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Crystal chemistry of the magnetite-ulvöspinel series

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Abstract

Spinel single crystals of 19 compositions along the magnetite-ulvöspinel join were synthesized by use of a flux-growth method. To obtain quantitative site populations, the crystals were analyzed by single-crystal X-ray diffraction, electron-microprobe techniques, and Mössbauer spectroscopy. All results were processed by using an optimization model.

The unit-cell parameter, oxygen fractional coordinate, and tetrahedral bond length increase with increasing ulvöspinel component, whereas the octahedral bond length decreases marginally. These changes result in sigmoidal crystal-chemical relationships consistent with cation substitutions in fully occupied sites. As a first approximation, the Akimoto model $^{T}(Fe^{3+}_{1-X}Fe^{2+}_{X})^{M}(Fe^{2+}Fe^{3+}_{1-X}Ti_{X})O_4$ describes the cation substitutions. Deviations from this model can be explained by an electron exchange reaction $^{T}Fe^{2+} + {}^{M}Fe^{3+} = {}^{T}Fe^{3+} + {}^{M}Fe^{2+}$, which causes $^{M}Fe^{2+} \neq 1$ and $^{T}Fe^{2+}/Ti \neq 1$. The resultant S-shaped trends may be related to a directional change in the electron exchange reaction at Ti ≈ 0.7 apfu. In general, variations in structural parameters over the whole compositional range can be split into two contributions: (1) a linear variation due to the $^{T}Fe^{3+} + {}^{M}Fe^{3+} = {}^{T}Fe^{2+} + {}^{M}Ti^{4+}$ chemical substitution and (2) non-linear variations caused by the internal electron exchange reaction.

In accordance with bond-valence theory, strained bonds ascribable to steric effects characterize the structure of magnetite-ulvöspinel crystals. To relax the bonds and thereby minimize the internal strain under retained spinel space group symmetry, the electron exchange reaction occurs.

Keywords: Spinel, Mössbauer spectroscopy, crystal synthesis, crystal structure