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Vacancy infilling during the crystallization of Fe-deficient hematite: An in situ synchrotron X-ray diffraction study of non-classical crystal growth

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Abstract

The crystallization of hematite from precursor ferrihydrite was studied using time-resolved, angle-dispersive synchrotron X-ray diffraction in aqueous solutions at pH 10 and 11 and at temperatures ranging from 80 to 170 °C. Rietveld analyses revealed a non-classical crystallization pathway involving vacancy infilling by Fe as defective hematite nanocrystals evolved. At 90 °C and pH 11, incipient hematite particles exhibited an Fe site occupancy as low as 0.68(2), and after 30 min, Fe occupancy plateaued at 0.84(1), achieving a metastable steady state with a composition corresponding to "hydrohematite." During crystal growth, unit-cell volume increased with an increase in Fe occupancy. The increase in Fe occupancy in hydrohematite was accomplished by deprotonation, resulting in a shortening of the long Fe-O(H) bonds and decreased distortion of the octahedral sites. Once the occupancy stabilized, the unit-cell volume contracted following further nanoparticle growth. Our study documented various synthetic routes to the formation of "hydrohematite" with an Fe vacancy of 10–20 mol% in the final product.

The structure refined for synthetic hydrohematite at 90 °C and pH 11 closely matched that of natural hydrohematite from Salisbury, Connecticut, with a refined Fe occupancy of 0.83(2). Dry heating this natural hydrohematite generated anhydrous, stoichiometric hematite, again by continuous infilling of vacancies. The transformation initiated at 150 °C and was complete at 700 °C, and it was accompanied by the formation of a minor amorphous phase that served as a reservoir for Fe during the inoculation of the defective crystalline phase.

Keywords: Hematite, 2-line ferrihydrite, crystal growth, time-resolved X-ray diffraction, kinetics