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asymmetric IVCT behavior. This, together with the relatively long Fe
IVCT mechanisms observed in other minerals. The latter typically have iron cations in octahedral or
quasi-octahedral coordination. The IVCT in aluminosilicate garnet can occur in different species that
grew under dissimilar P-T-X conditions. The resulting electronic absorption band affects color mark-
edly, because it is centered at higher energies in the blue visible region. It remains to be determined
why IVCT is observed in the spectra of some garnets but not others. The various proposed IVCT
mechanisms in Ca-Ti-bearing and aluminosilicate garnets are reviewed and analyzed.

**Keywords:** Garnet, UV/Vis absorption spectroscopy, IVCT, electronic transitions, iron, titanium

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**INTRODUCTION**

Most physical properties of solid materials are determined by how their electrons behave. Optical absorption behavior and color, for example, can be greatly affected by various electronic transition mechanisms. Intervalelence charge transfer (IVCT) is one type. It can occur in crystals having cations with different formal valence states and in terms of minerals it has received considerable study over the last five decades or so. IVCT in most silicates takes place between the electronic d orbitals of transition metals residing in neighboring coordination polyhedra. Hetero-
and homonuclear charge transfer can occur. A generalized example for the former, not considering the specifics of crystal chemistry, is Fe$^{2+}$ + Ti$^{4+}$ → Fe$^{3+}$ + Ti$^{3+}$ and for the latter Fe$^{2+}$ + Fe$^{3+}$ → Fe$^{3+}$ + Fe$^{2+}$. Both have been described for several different minerals. The energies and intensities of IVCT electronic transitions depend on the crystal structure and composition of the minerals in question. They can be excited by radiation often cor-
responding to the visible region of the electromagnetic spectrum. Optical absorption spectroscopy provides, therefore, an excellent method to investigate the process. Burns (1981, 1993) provides a very good and extensive treatment of the different electronic transitions that can occur in crystals as well as a discussion on optical absorption spectroscopy. He reviews the various known IVCT mechanisms known at the time for different minerals. Sherman (1987a, 1987b) analyzed, in an early computational and theoretical treatment, Fe$^{2+}$$\rightarrow$ Fe$^{3+}$ and Fe$^{3+}$$\rightarrow$ Ti$^{4+}$ charge transfer transitions and thermally induced electron delocalization involving edge-sharing octahedral clusters.

The subject of IVCT in silicate garnet, general formula \(\{X_3\}[Y_3](Z_3)O_{12}\), is not fully understood. This is because of the wide compositional range shown by different species, often ex-
tensive solid-solution behavior and the nature of the garnet crystal structure. Garnet can contain various transition metals, which can occur in different formal oxidation states. Cations are located at three different crystallographically special positions having different coordination, namely triangular dodecahedral-\{X\}, octahedral-\{Y\}, and tetrahedral-\{Z\}. The M(etal)-O distances are variable throughout the crystal structure. What is known? The Ca-Ti-bearing garnets are complex crystal chemically

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**Single-crystal UV/Vis absorption spectroscopy of aluminosilicate garnet: Part III. \(\{Fe^{2+}\} + [Fe^{3+}] \rightarrow \{Fe^{3+}\} + [Fe^{2+}]\) intervalence charge transfer**

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**ABSTRACT**

The various intervalence charge transfer (IVCT) mechanisms that can occur in silicate garnet, general crystal-chemical formula \(\{X_3\}[Y_3](Z_3)O_{12}\), are not fully understood. The single-crystal UV/Vis/NIR absorption spectra of two different almandine-rich, spessartine-rich and grossular-rich garnets, as well as an intermediate almandine-pyrope garnet, were measured. Absorption was observed from roughly 15 000 to 30 000 cm$^{-1}$. The spectra were deconvoluted and a very broad band with FWHM values ranging from 5000 to 7000 cm$^{-1}$ (except in the case of one grossular where the FWHM is 8700 cm$^{-1}$) and having an intensity maximum located between about 20000 and 22 000 cm$^{-1}$ in the visible region could be fit. Small weaker features located on this broad band were fit as well. The broad band is strongest in a nearly end-member composition almandine and weakest in a very grossular-rich iron-poor crystal. It is assigned to \(\{Fe^{2+}\} + [Fe^{3+}] \rightarrow \{Fe^{3+}\} + [Fe^{2+}]\) IVCT. This is the first recognition of this type of electronic transition mechanism in different aluminosilicate garnet species. Photon-induced electron transfer probably occurs through an overlap of the d orbitals of Fe$^{2+}$ and Fe$^{3+}$ in their edge-shared triangular dodecahedral and octahedral coordination polyhedra, respectively. The two Fe
cations with different formal charges should have markedly different energy potentials giving rise to asymmetric IVCT behavior. This, together with the relatively long Fe$^{2+}$-Fe$^{3+}$ distances (greater than 3.2 Å), could explain the higher energy of the IVCT in garnet compared to Fe$^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$
IVCT mechanisms observed in other minerals. The latter typically have iron cations in octahedral or
quasi-octahedral coordination. The IVCT in aluminosilicate garnet can occur in different species that
grew under dissimilar P-T-X conditions. The resulting electronic absorption band affects color mark-
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