

## **Thermodynamics and kinetics of cation ordering in $\text{MgAl}_2\text{O}_4$ spinel up to 1600 °C from in situ neutron diffraction**

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### **ABSTRACT**

The temperature dependence of the cation distribution in synthetic spinel ( $\text{MgAl}_2\text{O}_4$ ) was determined using in-situ time-of-flight neutron powder diffraction. Neutron diffraction patterns of stoichiometric  $\text{MgAl}_2\text{O}_4$  and slightly non-stoichiometric  $\text{Mg}_{0.99}\text{Al}_2\text{O}_4$  samples were collected under vacuum on heating from room temperature to 1600 °C, and the cation distribution was determined directly from site occupancies obtained by Rietveld refinement. The equilibrium non-convergent ordering has been analyzed using both the O'Neill-Navrotsky and Landau thermodynamic models, both of which fit the observed behavior well over the temperature range of the measurements. Fitting the data between 560 °C and 1600 °C using the O'Neill and Navrotsky (1983) thermodynamic model yields  $\alpha = 32.8 \pm 0.9$  kJ/mol and  $\beta = 4.7 \pm 2.0$  kJ/mol. The fit to the Landau expression for ordering gives values of  $T_c = 445 \pm 109$  K and  $c' = 1.62 \pm 0.21$ . This confirms suggestions that the sign of the  $\beta$  coefficient in  $\text{FeAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  is positive, and opposite to that found in other 2–3 oxide spinels. Non-equilibrium order-disorder behavior below 600 °C has been analyzed using the Ginzburg-Landau model, and successfully explains the time-temperature dependent relaxation behavior observed in the inversion parameter. Changing the stoichiometry, even by as little as 1 mol% Mg-deficiency, significantly reduces the degree of order.