In-situ neutron diffraction study of non-convergent cation ordering in the $(Fe_3O_4)_{1-x}(MgAl_2O_4)_x$ spinel solid solution

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ABSTRACT

Non-convergent cation ordering in the $(Fe_3O_4)_{1-x}(MgAl_2O_4)_x$ solid solution was investigated using in-situ time-of-flight neutron powder diffraction. The approach to equilibrium in a sample with $x = 0.75$ was observed at 923 K by performing in-situ structure refinements at intervals of 5 min, and the ordering behavior was traced through the time-dependence of the lattice parameter, the cation-oxygen bond lengths, and the cation-site scattering lengths. The data are consistent with a two-stage kinetic process in which relatively rapid exchange of Fe^{3+} with Mg and Fe^{2+} between tetrahedral and octahedral sites was followed by slower exchange of Mg with Al. The Fe^{3+} cations are shown to order onto tetrahedral sites, contrary to the predictions of thermodynamic models for the solid solution.

Equilibrium cation distributions in samples with $x = 0.4$, 0.5, and 0.75 were determined between 1073 and 1273 K by combining the structure refinements with measurements of saturation magnetization in quenched material. The adopted cation distribution was a compromise between the normal and inverse distributions observed in the end-members. The conflict of site preference between these two ordering schemes resulted in a simple behavior in the middle of the solid solution in which Al occurred predominantly on octahedral sites and the Mg, Fe^{2+}, and Fe^{3+} cations were distributed randomly over the remaining sites. The ordering scheme adopted away from the middle of the solid solution was obtained by combining this pseudo-random scheme with a tetrahedral site preference of Fe^{3+} relative to Mg and Fe^{2+}. Comparison of the structure refinements with published thermodynamic models demonstrates that quantitative agreement was poor between calculated and observed behavior in this system. Qualitative agreement with the O'Neill-Navrotsky thermodynamic model was found near the middle of the solid solution.