



1 Crystal chemistry of spinel and spinelloid solid solutions in the system $\text{Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4$

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Studies of the phase relations at high pressures and temperatures in the system $\text{Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4$ have shown that additionally to spinel solid solutions and spinelloid III, which is isostructural to wadsleyite, other polytypes of spinelloids occur [1]. These high-p,T phases are important minerals in the Earth's mantle, and extensive research has been done on their stabilities. The possible incorporation of Fe^{3+} into oxide minerals, silicate spinels, and spinelloids has implications for the redox state in the upper mantle and transition zone. The aim of our investigations was the crystal chemical characterization of experimentally synthesized samples of this system using a combination of transmission electron microscopy, electron energy-loss spectroscopy (EELS), and energy-dispersive X-ray microanalysis.

The crystal chemical substitution during polytype formation is read as: ${}^{IV}\text{Fe}^{3+} + {}^{VI}\text{Fe}^{3+} \leftrightarrow {}^{IV}\text{Si}^{4+} + {}^{VI}\text{Fe}^{2+}$. From this process, disorder phenomena in the different spinelloid structures are deduced in terms of $\text{Fe}^{3+} - \text{Si}^{4+}$ disorder on tetrahedral sites as well as $\text{Fe}^{2+} - \text{Fe}^{3+}$ disorder on octahedral sites. Therefore, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios have been quantified for the different spinelloids according to the method described in [2]. It is shown, that within experimental errors the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined from the Fe L_{23} EELS spectra yield identical results as the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, which are calculated from the Si/Fe concentration ratio assuming a stoichiometric composition of the spinelloids. Herewith, an indirect proof has been conducted, that the concentration of defects in the oxygen sublattice, if existing at all, is negligible.

Interestingly, a linear correlation between the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and the intensity of the O *K* pre-edge peak in the accordant EELS spectra has been found. The O *K* pre-edge feature is due to transitions of electrons from the O *1s* orbital into empty states above the Fermi level with O *2p* symmetry, whose origin result from the hybridization of O *2p* orbitals with Fe *3d* orbitals [3]. The relationship between the pre-edge peak intensity of the O *K* EELS spectra and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio has been explained by theoretical calculations of the O *K* near-edge structure for different spinels and spinelloid polytypes.

The Si *K* EELS spectra for the samples mentioned above have been measured and described by a superposition of Si *K* edge spectra following the technique described in [4] using iron-ringwoodite ($\gamma\text{-Fe}_2\text{SiO}_4$) and stishovite (SiO_2) as standards for Si in tetrahedral and octahedral coordination, respectively. Herewith, the results of Yamanaka et al. [5, 6] were confirmed, where octahedrally coordinated silicon was detected and its concentration was quantified for $\text{Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4$ spinel solid solutions using X-ray diffraction, and measurements of the magnetization and electrical conductivity.

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