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Kinetics of cation ordering in synthetic $MgAl_2O_4$ spinel

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ABSTRACT

The time and temperature evolution of intracrystalline Mg-Al exchange in synthetic $MgAl_2O_4$ spinel was studied by single-crystal X-ray diffraction of quenched samples, with the aim of contributing to rock cooling-rate estimation. Flux-grown, homogeneous crystals (0.1 mm in size) were annealed at 1000 °C and then were isothermally ordered at 900, 800, and 700 °C for 10 seconds to 40 days. The cation ordering process was investigated by measuring the spinel O atom positional parameter u, which had been previously demonstrated to be closely related to the inversion x at equilibrium by the linear equation ($R^2 = 0.995$):

$$x = 21.396 - 80.714\,u.$$

From $x = 0.27$ after annealing runs, the inversion decreased with time for all of the three ordering runs, and equilibrium was reached after about 4 min at $T = 900$ °C ($x = 0.25$), about 55 min at $T = 800$ °C ($x = 0.23$), and about 700 min at $T = 700$ °C ($x = 0.21$). The Mueller kinetic model was satisfactorily applied to the experimental data. Solution of Mueller's integral gave the kinetic ordering constants $K_{900} = 1.12 \pm 0.57$, $K_{800} = 0.112 \pm 0.047$, and $K_{700} = 0.0171 \pm 0.0045$ min^{-1}, corresponding to $t_{1/2}$ of 0.6, 6.2, and 40.5 min, respectively. The linear dependence of K with temperature ($R^2 = 0.99$) was observed, and may be expressed by the Arrhenius equation:

$$\ln K = 20.189 - 23722/T\ (\mathrm{K})$$

An activation energy of 197 ± 22 kJ/mol was obtained for the intracrystalline Mg-Al ordering reaction, which compares well with the value of 217 kJ/mol reported in the recent literature for Mg-Fe^{3+} exchange in spinels.