

Optical spectroscopic study of natural Fe-rich Pizzo Forno staurolite at different temperatures and pressures

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ABSTRACT

Polarized spectra of natural brownish-yellow Fe-rich staurolite from Pizzo Forno (Switzerland) evidence that its color is very likely due to an intervalence charge-transfer transition between Fe²⁺ and Ti⁴⁺ that causes a broad absorption band at ca. 25 400 cm⁻¹ superimposed on an intense high-energy edge. The polarization properties of the band and, also, the visible pleochroism $\gamma > \alpha \gg \beta$ of the sample studied, which is found to be different to previously published data viz. $\gamma > \beta \gg \alpha$, does not unambiguously give evidence of the structural positions of Ti⁴⁺ ions involved in the IVCT process. In the NIR-range, we observe a broad structured absorption envelope caused by an electronic spin-allowed band of ^{IV}Fe²⁺ containing three broad components at around 5445, 4625, and 3800 cm⁻¹ and strong narrow β - and γ -polarized lines of OH-vibrations in the range 3600 to 3400 cm⁻¹. Curve-fitting analysis suggests that the three crystal field bands are due to lowering of the local symmetry of the tetrahedral Fe²⁺ from T_d to ca. C_{2v} , so they are assigned to the split electronic ${}^5E \rightarrow {}^5T_2$ transition of ^{IV}Fe²⁺. Noticeable differences in the temperature- and pressure-induced effects on the spin-allowed bands of ^{IV}Fe²⁺ in staurolite compared to spinel—another ^{IV}Fe²⁺-bearing mineral—are observed. This implies a suppression of the Jahn-Teller effect in staurolite that is normally intrinsic to ions with doublefold degenerate electronic ground state such as ^{IV}Fe²⁺.

Keywords: Staurolite, optical absorption spectra, IVCT, *dd*-transitions, temperature and pressure effect