

Single-crystal UV/Vis optical absorption spectra of almandine-bearing and spessartine garnet: Part II. An analysis of the spin-forbidden bands of Fe²⁺, Mn²⁺, and Fe³⁺

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ABSTRACT

The UV/Vis single-crystal absorption spectra of two almandine-bearing and several spessartine garnets were measured and their respective Fe²⁺ and Mn²⁺ spin-forbidden electronic transitions analyzed. Spin-forbidden bands of Fe³⁺ are also considered, because many aluminosilicate garnets contain some Fe³⁺. The spectra of the almandine-bearing garnets were recorded at room temperature between about 10 000 and 30 000 cm⁻¹. The spectrum of a nearly end-member spessartine (97 mol% Mn₃²⁺Al₂Si₃O₁₂) was measured between about 15 000 cm⁻¹ and 30 000 cm⁻¹ at room temperature and 78 K, the latter for the first time. The 78 K spectrum shows absorption features not observed at room temperature. Five additional spessartine-rich garnets with different Mn²⁺/(Mn²⁺ + Fe²⁺) ratios, and two with unusual chemistries, were recorded up to 26 000 cm⁻¹. The spectra of the two almandine-bearing garnets agree well with published results and show several overlapping Fe^{2+/3+} bands located between about 14 000 and 25 000 cm⁻¹. The spectra were deconvoluted to gain more insight into the electronic transition behavior. These results, together with an analysis of other measured spectra, reveal several absorption features that were previously unrecognized or misassigned. The spectrum of spessartine shows several Mn²⁺ bands, and most are clearly spaced from one another. A synthesis of various UV/Vis spectroscopic results is made and assignments for the Fe^{2+/3+} and Mn²⁺ bands are attempted. The intensities of the Mn²⁺ spin-forbidden bands and the ligand → metal charge edge observed in the various spessartine spectra are discussed. Spectra of almandine and spessartine have been interpreted using Tanabe-Sugano diagrams that are constructed for cations in octahedral coordination, point symmetry *O_h*. However, such analysis does not appear to be fully successful because Fe²⁺ and Mn²⁺ in garnet have triangular dodecahedral coordination with point symmetry *D₂*. The interpretation of the spectrum of spessartine is especially problematic. An analysis shows that published model calculations of Fe²⁺ electronic transition energies in garnet are not in good agreement with each other and are also not in full agreement with experimental spectra. First principles calculations are needed to better understand the spin-forbidden transitions of Fe²⁺, Fe³⁺, and Mn²⁺ in garnet.

Keywords: UV/Vis absorption spectroscopy, garnet, almandine, spessartine, spin-forbidden electronic transitions, transition metals, crystal field theory