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Structural water in ferrihydrite and constraints this provides on possible structure models

Wenqian Xu,[1] Douglas B. Hausner,[2,3] Richard Harrington,[1,5] Peter L. Lee,[4] Daniel R. Strongin,[2] and John B. Parise[1,5,*]

[1]Department of Geosciences, Stony Brook University, Stony Brook, New York 11794-2100, U.S.A.
[2]Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, U.S.A.
[3]Department of Chemistry, Rutgers–Camden, Camden, New Jersey 08102, U.S.A.
[4]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.
[5]Department of Chemistry, Stony Brook University, Stony Brook, New York 11794-3400, U.S.A.

Abstract

The dry thermal transformation of 2-line ferrihydrite to hematite was investigated using combinations of thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis, along with in situ DSC and pair distribution function (PDF) analysis of X-ray total scattering data and in situ temperature controlled infrared (IR) spectroscopy. TG data show a 25.6 ± 0.1% weight loss below 300 °C, ascribed to the removal of surface water since PDF analysis shows no change in the structure of ferrihydrite up to this temperature. The transformation to hematite occurs at around 415 ± 1 °C (peak temperature) at a heating rate of 10 °C/min, with no obvious weight change during or after the transformation. In situ PDF analysis indicates that the ferrihydrite bulk structure remained intact up to the direct transition to crystalline hematite, with no intermediate phases, crystalline or amorphous, formed. In situ IR data shows the extent of absorption attributable to OH stretching in ferrihydrite at 215 °C dropped to 10% of its room-temperature value. These results suggest ferrihydrite contains very little structural OH: the molar ratio of OH/Fe is 0.18 ± 0.01. A recently proposed akdalaite-like ferrihydrite model has an OH/Fe equal to 0.2, consistent with this result. The 3-phase model proposed by Drits et al. (1993) has an average formula close to FeOOH, with an OH/Fe equal to 1.0, far more than suggested by our experiments. Based on the constraints set by the estimated water content and the PDF signatures, we examined possible anion packing types and local structural motifs in ferrihydrite, and demonstrate that ABAC is the only feasible packing type and that a peak at 3.44(2) Å in PDF provides indirect evidence for the presence of tetrahedral Fe.

Keywords: Ferrihydrite, hydrous ferric oxide, hydroxyl, hematite, goethite, pair distribution function, PDF analysis, tetrahedral iron in ferrihydrite