American Mineralogist, Volume 86, pages 896–903, 2001

Spectroscopic standards for four- and fivefold-coordinated Fe^{2+} in oxygen-based minerals

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ABSTRACT

Optical spectra are presented for seven oxygen based, four-coordinated Fe^{2+} bearing minerals, eudialyte, gehlenite, genthelvite, gillespite, pellyite, spinel, and staurolite, and two five-coordinated Fe^{2+} minerals, grandidierite and joaquinite. Broad, intense spin-allowed *dd* bands of tetrahedrally coordinated Fe^{2+}, originating from the $^5E \rightarrow {}^5T_2$ transition, appear in the spectral range 3000–7000 cm^{-1}. In the spectra of gillespite and eudialyte, minerals with square-planar coordination, the bands shift to higher energies, appearing in the range 7000–20 000 cm^{-1}. The amount of band splitting depends mainly on the distortion of the ligands surrounding four-coordinated Fe^{2+}. Splitting and distortion are minimal for spinel with a regular tetrahedral site, and maximal for eudialyte and gillespite. For the minerals in four-coordination, the barycenter of the split bands correlates with the sum of the bond-length and edge-length distortion parameters if the square planer sites are excluded from the correlation. Molar absorption coefficients (ε) of the spin-allowed tetrahedral Fe^{2+} bands range from ~20 $cm^{-1}\cdot L\cdot mol^{-1}$ to ~90 $cm^{-1}\cdot L\cdot mol^{-1}$. For eudialyte and gillespite, due to the centrosymmetric character of the ligand environment, the ε values ranges from about 0.5–10 $cm^{-1}\cdot L\cdot mol^{-1}$. For grandidierite and joaquinite, five-coordination causes spectra that resemble those of Fe^{2+} in highly distorted octahedral sites. The number of bands suggests, however, that the electronic level scheme of five-coordinated Fe^{2+} in grandidierite significantly differs from that of Fe^{2+} in octahedral coordination.