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Thermodynamics of the magnetite-ulvöspinel (Fe_3O_4-Fe_2TiO_4) solid solution

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Abstract

The thermodynamics of mixing and its dependence on cation distribution in the Fe_3O_4–Fe_2TiO_4 (magnetite-ulvöspinel) spinel solid solution were studied using high-temperature oxide melt solution calorimetry and a range of structural and spectroscopic probes. The enthalpies of formation of ilmenite and ulvöspinel from the oxides and from the elements were obtained using oxidative drop solution calorimetry at 973 K in molten sodium molybdate. The enthalpy of mixing, determined from the fit to the measured enthalpies of drop solution calorimetry, is endothermic and represented by a quadratic formalism, $\Delta H_{mix} = (22.60 \pm 8.46)x(1-x)$ kJ/mol, where x is the mole fraction of ulvöspinel. The entropies of mixing are more complex than those for a regular solution and have been calculated based on average measured and theoretical cation distributions. Calculated free energies of mixing show evidence for a solvus at low temperature in good agreement with that observed experimentally.

Keywords: Titanomagnetite, magnetite-ulvöspinel solid solution, enthalpies of mixing, calorimetry