IDENTIFICATION OF NEPHRITE JADE WITH RAMAN SPECTROSCOPY

APPLICATION NOTE RAMAN-018 (US)

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Abstract

This short application note documents the Raman spectroscopic analysis of several stones from a private collection that had been verified to be real nephrite jade samples. A TSI ChemLogix EZRaman-I instrument with a 532 nm laser was used for these measurements.

Motivation

Jade is a semiprecious stone, prized since prehistoric times. It has been carved into weapons and tools, statues and jewelry. Most people are familiar with jade as a green material, but it is known to exist in a wide variety of colors, from white to orange, from black to a delicate violet. The term “jade” is applied to two metamorphic materials that are composed of different silicate minerals: nephrite and jadeite. Nephrite alone was used in China until the 1700s, when jadeite began to be imported from Burma. Jadeite is the rarer and therefore more valuable material, and the differentiation between jadeite and nephrite is an important measurement.[1,2]

Nephrite is member of the tremolite-ferroactinolite mineral series: [$Ca_2Mg_5Si_8O_{22}(OH)_2$, $Ca_2Fe_5Si_8O_{22}(OH)_2$]. Nephrite jade is sometimes referred to as amphibole jade. Jadeite, or serpentine jade, is a sodium- and aluminum-rich pyroxene, $NaAlSi_2O_6$ or $Na(Al,Fe^{3+})Si_2O_6$, one of the end members of the clinopyroxene group. Compositional variation in these materials is reflected in the physical characteristics, including color. These materials are easily differentiated using Raman spectroscopy, as is shown in Figure 1. The Si-O-Si symmetric stretching feature is located at slightly different places in the materials, 675 cm^{-1} in nephrite and above 695 cm^{-1} in jadeite.

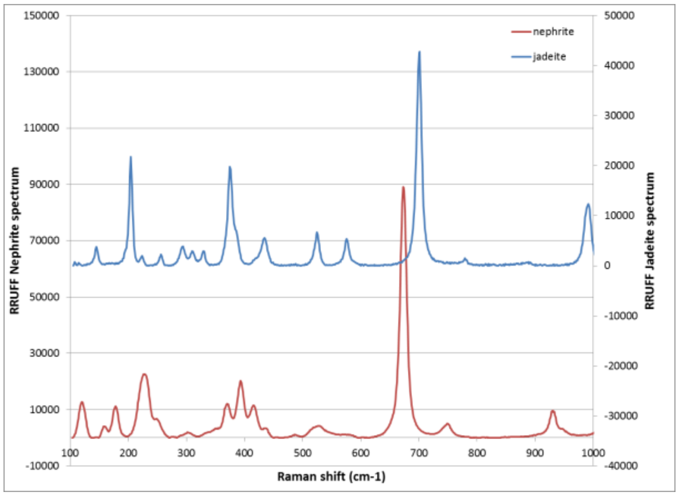

Figure 1. RRUFF Raman spectra of nephrite and jadeite, the two minerals that compose jade.

As was documented in an earlier application note (see RAMAN-012), many materials sold as jade, perhaps even a majority, are neither of these materials.

In a previous TSI application note, instead of jadeite or nephrite, the samples TSI had purchased as jade were identified by Raman spectroscopy as chrysotile and adventurine quartz. TSI was surprised to find that out of four samples, purchased from three different vendors, no genuine jade had been purchased.

The global interest in jade and the incredible prevalence of fakes have sensibly sparked a good deal of interest in their detection. There are a large number of websites, online videos and other documents devoted to the discovery of fake jade, both imitation jade (i.e. other minerals altogether) and processed jade, in which the minerals are heated, chemically altered, dyed or waxed. Now that TSI has documented such success in purchasing and identifying fake jade, in this application note, document the spectra acquired from one type of verified jade sample.[3,4]

Samples

Several verified nephrite jade samples from the collection of an anonymous individual were subjected to Raman analysis.

Measurements and Results

A TSI ChemLogix EZRaman-I with 532 nm excitation was used to acquire the spectra of the samples. The stones were set on a table with the probe suspended over them with ring stand and clamp. Approximately 35 mW of laser excitation was used for all the samples and acquisition times of 10s and 6x averages were used to accumulate data. Spectragryph software[5] was used to perform the comparison against the entries in the RRUFF mineral database, and then RRUFF spectra were superimposed with the sample spectra for demonstration purposes.[6]

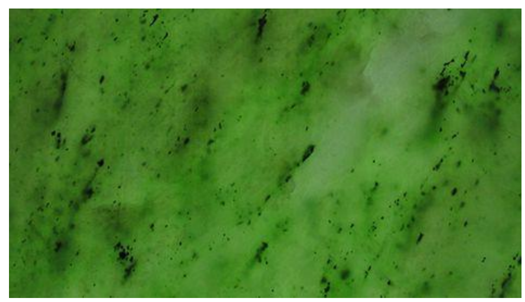

Figure 2. Photo of nephrite jade.

All of the samples that were analyzed were identified as nephrite.

The majority of the samples were identified by Raman comparison as actinolite, and a smaller number as ferroactinolite. Actinolite is an intermediate member in a solid-solution series between magnesium-rich tremolite, $Ca_2(Mg_{5.0\text{-}4.5}\ Fe^{2+}{}_{0.0\text{-}0.5})Si_8O_{22}(OH)_2$, and iron-rich ferro-actinolite, $Ca_2(Mg_{2.5\text{-}0.0}Fe^{2+}{}_{2.5\text{-}5.0})Si_8O_{22}(OH)_2$.

Actinolite is in between, with $Ca_2(Mg_{2.5\text{-}4.5}Fe^{2+}{}_{0.5\text{-}2.5})Si_8O_{22}(OH)_2$

Pure magnesium tremolite is a creamy white color; the stones become greener with increasing iron content. The change in color toward deep green-black upon increasing iron content is seen through the palette of colors in nephrite jade. Some of these minerals can be found in habits that are fibrous like asbestos and have similar hazards.

The RRUFF matches to the acquired spectra are shown in Figures 3 and 4 and demonstrate the way that the increase in the iron content of the mineral changes both color and structure. Figure 3 shows a greenish-blue jade superimposed on a RRUFF spectrum of actinolite. The stretching mode of the O-Si-O linkages in the green samples appears reproducibly at 668 cm^{-1}, while the white jade is at 670 cm^{-1} (ferroactinolite appears at 666 cm^{-1}). This feature approaches 695 cm^{-1} is the jadeite mineral. The feature near 220 cm^{-1} (A_1)[6-8] and the bands at 1030 and 1059 cm^{-1} (antisymmetric stretching vibrations of Si-O-Si) also shift as a result of composition change. The locations of these silicate features are very dependent upon the cation charge and ionic radius of the cations in nearby octahedral sites. These cations have an indirect effect upon the bond lengths and angles of the Si-O-Si and SiO_4 vibrations respectively; thus one can identify other cations simply by observing the appearance of Si–O bonds.[9]

The spectral differences caused by composition in this set of minerals is shown in Figure 5, which shows the RRUFF spectra of ferroactinolite, actinolite and tremolite in the spectral region from 200-1100 cm^{-1}.[6]

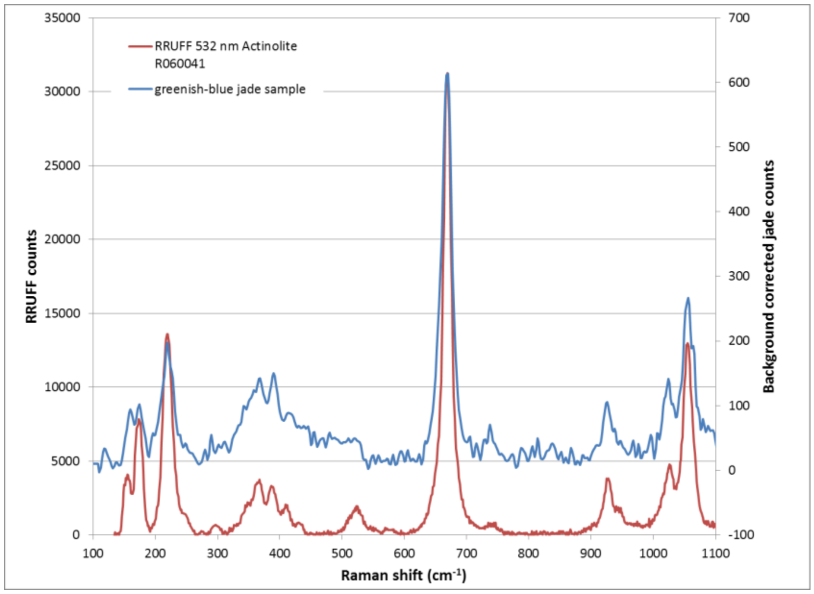

Figure 3. Raman spectrum of greenish-blue jade sample excited with 532 nm laser, plotted with actinolite spectrum from RRUFF database.

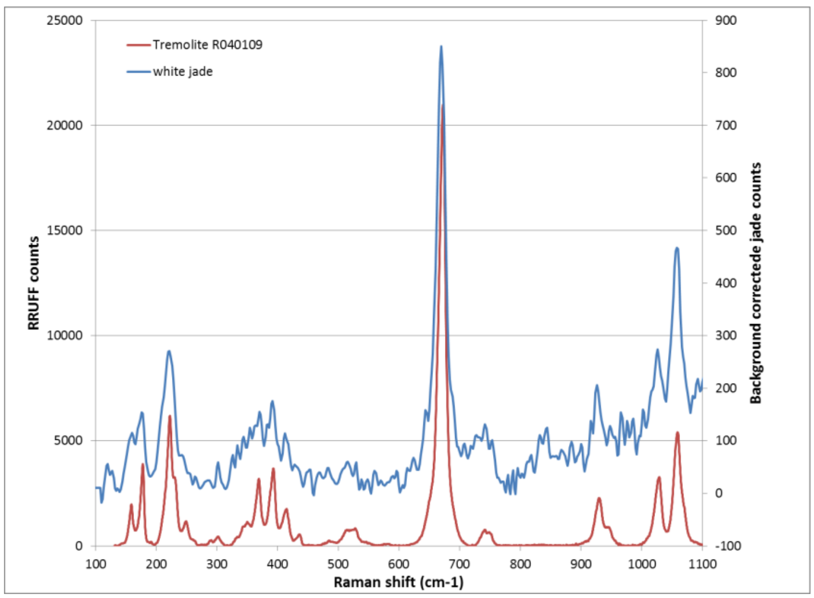

Figure 4. Raman spectrum of white jade sample excited with 532 nm laser, plotted with tremolite spectrum from RRUFF database.

Jadeite materials represent another color spectrum, including emerald green, pink, lavender, orange and brown. As with the nephrite, the color of the material is indicative of composition. Indeed, formulae based upon the frequency of the line near 660 cm^{-1} have been proposed for obtaining the jadeite proportion in the ternary mixture of diopside-hedenbergite-jadeite.[11]

In summary, Raman spectroscopy has long been recognized as an effective method for identification of nephrite jade, and our application note demonstrates this aptitude with a TSI ChemLogix EZRaman-I instrument.

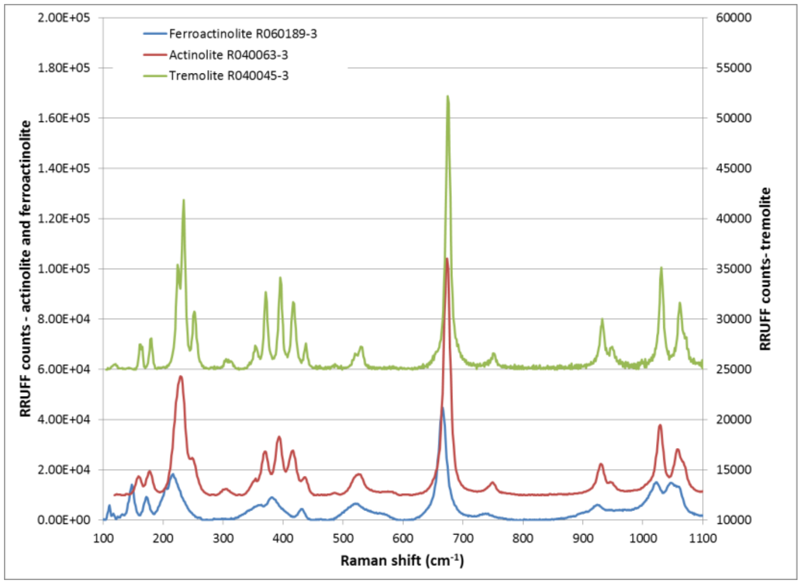

Figure 5. RRUFF spectra of ferroactinolite, actinolite and tremolite, demonstrating the change in vibrational features with composition.

References

1. http://asianart.com/articles/hoffman/index.html.
2. Smith, D.C. and R. Kaindl, "Raman spectroscopy: Analytical perspectives in mineralogical research," Chapter 7 of *EMU Notes in Mineralogy*, **Vol. 6** (2004).
3. http://www.noblejades.com/top-8-common-fake-jadeite-jade.html.
4. www.wikihow.com/Tell-if-Jade-Is-Real.
5. F. Menges "Spectragryph - optical spectroscopy software", **Version 1.2.4**, 2016-2017 http://www.effemm2.de/spectragryph/.
6. Lafuente B, Downs R T, Yang H, Stone N (2015) The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography, T Armbruster and R M Danisi, eds. Berlin, Germany, *W. De Gruyter*, pp 1-30.
7. Gates, W.P., Kloprogge, J.T., Madejová and F. Bergaya, Eds., *Infrared and Raman Spectroscopies of Clay Minerals*, Elsevier, Amsterdam 2017.
8. Kingma, K.J. and R.J.Hemley, "Raman spectroscopic study of microcrystalline silica," *Amer. Mineral*. **79**, 269-273, 1994.
9. Bersani, D. and P.P. Lottaci, "Applications of Raman spectroscopy to gemology," Anal Bioanal Chem, 397 (7), 2631 (2010)

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