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Neutron and temperature-resolved synchrotron X-ray powder diffraction study of akaganéite

JEFFREY E. POST,[1,*] PETER J. HEANEY,[2] ROBERT B. VON DREELE,[3] AND JONATHAN C. HANSON[4]

[1]Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560-0119, U.S.A.
[2]Department of Geosciences, 309 Deike, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.
[3]LANSCE-12, MS H805, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.
[4]Chemistry Department, Brookhaven National Laboratory, Upton, New York 11793, U.S.A.

ABSTRACT

Rietveld refinements using neutron powder diffraction data were used to locate H atom positions and obtain a more precise crystal structure refinement for akaganéite [$Fe^{3+}_{7.6}Ni^{2+}_{0.4}O_{6.35}(OH)_{9.65}Cl_{1.25}\cdot nH_2O$]. Difference Fourier maps clearly showed H atoms positions near those O atoms at the midpoints of the tunnel edges. The O-H vectors point toward the Cl sites at the center of the tunnel, and weak hydrogen bonds likely form between the framework O atoms and Cl. The Cl position is near the center of a prism defined by the eight hydroxyl H atoms. The Cl atoms fill ~2/3 of the tunnel sites, suggesting an ordering scheme in a given tunnel with every third tunnel site vacant. Such an arrangement allows the Cl anions to increase their separation distance along a tunnel by displacing away from one another toward their respective adjacent vacancies. The Fe-O octahedra in akaganéite are distorted with Fe-(O, OH) distances ranging from 1.94 to 2.13 Å and show three longer and three shorter Fe-O distances; as expected the longer distances are associated with the OH^- anions.

Temperature-resolved synchrotron X-ray powder diffraction data and Rietveld refinements were used to investigate changes in the akaganéite structure and its transformation into hematite as it was heated from 26 to 800 °C. Rietveld refinements revealed surprising consistency in all unit-cell parameters between room temperature and ~225 °C, resulting in nearly zero thermal expansion of the akaganéite structure over a 200 °C interval. Above ~225 °C, the unit-cell volume gradually decreased, primarily in response to decreases in *c* and *b*, and an increase in the β angle. The *a* parameter remained nearly constant until ~225 °C and increased thereafter. Akaganéite started to transform to hematite in the temperature range 290 to 310 °C with no evidence for maghemite as an intermediate phase.