



Comprehensive structural and chemical (CO₂, Fe/Fe Mg, H₂O) investigations of Mg-Fe cordierite with micro Raman spectroscopy

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The Mg-Fe silicate cordierite with the idealized formula (Fe, Mg)₂Al₄Si₅O₁₈ occurs as a hexagonal and an orthorhombic polymorph with disordered/ordered Al-Si distribution on the tetrahedral sites. Most of the natural cordierites are fully ordered. Six-membered rings of (Si,Al)O₄ are piled in the direction of the crystallographic c-axis and form channels, laterally and vertically linked by additional (Al, Si) tetrahedrons. Mg and Fe in varying fractions occupy the octahedrally coordinated M-sites. CO₂ and H₂O (and other volatiles) can be incorporated into the structural channels, thus cordierite can be used for paleofluid reconstruction. The vibration energies of incorporated volatiles, their interaction with the lattice and variations of certain lattice-vibration energies caused by the Mg-Fe exchange can be determined with Raman spectroscopy, allowing chemical quantifications and structural investigations. A method for the semi-quantitative determination of CO₂-contents of natural cordierites by Kaindl et al. (2006) was optimized and enhanced by Haefeker et al. (2007). CO₂ contents can be measured in single crystals and thin sections with an error of ± 0.05 - 0.09 wt.-%. Based on the Mg-Fe exchange with garnet, cordierite can be used as a geothermobarometer. Recent investigations of synthetic Mg-Fe cordierites with $X_{Fe} = 0 - 1$ have shown a linear downshift of six selected lattice peaks between 100 and 1250 cm⁻¹ with the Mg-Fe contents. Correlation diagrams allow an estimation of the Mg-Fe contents in synthetic and natural samples. The experimental data are in good agreement with the results of quantum-mechanical calculations of the Raman spectra of Mg- and Fe cordierite (Kaindl et al., 2011) allowing the assignment of the peaks to specific vibrations of tetrahedral and octahedral sites. Natural Mg-Fe cordierites are mainly orthorhombic with a fully ordered Al/Si distribution on the tetrahedral sites. However, the disordered hexagonal polymorph is observed in many experiments. Raman spectroscopy allows easy distinguishing between the two polymorphs by the splitting of a characteristic peak at ~ 569 cm⁻¹. Crystallographic and Raman spectroscopic data of the Fe endmember polymorphs are rare in literature, therefore, Raman and single-crystal x-ray data of synthetic samples were collected and compared with the well-known Mg and Mg-Fe cordierites. First compositional Raman maps show a relation between the degree of ordering of Fe cordierite and the amount of water incorporated into the channels. The effects of water incorporation on the Raman spectra of Mg cordierites is currently being evaluated. Preliminary investigations indicate a downshift of the peak at ~ 1186 cm⁻¹ with increasing water contents.

Literature:

Kaindl, R., Tropper P., Deibl, I. (2006) A semi-quantitative technique for determination of CO₂ in cordierite by Raman spectroscopy in thin sections. *Eur. J. Mineral.*, 18, 331-335

Haefeker, U. (2007) Verbesserte semiquantitative Analyse von CO₂ in natürlichem Cordierit mit Hilfe der Mikro-Raman-Spektroskopie. Unpublished master thesis. University of Innsbruck, 86p

Kaindl, R., Többens, D. M., Haefeker, U. (2011) Quantum-mechanical calculations of the Raman spectra of Mg- and Fe-cordierite. *American Mineralogist*, 96, 1568-1574