

## BRIEF COMMUNICATION

# A New Iron(III) Oxyhydroxynitrate

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A new Fe(III) oxyhydroxynitrate ( $\text{FeO}(\text{OH})_{1-x}(\text{NO}_3)_x$  with  $0.2 < x < 0.3$ ) was synthesized which, based on X-ray diffraction, FTIR, and Mössbauer spectroscopy, is considered to have an akaganeite ( $\beta\text{-FeOOH}$ )-like tunnel structure in which nitrate occupies the tunnel. © 1996 Academic Press, Inc.

One of the FeOOH polymorphs,  $\beta\text{-FeOOH}$  (akaganeite), has a structure in which four double chains of  $\text{FeO}_3(\text{OH})_3$  octahedra form a  $0.25 \times 0.25 \text{ nm}^2$  tunnel running along [010]. In akaganeite, ( $\text{FeO}(\text{OH})_{1-x}\text{Cl}_x$ ), the tunnel is partly occupied by chloride anions which appear essential for its structural stability. Recently, an analogous compound with sulfate occupying the tunnel position instead of  $\text{Cl}^-$  has been identified as a weathering product of pyrite,  $\text{FeS}_2$ , and the mineral form was named schwertmannite. Its idealized formula is  $\text{Fe}_8\text{O}_8(\text{OH})_5(\text{SO}_4)_{1.5}$  (1).

This note describes the nitrate member of this group. It was synthesized as follows: Two liters of 0.025 M  $\text{Fe}(\text{NO}_3)_3$  solution was hydrolyzed at  $75^\circ\text{C}$  for 12 min by adding solid Fe(III) nitrate into preheated water. The red sol was then shock-cooled and freeze dried. The resulting solid was either dried at  $55^\circ\text{C}$  for 10 days and then washed once with water and again freeze dried, or, alternatively, dried from acetone at  $40^\circ\text{C}$ .

Different preparations were analyzed for Fe and  $\text{NO}_3$  after dissolution in HCl. The composition depended on the treatment after synthesis. If dried from acetone, it contained between 33 and 43% Fe and between 17.5 and 18.6%  $\text{NO}_3$ . If dried from water, Fe rose to 48–50% and  $\text{NO}_3$  dropped to 9.8–11.9% indicating further hydrolysis. The weight loss after heating at  $110^\circ\text{C}$  for 16 h was ca. 10%. Since neither treatment led to a structural breakdown, the nitrate lost upon drying from water is presumably released mainly from the surface. The general formula for this compound is considered to be  $\text{FeO}(\text{OH})_{1-x}(\text{NO}_3)_x$ , where, on the basis of chemical analysis,  $x$  is  $\sim 0.2$  for the  $110^\circ\text{C}$  compound dried from water and  $\sim 0.3$  for the compound dried from acetone.

The compound, although poorly crystalline, shows six

broad XRD lines at 0.255(s), 0.224(m), 0.198(w), 0.168(w), 0.151(m), and 0.147(w) nm. They were indexed as 310, 212, 302, 412, 522, and 004, respectively (as for schwertmannite), with a primitive tetragonal unit cell (space group  $P4/m$ ). Thus, the compound is not the same as  $\text{Fe}_4\text{NO}_3(\text{OH})_{11}$  (JCPDS-ICBD, 44-520).

The Mössbauer spectrum at room temperature is a doublet, characteristic of paramagnetic Fe(III) and consisting of two broadened and significantly asymmetric lines. These are best fitted by two quadrupole doublets, of which the one with the larger splitting is of lower intensity. Mössbauer spectrum at 4.2 K shows two magnetically split sextets with hyperfine fields of  $\sim 45.0$  and  $\sim 47.6$  T, the latter being of higher intensity. These observations indicate two Fe(III) sites in the structure, one possibly influenced by neighboring nitrate anions as was proposed analogously for schwertmannite (1).

FTIR spectra show that the commonly used KBr must be avoided as a diluent because pressing a tablet or even grinding it with KBr partly destroys the material and forms  $\text{KNO}_3$  with a narrow band at  $1384 \text{ cm}^{-1}$ . In contrast, without KBr a strong, broad, poorly resolved band centered at about  $1400 \text{ cm}^{-1}$  which is interpreted as being derived from asymmetric stretch ( $\nu_3$ ) of nitrate, but partly perturbed in a similar way as  $\text{CO}_3^{2-}$  bound to goethite, shows up (2). In an ATR mode the broad bands split into two bands peaking at 1341 and  $1393 \text{ cm}^{-1}$  again indicating perturbation of  $\text{NO}_3^-$ . Bands at 680 and  $416 \text{ cm}^{-1}$  are due to Fe–O stretching. Characteristic bands for Fe(III) nitrate were not observed.

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