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A computational model of cation ordering in the magnesioferrite-qandilite ($MgFe_2O_4$-Mg_2TiO_4) solid solution and its potential application to titanomagnetite (Fe_3O_4-Fe_2TiO_4)

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Abstract

Cation ordering in the magnesioferrite-qandilite ($MgFe_2O_4$-Mg_2TiO_4) solid solution has been investigated using an interatomic potential model combined with Monte Carlo simulations. The dominant chemical interaction controlling the thermodynamic mixing behavior of the solid solution is a positive nearest-neighbor pairwise interaction between tetrahedrally coordinated Fe^{3+} and octahedrally coordinated Ti^{4+} (J^{TO}_{FeTi}). The predicted cation distribution evolves gradually from the Néel-Chevalier model to the Akimoto model as a function of increasing J^{TO}_{FeTi}, with $J^{TO}_{FeTi} = 1000 \pm 100$ K providing an adequate description of both the temperature and composition dependence of the cation distribution and the presence of a miscibility gap. Although Mg is a good analog of Fe^{2+} in end-member spinels, a comparison of model predictions for $MgFe_2O_4$-Mg_2TiO_4 with observed cation ordering behavior in titanomagnetite (Fe_3O_4-Fe_2TiO_4) demonstrates that the analog breaks down for Fe_3O_4-rich compositions, where a value of J^{TO}_{FeTi} closer to zero is needed to explain the observed cation distribution. It is proposed that screening of Ti^{4+} by mobile charge carriers on the octahedral sublattice is responsible for the dramatic reduction in J^{TO}_{FeTi}. If confirmed, this conclusion will have significant implications for attempts to create a realistic thermodynamic model of titanomagnetite.

Keywords: Magnesioferrite, qandilite, titanomagnetite, cation distribution, computer simulations