Cation ordering in MgTi$_2$O$_5$ (karrooite): Probing temperature dependent effects with neutrons

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ABSTRACT

MgTi$_2$O$_5$ (karrooite) exhibits cation exchange between the two non-equivalent octahedral M1 and M2 sites. The temperature dependence of Ti-Mg disorder has been determined using in situ time-of-flight powder neutron diffraction to establish the cation population of each site. The equilibrium Ti-Mg exchange commences above 700–800 °C, and continues up to 1300 °C. At ~1350 °C MgTi$_2$O$_5$ appears to undergo a reversible, displacive phase transition, although the structure can still be refined in space group 63. This transition shows discontinuities in the degree of order, the *c* cell parameter, and in the M-O bond lengths, quadratic elongation, and bond angle variance for the M1 octahedron, which becomes pseudo-tetrahedral. By contrast, the M2 octahedron shows no significant change. An Arrhenius plot exhibits linear behavior from 750–1300 °C, gives an exchange enthalpy of ordering of 33.6 kJ/mol, and a value of 10.7 kJ/mol for the entropy of disordering. A value of 5.92 cm^3/mol is deduced for the ΔV of the high-temperature reaction of geikielite (MgTiO$_3$) + rutile (TiO$_2$) to form fully disordered MgTi$_2$O$_5$ at an extrapolated temperature of 1860 °C.

Keywords: Crystal structure, high-temperature, neutron diffraction, order-disorder, oxides, karrooite, rutile, geikielite