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

INTRODUCTION

Over the last several decades, Earth scientists have documented that nanoparticles can control the aqueous geochemistry of surficial environments due to their enhanced reactivity and their catalytic proficiency (reviewed in Hochella et al. 2008 and Sharma et al. 2015). Traditionally, the amplified role of nanocrystals is attributed to their high ratios of reactive surface area to volume. In addition to their extensive surficial interfaces, however, nanocrystals may react more readily than their macroscopic counterparts because of structural changes arising from their sub-micrometer dimensionality. Variations in unit-cell dimension strongly influence electronic band structure, leading to disparities in the chemical behaviors of nano- and macro-particles (Solliard and Flueli 1985; Ayyub et al. 1995).

Nearly a century ago, Lennard-Jones and Dent (1928) theorized that lattice parameters of crystal surfaces will differ from those of the bulk, and by extension Lennard-Jones (1930) argued that nanoparticles dominated by surface structure will deviate in a predictable fashion from bulk materials. Specifically, he suggested that the unit-cells of “non-ionic” compounds should increase with decreasing particle size, whereas ionic crystals will behave in the opposite fashion. Some early X-ray (Randall and Rooksby 1932) and electron (Finch and Wilman 1934; Finch and Fordham 1936; Pickup 1936) diffraction experiments offered support for a dependence of lattice parameters on crystallite dimensions. Because of the small magnitudes of variation, however, these early studies offered contrasting interpretations for the effects of particle size on unit-cell dimensions (Boswell 1951).

MODELS OF SIZE-INDUCED LATTICE VARIATIONS

Modern investigative techniques offer much higher precision for the measurement of lattice parameters, and these issues have been revisited over the past two decades. In reviewing this recent work, Diehm et al. (2012) offer three generalizations regarding size-dependent lattice variations in nanoparticles.

(1) Metals and ionic crystals behave oppositely. Whereas the lattice parameters of noble metals tend to contract with decreasing particle size (Wasserman and Vermaak 1970, 1972), the unit cells of most metal oxides (e.g., MgO, Fe3O4, Fe2O3, MnCr2O4) expand as particles become smaller (Cimino et al. 1966; Bhowmik et al. 2006; Rodenbough et al. 2017). It should be noted, however, that the unit cells of Ni (Rollinghaus et al. 2001; Duan and Li 2004) and Fe (Choi et al. 2002) nanoparticles disobey this trend. Nanocrystals of these metals expand with smaller sizes, apparently due to oxide surface layers.

(2) For non-cubic metal oxides (e.g., TiO2-rutile, TiO2-anatase, t-BaTiO3), lattice expansion with diminishing size often is anisotropic (Tsunekawa et al. 2000; Kuznetsov et al. 2009; Ahmad and Bhattacharya 2009).

(3) Even today, reported magnitudes of lattice evolution with diminishing size often are highly variable for the same