American Mineralogist, Volume 84, pages 299–310, 1999

Thermodynamics and kinetics of cation ordering in $MgAl_2O_4$ spinel up to 1600 °C from in situ neutron diffraction

Simon A.T. Redfern,[1,*] Richard J. Harrison,[2] Hugh St.C. O'Neill,[3] and David R.R. Wood[1]

[1]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
[2]Institut für Mineralogie, Universität Münster, Corrensstrasse 24, D 48149, Münster, Germany
[3]Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

Abstract

The temperature dependence of the cation distribution in synthetic spinel ($MgAl_2O_4$) was determined using in-situ time-of-flight neutron powder diffraction. Neutron diffraction patterns of stoichiometric $MgAl_2O_4$ and slightly non-stoichiometric $Mg_{0.99}Al_2O_4$ 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 β coefficient in $FeAl_2O_4$ and $MgAl_2O_4$ 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.