

**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  $\text{Fe}_{0.40}^{3+}\text{Fe}_{1.80}^{2+}\text{Ti}_{0.80}\text{O}_4$  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,  $F_{\text{obs}}$ - and  $(F_{\text{obs}}-F_{\text{cal}})$ -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  $\text{Ti}^{4+}$  from the center of the octahedron. A further test refinement was successfully conducted with two mutually exclusive sites:  $^{\text{M}}\text{Ti}$  out-of-center (at 0.49, 0.49, 0.49) and  $^{\text{M}}\text{Fe}$  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  $^{\text{M}}\text{Ti}^{4+}$  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