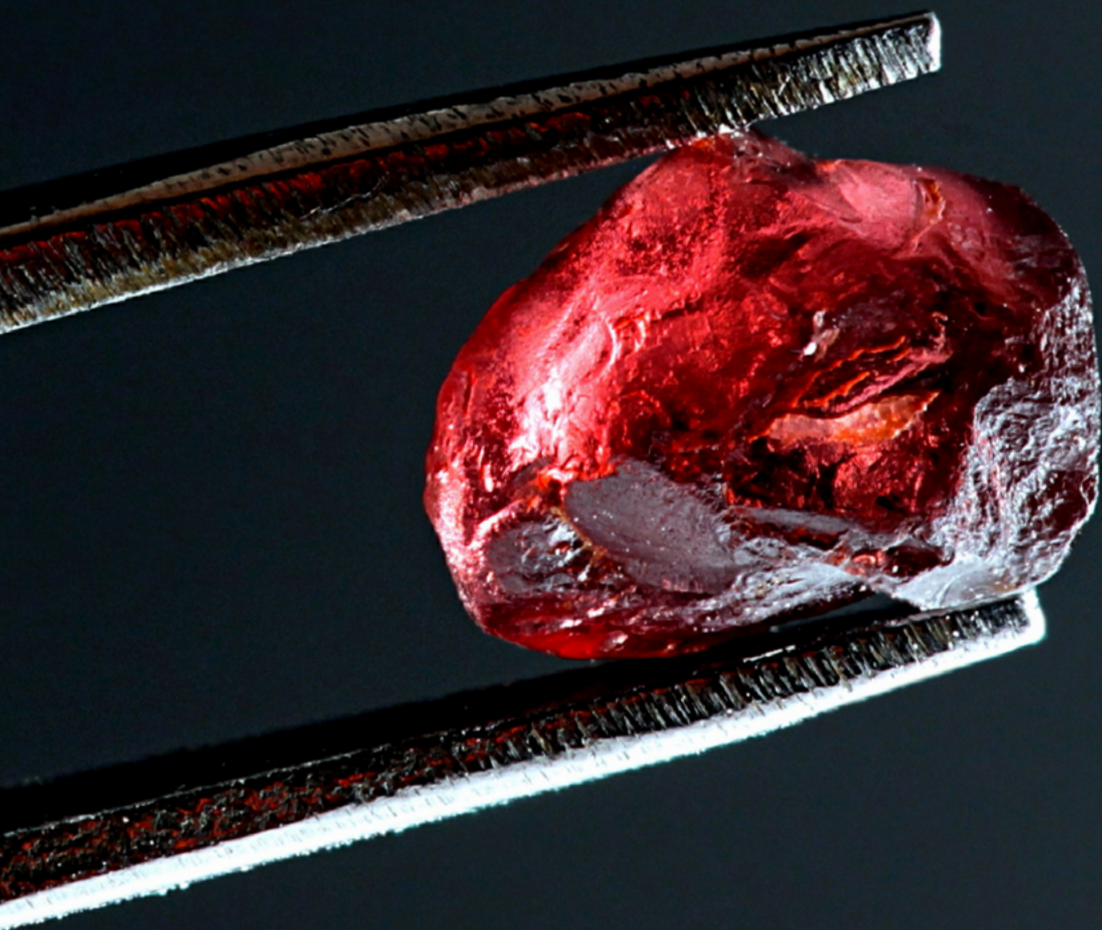




APPLICATION NOTE

RAMAN AND LIBS ANALYSIS OF GARNET SPECIES



INTRO

SPECTROSCOPY METHODS FOR GEMOLOGY

Earlier this year, we had the opportunity to analyze an extensive sampling of garnets from around the world, courtesy of collections from Dan Zellner of DanZ Rockshop and Nathan Robey, Sales Application Engineer at Avantes. In our first application note, “Characterization and Identification of Garnet Using Spectroscopy Techniques,” we focused on a specific garnet species known as spessartine. We examined color differences (reflection), absorption (transmission), and molecular structure (Raman), which highlighted the differences between spessartine garnets from the Fujian Province of China, Minas Gerais, Brazil, and the Federally Administrated Tribal Areas (F.A.T.A.) of Pakistan. However, we were still left with several unanswered questions about the nature of these differences. For example, why was the sample from Pakistan less absorbent in the near-infrared than the other samples? Why was the stone from Brazil a deep red color, while the other two appeared to be more amber? What caused the slight differences in the Raman spectra of all three? As a result, we decided to revisit our initial analysis with a twofold goal; expanding the Raman analysis to include additional garnet species and performing LIBS analysis to gain insight into the atomic differences between the different stones.



FIGURE 1: End member compositions of the garnet mineral group¹

Before diving into the details of this analysis, it is helpful to briefly review the fundamentals of garnet chemical structure, $X_3Y_2(SiO_4)_3$. 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. Garnets are first divided into two distinct groups, the aluminum group consisting of almandine ($Fe_2^{+3}Al_2Si_3O_{12}$), and 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 means that it can be considered 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. Not only is the bridge between the calcium and aluminum groups significant, but so is the bridge between species within a group (figure 1). For example, the aluminum group members are bridged by the ionic element. Spessartine and pyrope have a $Mn \leftrightarrow Mg$ bridge, spessartine and almandine have a $Mn \leftrightarrow Fe$ bridge, spessartine and grossular have a $Mn \leftrightarrow Ca$ bridge. This means that every spessartine garnet has some Mn, Mg, Fe, and Ca, but most of the ionic (X_3) elements must be Mn to be classified as spessartine.

SPECTRAL CORRELATION USING RAMAN SPECTROSCOPY

In this study, we exemplified a sample set of 14 different garnets, 12 of known species and origin and two of unknown species and origin. The known sample set included: 4 andradite stones, 2 from Stanley Butte, Arizona, and 2 (of the melanite variety of andradite) from the Kayes Region of Mali, six spessartine stones, two from Minas Gerais, Brazil, two from Fujian Province, China, two from F.A.T.A., Pakistan, and two grossular stones of the Tavorite variety, both from the Merelani Hills of Tanzania. The Raman spectra were acquired using an Avantes Avaspec-Mini4096CL ultra compact miniature spectrometer configured to measure from 785nm to 1100nm with a 50 μ m slit and an AvaLaser785 ultra-high throughput Raman probe with an integrated 785nm wavelength stabilized laser source (figure 2).

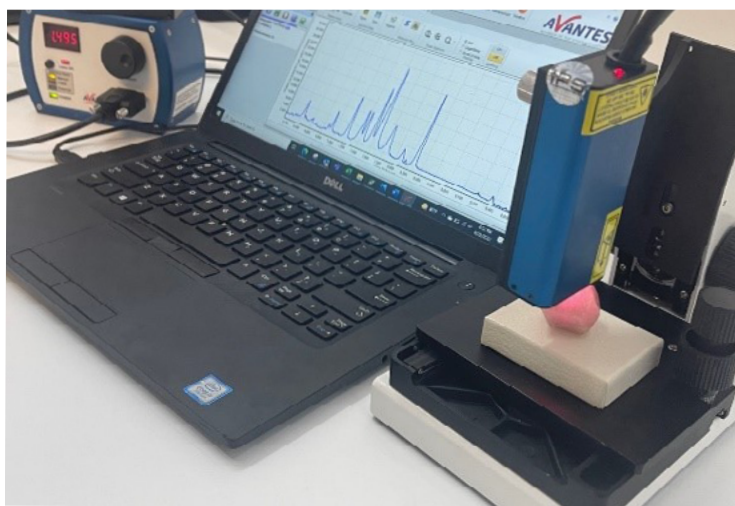


FIGURE 2 Raman spectroscopy experimental set-up

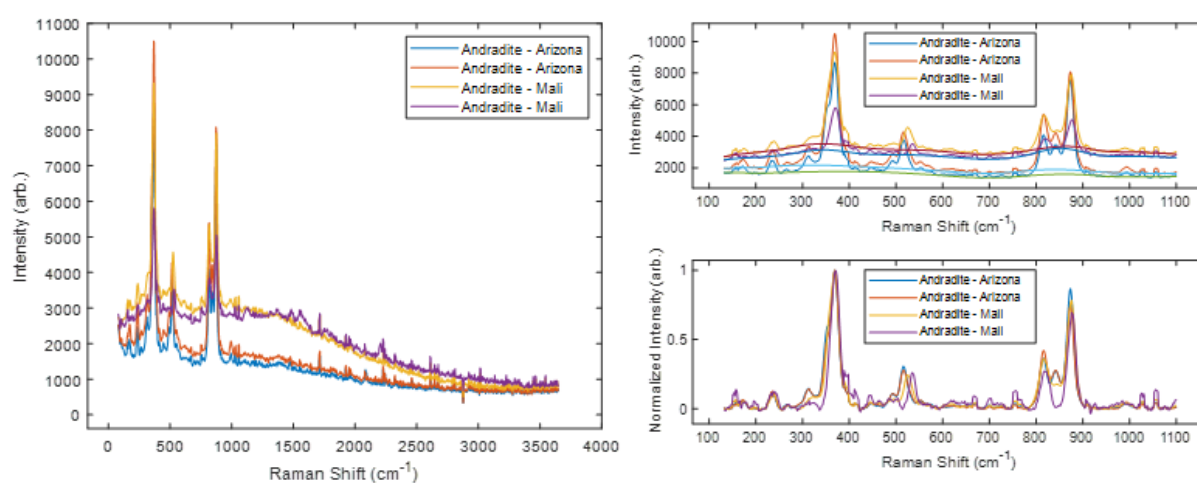
We employed a spectral correlation method called the hit quality index (HQI) or correlation coefficient to compare the Raman spectra from the various samples. The exact details of the mathematics behind this analysis are beyond the scope of this application note, but what is essential to understand is that it provides a single value to represent how well two spectra correlate to each other (with 1 being perfectly correlated and 0 being perfectly uncorrelated). It should be noted that while this method is relatively straightforward to implement, there are several steps along the way where human subjectivity comes into play. Therefore, we must take the time to walk through the assumptions/protocols followed in this analysis before moving on to any data interpolation.

In this analysis, our first step was removing the sample's background fluorescence to ensure that we only factored the Raman scattering in our correlation analysis. This was done using an adaptive iteratively reweighted penalized least squares (airPLS) algorithm to fit the fluorescence background and subtract it from the raw data. Next, we chose to normalize the data to the maximum peak height of each spectrum, ensuring that sample-to-sample measurement uncertainty would be removed. No other data preprocessing was done to the spectra. The spectra were then all compared to each other using a confusion matrix, where an $HQI > 0.85$ was defined as a strong correlation (green), $0.85 > HQI > 0.5$ weak correlation (yellow), and an $HQI < 0.5$ uncorrelated (red).

SPECTRAL CORRELATION USING RAMAN SPECTROSCOPY

Figure 3 shows a simple example of this process where the four different andradite samples were compared. As you can see, the two samples from Arizona are exceptionally well correlated with HQI values of 0.9912. The two samples from Mali are also well correlated with an HQI of 0.9026. Interestingly we also see that one of the Mali samples is strongly correlated to the Arizona samples (HQI = 0.9611). At the same time, the other one is only weakly correlated to the Arizona samples (HQI = 0.8130). This simple example illustrates two things simultaneously.

First, the fact that correlation is extremely powerful for identifying similar Raman spectra, but it doesn't tell the whole picture. For example, a close examination of the raw data indicates that both Mali samples have a higher fluorescence signal than the Arizona samples.



Andradite	Arizona 1	Arizona 2	Mali 1	Mali 2
Arizona 1	1.0000	0.9912	0.9611	0.8130
Arizona 2	0.9912	1.0000	0.9656	0.8265
Mali 1	0.9611	0.9656	1.0000	0.9026
Mali 2	0.8130	0.8265	0.9026	1.000

FIGURE 3 Example of spectral correlation procedure showing with the raw spectral data (upper left), baseline corrected and normalized spectra (upper right), and confusion matrix (bottom).

SPECTRAL CORRELATION USING RAMAN SPECTROSCOPY

Next, we applied the same protocol to the six spessartine samples to follow up on the previous application note. The resultant confusion matrix (see figure 4) shows that spessartine samples from Brazil and China strongly correlated, but the samples from Pakistan only correlated with each other. This was surprising since China and Pakistan samples appeared to be far more similar visually but provide a rationale for the NIR absorbance of the stone from Pakistan being much lower than the other two. We will further investigate these differences using LIBS in the following section.

Spessartine	Brazil 1	Brazil 2	China 1	China 2	Pakistan 1	Pakistan 2
Brazil 1	1.0000	0.9702	0.9162	0.9045	0.1350	0.1114
Brazil 2	0.9702	1.0000	0.8548	0.8499	0.1058	0.0876
China 1	0.9162	0.8548	1.0000	0.9916	0.2106	0.1782
China 2	0.9045	0.8499	0.9916	1.0000	0.2070	0.1792
Pakistan 1	0.1350	0.1058	0.2106	0.2070	1.0000	0.9770
Pakistan 2	0.1114	0.0876	0.1782	0.1792	0.9770	1.0000

FIGURE 4: Confusion matrix for the various spessartine garnets.

Finally, we attempted to classify the two unknown garnets by correlating the Raman spectra against our 12 known samples. Based on the confusion matrix (see figure 5), we could identify unknown sample 1 as spessartine and unknown sample 2 as grossular. Interestingly, the unknown spessartine appears to be more strongly correlated with the Brazil samples than China and not correlated with the ones from Pakistan. Unfortunately, we only have a grossular sample from one region, so it is hard to draw any more profound conclusions about the second unknown garnet other than the fact that it is grossular.

Garnets	Unknown 1	Unknown 2
Andradite Arizona 1	0.0396	0.0773
Andradite Arizona 2	0.0354	0.0725
Andradite Mali 1	0.0461	0.0877
Andradite Mali 2	0.0464	0.1715
Spessartine Brazil 1	0.7091	0.0087
Spessartine Brazil 2	0.8800	0.0051
Spessartine China 1	0.6119	0.0098
Spessartine China 2	0.6269	0.0102
Spessartine Pakistan 1	0.0277	0.0570
Spessartine Pakistan 2	0.0204	0.0740
Grossular Tanzania 1	0.0067	0.8713
Grossular Tanzania 2	0.0076	0.8945

FIGURE 5: Confusion matrix comparing two unknown garnets against the entire collection of known garnets.

ELEMENTAL ANALYSIS USING LIBS

To gain a deeper understanding of results from the last part of this study, we measured the LIBS spectra of all 14 garnets using the Avantes LIBS evaluation kit (see figure 6) with an AvaSpec-Mini2048CL configured with a 1200 groove grating and a 25-micron slit to provides 0.25nm resolution from 200 nm to 450nm. This spectral range is ideal for analyzing garnets because of the high density of LIBS bands for common garnet constituent elements such as Al, Ca, Si, Fe, and Mg.

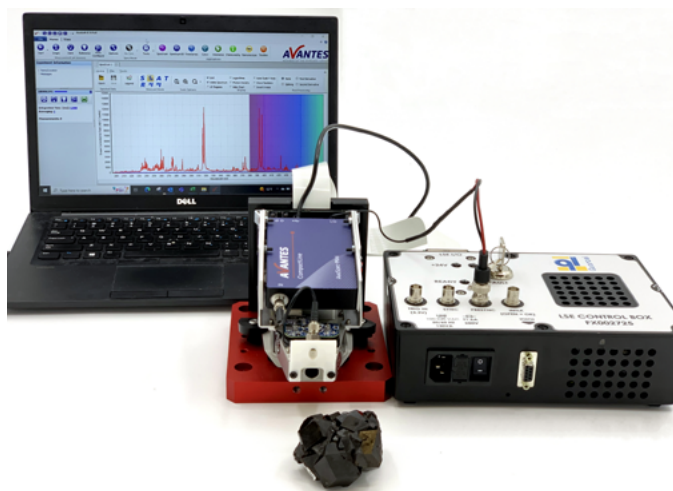


FIGURE 6: LIBS experimental set-up.

Since all garnets, regardless of species, have the same amount of Si, we normalized all the spectra to the 288nm band, allowing us to compare the relative peak intensities. The spectra shown in figure 7 indicate a substantially higher Mg concentration in the Brazil sample compared to the Pakistan sample, but not in comparison to the China sample. Interestingly though, when we look at the spessartine of unknown origin, we can see that it has the highest Mg concentration. This is consistent with the fact that the unknown sample has a deep red color (see figure 8) closer to that of pure pyrope than pure spessartine.

While we measured the LIBS spectra for all 14 garnets, we will limit the discussion in this section primarily to the spessartine samples since they showed the highest variability. Our first goal was to explore the hypothesis of the prior application note, which suggested that the Brazil sample may have more Mg (from the spessartine to pyrope bridge) than the China and Pakistan samples. We tested this hypothesis by looking at the Mg doublet band at 280nm compared to the Si band at 288nm.

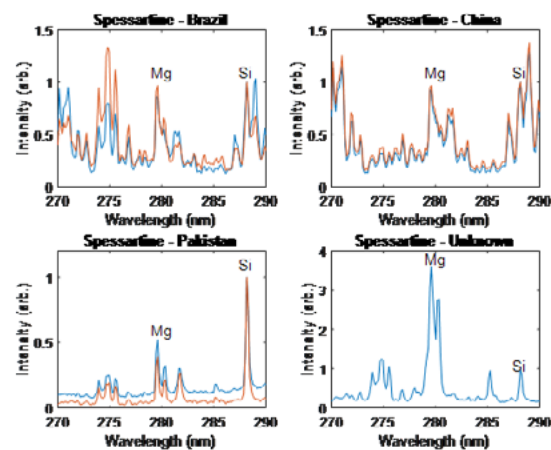


FIGURE 7: LIBS spectra of spessartine garnets zoomed in on the Mg / Si region of the spectrum.



FIGURE 8: Spessartine garnets from different regions - (a) China, (b) Brazil, (c) Pakistan, (d) unknown origin.

ELEMENTAL ANALYSIS USING LIBS

The second region of interest we examined was the Ca / Al region of the LIBS spectra centered around 395 nm, which is particularly interesting for exploring the spessartine to grossular bridge. In this region, we chose the Al band at 396 nm for our normalization since all spessartine garnets should have the same amount of Al (see figure 9). Based on the results, we can see that the Pakistan samples contain significantly more Ca than the others. Combining the abundance of Ca with the relatively low concentration of Mg in the Pakistan samples compared to the other localities, it is now apparent why the Raman spectra did not correlate to the samples from China and Brazil. This means that while they are all spessartine, Brazil, China, and unknown sample are more “pyrope-like,” whereas the Pakistan sample is more “grossular-like.” To further support the argument that the Pakistan sample is more “grossular-like” in nature, it is helpful to compare it with the LIBS spectra of the three grossular samples shown in figure 10. Additionally, the fact that there appears to be H (likely from water inclusions) in both Brazil and unknown samples but not in the China sample may indicate why the unknown sample is more strongly correlated to the Brazil samples.

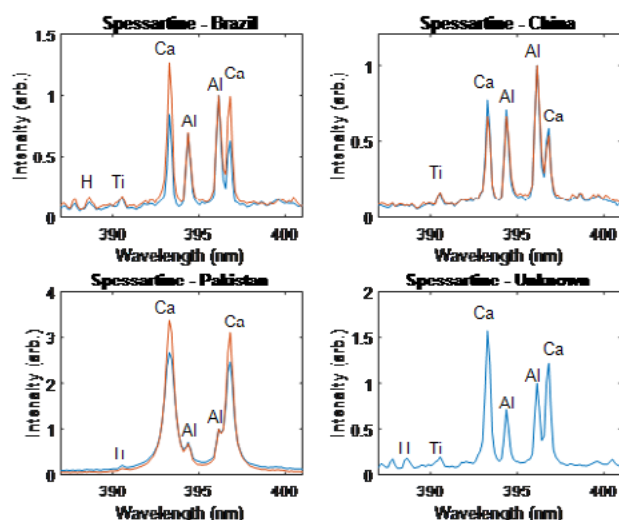


FIGURE 9: LIBS spectra of spessartine garnets zoomed in on the Ca / Al region of the spectrum.

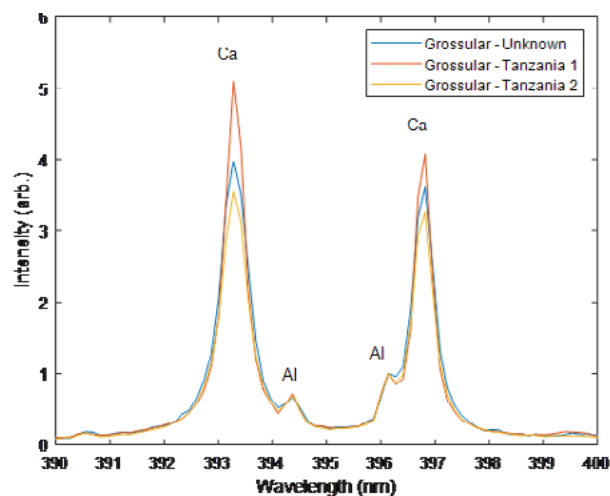


FIGURE 10: LIBS spectra of grossular garnets zoomed in on the Ca / Al region of the spectrum.

FINAL THOUGHTS

While each spectroscopic technique is extremely powerful in its own right, no one methodology can provide the complete picture, especially in systems like garnets, where the structure combines ionically and covalently bound species. This study focused on garnets, but it is important to note that the combination of molecular and atomic spectrometers is an extremely powerful tool for identifying and classifying complex structures.

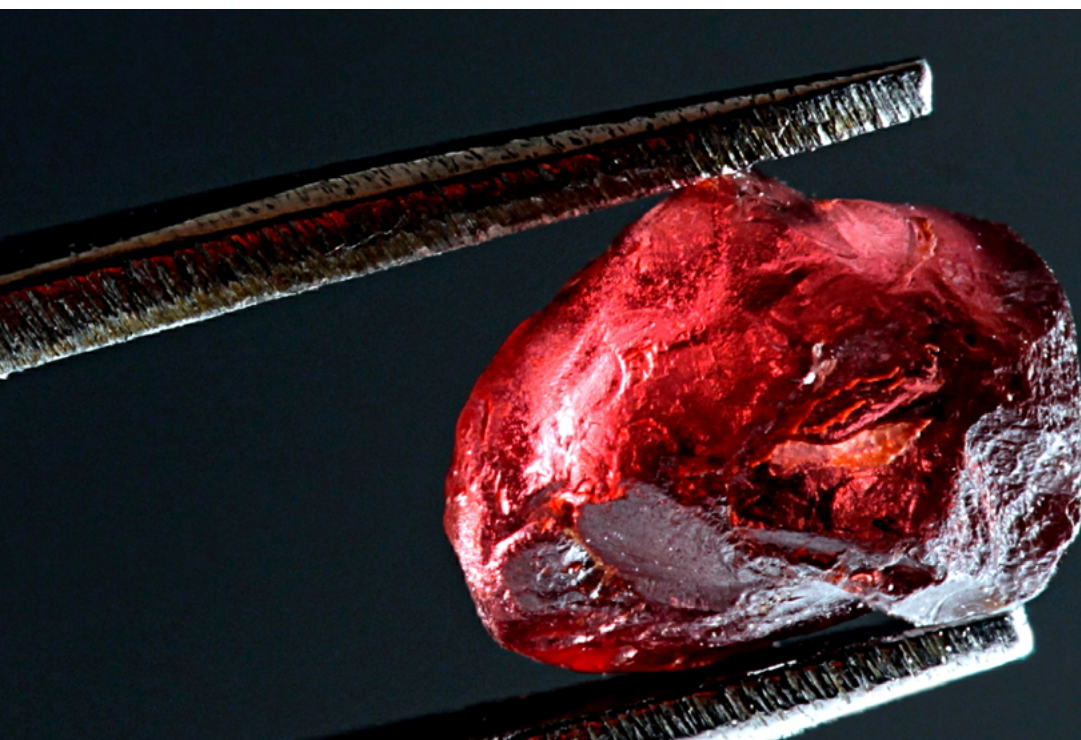
It is also important to note that while all the components used were standalone modules, they are also available as standalone units, OEM modules, or can be integrated into multichannel rack mount systems that are ideally suited to inline large-scale gemstone analysis. These units can communicate via USB, Ethernet, and the native digital & analog input/output capabilities of the Avantes AS7010 electronics board provide a superior interface with other devices. Additionally, the Avantes AvaSpec DLL package, with sample programs in Delphi, Visual Basic, C#, C++, LabView, MATLAB, and many other programming environments, enables users to develop their own code.

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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/3kcVFJI> 04.24.2022



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