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Stoichiometry of synthetic ulvöspinel single crystals

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Abstract

Spinel single crystals (up to 4 mm in size) of eight compositions along the $FeFe_2O_4$-Fe_2TiO_4 solid-solution join, with more than 75 mol% ulvöspinel, were synthesized by use of a flux-growth method. The crystals were characterized by electron microprobe and Mössbauer spectroscopy. Results demonstrated that these ulvöspinels are statistically stoichiometric. The atomic proportions of Ti^{4+} and Fe^{2+} progressively increase from 0.75 to 0.94 and from 1.75 to 1.94 apfu, respectively. Concomitantly the Fe^{3+} content decreases from 0.49 to 0.13 apfu. Consequently, the cation substitutions are restricted to the ideal classic substitution $2Fe^{3+} \leftrightarrow Fe^{2+} + Ti^{4+}$.

An average equilibrium temperature from coexisting spinel-ilmenite pairs of about 950 °C was estimated using the QUILF95 and Ghiorso-Sack models.

In contrast to previous studies based on non-stoichiometric samples sintered at higher temperatures, the present stoichiometric ulvöspinel samples were grown from a melt under moderate temperatures. This fact indicates that the formation of vacancies is related to high-equilibration temperatures or growth mechanisms, whereas natural ulvöspinel may very well be stoichiometric under normal magmatic conditions.

Keywords: Ulvöspinel, ilmenite, Mössbauer spectroscopy