
Mn-Substituted Goethite and Fe-Substituted Groutite Synthesized at Acid pH¹

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Abstract: Mn-substituted iron oxides were synthesized by coprecipitating Fe(NO₃)₃ and Mn (SO₄) solutions with NH₄OH, adjusting the suspensions to pH 4 or 6, and then keeping the suspensions at 55°C for 62 days. The Mn mole fraction of the final products ranged from 0 to 0.3. X-ray powder diffraction patterns showed that goethite and hematite formed in each Fe-containing system. Groutite formed in systems having initial Mn mole fractions ≥ 0.35 . Only manganite and hausmannite formed in the pure Mn systems. The oxalate-soluble Fe in the samples increased as the Mn mole fraction increased and was slightly larger for the pH 6 series.

For samples that contained the largest Mn mole fraction, the *b* and *c* dimensions of the goethite unit cell were shifted toward those of groutite, and the *b* and *c* dimensions of the groutite unit cell were shifted toward those of goethite. Assuming the Vegard rule holds for the unit-cell *c* dimension, the goethite accommodated a maximum Mn mole fraction of 0.34, and the groutite accommodated a maximum Fe mole fraction of 0.31. The unit-cell dimensions of hematite did not vary systematically with the mole fraction of Mn in solution, probably because little Mn substituted into the hematite structure.

Key Words: Goethite • Groutite • Iron • Manganese • Solid solution • Synthesis • Vegard's law • X-ray powder diffraction

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