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Cation ordering in magnesioferrite, $MgFe_2O_4$, to 982 °C using in situ synchrotron X-ray powder diffraction

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Abstract

Magnesioferrite spinel, $MgFe_2O_4$, was synthesized at 900 °C from equimolar amounts of reagent-grade oxides, MgO and Fe_2O_3, and quenched in air. The structural behavior of magnesioferrite was determined from in situ synchrotron X-ray powder-diffraction data [$\lambda = 0.92225(4)$ Å] at room pressure and temperatures from 28 to 982 °C on heating and cooling. The *a* unit-cell parameter increases linearly on heating, but deviates to give a discontinuity at 581 °C. Above 581 °C and on cooling from 982 °C, the *a* parameter varies linearly. The *a* parameter at 28 °C before heating [8.39704(5) Å] and after cooling to 47 °C [8.39514(4) Å] is different because the cation order frozen in the structure is not the same. Cation order, analyzed in terms of the inversion parameter, *x*, $\{^{iv}[Mg_{1-x}Fe_x]^{vi}[Mg_{x/2}Fe_{1-x/2}]_2O_4\}$, and the order parameter, $Q = 1 - (3/2)\,x$, show no change on heating until the temperature is high enough to cause exchange of Mg^{2+} and Fe^{3+} cations between the octahedral and tetrahedral sites. This activation barrier is overcome at 581 °C, where the sample achieves the maximum ordered state on heating [$x_{max} = 0.867(4)$] and begins to move toward equilibrium. This relaxation is toward a more ordered configuration and is a kinetically controlled process. Above 581 °C, the cations continuously disorder along the equilibrium pathway to the maximum temperature studied [T_{max} = 982 °C, $x = 0.769(3)$] and reverse along the equilibrium pathway on cooling. At T_B, the maximum equilibrium order is frozen in, and maintained to room temperature, where $x_{max} = 0.895(4)$. O'Neill-Navrotsky, Landau, and Ginzburg-Landau models give good descriptions of the ordering process in $MgFe_2O_4$. Simultaneous differential scanning calorimetry (DSC) and thermogravimetry (TG) data were obtained using a Netzsch STA 449C simultaneous TG-DSC instrument. The DSC curve for $MgFe_2O_4$ contains an irreversible exothermic peak at about 550 °C = T_{relax} in the first heating experiment, and the energy change associated with this peak is –162 J/g (= –32 KJ/mol), and corresponds to cation relaxation. From Rietveld refinements, $T_{relax} \approx 581$ °C. The $T_{Curie} \approx 360$ °C was obtained from TG experiments carried out in a magnetic field.