AVANTES
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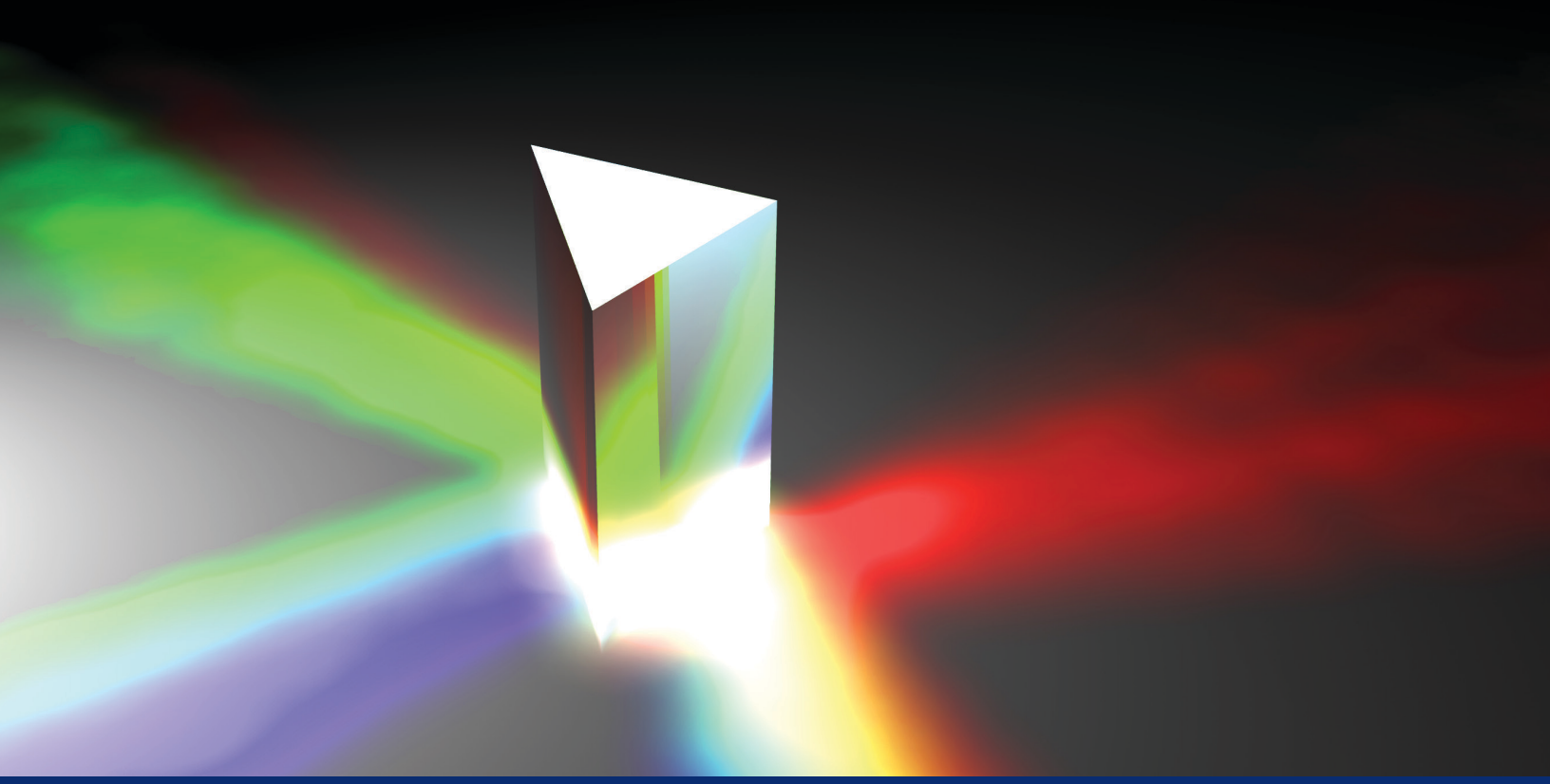
APPLICATION NOTE

CHARACTERIZATION AND IDENTIFICATION OF GARNET USING SPECTROSCOPY TECHNIQUES



INTRO

SPECTROSCOPY METHODS FOR THE GEMOLOGY INDUSTRY

Spectroscopy has been long used in the gemology industry for characterization and identification, with nearly every known spectroscopic method playing a critical role. Transmission provides insight into gemstone clarity, reflectance provides colorimetric data, fluorescence & absorption are excellent at detecting bulk defects, and Raman & laser-induced breakdown spectroscopy (LIBS) provides molecular and atomic composition.

These methodologies can be straightforward for some gemstones, such as diamonds. Since diamond is a simple single element face-centered cubic crystal, it is effortless to differentiate counterfeits such as zircon ($ZrSiO_4$ tetragonal crystal) using Raman spectroscopy. It is also extremely straightforward to distinguish between natural and lab-grown diamonds by examining their fluorescence spectrum since natural diamonds will have some impurities. Additionally, diamonds are often graded for color (colorless to faint) and clarity (flawless to included) by placing them into a calibrated integrating sphere and performing transmission/reflection spectroscopy. Colored precious and semi-precious stones having far more complex compositions (chemically and crystallographically), also benefit from spectroscopic analysis, especially garnets.

SPECTRAL ANALYSIS OF GARNET

Garnets are a class of silicate minerals that include several varieties with the general form $X_3Y_2(SiO_4)_3$. Their structure of isolated SiO_4 tetrahedra is interconnected by a combination of covalent (Y_2) and ionic (X_3) metal substitutions producing an isometric cubic unit cell with a typical lattice constant of 12Å. Therefore, when discussing garnets, it is more helpful to consider them as a family instead of one individual stone type. The garnet family is divided into two distinct groups referred to as the calcium and aluminum groups. The aluminum group members consist of almandine ($Fe_2^{+3}Al_2Si_3O_{12}$), spessartine ($Mn_2^{+3}Al_2Si_3O_{12}$), & pyrope ($Mg_3Al_2Si_3O_{12}$), and the calcium group members are andradite ($Ca_3Fe_3^{+2}Si_3O_{12}$), uvarovite ($Ca_3Cr_3^{+2}Si_3O_{12}$), & grossular ($Ca_3Al_2Si_3O_{12}$). It should be noted that while grossular is typically classified as a member of the calcium group, the fact that it contains both calcium and aluminum mean that it can be thought of as the bridge between the two groups. In fact, as shown in Figure 1, it can be used quite literally to bridge the two groups together physically. Each member can then be further broken down into different varieties (e.g., andradite can be divided into demantoid, melanite, and topazolite), further demonstrating the complexity of the garnet family.

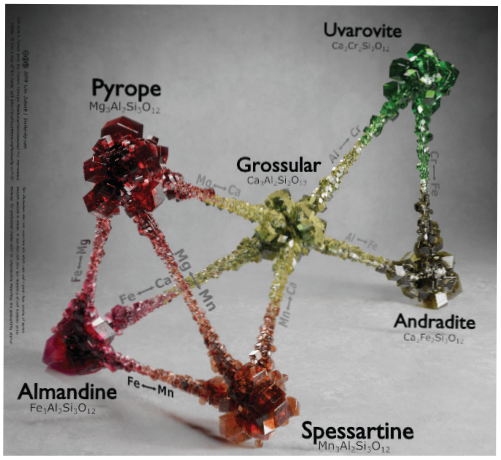


FIGURE 1: End member compositions of the garnet mineral group. [1]

Spessartine Garnets

This application note aims to show how easy it is to perform spectral analysis of garnets by comparing spessartine garnets from different geographic regions. While all these stones have the same base chemical structure ($Mn^{2+}_3Al_2Si_3O_{12}$), slight differences in impurities result in the vastly different appearances, as shown in figure 2. For example, while the spessartine garnets from China and Pakistan appear to have an orange/amber color, the sample spessartine from Brazil is much more of a deep dark red.

FIGURE 2: Spessartine garnets from different regions - (a) China, (b) Brazil, and (c) Pakistan.

REFLECTANCE SPECTROSCOPY

Because of the apparent colorimetric differences, first, we decided to measure the reflectance spectra of all three spessartine samples. For this experiment, we utilized an Avantes AvaSpec-ULS2048x64-EVO spectrometer configured to measure from 200 nm to 1100 nm, in conjunction with the AvaSphere-50-LS-HAL-12V 50 mm integrating sphere with an integrated 5W constant current halogen light source (see figure 3). The integrating sphere was secured in an inverted configuration with the stones placed on top of the 10mm diameter sample port.

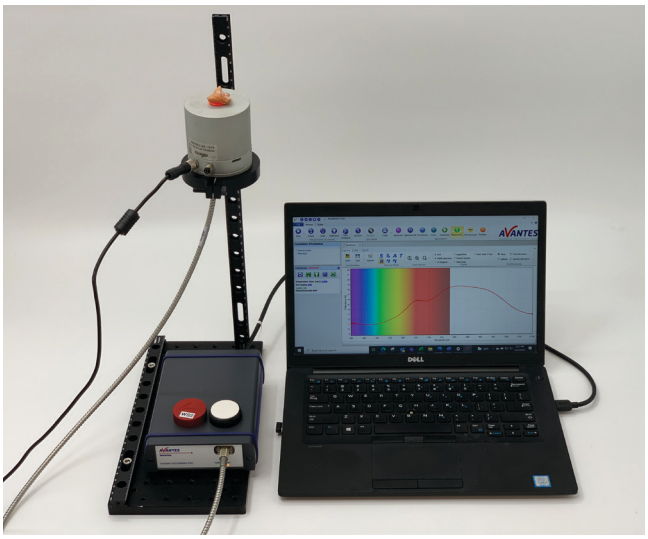
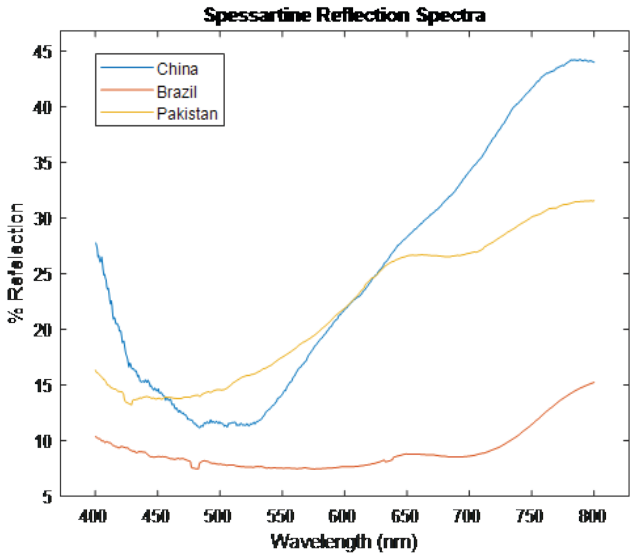


FIGURE 3 Reflectance spectroscopy experimental set-up.

Spessartine Garnet Reflectance Spectra

The spectra shown in figure 4 are consistent with the visual inspection while highlighting subtle differences not visible to the human eye. For example, the sample from Brazil has a significantly lower overall reflectance with a slight elevation in reflectivity in the red and violet regions of the spectrum, consistent with the deep (dark) red color visually observed. However, the results from the samples from China and Pakistan are a bit more intriguing since even though they both visually appear similar, their reflectance spectra are quite different. While both stones have roughly equal reflectance in the orange region of the spectrum, around 600nm, the stone from China has significantly more signals in the red and blue. But the sample from Pakistan has much higher reflectance in the green.



Since the human eye can only detect red, green, and blue, and our brains interpolate the rest of the color spectrum based on these parameters, it makes sense why these two different spectra would lead to the same apparent color. This example does an excellent job of showing how reflectance spectroscopy can potentially be used for both color analysis and regional identification.

TRANSMISSION SPECTROSCOPY

While reflectance is an excellent tool for surface-level characterization, we also decided to use transmission spectroscopy to see if we could further differentiate the stones based on their bulk absorption properties. For this experiment, we modified our experimental set-up by using a fiber-coupled Avalight-HAL-S-Mini2: 10W halogen light source with a COL-UV/VIS collimating less accessory. This allowed us to illuminate the sample from the top while still collecting the transmitted light through the integrating sphere. To extend our measurement capabilities into the near-infrared (NIR), we incorporated Avantes' AvaSpec-NIR256-1.7-EVO spectrometer configured to measure from 950 nm to 1700 nm. The output from the integrating sphere was directed to the two spectrometers using an FCB-UVIR-600-1-ME bifurcated fiber (see figure 5). It is important to note that due to the nature of the samples, it was not possible to ensure that all three spectra were measured with the sample optical pathlength. Therefore, the transmission spectra should not be analyzed quantitatively as we did for the reflection spectra.

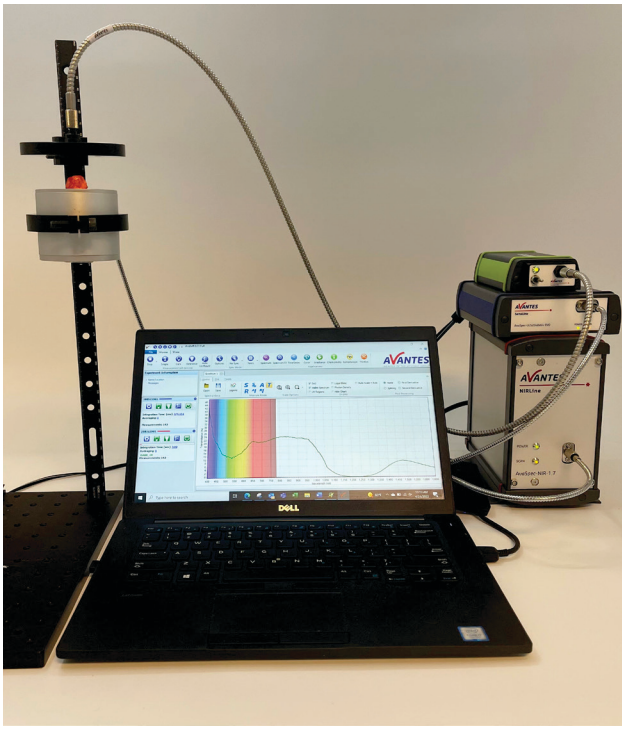


FIGURE 5
Transmission spectroscopy experimental set-up.

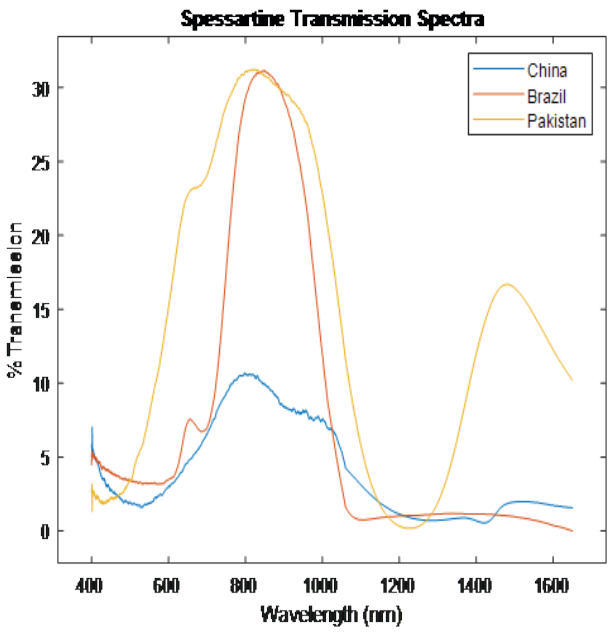


FIGURE 6
Transmission spectra of spessartine garnets from China, Brazil, and Pakistan.

While further investigation would be needed to identify the exact chemistry responsible for the transmission spectra shown in figure 6, it is abundantly clear that all three stones have extremely different transmission spectra. The most striking feature that we observed in the transmission spectra was the fact that both the China and Brazil samples appeared to be relatively opaque above 1100nm, whereas the Pakistan sample had a much higher transmissivity. This may be because of included water (liquid or gaseous) samples from China and Brazil, but further investigation would be needed to verify this.

RAMAN SPECTROSCOPY

Lastly, we measured the Raman spectra of all three samples to investigate the spessartine samples' molecular structure directly. Although, it should be noted that Raman spectroscopy is not sensitive to ionically bound atoms. Therefore, it can only directly measure the covalently bound $Y_2(SiO_4)_3$ portion of the crystal, not the ionically bound X_3 atoms. Still, the Van der Waals force and other steric effects from the X_3 ions do affect the vibrational modes of the covalently bound atoms allowing for indirect measurements to be taken. Although it wasn't investigated as part of this experiment, one could use LIBS to measure the full atomic structure of the sample directly. For the Raman measurements, we used an Avantes Avaspec-Mini4096CL ultra company miniature spectrometer configured to measure from 785nm to 1100nm with a 50µm slit and an AvaLaser785 ultra-high-throughput Raman probe with an integrated 785nm wavelength stabilized laser source (see figure 7). From the Raman spectra shown in figure 8, we can see that even though there are significant differences in the reflection and transmission spectra of the three spessartine samples, they are still extremely similar from a molecular standpoint. The spessartine spectra exhibit a prominent silicate peak around 900cm^{-1} and a series of smaller bands below 500cm^{-1}, likely combining Y-O (metal oxide) bonds and structural phonon modes.

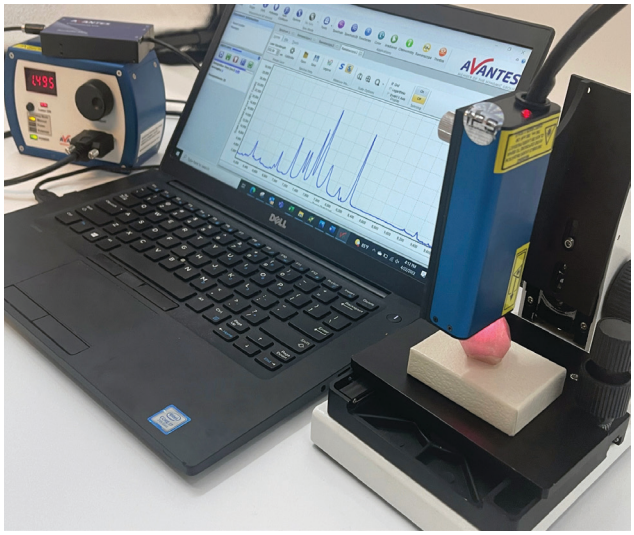


FIGURE 7: Raman spectroscopy experimental set-up.

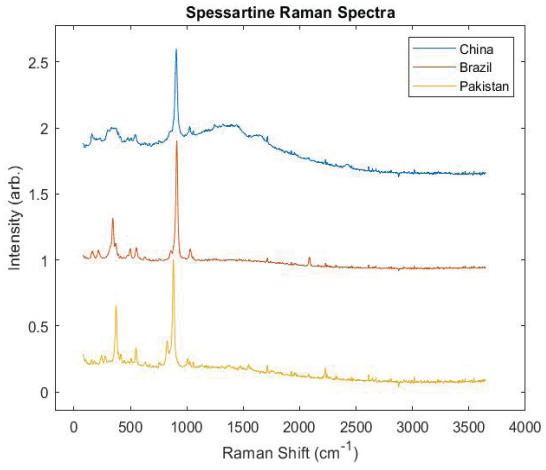


FIGURE 8: Raman spectra of spessartine garnets from China, Brazil, and Pakistan.

A small fluorescence band in the Raman spectra of the sample from China (1100cm^{-1} to 1600cm^{-1}) provides strong evidence of organic impurities not found in the other two samples. The broadening can be seen as further proof of impurities in the China sample of the Raman band centered around 342cm^{-1} compared to the other two samples. This would indicate that the 342cm^{-1} peak likely corresponds to an optical phonon (structural mode), and the presence of the impurities increases the disorder in the crystal lattice. This is a fascinating discovery because the China and Pakistan stone visually appears to the quite similar, but on a molecular scale, the Pakistan stone is much more like the stone from Brazil. Upon closer inspection of the 342cm-1 band in Brazil stone's spectra, it appears to be splitting into two "sub-bands." This feature, combined with the deep red color of the sample, is strong evidence of high concentrations of Mg, like pyrope garnets which are typically dark red. A much deeper analysis beyond the scope of this application note would be required to confirm these hypotheses.

FINAL THOUGHTS

We specifically chose to look at garnets to highlight their uniquely broad range of chemical and spectra characteristics in this application note. Still, it is important to remember that all the spectral analysis tools shown here can be employed to characterize virtually any precious and semi-precious gemstones. It is also important to note that while all the components used were stand-alone modules, they are also available as standalone units OEM modules or can be integrated into multichannel rack mount systems that are ideally suited to inline large scale gemstone analysis.

These units can communicate via USB, Ethernet, and the native digital & analog input/output capabilities of the Avantes AS7010 electronics board provides for a superior interface with other devices. Additionally, the Avantes AvaSpec DLL package, with samples programs in Delphi, Visual Basic, C#, C++, LabView, MATLAB, and many other programming environments, enables users to develop their own code.

Contact Us

For more information about the full range of spectrometer options available from Avantes for fluorescence spectroscopy, please feel free to visit the website at www.avantes.com or give us a call at +1 (303)-410-8668 (USA) or +31 (0) 313 670 170 (Europe) where our knowledgeable applications specialists are standing by to help

Reference

1) Jakaite, Lina. "A visual representation of the end members of garnet and the relationship of the elements that are substituted for each variety" wikipedia, https://bit.ly/3kcVFJl 04.24.2022

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