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Optical spectroscopic study of tetrahedrally coordinated Co^{2+} in natural spinel and staurolite at different temperatures and pressures

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Abstract

Optical absorption spectra of natural Co-bearing spinel and staurolite were studied at different temperatures and pressures. In both minerals, two broad, intense structured bands in the range 5500–8000 and 15 000–19 000 cm^{-1}, caused by electronic spin-allowed transitions $^4A_2 \rightarrow {}^4T_1(^4F)$ and $^4A_2 \rightarrow {}^4T_1(^4P)$ of $^{IV}Co^{2+}$ are the predominant absorption features. In addition, in both cases broad bands, derived from spin-allowed electronic transitions $^4E \rightarrow {}^4T_2$ of $^{IV}Fe^{2+}$, appear in the near infrared range partly overlapping the bands caused by $^{IV}Co^{2+}$. In staurolite the NIR range of the spectra are complicated by intense sharp lines of OH-vibrations at around 3400 cm^{-1}.

In spinel, with a regular tetrahedral site, the splitting of the spin-allowed bands I and II of $^{IV}Co^{2+}$ is assumed to be caused by spin-orbit and vibronic coupling. In staurolite, the splitting is stronger due to the additional low-symmetry crystal field effect of $^{IV}Co^{2+}$. It is found that the effect of temperature and pressure on the behavior of the $^4A_2 \rightarrow {}^4T_1(^4P)$ bands of $^{IV}Co^{2+}$ in the two minerals are rather similar, in contrast to our findings for the spin-allowed bands of $^{IV}Fe^{2+}$ in spinel and staurolite. This is interpreted as a manifestation of a dynamic Jahn-Teller effect for $^{IV}Fe^{2+}$ and lack of it in case of $^{IV}Co^{2+}$.

Keywords: Spinel, staurolite, tetrahedral coordination, Co^{2+}, optical absorption spectra, temperature and pressure effects