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Crystal structure refinement of ferrihydrite using atomic pair distribution function (PDF) analysis

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Ferrihydrite is a short-range ordered nano-crystalline iron (III) oxyhydroxide that has been recognized to play an important role in iron cycling in environmental, biological, and geochemical processes. Despite intensive research for the two last decades, the exact atomic structure of ferrihydrite is not fully established and is still matter of debate. Atomic pair distribution function (PDF) analysis is a powerful technique to obtain structural information of nanoparticulate materials. Michel et al. (2007) have recently presented a structure for ferrihydrite that was determined using the PDF method and synchrotron X-ray scattering technique. In the study, the PDF analysis is used to investigate and compare the structure of 6-line ferrihydrite and dehydrated ferrihydrite with the results of Michel et al. (2007). Ferrihydrite was synthesized by the method of Schwertmann and Cornell (1991). TEM observations show that the particle size of the ferrihydrite is highly uniform with a size distribution between 3 nm and 5 nm. X-ray measurements were performed on a Rigaku RAXIS RAPID imaging plate area detector with sealed-tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromated) operating at 50 kV and 40 mA. The X-ray total scattering data were collected up to 2theta = 72.2° that corresponds to the value of Qmax = 10.4 Å-1. The crystal structure of ferrihydrite was refined in space group P63mc, with a = 5.974(2), c = 9.130(2) Å, V = 282.18 Å3, spherical diameter = 2.09 (1) nm, and that of ferrihydrite heated was with a = 5.924(1), c = 9.130(2) Å, V = 277.48 Å3, spherical diameter = 2.002 (4) nm, respectively. The crystal structures are composed of edge-sharing FeO6 octahedra and corner-sharing FeO4 tetrahedra, which form a two-dimensional layer-like structure perpendicular to the c axis. The tetrahedra exhibit significantly distorted configuration such that three oxygen atoms are found at a distance of 1.96 A and the other at 2.08 A. The dehydration process causes a unit cell contraction accompanied by a shrinkage of the a lattice parameter. The release of water molecules enhances the bond length and angular distortions of the octahedra and tetrahedra in ferrihydrite.