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 $^4A_2 \rightarrow ^4T_1(2P)$ and $^4A_2 \rightarrow ^4T_1(4P)$ of $^{65}$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 $^{56}$Fe$^{2+}$, appear in the near infrared range partly overlapping the bands caused by $^{65}$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 $^{65}$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 $^{65}$Co$^{2+}$. It is found that the effect of temperature and pressure on the behavior of the $^4A_2 \rightarrow ^4T_1(2P)$ bands of $^{65}$Co$^{2+}$ in the two minerals are rather similar, in contrast to our findings for the spin-allowed bands of $^{56}$Fe$^{2+}$ in spinel and staurolite. This is interpreted as a manifestation of a dynamic Jahn-Teller effect for $^{56}$Fe$^{2+}$ and lack of it in case of $^{65}$Co$^{2+}$.

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

INTRODUCTION

Temperature and pressure effects on spin-allowed $dd$-bands originating from the $^4E \rightarrow ^4T_2$ transition of tetrahedral Fe$^{2+}$ in natural spinel have been found to be rather different from staurolite (Taran and Koch-Müller 2010). This was attributed to a dynamic Jahn-Teller effect, intrinsic to electronic centers with twofold degenerate ground state $^E$, in spinel (Taran and Langer 2001; Taran et al. 2005) and suppressed by a static crystal field distortion in staurolite (Taran and Koch-Müller 2010).

Co$^{2+}$, which also occupies tetrahedral sites in both spinel and staurolite structures (e.g., Burns 1993), is not expected to show a Jahn-Teller effect since the ground electronic level of $^{65}$Co$^{2+}$ is a non-degenerate $^4A_2$-state. Therefore, the effect of pressure or temperature on the behavior of the absorption crystal field bands of $^{65}$Co$^{2+}$ of the two minerals should be quite similar. In this paper, the results of a comparative optical spectroscopic study of natural Co$^{2+}$-bearing spinel and staurolite at different pressures and temperatures are presented.

EXPERIMENTAL METHODS

Samples and chemical composition

Staurolite and spinel for the present study were collected from a diaspore-bearing metabauxite lens on the eastern coast of the island of Samos (the eastern part of the Aegean Sea, Greece) near Mikri Lakka [the sample Sa9a of Feenstra et al. (2003)]. The rock consists of silicate- and oxide-rich domains or layers in a matrix of calcite with a minor amount of muscovite and paragonite. After crushing to a coarse powder and removing calcite by dissolution in concentrated HCl, several perfectly transparent and homogeneously colored, dark-blue, octahedral crystals of garnet spinel of “the second generation” (Feenstra et al. 2003), ~0.2 mm in diameter, were selected for an optical absorption spectroscopy study. The electron microprobe analysis (EMP) (Cammea SX100 electron microprobe) gives (Fe$_{0.004}$Mg$_{0.219}$Mn$_{0.009}$Zn$_{0.024}$Ni$_{0.006}$Co$_{0.001}$)O$_{2.986}$Al$_{0.002}$, similar to that of sample Sa9a(a) in Table 3 of Feenstra et al. (2003). Thin plates of thickness ~0.05 mm were prepared by polishing the crystals on two opposite sides with diamond pastes. They were used for optical absorption spectroscopy at ambient conditions, as well as at higher temperatures (up to 300 °C) and pressures (up to 12 GPa).

Two sections of Co-bearing staurolite, a-c (010) and a-b (001), prepared from fragments of a single crystal polished on both sides as thin plates of ~0.08 mm thickness were used for measuring polarized optical absorption spectra at ambient conditions and at different temperatures. In unpolarized transmitted illumination they are homogeneously colored in blue and violet-blue colors, respectively. Un-polarized high-pressure spectra were measured on a thinner plate (~0.05 mm) of a random orientation prepared from a tiny fragment of this same crystal.

Chemical compositions of the two plates in a-c (010) and a-b (001) orientation were measured close to the spots where the spectra were taken. Standards for the EMPA included the following synthetic and natural minerals and metals: garnet (Fe, Mn, Si, Al); ilmenite (Fe, Mn, Ti); rutile (Ti); wollastontite (Ca, Si, Mg); corundum (Al); periclase (Mg); garnet (Zn, Al); sphalerite (Zn); escolait (Cr); NiO (Ni); metallic V, Zn, Ni, and Co. The average crystal chemical formula for both sections, (010) and (001), calculated on the basis of 46 O atoms are presented in Table 1. For more clarity we also display it here:

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\begin{align*}
\text{(Fe}_{0.004}\text{Mg}_{0.219}\text{Mn}_{0.009}\text{Zn}_{0.024}\text{Ni}_{0.006}\text{Co}_{0.001})\text{O}_{2.986}\text{Al}_{0.002} & \rightarrow \text{the a-c section, (010);} \\
\text{(Fe}_{0.004}\text{Mg}_{0.171}\text{Mn}_{0.022}\text{Zn}_{0.024}\text{Ni}_{0.006}\text{Co}_{0.001})\text{O}_{2.986}\text{Al}_{0.002} & \rightarrow \text{the a-b section, (001).}
\end{align*}
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The Li content was determined by secondary ion mass spectrometry (SIMS). Because Fe > Co, Mg (Table 1) in our sample, the mineral is referred to as Co-

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