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Epitaxial overgrowth of goethite on hematite synthesized in phosphate media: A scanning force and transmission electron microscopy study

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ABSTRACT

We used X-ray diffraction (XRD), scanning force microscopy (SFM), transmission electron microscopy (TEM), and color to investigate the effect of phosphate on the crystallization rate, nature, and morphology of iron oxides prepared from ferrihydrite in the laboratory. Synthesis was performed at two temperatures (323 and 373 K) and two pH values (9 and 12) from ferric nitrate, for P/Fe atomic ratios ranging from 0 to 2.5%. The presence of phosphate retarded crystallization, tended to favor hematite over goethite, and markedly influenced the morphology of the goethite crystals formed at high pH. Application of SFM in the deflection mode was useful to investigate the morphology of the small goethite crystals, with careful attention paid to operating conditions; in particular, sharp silicon probes were found to produce fewer artifacts than coarser silicon nitride ones. At low P/Fe ratios ($<0.2\%$), the goethite crystals were thin, elongated, multidomain laths; at high P/Fe ratios ($>1.5\%$), star-shaped, twinned crystals were produced. All the theoretical shapes, derived from the assumption that star-shaped crystals result from the epitaxial growth of goethite on a hematite core, were observed by SFM and TEM. The presence of such hematite nuclei was supported by XRD, selected-area electron diffraction, color, and preferential dissolution of the samples in HCl, because it is known that hematite dissolves faster than goethite in acid. With increasing P/Fe ratio, the arms of the star-shaped crystals became shorter. This was likely due to the higher density of P-adsorbing pairs of singly coodinated OH groups on terminal {021} faces relative to prismatic {110} arm faces.