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Report

"High resolution X-ray diffraction analyses of synthetic green rust minerals"

Proposal CH2254-Beamline ID31 6 shifts from 23 to 25 August 2006
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I – Context and Objectives

Green rusts of bulk composition $[Fe^{II}_{(1-x)}Fe^{III}_{x}(OH)_2]^{x+}[(x/n)A^{n-}, m\ H_2O]^{x-}$ belong to the layered doubled hydroxide (LDH) family. They consist of the stacking of positively charged brucite like layers separated by interlayers made of anions A^{n-} and water molecules. The importance of these compounds increased recently since their discovery in a hydromorphic gley soil of the forest of Fougères (Britanny).

The goal of the experiments was to determine accurate structural models by recording high resolution powder diffraction patterns of GR[CO_3^{2-}], GR[SO_4^{2-}] and Al-GR[SO_4^{2-}] samples. High intensity and high resolution diffraction patterns delivered by the ESRF was used to determine both the structure and microstructure of synthetic green rust minerals.

II- Experiments

Green rust minerals were synthesised in aqueous solution and dried in a glove box filled with an N_2 inert atmosphere. The samples were introduced in 1 mm diameter glass capillaries that were sealed with a glue to avoid any air oxidation. First standard X-ray diffraction (XRD) analyses show that sulphated green rust ($GRSO_4$) and Al-substituted hydroxysulphate green rust (Al-$GRSO_4$) exhibit the expected diffraction patterns [1]. Despite the precaution utilised during the preparation of the samples, the unwanted presence of magnetite Fe_3O_4 was observed for the hydroxycarbonate green rust samples. Therefore, supplementary Fe_3O_4 free carbonated ferric green rust coated sand samples were also prepared. The samples were carried from the LCPME laboratory to ESRF in a box filled with N_2. Samples were loaded on line ID31 of ESRF and high resolution X-Ray powder diffraction (HRXRPD) patterns were recorded at 2 θ angles between 0.25° and 38° with a wavelength set at λ = 0.35015(6) Å.

III- First results and interpretations

III-1 Analyses of hydroxysulphate green rust GR(SO_4^{2-})

The GR[SO_4^{2-}] exhibit a well defined diffraction pattern with all main expected lines. Four models taking into account the two possible orientations of sulphate group (up and down) and two positions in (a, b) plane, one below Fe^{3+} , the other below Fe^{2+} have been proposed [1]. The model "down to Fe^{3+} " gives rise to the best Rietveld refinement (figure 1). The high intensity of the diffraction pattern allows distinguishing much more clearly the previously observed lines of superstructure [1]. The refined atomic parameters are given in table 1

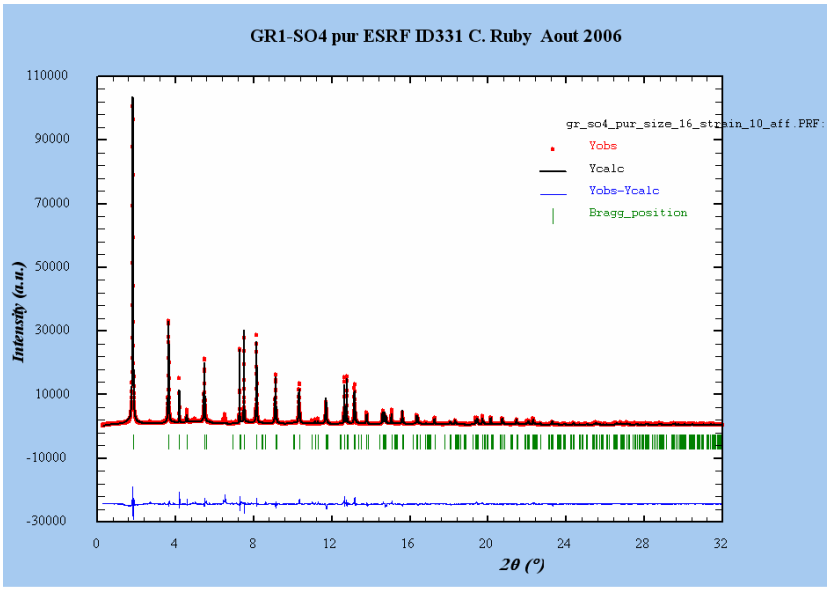

Figure 1 : HRXRPD pattern and Rietveld refinement of non-substituted GR(SO_4^{2-})

Table 1 **:** Refined atomic parameters for GR(SO_4^{2-}).

Atom	Site	*X*	*Y*	*Z*	*B* (nm^2)	Atoms/cell
Fe^{2+}	2c	0.666	0.3333	0.0	1.59(6)	2
Fe^{3+}	1a	0.0	0.0	0.0	0.558	1
OH^-	6k	0.338(1)	0	0.0776(5)	2.9(1)	6
H_2O	12l	-0.201(4)	0.627(2)	0.6271(6)	7.6(5)	4.36
S^{6+}	2e	0	0	0.3580(7)	3.2(3)	0.61
O_A^{2-}	2e	0	0	0.5	3.2(3)	0.61
O_B^{2-}	6k	-0.251 (1)	0	0.274(1)	3.2(3)	1.84

Rp = 0.077; Rwp = 0.10, Rexp = 3.4, R_F = 0.122 R_B = 0.081

III-2 Analyses of Al-substituted hydroxysulphate green rust Al-GR(SO_4^{2-})

A series of samples with increasing content of Al^{III} were prepared. They correspond to the general chemical formula $[Fe^{II}_{0.67}\ Fe^{III}_{(0.33-y)}\ Al^{III}_{y}\ (OH)_2]^{0.33+}$. $[1/6\ SO_4^{2-},\ 4/3\ H_2O]^{0.33-}$ with an Al^{III} molar fraction . y = 1%, 2 %, 4% and 8 %. The previously obtained structural model of GR(SO_4^{2-}) in which Al^{III} species are allowed to substitute either Fe^{II} or Fe^{III} species were used to do new Rietveld refinements attempts . As expected only the model where Al^{III} substitute Fe^{III} species gives rise to satisfactory results. A progressive shift and broadening of all the diffraction lines are observed and the microstructural refinement allows determining the cell parameters (figure 2), mean size and anisotropy of the crystals (figure 3).

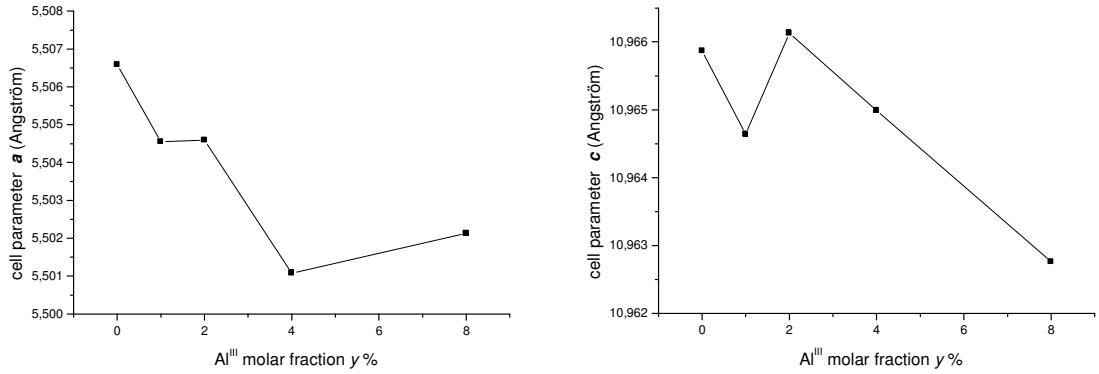

Figure 2 : Variation of the cell parameters ***a*** and ***c*** of Al-GR(SO_4^{2-}) for increasing Al^{III} content.

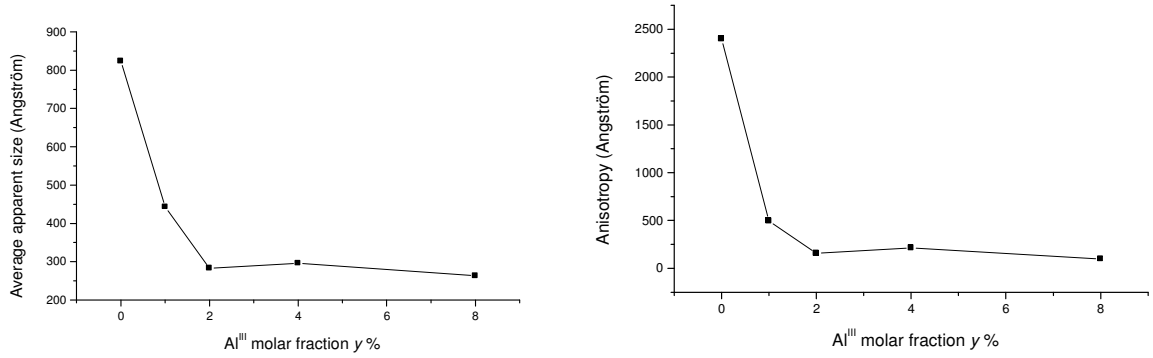

Figure 3 : Variation of the cell parameters average apparent size and anisotropy of Al-GR(SO_4^{2-}) for increasing Al^{III} content.

As expected (ionic radii of Al^{III} is smaller than ionic radii of Fe^{III}), a very small contraction of the unit cell is observed that corresponds to a relative variation of the parameters *a* and *c* of 0.08 % and 0.03 %, respectively. The decrease of average apparent crystal size and anisotropy is in very good agreement with previous results obtained by TEM that have shown a decrease of a factor ~ 10 for Al-GR(SO_4^{2-}) with a substitution rate y = 8 % [2, 3]. It was also shown that non-substituted GR(SO_4^{2-}) exhibits flat hexagonal shaped crystal and that Al-GR(SO_4^{2-}) was constituted of more rounded crystals in good agreement with the decrease of anisotropy observed in figure 3.

The results presented in tables 2 to 5 correspond to the refined atomic parameters of the Al-GR(SO_4^{2-}) samples. Despite the fact that the Al^{III} content is accurately determined for the synthesis of these compounds, the occupancy of the Al^{III} species was not fixed for this first series of refinement. The level of occupancy of the Al^{III} species does not increase proportionally with the value of the parameter *y*, showing that the method is not sufficiently sensitive for quantifying the aluminium content. The fact that the quantity of inserted aluminium is relatively low ($y \leq 8$ %) may explain this result.

Table 2 **:** Refined atomic parameters for Al-GR(SO_4^{2-}), Al^{III} content *y* = 1 %.

Atom	Site	*X*	*Y*	*Z*	*B* (nm^2)	Atoms/cell
Fe^{2+}	2c	0.666	0.3333	0.0	1.10(3)	2
Fe^{3+}	1a	0.0	0.0	0.0	1.10(3)	0.72
Al^{3+}	1a	0.0	0.0	0.0	1.102	0.28
OH^-	6k	0.323	0	0.071	3.94	6
H_2O	12l	-0.223(4)	0.654(4)	0.6333(8)	9.2(9)	4.54
S^{6+}	2e	0	0	0.3543(8)	0.8(3)	0.46
O_A^{2-}	2e	0	0	0.5	0.86(3)	0.46
O_B^{2-}	6k	-0.251 (2)	0	0.269(1)	0.8(8)	1.34

Rp = 0.097; Rwp = 0.14, Rexp = 3.5, R_F = 0.126 R_B = 0.087

Table 3 **:** Refined atomic parameters for Al-GR(SO_4^{2-}), Al^{III} content *y* = 2 %.

Atom	Site	*X*	*Y*	*Z*	*B* (nm^2)	Atoms/cell
Fe^{2+}	2c	0.666	0.3333	0.0	0.61(3)	2
Fe^{3+}	1a	0.0	0.0	0.0	3.5(2)	0.88
Al^{3+}	1a	0.0	0.0	0.0	3.5(2)	0.12
OH^-	6k	0.332(3)	0	0.0750(7)	3.4(2)	6
H_2O	12l	-0.196(5)	0.646(3)	0.6333(7)	10.9(9)	4.86
S^{6+}	2e	0	0	0.354(8)	3.7(6)	0.5
O_A^{2-}	2e	0	0	0.5	3.7(6)	0.5
O_B^{2-}	6k	-0.251 (2)	0	0.270(1)	3.7(6)	1.5

Rp = 0.094; Rwp = 0.13, Rexp = 3.1, R_F = 0.11 R_B = 0.079

Table 4 **:** Refined atomic parameters for Al-GR(SO_4^{2-}), Al^{III} content *y* = 4 %.

Atom	Site	*X*	*Y*	*Z*	*B* (nm^2)	Atoms/cell
Fe^{2+}	2c	0.666	0.3333	0.0	0.81(4)	2
Fe^{3+}	1a	0.0	0.0	0.0	2.2(2)	0.82
Al^{3+}	1a	0.0	0.0	0.0	2.225	0.18
OH^-	6k	0.322(2)	0	0.0775(6)	3.4(2)	6
H_2O	12l	-0.179(4)	0.635(2)	0.6310(6)	9.3(7)	4.7
S^{6+}	2e	0	0	0.3551(7)	2.3(4)40	0.53
O_A^{2-}	2e	0	0	0.5	2.3(4)	0.53
O_B^{2-}	6k	-0.252 (2)	0	0.272(1)	2.3(4)	1.58

Rp = 0.090; Rwp = 0.12, Rexp = 2.2, R_F = 0.11 R_B = 0.074

Table 5 **:** Refined atomic parameters for Al-GR(SO_4^{2-}), Al^{III} content *y* = 8 %.

Atom	Site	*X*	*Y*	*Z*	*B* (nm^2)	Atoms/cell
Fe^{2+}	2c	0.666	0.3333	0.0	2.7(3)	2
Fe^{3+}	1a	0.0	0.0	0.0	1.1(4)	0.89
Al^{3+}	1a	0.0	0.0	0.0	1.1(4)	0.11
OH^-	6k	0.326(8)	0	0.0532(9)	1.8(3)	6
H_2O	12l	-0.22(1)	0.65(1)	0.630(2)	10.9(9)	3.4
S^{6+}	2e	0	0	0.3544(8)	15.9(9)	0.44
O_A^{2-}	2e	0	0	0.5	15.9(9)	0.44
O_B^{2-}	6k	-0.252 (2)	0	0.269(1)	15.9(9)	1.34

Rp = 0.093; Rwp = 0.13, Rexp = 2.4, R_F = 0.13 R_B = 0.089

IV- Conclusion and perspectives

Rietveld refinements were performed to adjust the structure of GR(SO_4^{2-}) and Al-GR(SO_4^{2-}) samples against the experimental HRXRPD patterns. Refined atomic parameters and microstructure have been determined. For Al^{III} content as low as y = 1 %, strong effect on the microstucture parameters are observed: it corresponds to a global decrease of the crystal size and anisotropy with increasing aluminium content. Further Rietveld refinements are in progress to optimize the results. Diffraction patterns of iron coated sand samples are also currently analysed.

V- Publication related with this work

A part of this work will be presented in the next GFSM (Groupe Francophone de Spectrométrie Mössbauer) as an invited oral conference and proceeding (Caen 22-23 mai 2007). A publication is also in preparation and should be submitted in 2007.

V- References

[1] L. Simon, M. François, P. Refait, G. Renaudin, M. Lelaurain, J.-M. R. Génin, Solid State Sci. 5 (2003) 327.
[2] C. Ruby, R. Aïssa, A. Géhin, J. Cortot, M. Abdelmoula, J.-M. Génin, C. R. Geoscience, 338 (2006) 420.