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Study of cation order-disorder in $MgAl_2O_4$ spinel by in situ neutron diffraction up to 1600 K and 3.2 GPa

Fabienne Méducin,[1,*] Simon A.T. Redfern,[2] Yann Le Godec,[3] Howard J. Stone,[2] Matt G. Tucker,[2] Martin T. Dove,[2] and William G. Marshall[4]

[1]Centre de Recherche sur la Matière Divisée (CRMD) Unité Mixte de Recherche 6619 du CNRS et de l'Université d'Orléans, 1bis, rue de la Férollerie, 45071 Orléans Cedex 2, France
[2]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
[3]Laboratoire de Physique des Milieux Condensés, Université Pierre et Marie Curie, 75252 Paris, France
[4]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, U.K.

Abstract

The temperature-dependence of the cation distribution in synthetic spinel ($MgAl_2O_4$) was investigated using in situ time-of-flight neutron powder diffraction at ISIS, the pulsed-neutron source at the Rutherford Appleton Laboratory. Neutron diffraction patterns of stoichiometric $MgAl_2O_4$ were collected on heating from room temperature to ~1600 K at pressures of ~2.6 GPa. The cation distribution was determined directly from site occupancies obtained by Rietveld refinement. The equilibrium non-convergent ordering was analyzed using the O'Neill-Navrotsky (1983) thermodynamic model, which fits the observed behavior well over the temperature range of the measurements. Fitting the data between 790 and 1600 K yields $\alpha = 31(6)$ kJ/mol and $\beta = -20(13)$ kJ/mol in the expression for the free energy of ordering. The high-pressure temperature-dependent behavior, as compared to equivalent ambient-pressure behavior, demonstrates that disordering occurs to a much greater extent in $MgAl_2O_4$ at high pressure and that pressure favors disordering toward the inverse structure.