

## The temperature dependence of the cation distribution in synthetic hercynite ( $\text{FeAl}_2\text{O}_4$ ) from in-situ neutron structure refinements

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### ABSTRACT

The temperature dependence of the cation distribution in synthetic hercynite ( $\text{FeAl}_2\text{O}_4$ ) has been determined using in-situ time-of-flight neutron powder diffraction. The sample was synthesized from the oxides under controlled oxygen fugacity and then quenched in air. Neutron diffraction patterns were then collected under vacuum on heating from room temperature to 1150 °C, and the cation distribution was determined directly from site occupancies obtained by Rietveld refinement. The degree of inversion,  $x$ , decreased from 0.135(4) at room temperature to 0.112(4) at 600 °C. Thereafter the degree of inversion increases smoothly with increasing temperature, reaching a value of 0.219(5) at 1150 °C. The decrease in  $x$  on heating to 600 °C is a kinetic phenomenon caused by the system moving toward its equilibrium degree of order from the relatively disordered state maintained after quenching from the synthesis temperature. The equilibrium ordering behavior between 600 and 1150 °C has been analyzed using both the O'Neill-Navrotsky and Landau thermodynamic models. Although the data could be fitted with both models over the temperature range of the measurements, Landau theory predicts the incorrect curvature of the equilibrium  $x$ - $T$  curve, leading to a significant discrepancy in the calculated behavior when the model is extrapolated outside the calibrated temperature range. The correct  $x$ - $T$  curvature is predicted by the O'Neill-Navrotsky model, and values of the model coefficients  $\alpha = 31.3 \pm 1.1$  kJ/mol and  $\beta = 19.7 \pm 3.4$  kJ/mol were obtained by least-squares fitting to the equilibrium data. This confirms the results of a previous study using quenched material, which suggested that the sign of the  $\beta$  coefficient in  $\text{FeAl}_2\text{O}_4$  is opposite to that found in other 2–3 oxide spinels.