

A refined monoclinic structure for a variety of “hydrohematite”

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ABSTRACT

In ferruginous soils, nano- to microscale hematite (α -Fe₂O₃) plays a central role in redox processes and contaminant cycling. Hematite is known to incorporate structural OH⁻ and water, and the requisite charge balance is achieved by iron vacancies. Prior researchers have suggested that the defective hematite structures form unique phases called “protohematite” and “hydrohematite.” Infrared and Raman spectroscopic studies have assigned a lower-symmetry space group to “hydrohematite” ($R\bar{3}c$) relative to that of stoichiometric hematite ($R\bar{3}c$). However, the existence and structure of these phases have been contentious, largely due to the lack of in situ X-ray diffraction data

Here we present a new structure refinement for “hydrohematite” precipitated hydrothermally at 200 °C in a monoclinic space group ($I2/a$) using time-resolved synchrotron X-ray diffraction (TR-XRD) data collected during the in situ hydrothermal precipitation of akaganeite and its transformation to stoichiometric hematite. Distinct peak splitting was observed in the “hydrohematite” diffraction patterns, indicating a violation of the threefold rotational symmetry. A monoclinic unit cell with parameters of $a = 7.3951(10)$, $b = 5.0117(5)$, $c = 5.4417(7)$ Å, $\beta = 95.666(5)^\circ$ provided a good fit and significant reduction in χ^2 and R_{wp} relative to space group $R\bar{3}c$. Rietveld analyses revealed that water concentrations in the first-formed crystals of “hydrohematite” were comparable to water contents of akaganeite and goethite. Thus, the hydrothermal transformation of akaganeite to “hydrohematite” is promoted not by dehydration but by reconstruction of the oxygen framework.

Keywords: Hydrohematite, protohematite, hematite, akaganeite, X-ray diffraction