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Spinels Renaissance: The past, present, and future of those ubiquitous minerals and materials

Static positional disorder in ulvöspinel: A single-crystal neutron diffraction study†

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Abstract

A single-crystal neutron diffraction study of a synthetic ulvöspinel sample of composition $Fe^{3+}_{0.40}Fe^{2+}_{1.80}Ti_{0.80}O_4$ was performed to investigate the static positional disorder at the octahedrally coordinated *M* site. Anisotropic structural refinement was performed in the space group $Fd\bar{3}m$ against neutron Laue diffraction data collected at 298 K from two millimetric-sized crystals. Initial structure refinements were conducted with Fe and Ti sharing the *M* site (at 1/2, 1/2, 1/2), and their partial site occupancy was refined. The tetrahedrally coordinated *T* site (at 1/8, 1/8, 1/8) was modeled as fully occupied by Fe. For both crystals, the final R_1 index was about 3% for 9 refined parameters and 129 unique reflections, with no significant residuals.

As the atomic displacement factors obtained were anomalously high, according to the previous experimental findings, F_{obs}- and (F_{obs}–F_{cal})-difference Fourier maps of the nuclear density were generated. Fourier maps showed a significant minimum located out-of-center of the *M* site, and indicating a displacement of the Ti^{4+} from the center of the octahedron. A further test refinement was successfully conducted with two mutually exclusive sites: ^{M}Ti out-of-center (at 0.49, 0.49, 0.49) and ^{M}Fe on the center (at 1/2, 1/2, 1/2). The resulting displacement of Ti from the octahedral center appears to be shorter than 0.15 Å.

Using bond-valence theory, the out-of-center distortion of $^{M}Ti^{4+}$ is interpreted as a result of intrinsic distortions in the ulvöspinel structure. The potential implication of the octahedral distortion on the behavior of ulvöspinel at non-ambient conditions is discussed.

Keywords: Ulvöspinel, crystal chemistry, neutron Laue diffraction, static positional disorder, bond valence theory