sample and the resulting analysis report for this application.

The results of the analysis shown above can also be saved in an Excel® file or sent to another relevant software program. An important feature of the CLS technique is the calculation of a standard error term. In most cases, a concentration value that is several times larger than the reported standard error gives a very high confidence that the peak is present. In this example, the peak is 104 units and the standard error is less than 4.

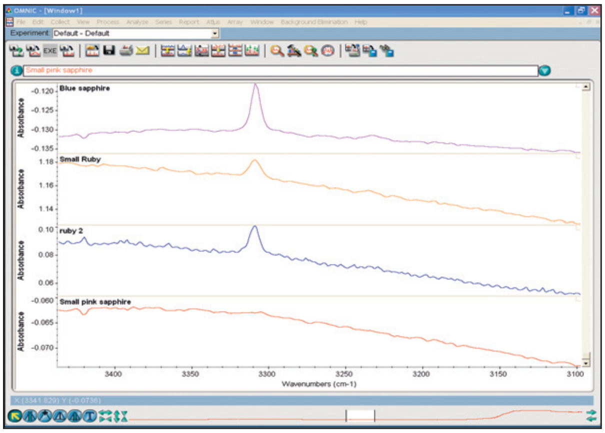


Figure 3: A comparison of the OH spectral region for four stones

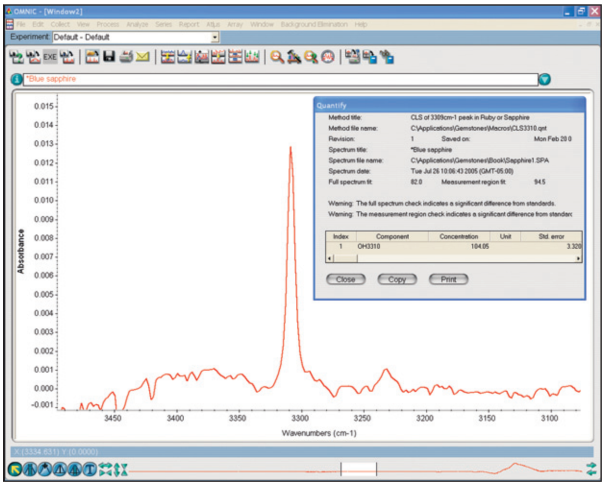


Figure 4: CLS analysis result for determining water in corundum

Conclusions

In this application note, we have provided several examples where the combination of a Nicolet series FT-IR spectrometer and an optimized accessory have been used with multivariate statistical analysis techniques to provide a rapid, reliable information source of great importance to classifying gemstones.

Additionally, we have described an example of using FT-IR spectroscopy to verify the presence of a specific peak in the infrared spectrum of corundum. The presence of this peak strongly suggests that a stone has not undergone the beryllium diffusion treatment. If this peak is not present in the spectrum, there is a good chance that the stone has been treated. Depending on the potential value of the stone, this rapid screen may be used to identify the need for more extensive testing. In many cases, a full FT-IR analysis can be performed in less than a minute, saving gemologists precious time.

The high-quality spectra easily obtained from rubies and sapphires with the Nicolet 6700 FT-IR spectrometer can provide valuable information to aid in verifying that a sample is an untreated natural ruby or sapphire. While no analytical technique can solve every problem, FT-IR spectroscopy plays a valuable role in modern gemological laboratories.

References

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