

the most commonly irradiated gemstone (to get various shades and tones of blue). This also is how fabulously colored diamonds are obtained. In fact, diamond was the first gemstone to be color treated by UV radiation (1, 3–6).

Another gemstone enhancement technique is stabilization. Stabilization traditionally was accomplished by filling the stone with natural oils; however, modern synthetic resins such as Opticon (Hughes Associates, Wayzata, MN) are being used now. Resin filling often is more permanent than the use of natural oils. Opals often are stabilized and emeralds have a long history of fracture filling due to the popularity of the gem and a tendency for the stones to be highly included or fractured. Another commonly used technique is diffusion, which embeds a very thin layer of an element into the surface to improve color. Laser drilling also is done to obtain access to enclosed crystal inclusions and remove them with acid. Stones also are bleached, dyed, waxed, coated, and painted (4–6).

One of the most controversial modification techniques is the so-called creation of gemstones. Synthetic gems are made on an industrial scale like chemicals and have been around since the late 1800s when ruby first was synthesized. Laboratory grown crystals of ruby, sapphire, diamond, emerald, and star sapphire bear the name of the mineral species they resemble because they have an identical appearance, atomic structure, and a similar (not always identical) chemical composition. Simulants or imitations are gemstones or other materials that alone or in combination with others are made to look like more valuable gemstones. Assembled stones are made by gluing layers of different gem materials together to create an apparently colored composite or to increase stone size. Glass and plastics, manufactured with a wide range of color, specific gravity and index of refraction can be used to simulate natural stones. Cubic zirconia, synthetic rutile, strontium titanate, zircon, and white sapphire include both synthetic and natural gemstones that are used to simulate natural gemstones, usually diamonds (3). From a buyer's point of view, the most impor-

tant issue with these simulants is proper disclosure (7–9).

Gem Examination and Identification

Gems often are examined by trained personnel using a variety of methods. The most common instrument in gem identification is the eye. Vision alone can be used to observe color, transparency, cut, phenomena, polish luster, dispersion, heft, fractures, and cleavage. However, a variety of analytical instruments also is available and some are explained here.

The refractometer probably is the most common instrument in gemstone identification. A special light source is used to project a beam of light into the refractometer and into a hemicylinder of very soft, highly leaded glass. A small drop of a special liquid with a high refractive index is used to form an optical bond (not physical) between the

sample stone and the hemicylinder. Observation through a calibrated scale allows the observer to see a partially shaded scale where the boundary defines the refractive index of the stone. If a yellow sodium light source is used, the observer can move the stone around to view different facets and determine both the upper and lower limits of the refractive index on doubly refractive stones and therefore the birefringence. Careful use of the refractometer with the stone in many positions also will allow determination of the optical characteristics (doubly or singly refractive) and the optical sign (positive or negative). These tests must be done with a well-polished, clean stone and great care must be taken so as not to scratch the hemicylinder (3, 10).

A thermal impedance tester is used to measure the thermal conductivity of a stone. It is of little value except for separating diamond from other stones.

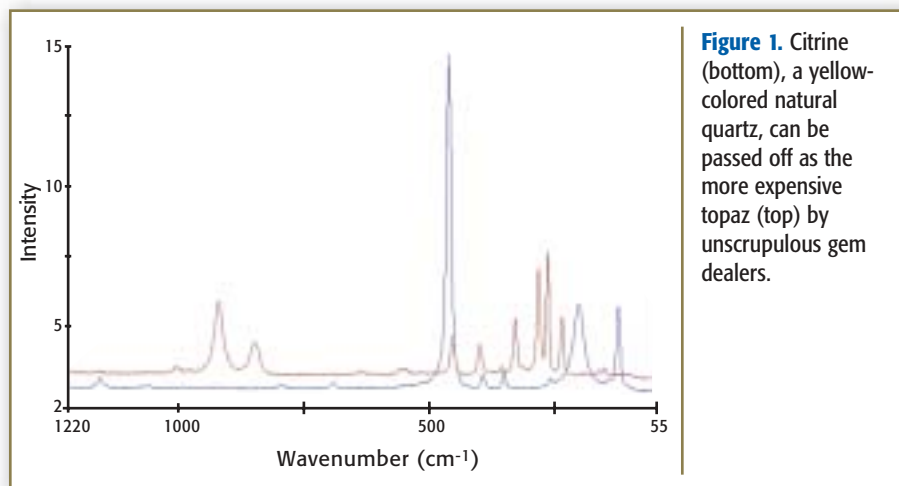


Figure 1. Citrine (bottom), a yellow-colored natural quartz, can be passed off as the more expensive topaz (top) by unscrupulous gem dealers.

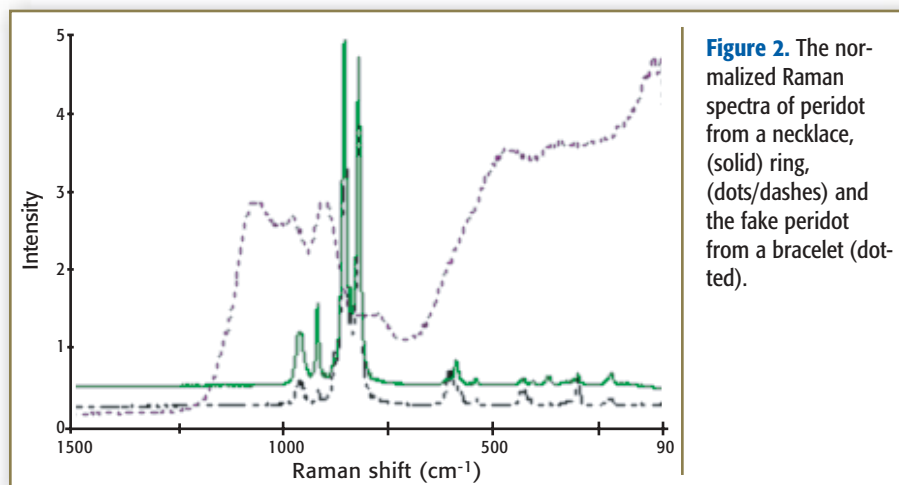


Figure 2. The normalized Raman spectra of peridot from a necklace, (solid) ring, (dots/dashes) and the fake peridot from a bracelet (dotted).

However, even a positive test using thermal impedance must be augmented by other gemological observations to differentiate diamond from moissanite. A UV cabinet uses both short- and long-wave UV light bulbs to illuminate the samples. Testing for UV fluorescence is useful in separating several gemstone types and is particularly useful in separating some synthetic materials from natural counterparts. Occasionally a gemstone will have phosphorescence, a persistent release of light for a short time after exposure to ultraviolet light. This is caused by a slower return of electrons from their excited state to the normal, or ground, state. In adequate darkness, such phosphorescence can be observed easily. A spectroscope is used to reflect a strong light source off the surface of a gemstone or project it through the stone. Either way, the gemstone will leave its spectral fingerprint on the light beam, which is spread into the visible spectrum for observation. The gemologist notes the wavelengths (spectral position) of the absorption line and bands, and compares them to known materials. Microscopes are used for close-up examination of the external and internal characteristics of gemstones (3, 10).

In some well-studied cases such as diamond, these techniques usually will suffice. However, imperfections can be filled readily 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 (7, 11). With lesser gemstones the analytical techniques are much less established and more reliant on long experience with mineralogical identification methods. Raman spectroscopy provides an ideal method for the examination of gemstones and semiprecious stones. Raman spectroscopy is a measurement of the reemission of light from interaction with an incident light source, usually a laser. Raman spectra result from vibrational motions of the molecular bonds in the material. As opposed to infrared spectra, which are a result of a change in the molecular dipole moment during the molecular vibration, Raman spectra result from a

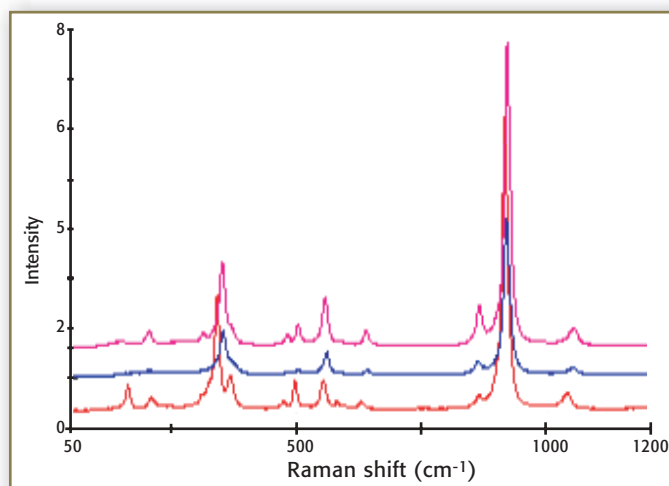


Figure 3. The Raman spectra of several cuts of garnet: square cut (top), oval (middle), and round (bottom).

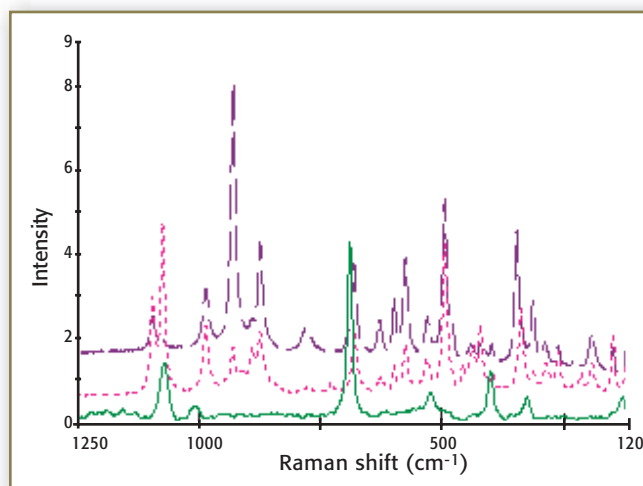


Figure 4. The Raman spectra of emerald (solid) and two tanzanites (dotted and dashed).

source-induced change in the polarizability of the molecular bond during the vibrational motion. With the ability to microscopically examine both loose and mounted stones, Raman can distinguish not only real versus artificial gemstones, but also can discriminate those that have been adulterated in addition to providing details of the alteration.

Experimental

Loose and mounted gemstones in different types of platinum gold jewelry settings (rings and pendants) were borrowed or purchased from various dealers. In several instances these gemstones had professional appraisals. Each gemstone then was placed into the sample compartment of a Jasco Ventuno, a benchtop-mounted fully integrated confocal micro-Raman spectrometer. The instrument was equipped with a 488-nm argon ion laser (Melles Griot, Carlsbad, CA) and a 532-nm diode laser (Torsana

Laser Technologies AVS, Skodsborg, Denmark); two gratings and an Andor (South Windsor, CT) air-cooled, front-illuminated CCD detector. The integration time for spectral collection was 20 s per acquisition. The confocal aperture of 50 mm gives an approximate 1 mm (x, y) \times 2 mm (z) sample volume. The laser power at the sample was approximately 10 mW or less.

Results and Discussion

Citrine, Topaz, and Amethyst. The most commonly occurring form of silica (SiO_2) is quartz, which appears in impure form as amethyst, citrine, onyx and jasper (12). Citrine is the most valuable quartz gem. Almost all citrine on the market is heat-treated amethyst (13). Natural citrine is yellow to orange, and occurs in much lighter hues than the heat-treated material. Amethyst traditionally is purple. The color in both amethyst and citrine is due to impurities

of iron at parts per million levels. The iron substitutes for silica in the quartz structure. The iron is trivalent and gives the yellow color seen in citrine. If it is irradiated, most of it will turn purple, but not all citrine will change color (11). In some amethyst deposits, the amethyst has been partially or fully changed to brown citrine by geothermal heating. Citrine also can be produced by heat-treating smoky quartz from certain localities. Citrine also closely resembles topaz (14). 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 1 clearly indicate the differences between citrine and topaz.

Peridot, Emerald, Garnet, and Tanzanite.

Peridot is the well-known gem variety of olivine ($[\text{Mg,Fe}]_2\text{SiO}_4$), a species name for a series of magnesium-iron rich silicate minerals known for their green

color (12). The ancient Egyptians called peridot "the Gem of the Sun" because it supposedly was too bright to be visible in the sunny Egyptian desert. Legend also suggests that peridot can glow at night which made it easier for the Egyptians to see (and mine it) after sunset (11–15). We analyzed several peridot stones in various shapes and settings. The first two stones were trillion cut, one mounted in a ring and the other in a pendant. Two oval peridot stones from a ring and a pendant also were evaluated. Finally a series of peridot stones from a tennis bracelet were examined by Raman spectroscopy. The Raman spectra from each of the first four stones were almost identical, independent of stone cut. Figure 2 shows the Raman spectra from the oval peridot pendant and the triangular peridot ring. Some minor variations in some of the weaker bands are indicative of the stone cut. The peridot spectra from the tennis bracelet, however, had a large fluorescence and were missing the peridot bands. Instead, these so-called peridot exhibited the charac-

teristic silicon bands from 900–1150 cm^{-1} , which indicated that these stones were merely green glass. Thus Raman analysis proved the peridot in this bracelet to be a fake.

Another orthosilicate gemstone is garnet, which is a group of compounds with the structure, $\text{M}^2_3\text{M}^3_2(\text{SiO}_4)_3$ where M^2 are eight-coordinate (Ca, Mg, Fe) and M^3 are six-coordinate (Al, Cr, Fe) (12). The name garnet can be applied to six similar mineral species, namely almandine, pyrope, spessartine, grossular, andradite, and uvarovite. To further complicate matters, many garnets actually are a combination of these minerals. Rhodolite, for instance, is a combination of almandine and pyrope (13). There also are many trade names and other commonly used names which only adds to the confusion, such as Rhodolite, Tsavorite, Malaya, Mozambique, Mandarin, Melanite, Topazolite, and Thai (2, 15). The most common forms of garnet all contain iron and adopt one of the spinel structures (12). We evaluated several different garnets, including

two oval shaped garnets mounted as pendants, two square garnets mounted as earrings, and several small round garnets in an earring cluster. Figure 3 illustrates the Raman spectra from each garnet shape. The top square garnet was identified as being spessartine-zz. The middle spectrum of the round stone was determined to be an almandine-xx, while the bottom spectrum of the oval garnet is an example of the pyrope-zz.

Tanzanite is a unique gemstone as it occurs in only one specific location in the east African state of Tanzania. It has a characteristic blue color that shimmers in a slightly purplish hue. Tanzanite is a blue variety of zoisite gemstone. However, this hydrated calcium aluminum silicate mineral $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ achieves only hardness 6.5 – 7 on the Mohs' scale, and is thus not very resistant to abrasions (16, 17). Tanzanite is a natural gemstone whose color is enhanced by heat-treating. When found in nature, tanzanite crystals are a muddy reddish-brown color. The crystals then are heated to approximately 650–700 °F to bring out the permanent rich blue, purple, and violet colors. Tanzanite is one of the few gemstones that are pleochroic, meaning it exhibits two or more separate colors when viewed at different angles. The more common colors are blues and purples but one might also see flashes of red, green, yellow, orange, or brown. The color that gemologists predominantly speak of is the “deep royal blue” (18–21). Tanzanites, which are more blue than purple, usually are more expensive because the crystals tend to form with the blue color axis oriented along the width of the crystal instead of the length (22).

Several synthetic gemstones and nongem materials have been offered as substitutes for tanzanite. For example, synthetic fosterite simulates the color and look of tanzanite but is significantly less expensive. Synthetic sapphires also have been offered as imitators of the bluer varieties of tanzanite (18). We evaluated several tanzanite stones and compared them with a reference database (21). One stone was a triangular shaped stone, two others were oval, and one was round. The Raman spectrum of tanzanite has a characteristically complex spectrum

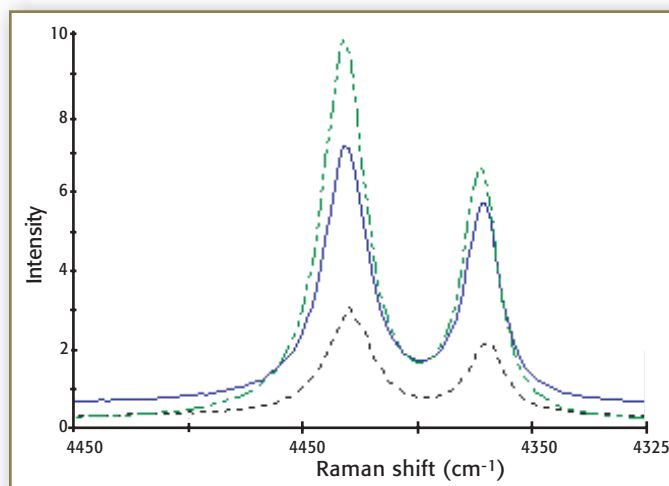


Figure 5. Three rubies: maternal stone (dot/dash), paternal stone (solid), and ruby ring (dashed). All have the same characteristic ruby peaks.

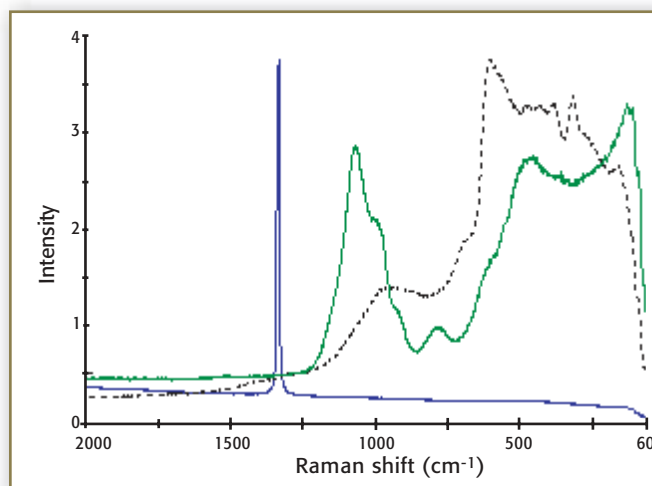


Figure 6. The 1332 cm^{-1} diamond Raman band (bottom) is clearly distinguishable from the luminescence of the glass imposters (top solid and dashed).

from about 50 to 2000 cm^{-1} (Figure 4). All four tanzanite examined had spectra with identical peak locations, but the individual spectra exhibited different peak height ratios. These slight intensity differences are attributed to the alignment of the crystals along the color axis.

Emerald is in the beryl family (beryllium aluminum metasilicate) with a chemical formula of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. The emerald differs from other beryls in its deep green color (7). Its intense green coloring is due to a trace of chromium or vanadium replacing the aluminum in the beryl structure. Because of the nature of this replacement, almost no emeralds with intense color are free from inclusions. Imitation emeralds are found most commonly as composite stones, which are jewelry pieces comprising more than one stone bonded together. False emerald doublets consist of a thin slab of emerald that is

glued on top of a colored glass bottom to form a large composite emerald. Soude emeralds are false emerald doublets that consist of a colorless spinel top and bottom pieces fused together with a green bonding agent. Emerald triplets can be detected by immersing the stone in a liquid such as alcohol — the top and bottom pieces seem to disappear and all that is visible is the green bonder at the girdle. Another common emerald imitator is green glass (19). We examined emeralds in an antique platinum ring consisting of 10 square cut emeralds surrounding a round diamond. The emerald Raman spectra are shown in Figure 4 along with the tanzanite.

A Tale of Two Rubies. We examined two large blue–purple gemstones mounted in separate rings. The amethyst from the first ring was a large teardrop shape and mounted in 14-karat yellow gold. It was purchased at

an antiques store in rural Maryland and had been appraised independently twice by two separate lapidaries as amethyst. The stone from the second ring was a large round stone with the same blue–purple color mounted in 18-karat rose gold. It was purchased in Egypt and was sold as alexandrite. This ring also was appraised due to the rarity of the alexandrite. This stone was determined to be amethyst. This seemed reasonable because the other ring with the similar stone was also appraised as amethyst.

Raman analysis of both stones provided an interesting discovery. Neither stone had the characteristic amethyst Raman bands; however both stones did display the strong bands at 4392 and 4360 cm^{-1} , characteristic of ruby. Comparison of the spectra of these stones versus that of a known ruby, proved that these two amethysts were indeed rubies despite their purple coloring (Figure 5). In this instance three separate lapidaries gave three incorrect appraisals of the stones. We also evaluated two synthetic rubies and found them to be indistinguishable from their natural counterparts. Throughout history, ruby has been considered the most prized of red gemstones and is considered to be the medium-to-dark orangey red to purplish red variety of corundum, a mineral composed of aluminum oxide (Al_2O_3) (20). Colored metal ion impurities create the gemstone color, such as Cr^{3+} -ruby, and $\text{Fe}^{2/3}$, Ti^{4+} -sapphire (12). The sapphires that we evaluated had spectra virtually indistinguishable from the ruby (11).

Diamonds. Diamond has been prized for centuries as a gemstone of exceptional brilliance and for its range of exceptional chemical properties. When compared with almost any other material, diamond is almost always the most valuable. As well as being the hardest known material, it is also the least compressible, the stiffest, the best thermal conductor with an extremely low thermal expansion, chemically inert to most acids and alkalis, and transparent from the deep UV through the visible to the far infrared, and it is one of the few materials known with a

negative electron affinity (or work function) (22).

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 when excited by laser light. A Raman spectrometer used to measure photoluminescence is a powerful characterization tool to identify artificially reprocessed, so-called exotic colored diamonds. 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 is fancy yellow or brown.

Cubic zirconia is now one of the most common substitutes for diamond. The original manufacturing process was developed in Russia and now is performed all over the world. Cubic zirconia can be manufactured in several different colors due to the addition of other minerals, but only the clear white is preferred as a substitute for diamond. With a distinctly different Raman spectrum, cubic zirconia gemstones can be distinguished easily from diamond. Common glass also is a cheap substitute for diamond. Glass is distinguished easily from the diamond in the Raman spectra because glass has a large photoluminescence. Diamond is characterized readily by a sharp Raman band at 1332 cm^{-1} (Figure 6).

Conclusions

Raman spectroscopy has been demonstrated as an ideal method for the analysis of gemstones, both real and fake. With the ability to examine both loose and mounted stones of any size or configuration, Raman can be used to rapidly distinguish various gemstones that do not readily lend themselves to identification by other, more traditional gemological identification methods. Raman spectra also can provide a unique fingerprint of the gemstone with the ability to distinguish any future alteration of the gemstone. The photoluminescence of colored diamonds offers a method for the determination of the color of diamonds and provide a further discrimination of the diamond color scale.

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