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Cation mixing in natural $MgAl_2O_4$ spinel: A high-temperature ^{27}Al NMR study

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Abstract

The positional disorder of Mg^{2+} and Al^{3+} cations between the tetrahedral and octahedral sites in natural $MgAl_2O_4$ spinel has been investigated by ^{27}Al MAS NMR at room temperature and in-situ high-temperature ^{27}Al NMR spectroscopy up to 1600 °C. The inversion parameter describing the disorder, *x*, where *x* stands for the positional disorder between Mg and Al cations in $Mg_{1-x}Al_x(Mg_xAl_{2-x})O_4$, increased with temperature. Below 1100 °C the inversion parameter, *x*, can be determined from MAS NMR measurements of quenched samples at room temperature. Above 1100 °C, *x* was estimated from the peak position in the high-temperature ^{27}Al NMR spectra up to 1600 °C. The observed dependence of *x* with temperature was fitted using the model of O'Neill and Navrotsky (1983). The coefficients of the model obtained are $\alpha = 35 \pm 5$ kJ and $\beta = -32 \pm 5$ kJ, which are approximately equal in magnitude and opposite in sign. The *x* values observed in the present investigation are in agreement with the model. However the introduction of an additional entropy term, ΔS_D, improved the fitting. ΔS_D reduces the entropy of disorder relative to a random mixing model. This would reflect either a nonconfigurational entropy contribution or short-range Mg-Al order because of local charge balance. On the other hand, above 1400 °C a narrow peak appeared at about 60 ppm. This peak became narrower with increasing temperature up to 1600 °C. This behavior might suggest that a rapid exchange process among the fourfold-coordinated Al sites occurs in this temperature range.