Kinetics of cation ordering in synthetic MgAl$_2$O$_4$ spinel

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ABSTRACT

The time and temperature evolution of intracrystalline Mg-Al exchange in synthetic MgAl$_2$O$_4$ 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 ($R^2 = 0.995$):

$$x = 21.396 - 80.714u.$$  

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:

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

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.

INTRODUCTION

Many studies have been done on intersite cation exchange in rock-forming minerals with the aim of quantifying cation ordering as a function of chemical composition, equilibration temperature, and time. This makes it possible to estimate both the closure temperature and the cooling rate of silicates from terrestrial rocks and meteorites (e.g., Ganguly and Stimpfl 2000; Ganguly and Domenechetti 1996; Ganguly and Tazzoli 1994; Molin et al. 1994; Skogby 1992; Seifert and Virgo 1975). Pyroxenes, olivines and amphiboles have been largely investigated for this purpose, whereas spinels—oxides nearly ubiquitous in low crust and upper mantle—have been relatively less carefully examined. As well as the above-mentioned mineral species, spinels show temperature-dependent cation ordering that is non-convergent, i.e., no changes in symmetry are caused by order-disorder reactions. The spinel structure ($Fd\overline{3}m$) is formed of an approximately cubic, close-packed array of O atoms. Bivalent A and trivalent B cations—which partially fill the tetrahedral T and octahedral M cavities—undergo continual intersite exchange with temperature. Cation distribution in spinels is described by the following structural formula:

$$^{IV}(A_{1-x}B_x)^{VI}(B_{2-x}A_x)O_4$$

where IV refers to the T site and VI to the M site, and $x$ is the inversion parameter. At low temperatures ($T \rightarrow 0$ K), $x$ tends toward 0 for normal spinels (e.g., MgAl$_2$O$_4$) and toward 1 for inverse spinels (e.g., MgFe$_2$O$_4$), both values corresponding to a low-entropy, completely ordered state. At high temperatures ($T \rightarrow \infty$), both normal and inverse spinels are expected to have $x$ tending to 2/3, a fully disordered state corresponding to maximum entropy and random distribution of cations. This is confirmed by experimental data, because high-temperature investigations of cation distribution have shown $x$ up to 0.35 in MgAl$_2$O$_4$ (Maekawa et al. 1997; Redfern et al. 1999), and up to 0.72 in MgFe$_2$O$_4$ (O’Neill et al. 1992).

The kinetics of cation ordering in spinels is definitely less well known than the thermodynamics: this is mainly due to the scarcity of experimental data and to difficulties in interpreting non-equilibrium behavior of intracrystalline cation exchange. Ordering kinetics of MgFe$_2$O$_4$ have been investigated by O’Neill (1994) and Harrison and Putnis (1999), who measured the evo-