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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

Charles A. Geiger[1,*], Michail N. Taran[2], and George R. Rossman[3]

[1]Department of Chemistry and Physics of Materials, University of Salzburg, Jakob Haringer Str. 2a, A-5020 Salzburg, Austria
[2]M.P. Semenenko Institute of Geochemistry and Mineralogy and Ore Formation, National Academy of Sciences of Ukraine, Palladin Avenue 34, 03142 Kyiv-142, Ukraine
[3]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125-2500, U.S.A.

Abstract

Aluminosilicate garnet is an excellent phase to research solid-solution behavior in silicates. Natural almandine-pyrope, $\{Fe^{2+}_{3x},Mg_{3-3x}\}[Al_2](Si_3)O_{12}$, and almandine-spessartine, $\{Fe^{2+}_{3x},Mn^{2+}_{3-3x}\}[Al_2](Si_3)O_{12}$, crystals were measured by UV/Vis/NIR (~29 000 to 10 000 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^{3+}-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