The Influence of Aluminum on Iron Oxides: XIV. Al-Substituted Magnetite Synthesized at Ambient Temperatures

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Abstract: Mixtures of magnetite and goethite were formed by the slow oxidation of mixed $FeCl_2$-$AlCl_3$ solutions in an alkaline environment at room temperature. The compositions of the products ranged from almost exclusively magnetite in Al-free systems to goethite only at Al/(Al + Fe) $\approx$ 0.3. The magnetic phase consisted of a partly oxidized ($Fe^{2+}/Fe^{3+} < 0.5$), Al-substituted magnetite. The unit-cell edge length *a* of the magnetite decreased with increasing Al (Al = 0 − 0.37 per formula unit, corresponding to 0 − 14 mole % Al) and decreasing Fe^{2+} in the structure as described by the empirical relationship a(A) = 8.3455 + 0.0693 Fe^{2+} - 0.0789 Al. A correlation between the experimentally determined *a* and that calculated from the unit-cell edge lengths of end-member magnetite, maghemite, and hercynite was highly significant (r = .96) although shifted by about 0.01 Å. Mössbauer spectra showed Al to have entered preferentially the tetrahedral rather than the octahedral sites at low Al substitutions (<0.15 per formula unit), perhaps because of steric reasons. With increasing Al substitution the crystal size of magnetite decreased and structural strain increased, indicating that the structure had a limited capability to incorporate Al under these synthesis conditions. The capacity of the goethite structure to tolerate more Al may explain why goethite replaced magnetite at higher Al concentrations.

Key Words: Aluminum • Goethite • Iron oxide • Magnetite • Mössbauer spectroscopy • X-ray powder diffraction

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