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A structural study of size-dependent lattice variation: In situ X-ray diffraction of the growth of goethite nanoparticles from 2-line ferrihydrite

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Abstract

Unlike most native metals, the unit cells of metal oxides tend to expand when crystallite sizes approach the nanoscale. Here we review different models that account for this behavior, and we present structural analyses for goethite (α-FeOOH) crystallites from ~10 to ~30 nm. The goethite was investigated during continuous particle growth via the hydrothermal transformation of 2-line ferrihydrite at pH 13.6 at 80, 90, and 100 °C using time-resolved, angle-dispersive synchrotron X-ray diffraction. Ferrihydrite gels were injected into polyimide capillaries with low background scattering, increasing the sensitivity for detecting diffraction from goethite nanocrystals that nucleated upon heating. Rietveld analysis enabled high-resolution extraction of crystallographic and kinetic data. Crystallite sizes for goethite increased with time at similar rates for all temperatures.

With increasing crystallite size, goethite unit-cell volumes decreased, primarily as a result of contraction along the *c*-axis, the direction of closest-packing (space group *Pnma*). We introduce the coefficient of nanoscale contraction (CNC) as an analog to the coefficient of thermal expansion (CTE) to compare the dependence of lattice strain on crystallite size for goethite and other metal oxides, and we argue that nanoscale-induced crystallographic expansion is quantitatively similar to that produced when goethite is heated. In addition, our first-order kinetic model based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation yielded an activation energy for the transformation of ferrihydrite to goethite of 72.74 ± 0.2 kJ/mol, below reported values for hematite nucleation and growth.

Keywords: Goethite, 2-line ferrihydrite, nanoparticle research, time-resolved X-ray diffraction, kinetics