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Thermodynamics and kinetics of cation ordering in natural and synthetic $Mg(Al,Fe^{3+})_2O_4$ spinels from in situ high-temperature X-ray diffraction

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ABSTRACT

One natural and two synthetic spinels with compositions $Mg(Al_{1-z}Fe^{3+}_z)_2O_4$ (with $2z = 0.078$, 0.138, and 0.200, respectively) were studied by in situ, high-temperature, single-crystal X-ray diffraction. All samples were heated from room temperature to 1050 °C. Thermal expansion was monitored by measuring the cell edge variation. Cation disorder was monitored by measuring the variation of the oxygen positional parameter *u*, which is closely correlated with the inversion parameter *i*. All samples showed extensive Al reordering at the M site between 550 and 650 °C, followed by an increase of disorder at $T > 650$ °C due to both Mg-Al and Mg-Fe^{3+} intersite exchanges.

The measured cation distributions were compared with those calculated using the general thermodynamic model for spinel binary solid-solutions of O'Neill and Navrotsky (1984). Measured and calculated inversion parameters compare satisfactorily at $T > 650$ °C, i.e., at conditions under which equilibrium was achieved at any temperature. In fact, at $T > 650$ °C, both $^{IV}Fe^{3+}$ and ^{IV}Al increase with increasing *T*, following the equilibrium path. The reproducibility of ^{IV}Al occupancies was very high, whereas $^{IV}Fe^{3+}$ occupancies were not satisfactorily matched. The cation distribution relaxation observed between 550 and 650 °C was interpreted on the basis of kinetic considerations. In this temperature range, inversion decreases to a minimum because the amounts of Al that reorder are far more abundant than those of Fe^{3+} that disorder. The Mg-Fe^{3+} exchange was confirmed to proceed at a faster rate than the Mg-Al exchange. Moreover, the Mg-Fe^{3+} exchange was found to be active at laboratory times at about 550 °C, whereas the Mg-Al exchange was hard to monitor below 600 °C.

Keywords: X-ray diffraction, in situ-HT, order-disorder, spinels