UV/Vis single-crystal spectroscopic investigation of almandine-pyrope and almandine-spessartine solid solutions: Part I. Spin-forbidden Fe$^{2+,3+}$ and Mn$^{2+}$ electronic-transition energies, crystal chemistry, and bonding behavior

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ABSTRACT

Aluminosilicate garnet is an excellent phase to research solid-solution behavior in silicates. Natural almandine-pyrope, $\{\text{Fe}^{2+},\text{Mg}^{2+}\}_3\text{[Al}_2\text{](Si}_3\text{)O}_{12}$, and almandine-spessartine, $\{\text{Fe}^{2+},\text{Mn}^{2+}\}_3\text{[Al}_2\text{](Si}_3\text{)O}_{12}$, crystals were measured by UV/Vis/NIR (~29000 to 10000 cm$^{-1}$) optical absorption spectroscopy using a microscope. The spectra and changes in energy of several Fe$^{2+}$ and Mn$^{2+}$ spin-forbidden electronic transitions of different wavenumber were analyzed as a function of garnet composition across both binaries. The spectra of Alm-Pyp garnets are complex and show several Fe$^{2+}$ and Fe$^{3+}$ transitions manifested as overlapping absorption bands whose intensities depend on composition. There are differences in energy behavior for the various electronic transitions, whereby lower wavenumber Fe$^{2+}$ transitions decrease slightly in energy with increasing pyrope component and those of higher wavenumber increase. The spectra of Alm-Sps solid solutions show both Fe$^{2+}$ and Mn$^{2+}$ spin-forbidden bands depending upon the garnet composition. The variations in energy of the different wavenumber Fe$^{2+}$ transitions are unlike those observed in Alm-Pyp garnets. The three lowest wavenumber electronic transitions appear to vary the most in energy across the Alm-Sps join compared to those at higher wavenumber. Four narrow and relatively intense Mn$^{2+}$ spin-forbidden bands between 23 000 and 25 000 cm$^{-1}$ can be observed in many Sps-Alm garnets. Their transition energies may increase or decrease across the join, but scatter in the data prohibits an unequivocal determination. A consistent crystal-chemical model and Fe$^{2+}$-O bond behavior, based on published diffraction and spectroscopic results, can be constructed for the Alm-Pyp binary but not for the Alm-Sps system. The spectra of the former garnets often show the presence of high-wavenumber spin-forbidden bands that can be assigned to electronic transitions of Fe$^{3+}$ occurring at the octahedral site. The most prominent band lies between 27 100 and 27 500 cm$^{-1}$ depending on the garnet composition. Fe$^{2+}$-O$^{2-}$ bonding is analyzed using Racah parameters. State-of-the-art electronic structure calculations are needed to understand the precise physical nature of the electronic transitions in garnet and to interpret better UV/Vis/NIR spectra.

Keywords: UV/Vis/NIR spectroscopy, garnet, solid solutions, electronic spin-forbidden transitions, crystal chemistry

INTRODUCTION

Aluminosilicate garnet, general formula $\{X_3\}[\text{Al}_2\text{](Si}_3\text{)O}_{12}$, where $X = \text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{and Ca}$, is a key rock-forming mineral occurring in different geologic settings. Many upper-mantle and some crustal garnets are largely pyrope-almandine solid solutions, $\{\text{Mg}_3,\text{Fe}^{2+}\}_3\text{[Al}_2\text{](Si}_3\text{)O}_{12}$, and almandine-spessartine-almandine garnets, $\{\text{Mn}_3,\text{Fe}^{2+}\}_3\text{[Al}_2\text{](Si}_3\text{)O}_{12}$, occur in certain crustal granites and pegmatites. Atomic mixing at $\{X\}$ can be complete for both binaries as shown by compositional analyses of natural garnets (Boeke 1914; Sobolev 1964) and the successful laboratory synthesis of crystals along both joins at elevated pressures and temperatures (e.g., Geiger and Feenstra 1997).

Investigation of the solid-solution behavior of aluminosilicate garnets, both at the micro- and macroscopic scale, is a long, continuous work in progress (Geiger 2008, 2016) and still needs to be researched. A fundamental problem is in trying to understand the nature of local structural heterogeneity that arises through the exchange of different atoms of varying sizes and electronic properties. Local X$^{2+}$-O chemical bonds must vary slightly as a function of crystal composition. Garnet is an excellent phase to study solid solutions, because Fe$^{2+}$, Mg, and Mn$^{2+}$ mix at the single crystallographic $\{X\}$ site. All three cations have relatively similar ionic radii, but Mg does not have a $d$ electron unlike Fe$^{2+}$ (3$d^6$) and Mn$^{2+}$ (3$d^5$). The chemical-bonding behavior of the latter two transition metals with oxygen should differ between each other and both most certainly with respect to the alkaline Mg cation. A notable crystal-chemical feature of the aluminosilicate garnets is the anisotropic vibrational behavior of the different X$^{2+}$ cations and their probable anharmonic potentials (Geiger 2013). To understand a wide range of atomic-scale and bonding behavior in crystals various spectroscopic measurements are necessary (Geiger 2004).

Optical absorption spectroscopy is a powerful tool for in-