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Optical absorption study of natural garnets of almandine-skiagite composition showing intervalence $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge-transfer transition

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Abstract

A broad (FWHM ≈ 7300 cm^{-1}) intense band at ~21 700 cm^{-1} in the optical absorption spectra of natural Fe^{2+}, Fe^{3+}-rich garnets is attributed to electronic intervalence charge-transfer transitions (IVCT), $^{VIII}Fe^{2+} + {}^{VI}Fe^{3+} \rightarrow {}^{VIII}Fe^{3+} + {}^{VI}Fe^{2+}$. In Fe^{3+}, Fe^{2+}-bearing garnets of predominantly almandine compositions, this band causes yellowish tinges in addition to the pink color, typical of pure Fe^{3+}-free almandines. In garnets from deeper-seated mafic granulites from kimberlite pipes in Siberia with high skiagite ($Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$) contents, IVCT causes intense brownish-yellow colors. The relatively high energy of the band (~21 700 cm^{-1}) compared to diverse minerals showing IVCT between Fe^{2+} and Fe^{3+} in adjacent octahedral sites, is attributed to the charge-transfer transition taking place between Fe^{2+} and Fe^{3+} in non-equivalent, dodecahedral and octahedral sites of the garnet structure. Band intensity is directly correlated with the product of Fe^{2+} and Fe^{3+} as measured by Mössbauer spectroscopy. The energy of the IVCT band is nearly independent of temperature, whereas its intensity decreases slightly with increasing temperature. Pressure induces a weak shift of the band to lower energies, $\Delta\nu/\Delta P \approx -75$ cm^{-1}/GPa, but intensity of the bands remains practically unchanged. Such temperature and pressure dependencies are quite different from those in other minerals showing IVCT between Fe^{2+} and Fe^{3+} in equivalent octahedral positions of structure.

Keywords: Garnets, optical absorption spectra, Mössbauer spectra, iron ions, electronic dd transitions, intervalence charge-transfer transitions