Energetics of Fe^{II}-Fe^{III} Spinel Solid Solutions on Macroscopic and Nanoscale

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The thermodynamics of mixing of the bulk and nanosized magnetite-maghemite and magnetite-ulvöspinel solid solution sare of interest for understanding the extent of solid solution formation and also for providing a basis to define effective half-cell reduction potentials for heterogeneous electron transfer reactions with environmentally relevant species. The "tunable" solid-state Fe2+/Fe3+ ratio provides an ideal parameter to systematically examine the relationship between thermodynamics, kinetics, and environmental impact.

The mixing properties of the macroscopic and nano solid solutions in the Fe-TI-O system were determined using high temperature oxide melt solution calorimetry and the effect of particle size was assessed. The entropies of mixing of were calculated from the cation distributions. The surface energies of the nanosized materials were found to be similar regardless of the composition and were consistent with those determined for other spinels.