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Investigation of Fe-based oxyhydroxy-fluoride with hollandite-type structure☆

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ABSTRACT

Well crystallized Fe-based oxyhydroxy-fluoride with the $FeO(OH_{0.2}F_{0.8})\cdot 0.2H_2O$ chemical composition has been prepared from hydrolysis of Fe trifluoride under supercritical CO_2 conditions. Investigation by Mössbauer spectroscopy and neutron diffraction show that this compound crystallize in the monoclinic symmetry (SG: $I2/m$, a = 10.447(7) Å, b = 3.028(2) Å, c = 10.445(4) Å, β = 90.00(3)°). Taking into account the Fe–O(F) bond distances, F^- anions are mainly located on the common vertices of Fe octahedra whereas OH^- groups occupy mainly the shared edges of the Fe octahedra. Two various highly distorted octahedral sites have been identified with Fe–O/F bond distances varying from 1.90 Å to 2.31 Å. One Fe site is more distorted than in $FeO_{0.8}OH_{1.2}\cdot 0.2Cl$ akaganeite because of the random distribution of $F^-/OH^-/O^{2-}$ in the vicinity of this Fe cation.

1. Introduction

Numerous oxyhydroxides adopt 2D-type networks where protons are delocalized between layers. In the case of nickel or cobalt, these materials can be used as positive electrode materials in secondary batteries. However in the case of Cr^{3+}, Fe^{3+} or Al^{3+} oxyhydroxides, 3D as well as 2D-type structures can be stabilized. The formation of the different phases and various allotropic forms can be explained by thermodynamics and kinetics considerations. Thus, whereas Cr^{3+} or Al^{3+} hydroxides do not transform spontaneously to oxyhydroxides, Fe^{3+}-based hydroxides are unstable and α (goethite), β (akaganeite) or γ (lepidocrocite) oxyhydroxides are obtained by thermohydrolysis of ferric solutions. The relative low stability of the hydroxides can be related to the faster kinetics of water molecules exchange in the case of Fe^{3+} cations [$k = 10^2\ s^{-1}$ (Fe^{3+}), $k = 1\ s^{-1}$ (Al^{3+}), $k = 10^{-6}\ s^{-1}$ (Cr^{3+})]. The β form of ferric oxyhydroxide (named akaganeite) has been prepared by various routes, involving the presence of halide ions, in particular chloride [1–5]. It is generally obtained from ferric chloride aqueous solutions, by adding sodium hydroxide, ammonia, carbonate or sulfate at various pH [1–3]. The akaganeite has been firstly described on the basis of a tetragonal unit cell (space group: $I4/m$, a = 10,480 Å, c = 3,023 Å) isostructural with the hollandite-type [4–6]. The structural network exhibits tunnels, running parallel to the c-axis; the large cavities are surrounded by double rows of edge-shared octahedra containing Fe^{3+}, water molecules or Cl^- occupying these large cavities. The double chains are corner-shared to neighboring double chains in order to form a 3D network. However, based on a structure refinement (Powder X-Ray and neutron diffraction) and Mössbauer spectroscopy studies, a monoclinic unit cell (space group: $I2/m$, a = 10,600 Å, b = 3,034 Å, c = 10,513 Å, β = 90,24°) has been proposed [7,8]. Two various Fe sites have been identified in the monoclinic cell (SG: $I2/m$) whereas only one Fe site occurs in the tetragonal cell (SG: $I4/m$). The akaganeite can be formulated $Fe_8(O,OH)_{16}$, $x(Cl,H_2O)$, where chloride ions and water are trapped into the tunnels. This structure is stable below 200 °C and a template effect occur as chloride is released leading to the transformation of hematite. Generally the amount of inserted species is low but Kamoun et al. [9] have considered a substitution of F^- for OH^- leading to a higher fluorine content, i.e. $FeO(OH_{0.4}F_{0.6}),yH_2O$, and a decrease of the lattice constants. The porous structure of akaganeite has been examined [4,6] and the applications of this material as pigment, catalyst or ionic exchange membrane have been proposed. We decided to investigate the stabilization of akaganeite/hollandite type with fluoride ions by developing new syntheses routes because the structural features were unknown [7,8]. The aim of this study is to understand the influence of chloride, fluoride, hydroxyls and water on the stabilization of various hollandite-type networks. On the basis of the structure determination, Fe–O/F bond distances will be discussed. These compounds have been characterized by chemical

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☆ Dr. A. Tressaud worked at the beginning of his career on Fe-based fluorides adopting Bronze's structures. This Work on Fe-based oxyhydroxy-fluoride is dedicated to Dr. Alain Tressaud, recipient of the 2011 ACS award for Creative Work in Fluorine Chemistry.

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analysis, TGA coupled with mass spectrometry, X-ray and neutron diffraction, Mossbauer and infrared spectroscopies.

2. Experimental

2.1. Preparation of the akaganeite form of the β-ferric oxyhydroxide stabilized with chloride ions

The akaganeite form of the ferric oxyhydroxide with $FeO(OH){\cdot}x(Cl,H_2O)$ formula was prepared by the hydrolysis of an $FeCl_3$ solution according to previous works [1–3]. A solution of 20 mL containing 0.6 g of $FeCl_3$ and 20 mL of water was prepared at room temperature in a 200 mL PFA flask; 5 mL of oxygen peroxide H_2O_2 (30%) was then added. The thermolysis was maintained at 363 K overnight. The flask was equipped with a column cooled with water in order to keep the same amount of liquid. The heat was then turned off, and the precipitate was filtered and washed with water and ethanol. The sample was dried at 363 K for one night. The powder exhibited a light brown coloration.

2.2. Preparation of hollandite-type ferric oxyhydroxyfluoride

2.2.1. Conventional hydrolysis route

A suitable method to obtain iron oxyhydroxyfluoride consists of a partial hydrolysis of α-FeF_3 with a replacement of F^- by OH^-/O^{2-} in an aqueous medium. This synthesis route is slightly different from that of akaganeite. A solution of 20 mL containing 0.6 g of α-FeF_3 and 20 mL of water was mixed at room temperature in a 200 mL PFA balloon. The pH of the medium was then adjusted to 9 with a buffer solution in order to keep a high fluorine rate. The temperature was maintained at 363 K overnight in the same conditions as previously described for the preparation of akaganeite. After reaction the precipitate was filtered and washed with water and ethanol. Then, the sample was dried at 363 K for one night. The powder exhibited a yellow-brown coloration brighter or more yellow than akaganeite.

2.2.2. Hydrolysis in supercritical (sc) media

A more efficient route of synthesis has been developed [10,12], when β-$FeO(OH,F){\cdot}zH_2O$ was prepared from NH_4FeF_3 in H_2O_2 solution in a supercritical (sc) media. After optimization of the experimental supercritical conditions and the use of various starting materials, β-$FeO(OH,F){\cdot}zH_2O$ was prepared by hydrolysis of α-FeF_3 in sc-CO_2. The α-FeF_3 powder was treated at 453 K for 90 min under a sc-CO_2 pressure of 30 MPa in an alcoholic solution at pH 9 using a buffer solution. Stainless reactors fitted with Teflon foil have been used. After reaction the pressure was decreased to standard conditions. The powder was then dried with sc-CO_2 until room temperature was reached. The β-$FeO(OH,F){\cdot}zH_2O$ powder was washed with water and ethanol. The sample was finally dried at 363 K for one night. The powder exhibited a yellow-brown coloration brighter or more yellow than akaganeite.

2.3. Powder X-ray diffraction

The various phases were characterized by X-ray powder diffraction. X-ray powder diffraction patterns were recorded at room temperature on a Philips PW diffractometer in Bragg-Brentano geometry, using graphite-monochromated CuKα radiation. The 2θ range was 5–120°, with a step of 0.02°; the counting time was 25 s. Cell parameters were first refined on the basis of a tetragonal cell (SG: $I4/m$) and then considering a monoclinic cell (SG: $I2/m$) as mentioned in the literature [7,8]. Atoms positions have been refined on the basis of powder neutron diffraction data.

2.4. Chemical analysis, thermogravimetric analysis coupled with mass spectrometry (TGA/MS)

The Fe and F elemental analysis have been performed by ICPMS and by conventional titration in the CNRS facility at Vernaison (France) and provided a F/Fe molar ratio.

The thermal degradation of the different compounds was followed by a thermogravimetric analyzer (Setaram TAG 24) coupled with a quadripolar mass spectrometer (Balzers Thermostar) which allowed to detect HF ($M_F = 19$ g) and water ($M_{H_2O} = 18$ g) release [11]. Each sample was heated under argon atmosphere (heating rate 1 K/min). The release of water and hydroxyl groups starts before and during fluorine species evolution.

2.5. Mössbauer spectroscopy

Mössbauer measurements were performed at room temperature using a constant acceleration HALDER – type spectrometer with a room temperature ^{57}Co source (Rh matrix) in transmission geometry. The polycrystalline absorbers containing about 10 mg cm^{-2} of iron were used to avoid the experimental widening of the peaks. The velocity was calibrated using pure α-Fe as the standard material. The refinement of the Mössbauer spectra showed an important and abnormal widening of the peaks, so that the spectra have been fitted assuming a distribution of quadrupolar splittings.

2.6. FTIR spectroscopy: nature of the hydroxyl groups

The powdered samples ($\approx$20 mg) were pressed into self-supported wafers of about 10 mg cm^{-2} and activated *in situ*, in a quartz cell connected to a high vacuum system (10^{-4} Pa) and placed into the IR beam. The procedure started with a 2 h treatment under vacuum at 413 K in order to eliminate a large amount of water. The spectrum of the outgassed sample, that is the so-called "activated" sample, was recorded at room temperature. Spectra were recorded on a Nicolet Magna 750 spectrophotometer, equipped with a MCT detector and an extended KBr beamsplitter. Spectra were recorded in transmission or diffuse reflectance (DRS) depending on the difficulty to prepare pellets.

2.7. Powder neutron diffraction

Akaganeite and iron oxyhydroxy-fluorides powders were characterized by neutron diffraction at 300 K on the D1B station with a 1.28 Å radiation and a graphite monochomator at the Laüe-Langevin Institute in Grenoble, France. The 2θ range was 9.7–87.86°, with a step scan of 0.2°. Intensity treatments (profiles, cell parameters, atomic positions and isotropic thermal displacement) and refinements based on the Rietveld method [12] were performed using the JANA2006 program [13]. The quality of the acquisition and refinement was based on the conventional reliability factors R_p, R_{wp} and χ^2, respectively.

3. Results

3.1. Powder X-ray diffraction analysis

Whatever the synthesis route, akaganeite and iron oxyhydroxyfluorides exhibit characteristic X-ray diffraction peaks of the hollandite-type structure. The X-ray diffractograms and their simplified indexation (tetragonal unit cell, SG: $I4/m$) have been given in Fig. 1. However, it can be noticed that the X-ray diffraction patterns show small impurity peaks attributed to HTB (Hexagonal Tungsten Bronze) or pyrochlore forms of hydroxyfluorides. Powder X-ray diffraction and powder neutron diffraction data lead to the

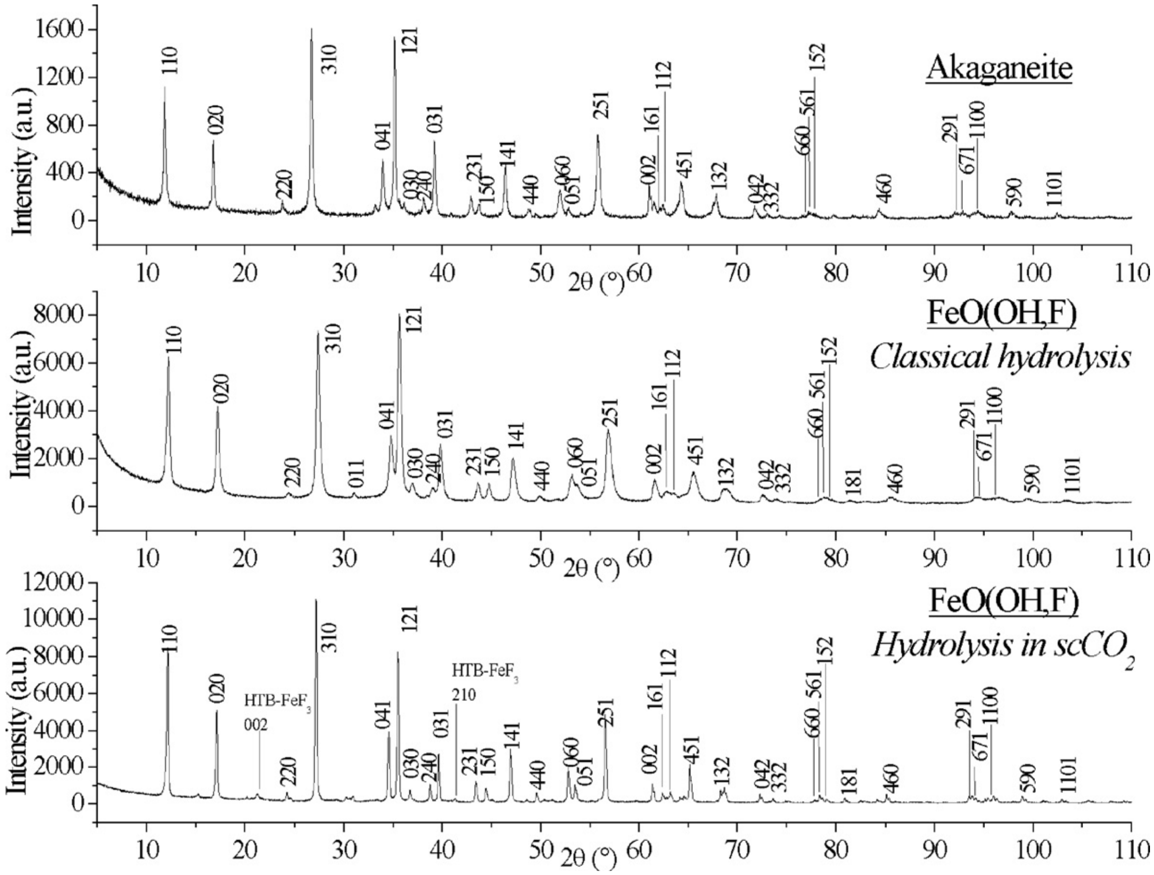

Fig. 1. Powder X-ray diffraction patterns of akaganeite (a) and as-prepared iron oxyhydroxyfluorides (b and c). The simplified indexation with a tetragonal cell (SG: *I*4/*m*) are given.

same refined cell parameters. The unit cell parameters obtained on the basis of a monoclinic unit cell (SG: *I*2/*m*) are reported in Table 1.The *a* and *c* parameters strongly decrease as well as the cell volume with the presence of fluorine atoms and the absence of chlorine atoms in the oxyhydroxy-fluoride. Moreover, taking into account the *a* and *c* parameters as well as the β angle, the deviation from the tetragonal symmetry (SG: *I*4/*m*) is higher for the akaganeite without fluorine substitution and the occurrence of chloride anions trapped in the tunnels.

Table 1
Reliability factors (powder neutron diffraction data), space group, cell parameters, unit cell volume and theoritical density of akaganeite $FeO_{0.8}OH_{1.2}\cdot0.2Cl$ and oxyhydroxy-fluoride, $FeO(OH_{0.2}F_{0.8})\cdot0.2H_2O$ (sc-CO$_2$).

Akaganeite $FeO_{0.8}OH_{1.2}\cdot0.2$ Cl		
Reliability factors		
R_p	R_{wp}	χ^2
0.88	1.16	25.32
Symmetry: tetragonal		SG: *I*2/*m* (12)
hkl: $h+k+l=2n$	$Z=8$	
$a=10.561(7)$ Å	Unit cell vol.: 339.54(8) Å^3	
$b=3.040(2)$ Å	Theor. density: 3.788(2) g cm^{-3}	
$c=10.576(4)$ Å		
$\beta=90.17(2)^\circ$		
Oxyhydroxyfluoride, $FeO(OH_{0.2}F_{0.8})\cdot0.2H_2O$ (sc-CO$_2$)		
Reliability factors		
R_p	R_{wp}	χ^2
0.88	1.15	12.34
Symmetry: tetragonal	SG: *I*2/*m* (12)	
hkl: $h+k+l=2n$	$Z=8$	
$a=10.447(7)$ Å	Unit cell vol.: 330.41(7) Å^3	
$b=3.028(2)$ Å	Theor. density: 3.724(2) g cm^{-3}	
$c=10.445(4)$ Å		
$\beta=90.00(3)^\circ$		

3.2. Chemical and thermogravimetric analyses

The approximated formulae have been determined by taking into account elemental and thermogravimetric analysis. Thus, experimental elemental ratio F/Fe of oxyhydroxy-fluorides prepared by conventional hydrolysis and supercritical CO$_2$ routes are equal to 0.7 and 0.8, respectively. The chemical analysis of akaganeite reveals a large amount of Cl$^-$ around 7% in weight corresponding to 0.2 mole of Cl per mole of Fe. Thermogravimetric analysis and the identification of outgassed species by mass spectrometry have been represented in Figs. 2 and 3. The thermal decomposition of akaganeite at 500 °C under Ar leads to hematite Fe_2O_3. In the case of iron oxyhydroxyfluorides prepared by supercritical route or thermolysis of iron trifluoride, F ($M = 19$ g) departure is identified above 260 °C and the amount remains high corresponding to an F/Fe molar ratio around 0.8 and 0.7, respectively. An interesting observation derived from the mass spectrometry study is that as the signal corresponding to fluorine or HF departure appears and increases, the signal corresponding to water and OH groups decreases and become weaker. After the water loss of about 4% (0.2 moles of H_2O), two plateau can be identified in the case of the sample prepared by supercritical means, whereas only one plateau can be distinguished with smooth signals for the sample prepared by conventional hydrolysis. For these last compounds the complete thermal decomposition under Ar at 600 °C leads to the formation of $Fe_{1-x}O$ wustite. Taking into account such analyses, the following formula can be proposed for akaganeite and the two oxyhydroxyfluorides, respectively:

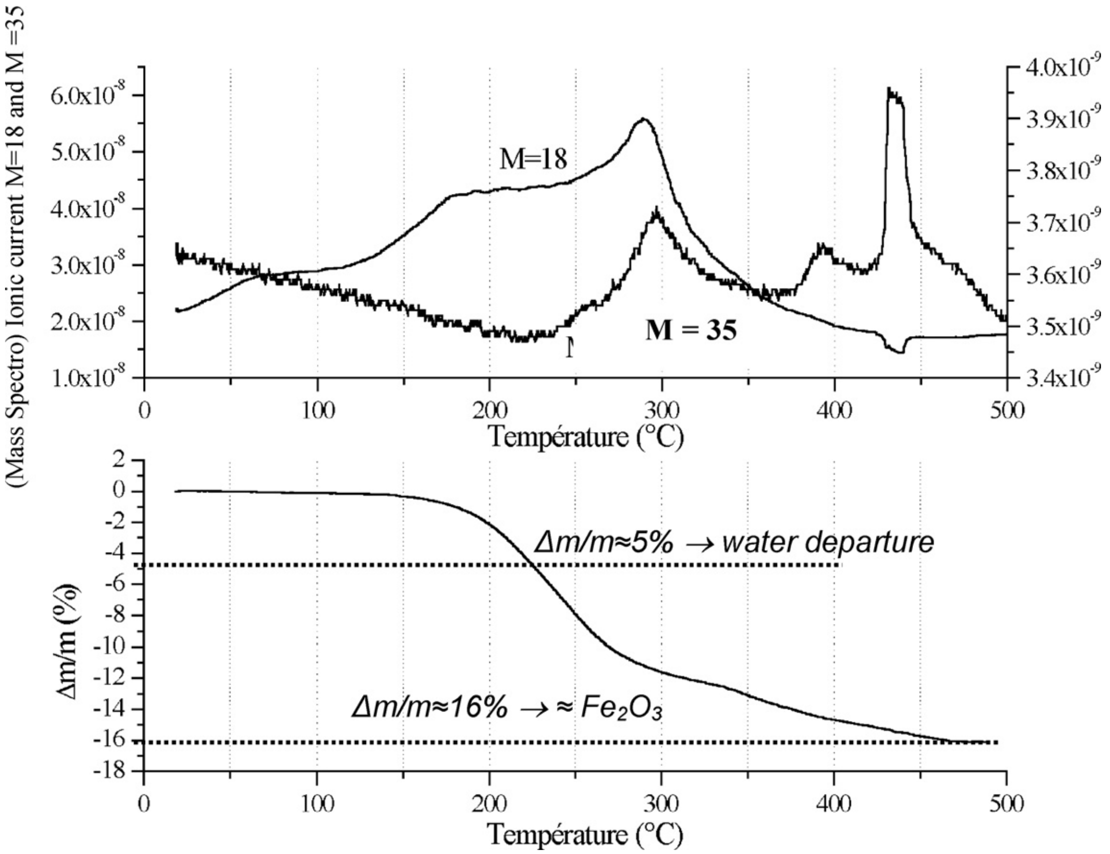

Fig. 2. Thermogravimetric analysis coupled with mass spectrometry of akaganeite.

$FeO_{0.8}OH_{1.2}\cdot 0.2Cl$ - $FeO(OH_{0.2}F_{0.8})\cdot 0.2H_2O$ (sc-CO_2) - $FeO(OH_{0.3}F_{0.7})\cdot 0.15H_2O$ (conventional hydrolysis).

3.3. Mössbauer spectroscopy

All Mössbauer spectra can be described with two quadrupolar doublets. For akaganeite, the Mössbauer spectra recorded at room temperature reveal two octahedral Fe(III) components contributing around 50% for each (Fig. 4 and Table 2). The isomer shifts remain similar for the two sites (δ = 0.387 mm/s and 0.378 mm/s) but the average quadrupole splitting Δ based on a distribution of quadrupole splitting is higher for the first site and related to a larger and more distorted octahedral site (Table 2). In oxyhydroxyfluorides prepared by the two routes, the proportion of two iron

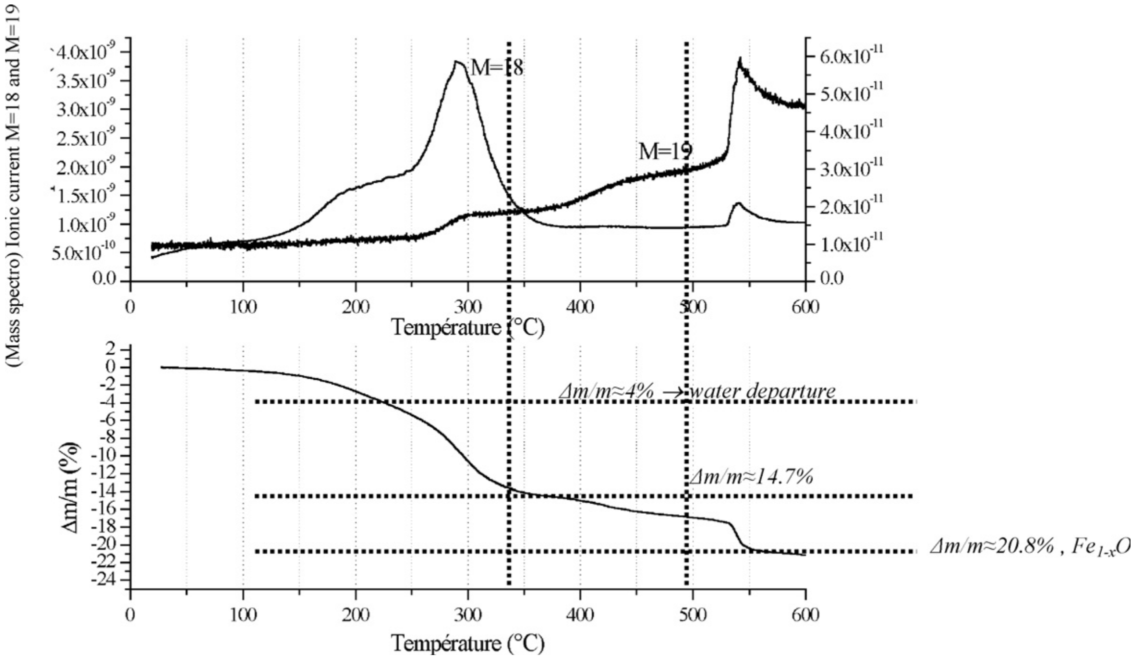

Fig. 3. Thermogravimetric analysis coupled with mass spectrometry of iron oxyhydroxyfluoride prepared in supercritical CO_2 media.

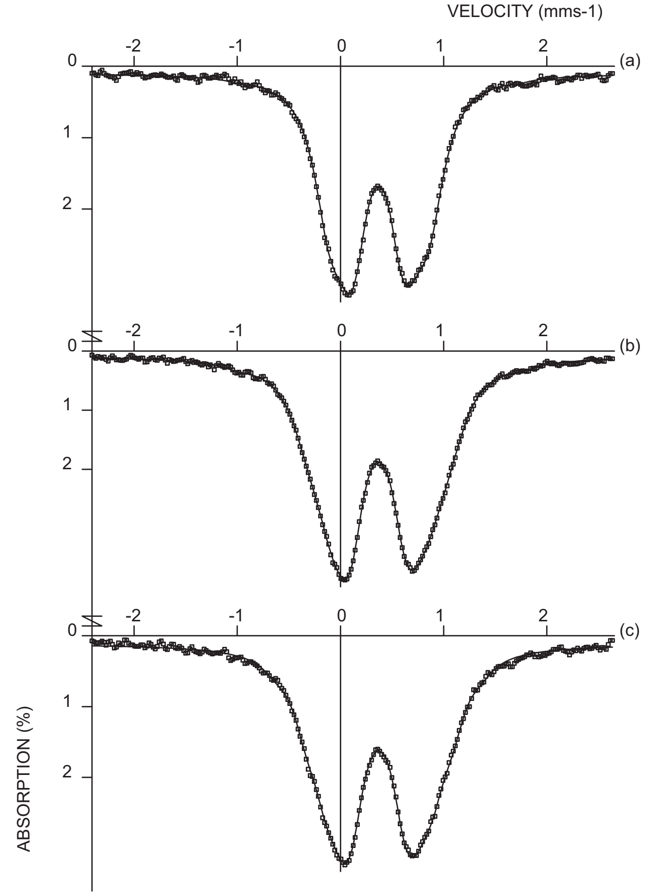

Fig. 4. Iron-57 Mössbauer spectra recorded at room temperature for akaganeite (a) and Fe oxyhydroxyfluorides obtained by conventional hydrolysis route (b) and in supercritical CO_2 media (c). The fits correspond to the two Fe quadrupolar splitting distributions.

octahedral sites remains the same, around 50%. However in these last compounds, one should have to note the increase of the peaks widening and consequently the width of the quadrupole splitting distribution attributed to first Fe octahedral site. Thus, based on a distribution of quadrupole splitting, the calculation of average quadrupole splitting Δ_1 leads to 1.08 mm s^{-1} ($0.50 < \Delta_1 < 1.60$ mm s^{-1}, conventional hydrolysis) and 1.15 mm s^{-1} ($0.35 < \Delta_1 < 1.60$ mm s^{-1}, sc-CO_2) whereas a value of 0.92 mm s^{-1} ($0.50 < \Delta_1 < 1.20$ mm s^{-1}) is found in the case of akaganeite. A comparison between akaganeite and the oxyhydroxy-fluorides shows as well that no strong variation of quadrupole splitting Δ_2 is detected for the second site and these values remain smaller than in the case of the first iron site. The broader octahedral component identified for the first site shows that the sites distribution increases with the F substitution. As far as the second iron site is concerned, whatever the synthesis route, these octahedra are more regular and less distorted. For all of these compounds, the occurrence of two sites identified by Mössbauer spectroscopy leads to consider the $I2/m$ space group instead of $I4/m$ structural hypothesis where only one site can be identified.

3.4. Nature of hydroxyl groups

Previous works [13] have been devoted to IR studies of akaganeite. The FTIR technique is able to detect the presence of hydroxyl groups in the network and to give important information on the nature and the localization of the OH^- groups. Various types of OH^- groups can be defined according to their nearest neighbors. If a hydroxyl does not have any other hydroxyl groups or water molecules, ammonia or organics containing protons as nearest neighbors, this OH^- group is called "free-OH" group. If a substituting OH^- group interacts with other surrounding OH^- groups or impurities, this OH^- group is called "linked-OH" group, and the hydroxyl band on the FTIR spectra becomes broader and moves to smaller wavenumbers. The absorption bands assigned to the ν(OH) vibrations of the hydroxyls groups present at the surface of activated oxyhydroxyfluorides are observed in the 4000–3000 cm^{-1} range (Fig. 5a–c). The IR spectrum of akaganeite exhibits a sharp band at 3597 cm^{-1} which can be attributed to free-hydroxyl groups. Two other broad IR bands are also observed around 3180 cm^{-1} and 3410 cm^{-1} and are characteristic of two different kinds of linked-OH groups. The FTIR spectrum of iron oxyhydroxy-fluoride prepared by conventional hydrolysis shows a sharp IR band at 3615 cm^{-1} which is assigned to free-OH groups and two broad IR bands at 3480 cm^{-1} and 3240 cm^{-1} which are assigned to linked-OH groups. In the case of iron oxyhydroxy-fluoride prepared under supercritical conditions two large IR bands are observed at 3198 cm^{-1} and 3482 cm^{-1} which are attributed to two types of linked-hydroxyl groups and no free-hydroxyls are detected. It is relevant to note the overall displacement of the IR bands to larger wavenumber compared to the akaganeite spectrum due to the presence of F^- ions which contribute to strengthen the Fe–OH bond.

3.5. Neutron diffraction study

Experimental and calculated neutron diffraction profiles and differences are represented in Fig. 6a and b. In the neutron case, the signal over noise ratio remains high because of the presence of a large amount of protons in the samples. The structures have been first refined considering a tetragonal cell with the $I4/m$ space group and then on the basis of a monoclinic unit cell with the $I2/m$ space group taking into account the two Fe(III) sites identified by Mössbauer spectroscopy. The refinement has been carried out using the Rietveld method [14] with the JANA2006 [15] system. Reliability factors discussed in this paper were the usual ones defined by the Rietveld refinement guidelines [14]. Cell parameters were refined considering X-Ray diffraction patterns. Profile functions and background (five order polynomial function) have been refined. Zero and scale factor were then estimated. Taking into account the neutron scattering (Fermi) lengths of Fe (9.45), O(5.803), F(5.654), Cl(9.577) and H (−3.739), oxygen atoms can not be distinguished from fluorine atoms.

Table 2

Refined Mössbauer data for both Fe sites (isomer shift δ, average quadrupole splitting Δ, peak width Γ (imposed value) and percentage of each sites) for akaganeite $FeO_{0.8}OH_{1.2}\cdot 0.2Cl$, oxyhydroxyfluorides $FeO(OH_{0.3}F_{0.7})\cdot 0.15H_2O$ (conventional hydrolysis) and $FeO(OH_{0.2}F_{0.8})\cdot 0.2H_2O$ (sc-CO_2).

Compounds	DIS1				DIS2			
	δ_1 (mm s^{-1})	Δ_1 (mm s^{-1})	Γ_1 (mm s^{-1})	%1 ± 2	δ_2 (mm s^{-1})	Δ_2 (mm s^{-1})	Γ_2 (mm s^{-1})	%$_2$ ± 2
FeOOH/$FeCl_3$	0.387(2)	0.92(1)	0.30	52	0.377(2)	0.53(1)	0.30	48
FeO(OH,F)/FeF_3	0.392(2)	1.08(1)	0.30	53	0.377(2)	0.65(1)	0.30	47
FeO(OH,F)/FeF_3 sc	0.389(2)	1.15(1)	0.30	53	0.378(2)	0.62(1)	0.30	47

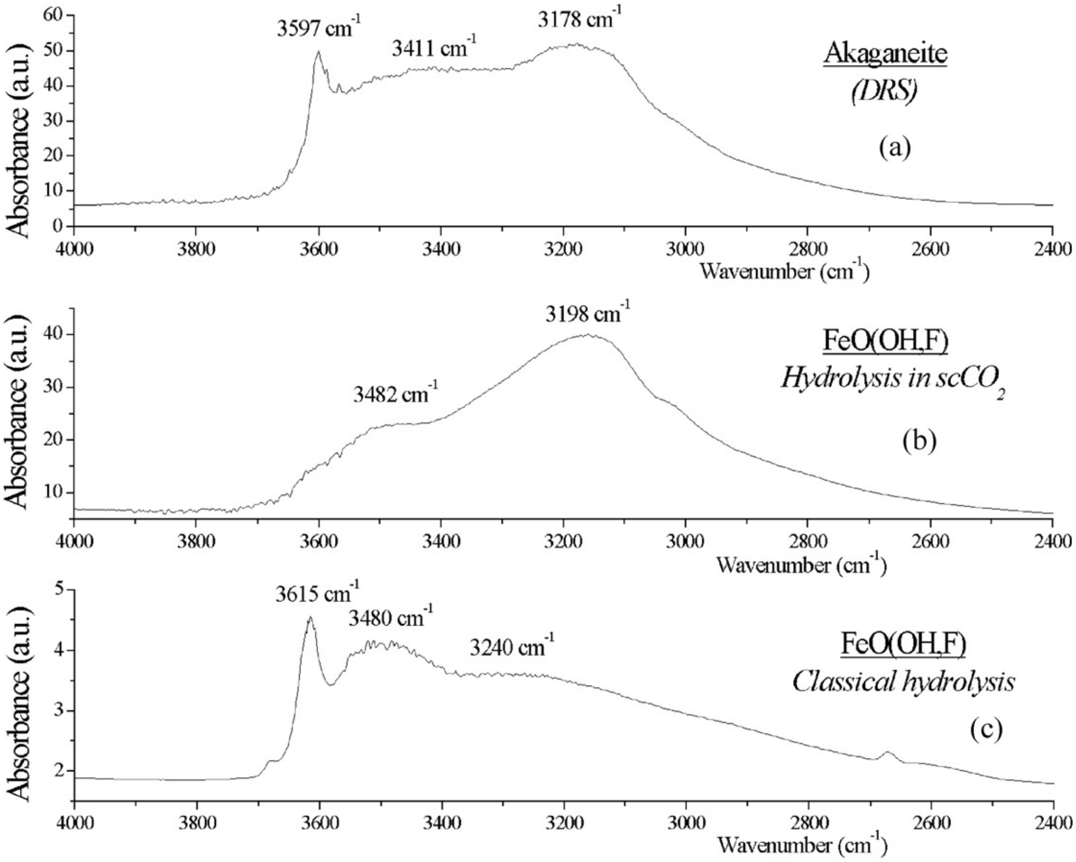

Fig. 5. FTIR spectra to illustrate the nature of hydroxyl groups in akaganeite (a) and in iron oxyhydroxyfluorides (b,c).

The structure of β-FeOOH·*x*(Cl,H_2O) has been described in previous work [5–8]. Neutron diffraction pattern of iron oxyhydroxyfluoride prepared under supercritical conditions corresponding to well crystallized samples has been refined and displayed in this paper. Fe (2 sites) and O (4 sites) atoms are located on 4i (*x*,0,*z*) positions. The O1/O3 positions are located at the common edges of Fe^{3+} octahedra whereas the F2/F4 positions correspond to shared vertices of octahedra. Both the O1 and O3 atomic positions correspond to the highest Fe–OH(O) bond distances whereas the shortest Fe–F(O) bond distances are associated with F2/F4 atomic positions in agreement with the literature [19,20] and the structures of Fe trifluorides. The H1 and H3 hydrogen atoms are located only in two 8j (*x*,*y*,*z*) positions near the O1 and O3 positions at the common edges of Fe(III) octahedral site. The oxygen atom (O5) associated to H_2O molecules is then placed in the center of tunnels in 2b (0,1/2,0) position. No protons have been added in the vicinity of O(H_2O) oxygens attributed to water in the tunnels. The isotropic thermal displacements of Fe1, Fe2, O1, F2, O3 and F4 atomic positions have been refined whereas the isotropic thermal displacement of H1/H3 and O5 are fixed to 1 Å^2 and 1.5 Å^2, respectively. However the occupancies of these three atomic positions have been refined. The O1–H1 bond distances remain equal to 1.10 Å and H1 protons exhibit slight interactions with the oxygen O5 from the water molecules (O5–H1 = 1.68 Å). The O3–H3 bonds are equal to 1.25 Å and the H3–O5(H_2O) is around 1.54 Å implying that the H1/H3 protons exhibit interactions with water. Nevertheless, the refined values of H1/H3 occupancies are rather high considering the $FeO(OH_{0.2}F_{0.8})\cdot 0.2H_2O$ (sc-CO_2) composition determined by chemical analysis. Based on this refinement, 0.7 moles of hydrogen per Fe moles can be determined leading to the following formula: $FeO(OH_{0.3}F_{0.7})\cdot 0.2H_2O$. The H1, H3, O1, O3 atomic coordinates obtained in this refinement lead to the following shortest bond distances Fe1–H1 = 2.70 Å, Fe2–H3 = 2.72 Å, O1–O1 = 2.69 Å and O3–O3 = 2.58 Å. Such short O–O bondlengths have been identified in silicates. In the case of γ-FeOOH lepidocrocite [16], or γ-MnOOH manganite [17], Fe–H and O–H bond distances are of the same order of magnitude than that found in this refinement. Under these conditions, the final reliability factors correspond to $R_p = 0.88$, $R_{wp} = 1.15$ and $\chi^2 = 12.34$. The atomic positions and shortest interatomic distances are collected in Tables 3 and 4, respectively. Two Fe octahedral sites can be distinguished (Fig. 7). The first site remain highly distorted (Fe–O(F): 1.90 Å–2.31 Å) and the sum of difference between each distances and the average distance (2.05 Å) characterizing the octahedral distortion, is larger than in the case of akaganeite [5–8]. The second iron site which is more regular, is also smaller (Fe–O(F): 1.92–2.12 Å, average distance 2.00 Å) than the first one. Moreover the distortion of the second Fe site calculated by considering the deviation between Fe–O(F) bond distances and the average one's, is also smaller.

4. Discussion

The hydrolysis in sc-CO_2 medium enables the preparation of an iron oxyhydroxy-fluoride powder with better crystallized particles than those prepared by conventional hydrolysis. Supercritical conditions lead to a better diffusion around cationic centers, which favors reactivity. Furthermore, the synthesis of this compound is carried out at high pressure (300 bar) and 453 K. These conditions can be considered as hydrothermal conditions which favor the crystallization of iron oxyhydroxyfluoride.

Whatever the synthesis route, the two final hollandite-type iron oxyhydroxyfluorides exhibit a large amount of fluorine. This partial hydrolysis can be explained by the stability of Fe^{3+} aquo

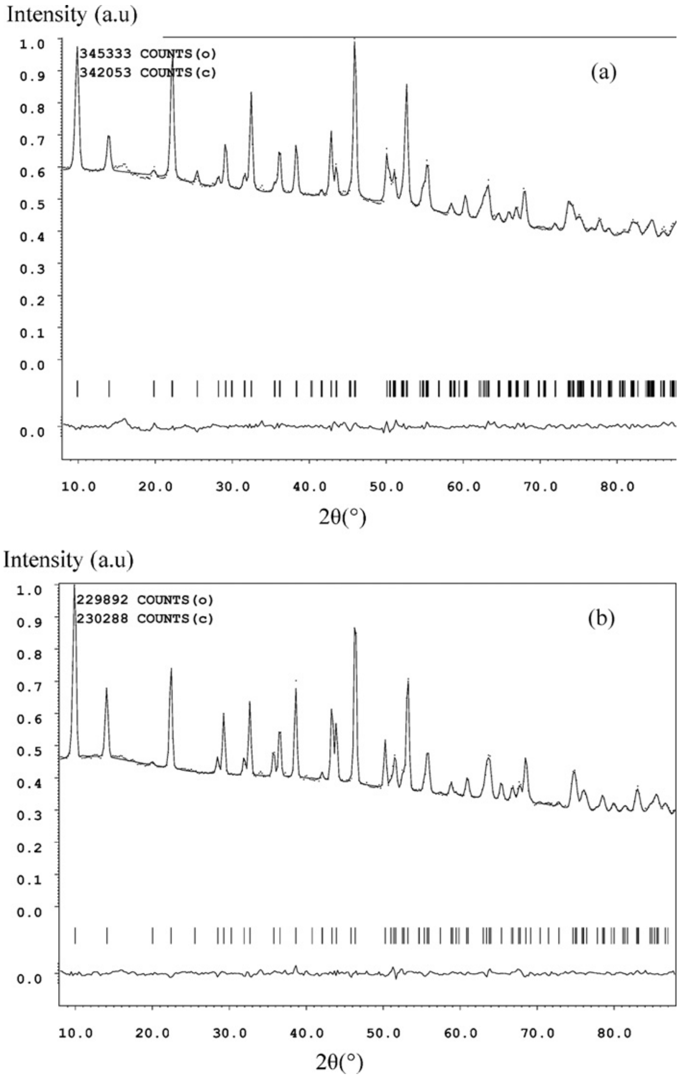

Fig. 6. Calculated and experimental neutron diffraction patterns of akaganeite $FeO_{0.8}OH_{1.2}{\cdot}0.2Cl$ (a) and iron oxyhydroxyfluoride $FeO(OH_{0.2}F_{0.8}){\cdot}0.2H_2O$ (sc-CO_2) (b). The lower line is the difference function.

complex. If from a thermodynamical point of view, the hydrolysis of trivalent iron is favored ($\Delta H = -4450$ kJ mol^{-1}), from a kinetical point of view, the fast exchange of water molecules is not advantageous for the hydrolysis ($k = 10^2$ s^{-1}). Iron oxyhydroxyfluoride prepared under supercritical conditions does not exhibit any free or isolated hydroxyl groups. Since supercritical conditions enable a better diffusivity, the homogenization does not favor the presence of free-hydroxyl groups.

In the case of iron oxyhydroxyfluoride prepared under supercritical conditions or by conventional hydrolysis, fluorine atoms could be located both at the common vertices and shared edges of octahedra. Hydrogen H1 has been detected in the vicinity of oxygen O1 which share edges of octahedron and contribute to the distortion of site Fe1. As far as hydroxyls H3 are concerned, they are located between O3 and O5 (H_2O inside the tunnels) and the distortion of Fe2 is smaller. As in akaganeite, for both of the Fe1/Fe2 sites, the anions O1/O3 located at the edges generate longest Fe–O(OH) (d[Fe1-O1] = 2.31 Å/d[Fe2-O3] = 2.12 Å) distances than F(O)4 anions placed at the common vertices which give shortest Fe–F(O) bond distances (d[Fe1–F4] = 1.90 Å/d[Fe2–F4] = 1.92 Å). Thus, the sites Fe1 are more distorted than those in akaganeite [18] and this distortion is associated to the presence of fluorine, water and hydroxyl groups in the vicinity of trivalent Fe, in good agreement with Mössbauer spectroscopy. However, the Mössbauer spectroscopy for akaganeite and Fe-based oxyhydroxyfluorides does not detect any strong differences for the second distribution. The longest Fe–(O/F) average bond distance and the highest dispersion of Fe–(O/F) bond distance attributed to Fe1 site can be associated to the DIS1 distribution with the largest isomer shift and quadrupole splitting. The large rate of fluorine as well as hydroxyl group around Fe1 atoms contributes to distort this site. For the second Fe site, the distortion as well as the average Fe–O(F) bond distances are close to that found in akaganeite. Then, it is reasonable to consider that the fluorine content around Fe2 atom is smaller. In the case of $FeO(OH_{0.2}F_{0.8}){\cdot}0.2H_2O$ (sc-CO_2), the FTIR studies have shown the presence of two types of linked hydroxyl groups and no free-OH groups. Structural refinement has shown the presence of hydroxyl groups substituting fluorine. These anions are located at the common edges of octahedra. Thus the

Table 4
Shortest bond distances in oxyhydroxyfluoride, $FeO(OH_{0.2}F_{0.8}){\cdot}0.2H_2O$ (sc-CO_2).

Atom 1	Atom 2	Distance (Å)
Fe-1	O-1	2.054(3)
Fe-1	O-1	2.054(3)
Fe-1	O-1	2.315(3)
Fe-1	(F/O)-2	2.003(3)
Fe-1	(F/O)-2	2.003(3)
Fe-1	(F/O)-4	1.900(2)
O-1	H-1	1.10(2)
O-1	O-1	2.694(4)
O-1	(F/O)-2	2.673(4)
O-5	H-1	1.68(2)
Fe-1	H-1	2.698(4)
Fe-2	O-3	2.123(3)
Fe-2	O-3	2.123(3)
Fe-2	O-3	1.959(3)
Fe-2	(F/O)-2	1.954(3)
Fe-2	(F/O)-4	1.914(3)
Fe-2	(F/O)-4	1.914(3)
O-3	H-3	1.25(2)
O-3	O-3	2.580(4)
O-3	(F/O)-4	2.644(4)
O-5	H-3	1.54(2)
Fe-2	H-3	2.725(4)

Table 3
Atomic positions, isotropic thermal displacements and occupancies in oxyhydroxyfluoride, $FeO(OH_{0.2}F_{0.8}){\cdot}0.2H_2O$ (sc-CO_2).

Atoms	Site	x	y	z	B (Å)	n
Fe1	4i	0.8656(5)	0	0.3429(4)	0.686(4)	1
Fe2	4i	0.3424(5)	0	0.1540(4)	0.722(4)	1
O1	4i	0.8493(5)	0.5	0.2111(7)	0.809(7)	1
H1	8j	0.608(7)	0.078(3)	0.383(7)	1.0	0.36(5)
F2	4i	0.8455(8)	0.5	0.4670(7)	0.508(7)	1
O3	4i	0.2002(5)	0.5	0.1633(7)	0.627(5)	1
H3	8j	0.372(7)	0.077(3)	0.429(7)	1.0	0.34(7)
F4	4i	0.0469(8)	0	0.3278(7)	0.508(7)	1
O5	2b	0	0.5	0	1.5	0.70(8)

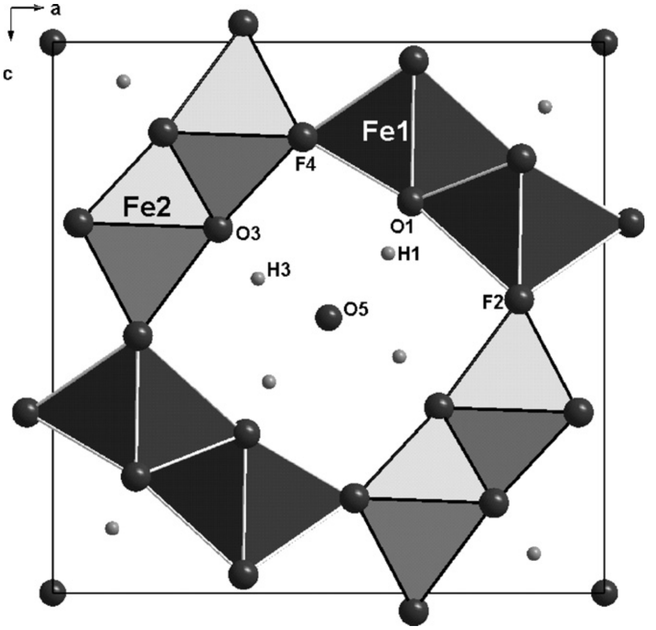

Fig. 7. Representation of as-prepared iron oxyhydroxyfluoride structure along *b*-axis. The two Fe sites, the four anionic sites (O/F) and the hydrogen atoms are represented.

large band around 3480 cm^{-1} must correspond to OH–OH interactions only involving hydroxyl groups located at the shared edges (shortest distance: OH–OH = 2.58 Å). The other-band at 3200 cm^{-1} corresponds, as in akaganeite to OH–O(F) interactions (shortest distance: OH–O(F) = 2.67 Å), oxygen and fluorine because of their high electronegativities affecting the O–H stretching mode. The overall displacement of IR band to high wavenumber in Fe-based oxyhydroxy-fluoride compared to akaganeite is thus related to the incorporation of F^- which contributes to reinforce the O–H bond. Surprisingly, in the sample prepared by conventional route, an additional peak appears at 3615 cm^{-1} which is absent in the sample prepared by supercritical route. The isolated-OH groups characterized by an IR peak at 3597 cm^{-1} have been identified in HTB-$FeF_{3-x}(OH)_x$ [21] where the network is constituted by corner-shared octahedra forming hexagonal tunnels. By comparison with akaganeite [13] or HTB-$FeF_{3-x}(OH)_x$ [21], this peak can be attributed to isolated OH-groups, probably located at the shared vertices of octahedral sites, despite the absence of hydroxyls in this position determined by neutron data refinement in the case of a sample prepared by conventional route.

By comparing akaganeite and iron oxyhydroxy-fluoride, it is important to note that the substitution of hydroxyl groups by fluorine leads to a significant decrease of the *a* and *c* unit cell parameters (Table 1). The monoclinic distortion of the hollandite-type network is less pronounced in the oxyhydroxyfluorides where the symmetry is almost tetragonal. The stabilization of fluorine around Fe^{3+} and the random distribution of O^{2-}, OH^- and F^- anions create a perturbation in charges distribution and octahedral sites distortion. The F^- anions are mainly distributed over two sites corresponding to the common vertices of the octahedra because the refined Fe–F bond distances are in good agreement with the literature [19,20]. The absence of protons in the vicinity of these positions as well as the absence or the small proportion of free OH groups detected by FTIR, contribute also to conclude that F^- anions are mainly located at the common vertices of octahedral sites. Moreover, the enhancement of the site 1 distortion identified by Mössbauer spectroscopy is due to the incorporation of a larger rate of fluorine and a smaller content of hydroxyls/oxygen mainly at the common vertices of the octahedral sites but also to the presence of water trapped in the tunnel.

5. Conclusion

New oxyhydroxyfluorides containing Fe^{3+} have been prepared from thermohydrolysis of Fe trifluoride in basic medium (pH 8–9). New routes using sc-CO_2 fluids have been used leading to well crystallized compounds with small particles. The compositions have been evaluated from chemical analysis as well as thermogravimetric analysis with the fluorine departure detected above $T = 260\,^{\circ}C$. The structure of iron oxyhydroxyfluoride $FeO(OH_{0.2}F_{0.8})\cdot 0.2H_2O$ (sc-CO_2) has been determined by neutron diffraction and compared to akaganeite β-$FeO_{0.8}OH_{1.2}\cdot 0.2Cl$. The occurrence of two Fe sites determined by Mössbauer spectroscopy leads to consider a monoclinic symmetry with the $I2/m$ space group. The cell parameters are smaller in iron oxyhydroxyfluoride than in the case of akaganeite as well as the distortion from the tetragonal cell (SG: $I4/m$). The presence of water, trapped in the tunnels instead of Cl^- anions as well as fluorine atoms substituted for hydroxyl groups, account for such variation. In the iron oxyhydroxy-fluoride and based on the Fe–O(F) bond distances, the F^- anions are mainly distributed on the common vertices of octahedra whereas OH^- groups occupy mainly shared edges of octahedra. On the basis of Mössbauer and neutron diffraction investigations, one Fe site is more distorted in oxyhydroxyfluoride than in akaganeite whereas the other one is comparable. This is due to the random distribution of fluorine into the anionic sites and the occurrence of F^-, OH^- and O^{2-} which contribute to create such distortion. The FTIR investigations confirm these results and show various OH^- interactions attributed to different anionic crystallographic sites. This is a very interesting example where $O^{2-}/OH^-/F^-$ anions can be stabilized on various atomic positions and the polarizing character of Fe allows the formation of various Fe–O(F) bond distances varying from 1.90 Å to 2.31 Å.

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