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An in situ neutron diffraction study of cation disordering in synthetic qandilite Mg_2TiO_4 at high temperatures

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ABSTRACT

Temperature-dependent cation order-disorder has been studied in many 2+ – 3+ oxide spinels but 4+ – 2+ spinels have been found to be either completely normal or completely inverse when examined at room temperature. Here we report the temperature dependence of the cation distribution in the 4–2 spinel synthetic qandilite (Mg_2TiO_4) from in situ time-of-flight neutron powder diffraction experiments to 1416 °C. At room temperature, Mg_2TiO_4 is confirmed to have completely inverse cation distribution, with Ti atoms occupying half the octahedrally coordinated cation sites. Cation disordering becomes observable above about 900 °C, with 4% of the Ti occupying the tetrahedral site by 1416 °C. The rate of reordering on cooling is fast, such that high-temperature disorder is not preserved on cooling to room temperature. The thermodynamics of the change in cation distribution with temperature can be described by an enthalpy of Mg-Ti disorder of -46.1 ± 0.4 kJ/mol.