Identification of the garnet chemical composition and color causes by express Raman and visible spectroscopy

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Introduction

In terms of mineralogy garnet group is a family of minerals having variable chemical composition, but similar structure. Many natural garnets have complex chemical composition being a mixture of several garnet minals (end-members). Gemological identification of garnet family minerals in laboratory is mainly bases on color, optical constants and inclusions. Whereas garnets of the same color (for example green or orange) may relate to different garnet varieties the diagnostic of mineral species based on the gemological features is not always possible.

The similarity of garnets physical properties has posed some challenge of the garnet variety identification by standard gemological equipment. The same problem usually can be found with the identification of the chromophores. However with the help of express Raman and visible spectroscopic techniques it can give the precise and relatively inexpensive solution on those problems.

Samples and Methods

We examined 56 faceted gem-quality transparent garnet samples from different locations. The garnets had wide color varieties (Fig.1). These samples represent the collection of major garnet varieties (i.e., pyrope, almandine, spessartine, grossular and andradite, except of uvarovite) and its solid solutions.

Figure 1. Range of color variation in garnet specimens. These samples are among those studied for this report: 1 – spessartine-pyrope; 2, 3, 4 – almandine-pyrope; 5 – grossular-andradite; 6 – pyrope; 7 – spessartine; 8 – spessartine-pyrope; 9 – grossular; 10 – andradite (demantiod); 11 – grossular (tsavorite); 12 – grossular.

Raman spectra were recorded using EnSpectr R532 Raman spectrometer with excitation laser wavelength 532 nm, laser power 30 mW, spectral range 140-6000 cm^{-1}, spectral resolution 6 cm^{-1}, slit width of 20 μm and a grating with 1200 grooves per mm.

Visible transmission spectra were recorded at room temperature at Ocean Optics QE65000 spectrometer with FOIS-1 integral sphere and HL-2000-HP light source, with 400-1000 nm spectral range, using 50 μm slit, 1 sec exposure time and averaging by 50 scans.

Chemical composition was measured on 7 samples to verify the data (garnet varieties and chromophores) obtained from Raman, UV-Vis-NIR spectroscopic measurements. We used a LEO Supra 50 VP electron microprobe in energy-dispersive mode.

Results

The Raman spectra of garnets contain three most intense lines around 350, 550 and 900 cm^{-1}, related to (Si-O) stretching, (Si-O) bending and $R(SiO_4)^{4-}$ rotational vibrations, respectively (Kolesov and Geiger, 1998). Those lines are sensitive to the garnet chemical composition.

The shift of the lines in Raman spectrum from the end-members to solid-solution members can give the possibility to calculate the approximate chemical composition of the garnet using the positions of the lines in the Raman spectrum.

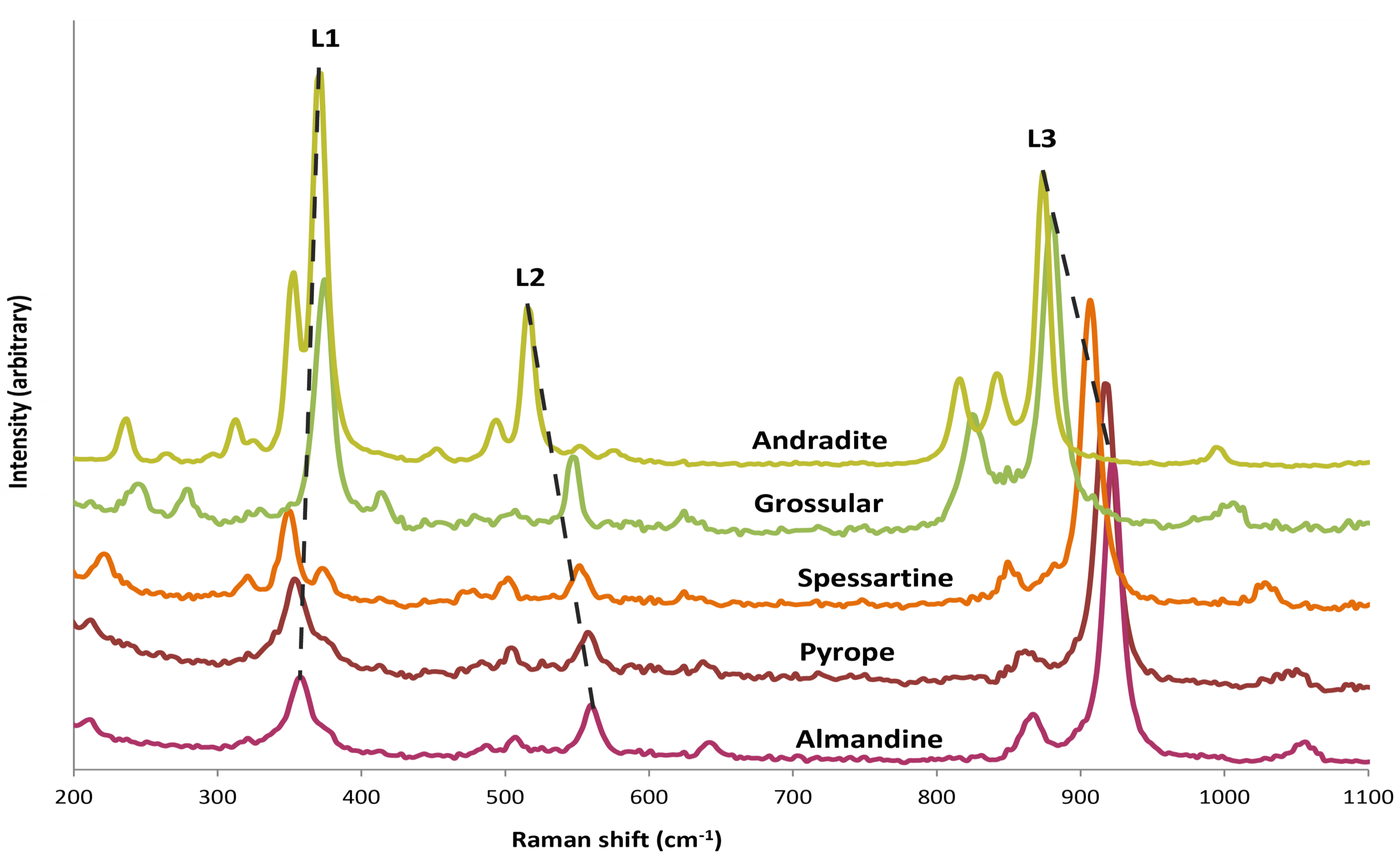

Figure 2. Raman spectra of garnet minals. Three the most intense lines are marked L1, L2, L3.

For our research we used three the most intense Raman lines (Fig. 2) because it gives better repeatability and needs less time to collect sufficient spectrum.

Using calculation of the positions of the Raman lines we have determined that 35 garnets from our collection are almandine-pyrope (solid solutions), 9 – grossular- andradite, 4 – andradite, 4 – grossular, 4 – spessartine.

Visible spectra of garnets can display the presence of Fe^{2+}/Fe^{3+}, V^{3+} and Cr^{3+} - related lines. The position of absorption lines could correspond with a garnet chemical composition. Thus the same chromophore in the different garnet varieties may give different absorption patterns and visible colors. As such it is possible to know roughly a garnet variety by using the visible spectrum.

For instance, visible transmission spectra for green grossular and andradite garnets colored by Fe^{3+}, V^{3+} and Cr^{3+} are shown in Figure 3, a. Grossulars are colored by Fe^{3+} (lines 408, 435, 501, 855 nm) and V^{3+} (lines 426 and 606 nm) whereas the andradite garnets colored by Fe^{3+} (lines 441, 575, 617, 855 nm) and Cr^{3+} (line 621 nm) (Platonov, 1984).

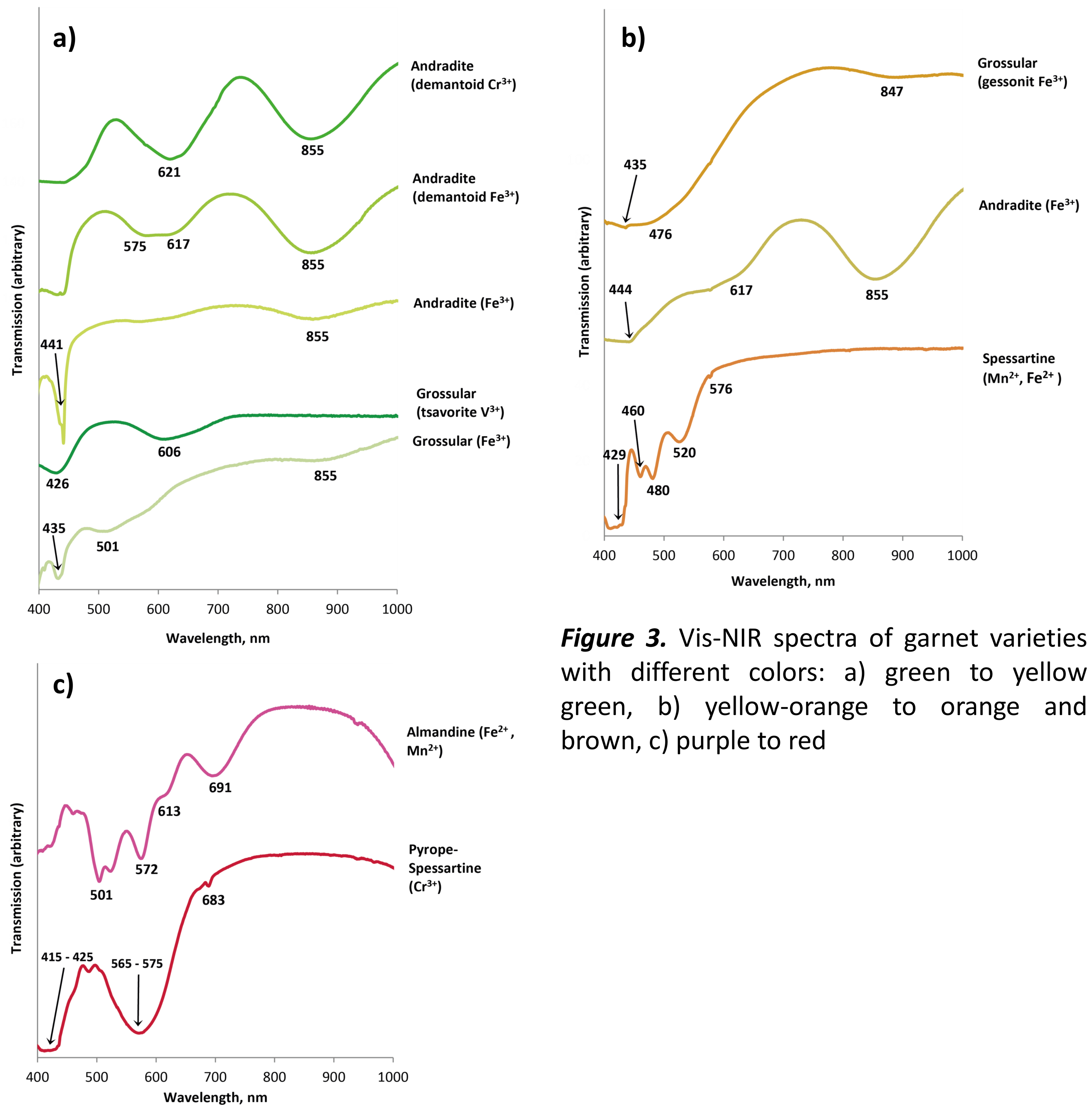

Figure 3. Vis-NIR spectra of garnet varieties with different colors: a) green to yellow green, b) yellow-orange to orange and brown, c) purple to red

Comparison of the data from electron microprobe with Raman, UV-Vis-NIR spectroscopic measurements demonstrates that determination of garnet varieties using Raman spectroscopy is more reliable for end-members, or for solid solutions composed of two minals. If chemical composition of garnet is more complex and includes several minals this express method may not work correct (if do not consider other cation lines in Raman spectrum, but it takes more time to collect sufficient spectrum).

In any case, the assignment of the garnets with complex chemical composition to certain solid solution series can be done.

Discussion

It is important to notice that the garnets of similar color (Fig. 1) can be colored by different chromophores and also have very different chemical compositions. Thus the precise identification of the garnet species cannot be reliable only on their physical properties and the color of stone. The advanced methods such as Raman and visible spectroscopy or microprobe/EDXRF analyses should also be carried out at the same time.

This study has shown that the routine express Raman and visible spectroscopic techniques could give enough precise data for the determination of garnet chemical compositions and their color origins.

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