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Goethite, a tailor-made host for the critical metal scandium: The $Fe_xSc_{(1-x)}OOH$ solid solution

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Supplementary Information

The Supplementary Information includes:

- Sample Characterisation
- Table S-1
- Figures S-1 and S-2
- Supplementary Information References

Sample Characterisation

The chemical composition of the samples was determined by induced coupled plasma atomic emission spectrometry (ICP-AES). Aliquots (50 mg) of each Sc doped goethite (0 to 100 mol %) were dissolved in 3 mL HNO_3 (UP, 15N) then diluted with 2 % HNO_3 to obtain a final volume of 50 mL. Fe and Sc were analysed using ICP-AES, Optima DV 3000 (PerkinElmer) and a calibration curve with certified solutions of Fe and Sc. Y was used as internal standard.

X-ray diffraction (XRD) was used for phase identification. Powder samples were disaggregated in an agate mortar and deposited on a zero background silicon plate (Sil'Tronix ST, Archamps, France) with a drop of ethanol to obtain a thin homogeneous layer of powder. X-ray diffraction was performed using a PANalytical X'Pert Pro MPD diffractometer running at 40 kV and 40 mA equipped with a cobalt anode (λ = 1.79 Å), a secondary monochromator and a fast X'Celerator X-ray detector. Samples were spun at 15 rpm to improve statistics and scanned from 20 to 70° (2θ) with a step size of 0.033° and a counting time of 4.5 s per step. Phase identification was checked using X'Pert Highscore Plus (PANalytical) and ICDD PDF2 database. Profex software (Doebelin and Kleeberg, 2015) was used for Rietveld refinement to determine the cell parameters of the (Fe,Sc)OOH samples starting with the ICDD PDF files 29-713 (goethite) or 73-1790 (ScOOH) and Pbnm space group. The following parameters were refined: zero point shift, sample displacement, cell parameters, preferred orientation and peak broadening resulting from the size of the crystallite and the micro strain.

The particles in the crystal suspensions deposited on carbon-coated copper grids were characterised using a transmission electron microscope (TEM, JEOL JEM 2011) coupled with an energy-dispersive X-ray spectrometer (EDX, X-Flash Silicon Drift Detector 5030, Bruker).

TEM-EDX microanalyses were conducted on individual particles. Data collection parameters were set as follows: magnification 50 000 x, 4L spot size, angular tilt of 20° towards the detector, time constant of 60 $kcp.s^{-1}$, energy range of 40 keV, and corrected counting time of 30 seconds. The beam diameter was set to ~ 20 nm (200 Å) in order to reach the smallest particles. The constant beam density was ~ 63.5 $pA.cm^{-2}$. Sc and Fe were quantified using the Bruker AXS MET line mark data quantification procedure, which is close to the original Cliff and Lorimer method (Cliff and Lorimer, 1975). In this procedure, the acquired EDX

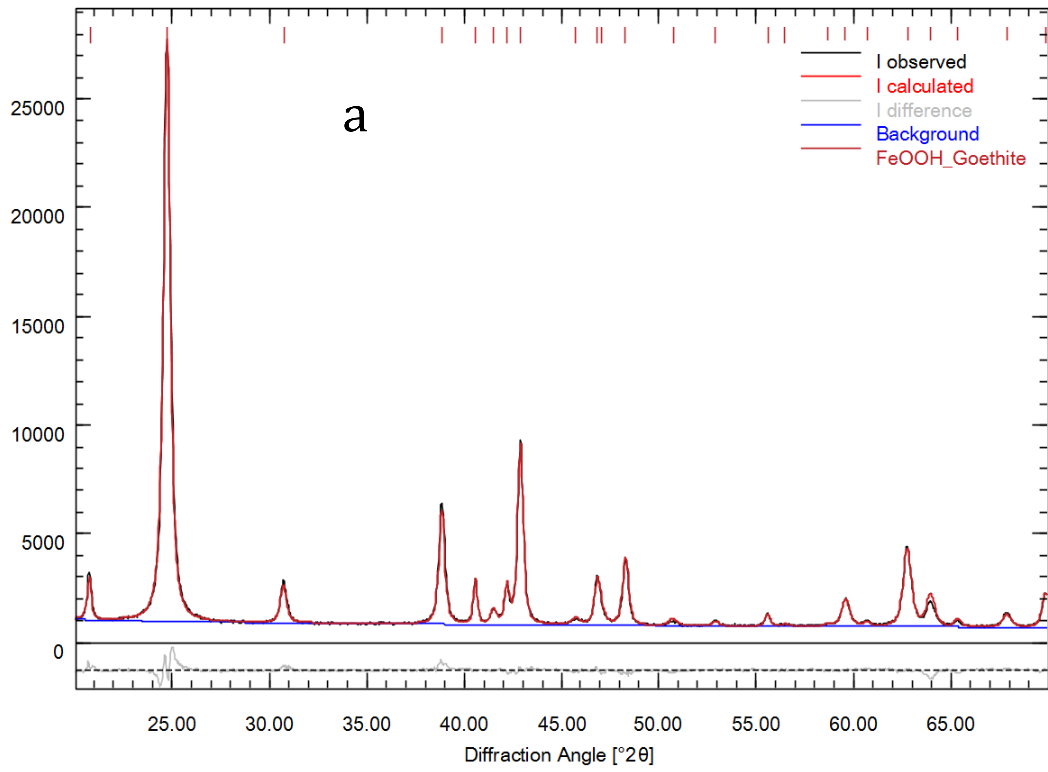
spectra are corrected by background subtraction (Bremsstrahlung calculation), Gaussian deconvolution, and *k* factor corrections using previously calculated values.

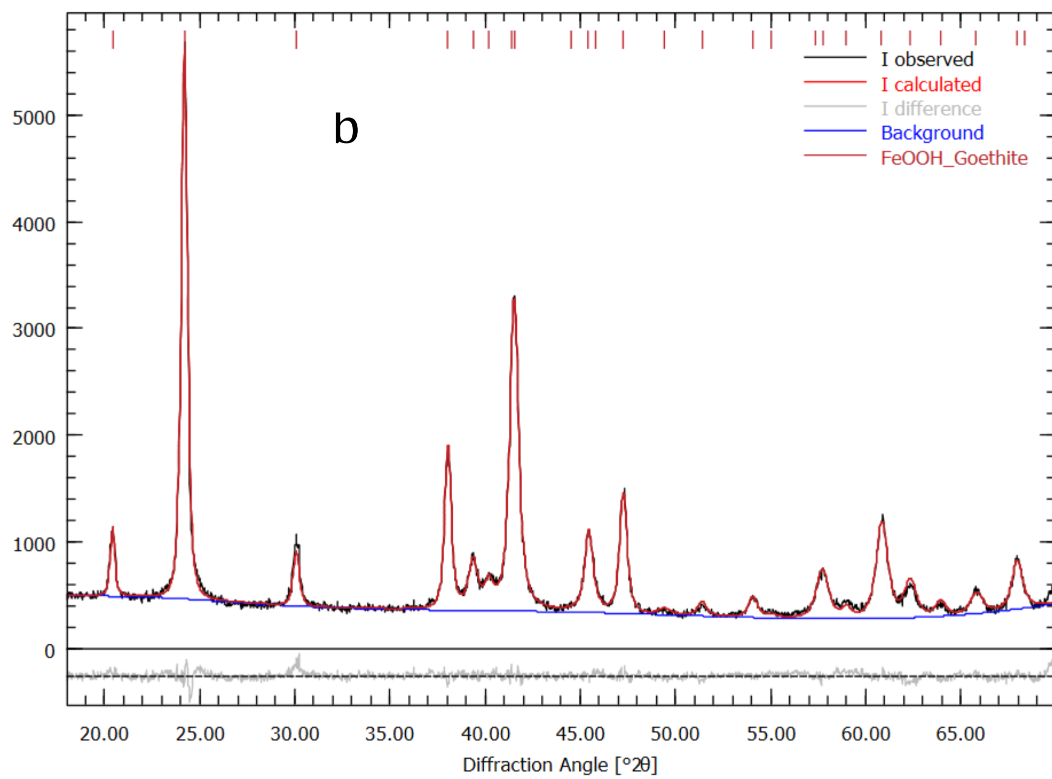
Supplementary Table

Table S-1 Refined cell parameters from Rietveld analysis.

Samples	a (nm)	b (nm)	c (nm)
S #1	0.461288 ± 0.000029	0.995894 ± 0.000051	0.302430±0.000014
S #2	0.46188 ± 0.00034	0.99644 ± 0.00068	0.30269±0.0002
S #3	0.46303 ± 0.00022	0.99752±0.00046	0.30338±0.00013
S #4	0.465786 ± 0.000059	1.001065±0.000077	0.304996±0.000024
S #5	0.469126 ± 0.000063	1.006237±0.000085	0.307784±0.000029
S #6	0.473829 ± 0.000072	1.01646±0.00010	0.313386±0.000032
S #7	0.477482 ± 0.000054	1.024749±0.000080	0.318170±0.000027
S #8	0.47934 ± 0.00022	1.03146±0.00046	0.32192±0.00014

Supplementary Figures





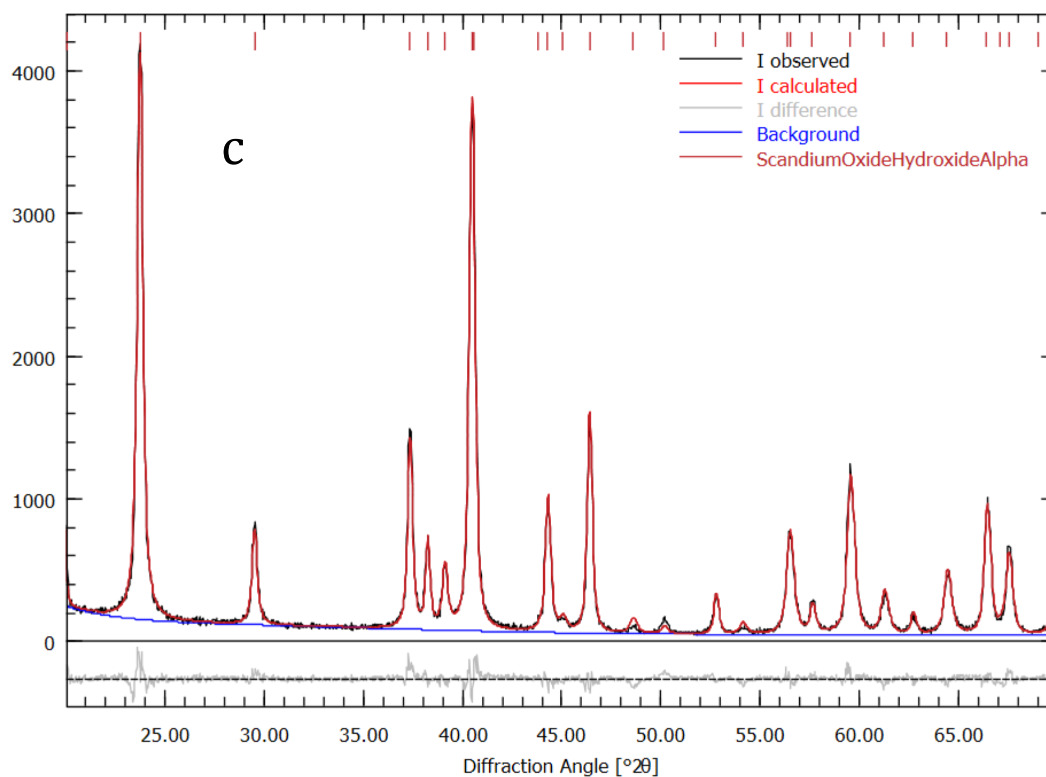


Figure S-1 Rietveld refinement of X-ray powder diffraction patterns of samples **(a)** #1, **(b)** #6 and **(c)** #8 between 20 and 70° (2θ). The black curve represents experimental data, the red curve calculated data, blue represents the background and grey the residue.

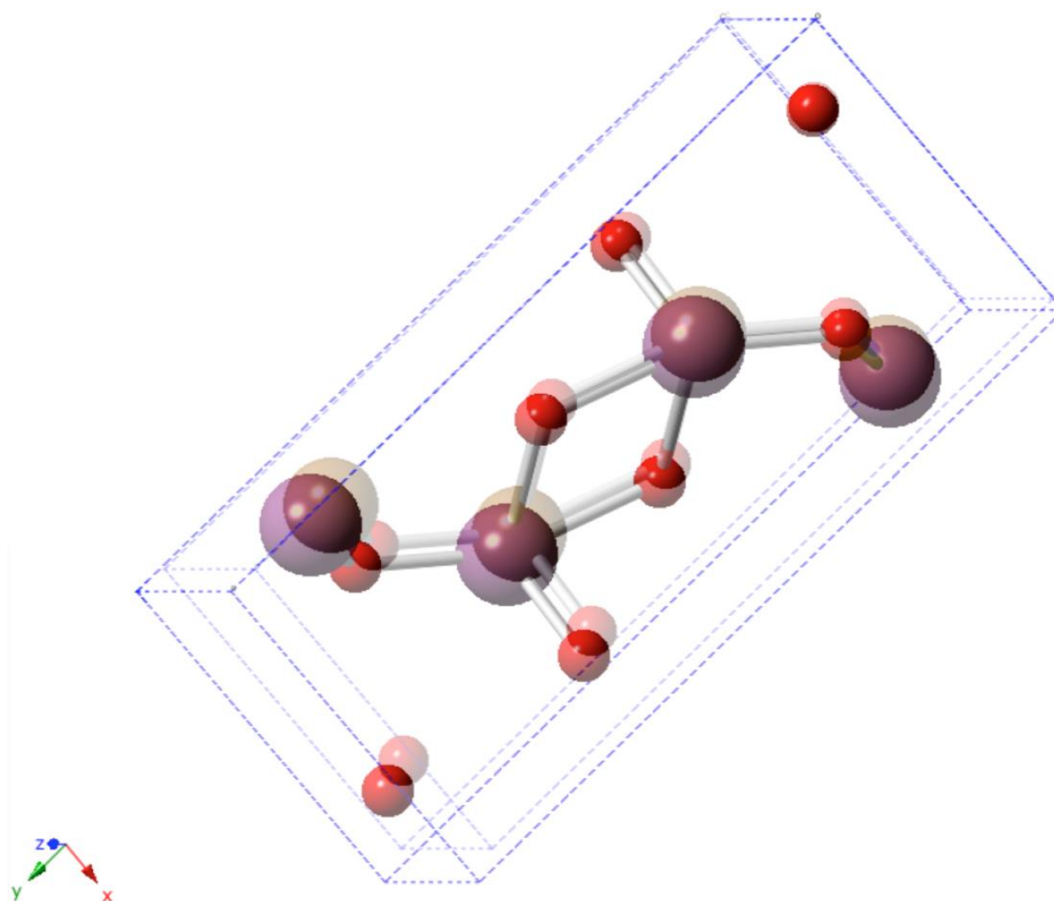


Figure S-2 Superimposition of atomic cell for FeOOH (Fe atoms in brown) and ScOOH (Sc atoms in purple).

Supplementary Information References

Cliff, G., Lorimer, G.W. (1975) The quantitative analysis of thin specimens. *Journal of Microscopy* 103, 203-207.

Doebelin, N., Kleeberg, R. (2015) Profex: a graphical user interface for the Rietveld refinement program BGMN. *Journal of Applied Crystallography* 48, 1573-1580.