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Kinetics of cation ordering in natural $Mg(Al,Cr^{3+})_2O_4$ spinels

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ABSTRACT

The kinetics of cation ordering (quench method) in two natural $Mg(Al_{2-y}Cr_y)O_4$ spinels (y~ 0.03–0.06 and 0.24), highly ordered in terms of Mg-Al, were studied by means of X-ray single-crystal diffraction. The equilibrium distribution of Mg and Al between tetrahedral and octahedral sites was investigated at 650 °C (in disordering and ordering) and at 850 °C (in ordering), through several time-steps to monitor the rate of cation distribution before equilibrium was achieved. The cation distributions for both disordering and ordering experiments were obtained by measuring the oxygen positional parameter *u*, which is correlated to the inversion parameter *x* (Al in T site), and then to the composition of the samples.

The Mueller kinetic model, satisfactorily applied to the experimental data, allowed the calculation of the kinetic ordering constants K, linearly related to temperature by means of Arrhenius equations.

The kinetics of ordering processes are influenced by Cr content. The equilibrium for both the isotherms at 650 and 850 °C was reached at different elapsed times by the low- and high-Cr spinels: the time for the low-Cr sample was, in both the ordering experiments, about double that of the high-Cr sample. Consequently, the activation energy (186 and 175 kJ/mol for low- and high-Cr samples, respectively) for the intracrystalline Mg-Al ordering decreases with Cr increase.

Keywords: Kinetics, cation distribution, order-disorder, spinels