RM APPLICATION NOTE 01-03

Gemstone Identification Using Raman Spectroscopy

In recent years, the gemstone market has been flooded with stones of questionable origin. Frequently, even thorough analysis by a qualified jeweler cannot unequivocally reveal whether a gemstone is genuine or fake. In the worst case, even sophisticated analytical methods struggle to differentiate modified diamonds, causing considerable concern to the international gemstone trade. Raman micro-spectroscopy is an ideal method for the examination of marketable gemstones. The lack of sample preparation and the non-destructive nature of Raman analysis make it ideal for the analysis of even high-value gems. Plus, the micro-Raman study of a stone provides a unique record for identification purposes. We will discuss the variety of Raman spectra that can be obtained from different families of gemstones, comparing and contrasting spectra from genuine and artificial materials.

Introduction

Gemstones and semi-precious stones have been modified for centuries to make them more colorful, more eye-catching, and easier to work with. One such technique is heat treating (the most common) to enhance, clarify or create color in a stone. Amethyst is heated for citrine. Zircon is heated to clarify the stone to clear white. Sapphires are heated to get amazing pinks and blues. Rubies lose a purplish tint while iolite may be turned a deep blue. Heat treating can also be used to enhance the 'color change' of gems such as tanzanite. Dying of stones is also a very common practice. Agate is dyed to get pinks, purples, orange and blues. Chalcedony is also dyed; black chalcedony sold as onyx. Irradiation is another common treatment. Topaz is currently the most commonly irradiated gemstone (to get various shades and tones of blue). This is also how one obtains fabulously colored diamonds. In fact, diamond was the first gemstone to be color treated by radiation. (Figure 1) Another gemstone modification is stabilization. Stabilization was traditionally accomplished by filling the stone with natural oils; however, modern synthetic resins such as Opticon are now being used. Resin filling is often more permanent than the use of natural oils. Opals are often stabilized and emeralds have a long history of fracture filling due to their popularity and a tendency to be highly fractured or contain multiple inclusions.

The most controversial of all the modification techniques is the "creation" of gemstones. Cultured pearls are genuine but are created by using a center of plastic or mother of pearl, rather than sand. Still a pearl, just helped to grow by human intervention.

Figure 1. Diamonds of varying color.

Laboratory grown crystals of ruby, sapphire, diamond, emerald, and star sapphire are real semiprecious stones. They just weren't grown in the earth. So what is the answer: Real or Fake? This argument can be discussed with all sides being technically correct, but it is not the most important information. From a lapidary or jeweler's point of view, the most important topic is proper disclosure. Does the buyer know up front that the stone he is purchasing has been 'helped along' by the human touch?

Gems are often examined by trained personnel using optical microscopy and other methods. In some well-studied cases like diamond, these techniques will usually suffice. However, imperfections can be readily filled with synthetic materials or the stone can be processed to alter the color and increase market value, with the unsuspecting consumer convinced that he has purchased a stone of greater value. With lesser gemstones the analytical techniques are much less established and more reliant on long experience with mineralogical identification methods. Raman spectroscopy however provides an ideal method for the examination of gemstones and semi-precious stones. With the ability to microscopically examine both loose and mounted stones, Raman can distinguish not only real versus artificial gemstones, but can also discriminate those that have been adulterated in addition to providing details of the alteration.

Experimental

Gemstones loose and mounted in different types of 14K gold jewelry settings (rings and pendants) were purchased from various dealers. The gemstone was then placed into the sample compartment of a JASCO *Ventuno*; a benchtop mounted, fully integrated confocal micro-Raman spectrometer. The instrument was equipped with a 532 nm diode laser; 2 gratings and an air cooled CCD detector. The integration times for spectral collection were 20 seconds per acquisition. The confocal aperture used (50mm), gives an approximate 1mm (x,y) and 2mm (z) sample volume. The laser power at the sample was 10 mW or less.

Results and Discussion

Citrine is the most valuable Quartz gem. Almost all Citrine on the market is heat-treated Amethyst. Natural Citrine is yellow to orange, and occurs in much lighter hues than the heat-treated material. In some Amethyst deposits, the Amethyst has been partially or fully changed to brown Citrine by geothermal heating. Citrine may also be produced by heat-treating Smoky Quartz from certain localities. Citrine also closely resembles topaz. Unfortunately, unscrupulous dealers label Citrine in such a way that unassuming buyers think they are buying the more valuable topaz. It should be understood that any "Topaz" labeled with a prefix (such as Gold Topaz, Brazilian Topaz, and Citrine Topaz) is heat-treated Citrine. The Raman spectra in Figure 2 clearly indicate the difference in the two gemstones.

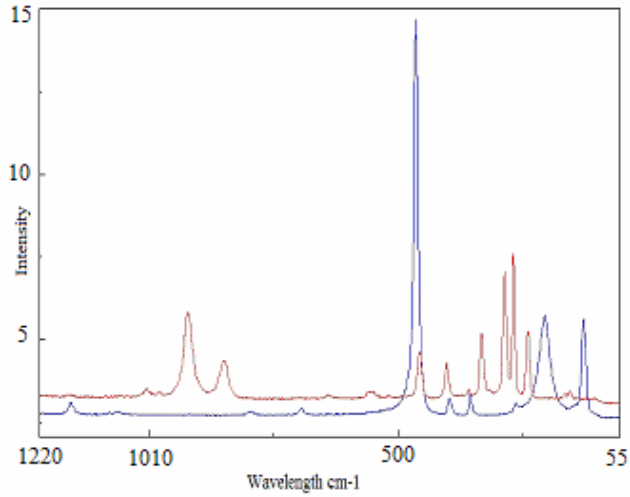

Figure 2. Citrine (blue), a yellow-colored natural quartz, can be passed off as the more expensive topaz (red) by unscrupulous gem dealers.

All natural diamonds are “flawed”, often by color or impurities. Most diamonds have some yellow or brown color. Defects mark the diamond as unique. Color centers in diamond photoluminesce (PL) when excited by laser light. A Raman spectrometer used to measure PL is a powerful characterisation tool to identify artificially reprocessed, “exotic” colored diamonds. (Figure 3) The diamond grading system is as follows: D and F are colorless, G through J are near colorless, K through M are faint yellow or brown, N through Z are light yellow, brown or grey, and Z’s are fancy yellow or brown.

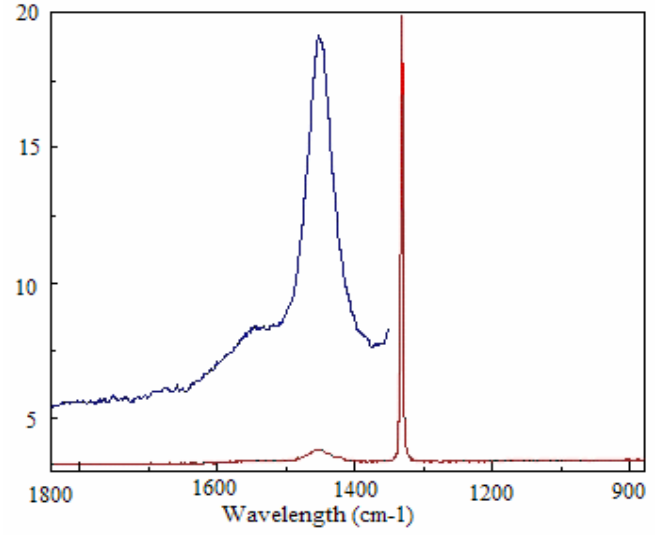

Figure 3. The 1332 cm^{-1} diamond band (red) along with the yellow 1576 cm^{-1} PL emission (blue).

The spectra of two other gemstones mounted as jewelry are shown in Figure 4. In these spectra the differences between the green peridot and the purple tanzanite are clearly identifiable. In conclusion Raman is a powerful tool for the identification and qualification of gemstones.

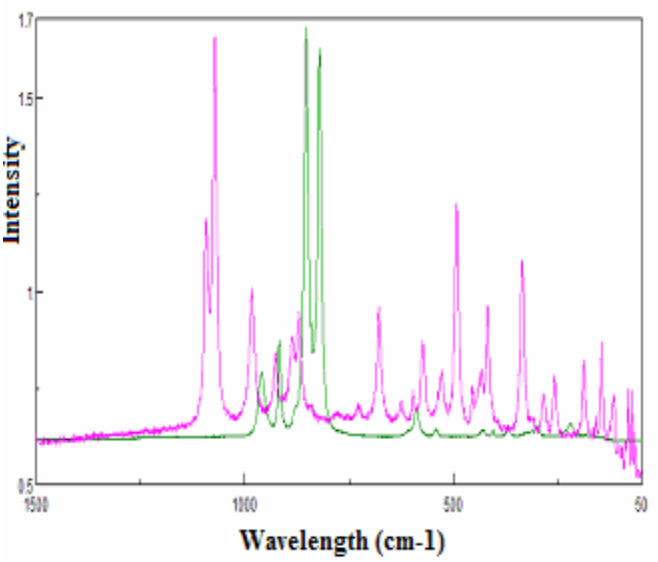

Figure 4. The Raman spectra of peridot (green) and tanzanite (pink)

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