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One-shot versus stepwise gas-solid synthesis of iron trifluoride: investigation of pure molecular F_2 fluorination of chloride precursors

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Crystal structures of iron fluorides: an overview

Rhombohedral FeF_3 (anhydrous)

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeF3	41120	01-088-2023	00-033-647	5.362(1)	5.362(1)	5.362(1)	103.86
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
Perovskite		*R*-3*c*		57.94(2)	57.94(2)	57.94(2)	2
Ref.	M. Leblanc, J. Pannetier, G. Férey, R. de Pape, *Revue de Chimie Minérale*, **1985**, 22, 107-114; *Phase Transition*, **1992**, 38, 127-220						

Crystal structure images

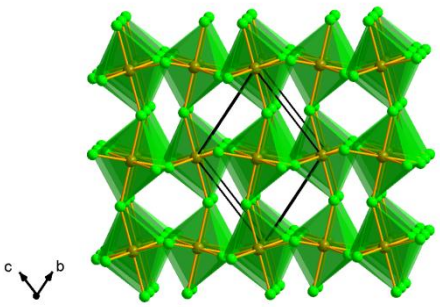

Fig. S1 Crystal structure of rhombohedral FeF_3 (r-FeF_3) viewed along the *a* axis

Hexagonal tungsten bronze $FeF_3 \cdot 0.33H_2O$ and FeF_3 (anhydrous)

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeF3(H2O)0.33	35359	01-076-1262	none	7.423	12.73	7.526	711.17
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
HTB		*Cmcm*		90	90	90	12
Ref.	M. Leblanc, G. Férey, G. Chevalier, P. Calage, R. de Pape, *Journal of Solid State Chemistry*, **1983**, 47, 53-58						

Notes

To the best of our knowledge, no structural data is to be found for the dehydrated compound, neither from the ICSD nor the PDF database. Nonetheless the dehydration of $FeF_3 \cdot 0.33H_2O$ has been studied and it unambiguously leads to the anhydrous HTB-FeF_3 discussed in the main text of the article.

Crystal structure images

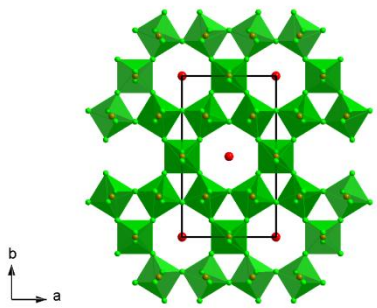

Fig. S2 Crystal structure of HTB $FeF_3 \cdot 0.33H_2O$ viewed along the *c* axis; the open channels where water molecules are accommodated are directed along the *c* axis

Pyrochlore FeF_3

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeF3	202047	01-084-1101	00-038-1305	10.325	10.325	10.325	1100.7
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
Pyrochlore		*Fd*-3*m*		90	90	90	16
Ref.	R. de Pape, G. Férey, *Materials Research Bulletin*, **1986**, 21, 971-978; *Golden Book of Phase Transitions*, Wroclaw, **2002**, 1, 1-123						

Crystal structure images

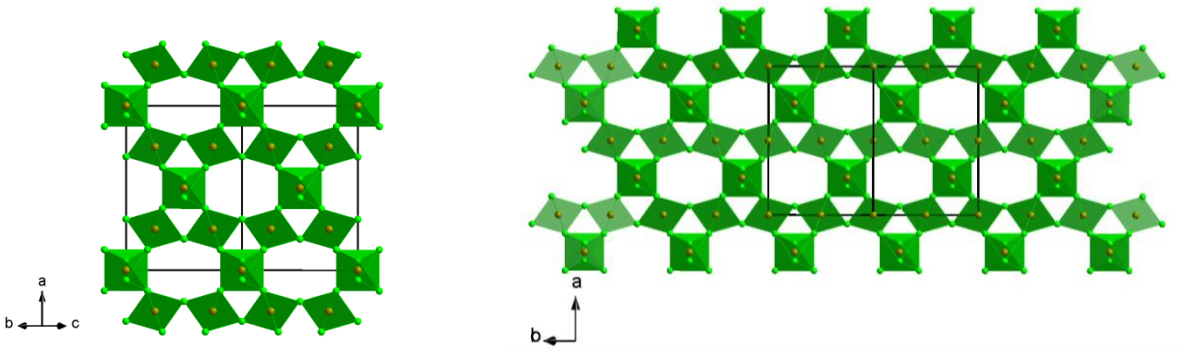

Fig. S3 Crystal structure of pyrochlore FeF_3 viewed along the [011] (left) and [0-11] directions (right), thus showing the 3D channels network

***β*-$FeF_3 \cdot 3H_2O$**

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeF3(H2O)3	14134	01-85-0404	00-032-0464	7.846	7.846	3.877	238.67
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
1D chains		*P*4/*n*		90	90	90	2
Ref.	G. Teufer, *Acta Crystallographica*, **1964**, 17, 1480						

Crystal structure images

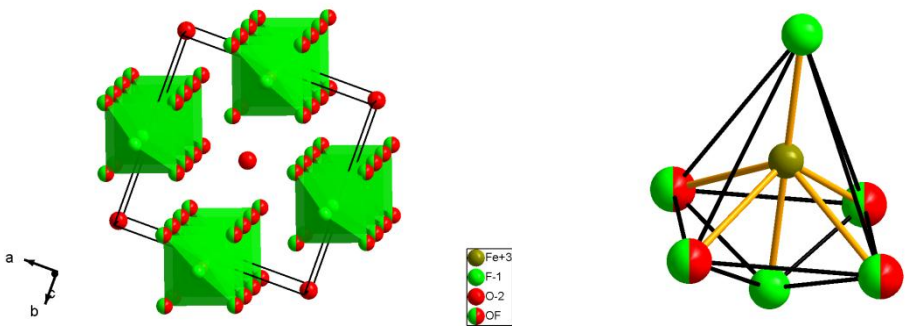

Fig. S4 Crystal structure of $FeF_3 \cdot 3H_2O$ viewed along the *c* axis (left); detailed geometry of the distorted Fe^{3+} octahedra, showing the positional disorder of the oxygen and fluorine atoms around the iron (right)

Notes

As it can be seen from the Fig. S4, there are one water molecule coordinated to the Fe(III), disordered over four positions, and the two remaining molecules are located in between the iron fluoride chains by van der Waals interactions. Therefore, it seems possible to obtain the dehydrated compound, $FeF_3 \cdot H_2O$. Although this formulation has been used in the past for thermally-treated iron fluoride hydrates,

there is no structural report about it, only a referenced experimental pattern in the PDF database (#00-026-0783, B quality).

$Fe_2F_5 \cdot 7H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(I)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
Fe2F5(H2O)7	none	None	00-045-0883	6.582	8.988	10.542	501.38
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
undescribed		*P*-1		105.81	123.28	82.93	2
Ref.	K. Gallagher, M. Ottaway, *Journal of the Chemical Society, Dalton Transactions*, **1975**, 11, 978-982						

Notes

To the best of our knowledge, this structure is not reported in any database, except for the indexed XRD pattern from the PDF database. According to the authors (*vide infra*), the dehydration of this compound under flowing nitrogen supposedly leads to $Fe_2F_5 \cdot 2H_2O$.

$Fe_2F_5 \cdot 2H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
Fe2F5(H2O)2	1167	01-070-0504	00-049-1263	7.489	10.897	6.671	544.4
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
Pyrochlore		*Imma*		90	90	90	4
Ref.	W. Hall, S. Kim, J. Zubieta, E. G. Walton, D. B. Brown, *Inorganic Chemistry*, **1977**, 16, 1884-1887 Worzala, H., Calov, U., Wilde, W., Inst. f. Angewandte Chemie e. V., Berlin, Germany, ICDD Grant-in-Aid, (**1997**)						

Notes

At least four other structures of $Fe_2F_5 \cdot 2H_2O$ are reported in the ICSD database under the ICSD codes: #201737, #201797, #201798, #201799. Their calculated patterns are referred to as PDF #01-086-1658, PDF #01-084-0878, PDF #01-084-0879, PDF #01-084-0880, respectively.

Crystal structure images

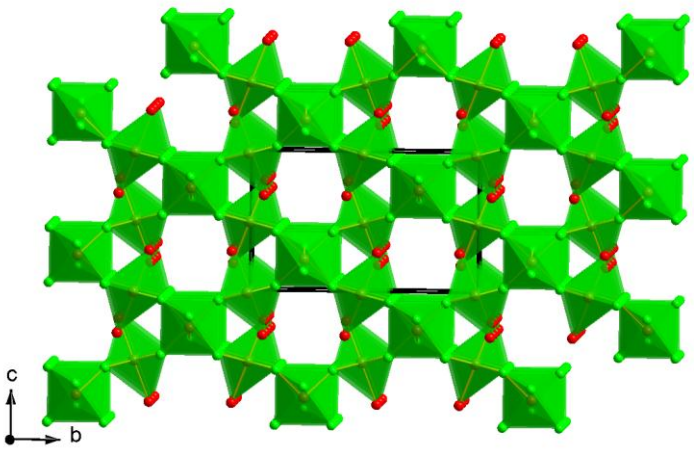

Fig. S5 Crystal structure of $Fe_2F_5 \cdot 2H_2O$ viewed along the *a* axis

$Fe_{1.9}F_{4.75}\cdot 0.95H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(B)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
Fe1.9F4.75(H2O)0.95	none	none	00-028-0483	10.35	10.35	10.35	1108.72
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
Pyrochlore		Cubic		90	90	90	4
Ref.	Charpin, P., Macheteau., *C. R. Seances Acad. Sci.*, Ser. C 280, 61 (**1975**) C. Li, L. Gu, S. Tsukimoto, P. A. Van Aken, J. Maier, *Advanced Materials*, **2010**, 22, 3650-3654						

$Fe_3F_8\cdot 2H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
Fe3F8(H2O)2	37140	01-076-2285	none	7.612	7.5	7.469	375.16
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
HTB		*C*2/*m*		90	118.38	90	2
Ref.	E. Herdtweck, *Zeitschrift fur Anorganische und Allgemeine Chemie*, **1983**, 501, 131-136 M. Leblanc, G. Férey, Y. Calage, R. de Pape, *Journal of Solid State Chemistry*, **1984**, 53, 360-368						

Notes

Another structure of $Fe_3F_8\cdot 2H_2O$ is reported in the ICSD database under the ICSD code #38366. Its calculated pattern is referred to as PDF #01-077-0306.

Crystal structure images

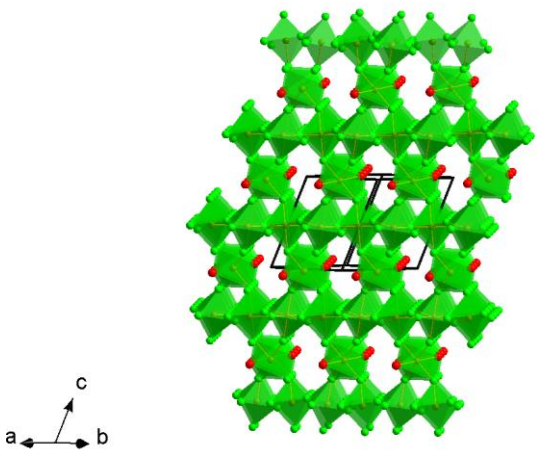

Fig. S6 Crystal structure of $Fe_3F_8\cdot 2H_2O$ viewed along the [110] direction

FeOF

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(I)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeOF	2875	01-070-1522	00-018-0648	4.654(3)	4.654(3)	4.654(3)	66.24
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
Rutile		*P*4$_2$/*mnm*		90	90	90	2
Ref.	M. Vlasse, J. C. Massies, G. Demazeau, *Journal of Solid State Chemistry*, **1973**, 8, 109-113 Hagenmuller, Portier et al., *C. R. Seances Acad. Sci.* (Paris) 260, 4768 (**1965**)						

Crystal structure images

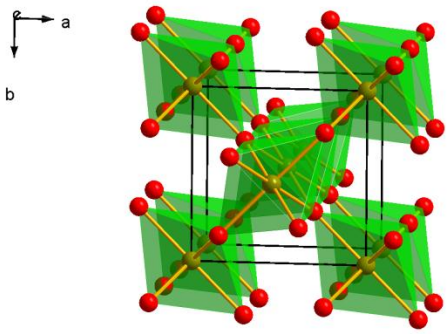

Fig. S7 Crystal structure of FeOF viewed along the *c* axis

Crystal structures of iron chlorides

$FeCl_2 \cdot 4H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
$FeCl_2 \cdot 4H_2O$	9488	01-071-0917	00-016-0123	5.885(3)	7.180(6)	8.514(4)	335.66
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
none		$P2_1/c$		90	111.09(2)	90	2
Ref.	Verbist, J.J.;Hamilton, W.C.;Koetzle, T.F.;Lehmann, M.S., *Journal of Chemical Physics* (**1972**), 56, 3257-3264						

Notes

Two other structures of $FeCl_2 \cdot 4H_2O$ are reported in the ICSD database under the ICSD codes #9198 and #26508. Their calculated patterns are referred to as PDF #01-071-0668 and #01-074-0833.

Crystal structure images

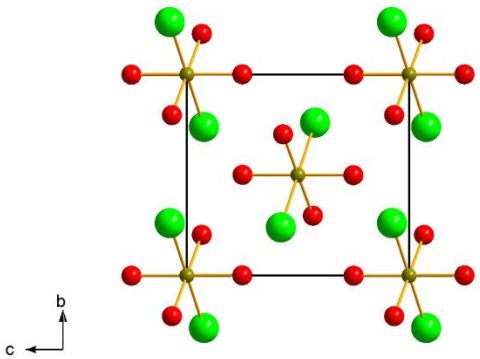

Fig. S8 Crystal structure of $FeCl_2 \cdot 4H_2O$ viewed along the *a* axis

$FeCl_2 \cdot 2H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
$FeCl_2 \cdot 2H_2O$	38012	01-077-0044	00-025-1040	7.25(3)	8.40(3)	3.60(2)	217
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
CoCl2(H2O)2		*C*2/*m*		90	98.2	90	2
Ref.	Schneider, W.;Weitzel, H., *Acta Crystallographica A* (24,1968-38,1982) (**1976**), 32, 32-37						

Notes

Another structure of $FeCl_2 \cdot 2H_2O$ is reported in the ICSD database under the ICSD code #15597. Its calculated pattern is referred to as PDF #01-072-0268.

Crystal structure images

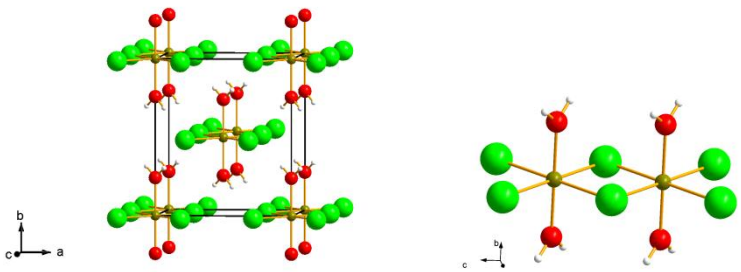

Fig. S9 Crystal structure of $FeCl_2 \cdot 2H_2O$ viewed along the *c* axis (left); detailed view of one edge-sharing chain (right)

$FeCl_2$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(B)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
$FeCl_2$	27810	01-074-1862	00-001-1106	3.58	3.58	17.53999	194.68
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
CdCl2(3R)		*R*-3*m*		90	90	120	3
Ref.	Herpin, A.;Meriel, P., *Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences* (1884 - 1965) (**1957**), 245, 650-653 ; *Atti della Accademia Nazionale dei Lincei, Classe di Fisiche, Matematiche e Naturali, Rendiconti* (**1929**), 9, 782-789						

Notes

Four other structures of $FeCl_2$ are reported in the ICSD database under the ICSD codes #4059, #64831, #64830 and #44397. Their calculated patterns are referred to as PDF #01-070-1634, #01-085-1438, #01-085-1437 and #01-089-3732.

Crystal structure images

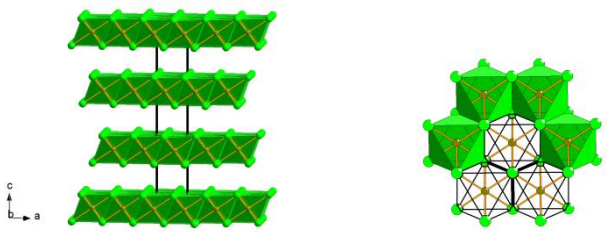

Fig. S10 Crystal structure of $FeCl_2$ viewed along the *b* axis (left); detailed view of one layer showing the edge-sharing geometry (with bold black lines; right)

$FeCl_3 \cdot 6H_2O$

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
$FeCl_3 \cdot 6H_2O$	30453	01-075-1069	00-033-0645	11.89(2)	7.07(1)	5.99(1)	495.1
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
-		*C*2/*m*		90	100.5(2)	90	2
Ref.	Lind, M.D., *Journal of Chemical Physics* (**1967**), 47, 990-993						

Crystal structure images

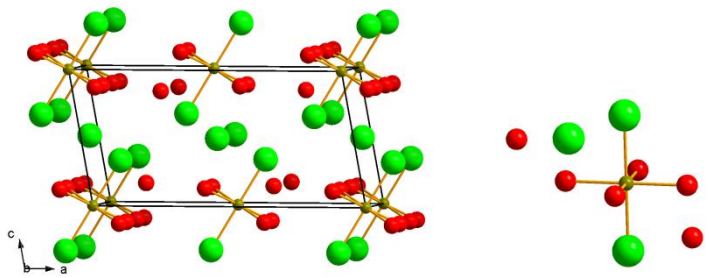

Fig. S11 Crystal structure of $FeCl_3 \cdot 6H_2O$ viewed along the *b* axis (left); asymmetric unit (right)

FeOCl

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(I)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeOCl	40963	01-073-2229	00-039-0612	3.773(1)	7.9096(1)	3.3010(1)	98.51
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
FeOCl		*Pmnm*		90	90	90	2
Ref.	Kauzlarich, S.M.;Stanton, J.L.;Faber, J.jr;Averill, B.A., *Journal of the American Chemical Society* (**1986**), 108, 7946-7951						

Notes

Three other structures of FeOCl are reported in the ICSD database under the ICSD codes #16013, #27136 and #167393. Their calculated patterns are referred to as PDF #01-072-0619, #01-074-1369 and none.

Crystal structure images

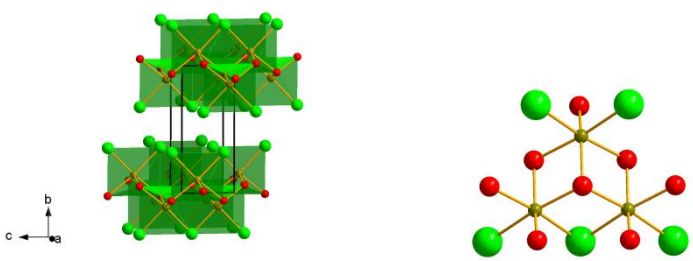

Fig. S12 Crystal structure of FeOCl viewed along the *a* axis (left); detailed view of one layer showing the edge-sharing geometry (right)

$FeCl_3$

Structural parameters

Formula	**ICSD #**	**PDF #(c)**	**PDF #(B)**	***a*, Å**	***b*, Å**	***c*, Å**	***V*, Å^3**
$FeCl_3$	39764	01-077-0997	00-001-1059	6.056(2)	6.056(2)	17.407(7)	552.87
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
BiI3		*R*-3		90	90	120	6
Ref.	Troyanov, S.I., *Zhurnal Neorganicheskoi Khimii* (**1993**), 38, 1946-1949						

Notes

Five other structures of $FeCl_3$ are reported in the ICSD database under the ICSD codes #27500, #39766, #39765, #63329 and #151400. Their calculated patterns are referred to as PDF #01-074-1658, #01-077-0999, #01-077-0998, #00-078-2123 and none.

Crystal structure images

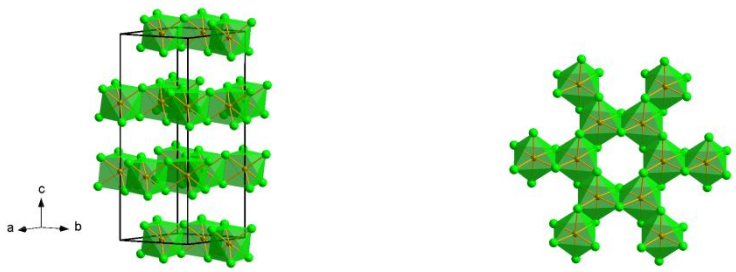

Fig. S13 Crystal structure of $FeCl_3$ viewed along the [110] direction (left); detailed view of one layer showing the edge-sharing geometry (right)

Crystal structures of iron oxide hydroxides

γ-FeOOH

Structural parameters

Formula	ICSD #	PDF #(c)	PDF #(*)	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
FeOOH	93948	01-074-1877	00-044-1415	3.072(2)	12.516(3)	3.873(2)	148.91
Type		**Space group**		***α*, deg.**	***β*, deg.**	***γ*, deg.**	**Z**
AlOOH(oS16)		*Cmcm*		90	90	90	4
Ref.	Zhukhlistov, A.P., *Kristallografiya* (**2001**), 46(5), 805-808; *Crystallography Reports* (**2001**), 46, 730-733; *Golden Book of Phase Transitions* (**2002**), 1, 1-123						

Notes

Four other structures of γ-FeOOH are reported in the ICSD database under the ICSD codes #24885, #27846, #37159 and #108876. Their calculated patterns are referred to as PDF #01-073-2326, #01-074-1877, #01-076-2301 and none.

Crystal structure images

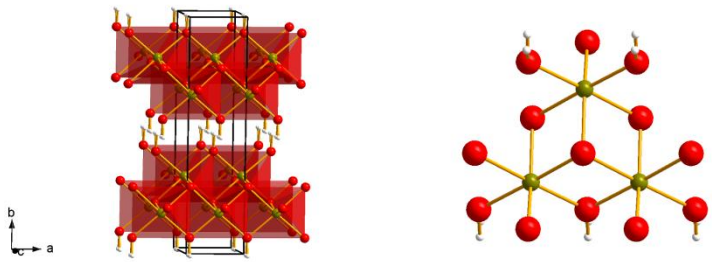

Fig. S14 Crystal structure of γ-FeOOH viewed along the *c* axis (left); detailed view of one layer showing the edge-sharing geometry (right)

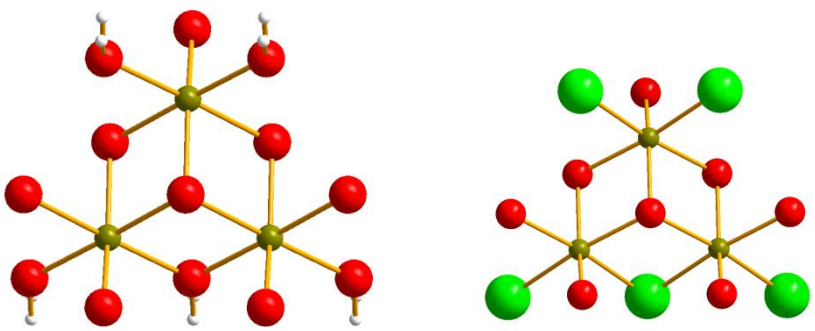

Fig. S15 Comparison of the crystal structure of γ-FeOOH (left) and FeOCl (right); this shows the similarity between the two structures where the chlorides Cl^- and hydroxides OH^- occupy the same positions

Thermogravimetric analysis

The thermal behaviour of each precursor and product has been investigated by thermogravimetric analysis under inert nitrogen gas on a Shimadzu TGA-50 thermogravimetric analyser instrument from 25 to 600 °C with a heating ramp of 5 °C.min^{-1}.

TG analysis of the iron chloride precursors

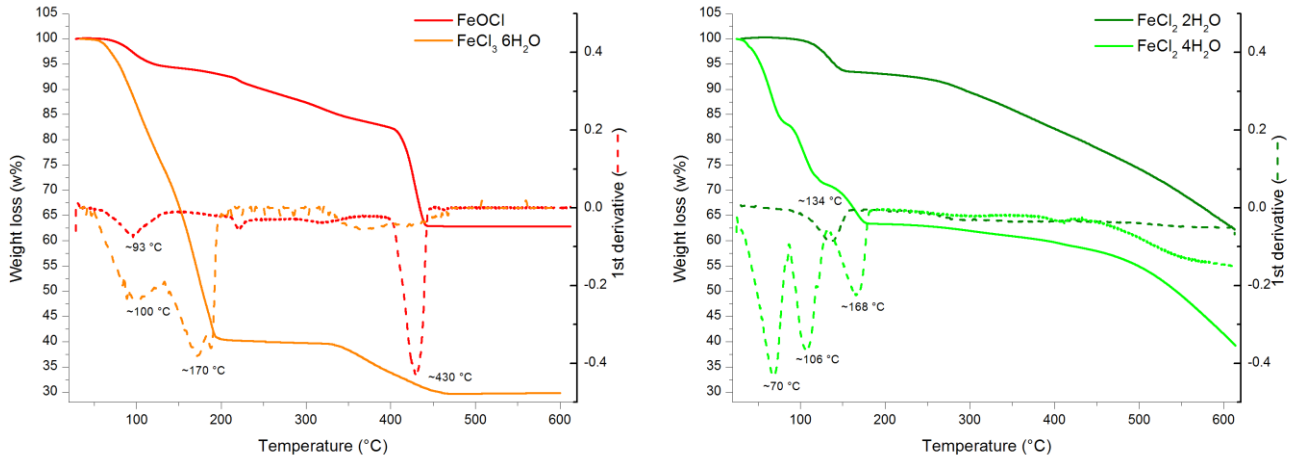

Fig. S16 TGA diagrams (and their 1st derivative) of $FeCl_3 \cdot 6H_2O$ (orange line), FeOCl (red line) obtained by thermal treatment of $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ (green line) and $FeCl_2 \cdot 2H_2O$ (dark green line) obtained by thermal treatment of $FeCl_2 \cdot 4H_2O$

Note on the TG profile of the FeOCl sample obtained by thermal treatment of $FeCl_3 \cdot 6H_2O$ under vacuum:
According to the TG curve, the compound loses 20.35% of weight at 430 °C. This loss is characteristic of FeOCl, which decomposes into Fe_2O_3 and gaseous $FeCl_3$. Considering the initial weight used for the measurement (10.568 mg), 20.35% corresponds to 2.15 mg, i.e. 0.01325 mmol of $FeCl_3$. According to the chemical reaction of decomposition, 3 FeOCl give rise to 1 $FeCl_3$; therefore the initial amount of FeOCl is 4.26 mg. Finally, we can conclude that FeOCl contributes to 40.3% of the total weight of the thermally treated $FeCl_3 \cdot 6H_2O$.

TG analysis of the fluorinated powders

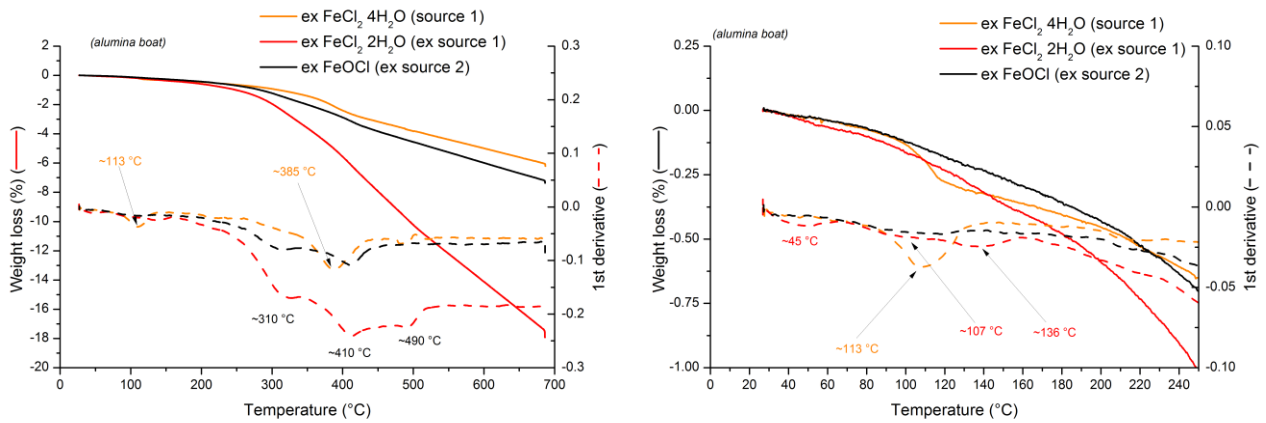

Fig. S17 TGA diagrams of the fluorinated powders of $FeCl_2 \cdot 4H_2O$ (orange line), $FeCl_2 \cdot 2H_2O$ (red line) and FeOCl (black line), obtained by the one-shot procedure at 350 °C for 15 hrs (left); zoom on the range 25-250 °C (right)

Mössbauer spectroscopy

Iron chloride precursors

Mössbauer spectra

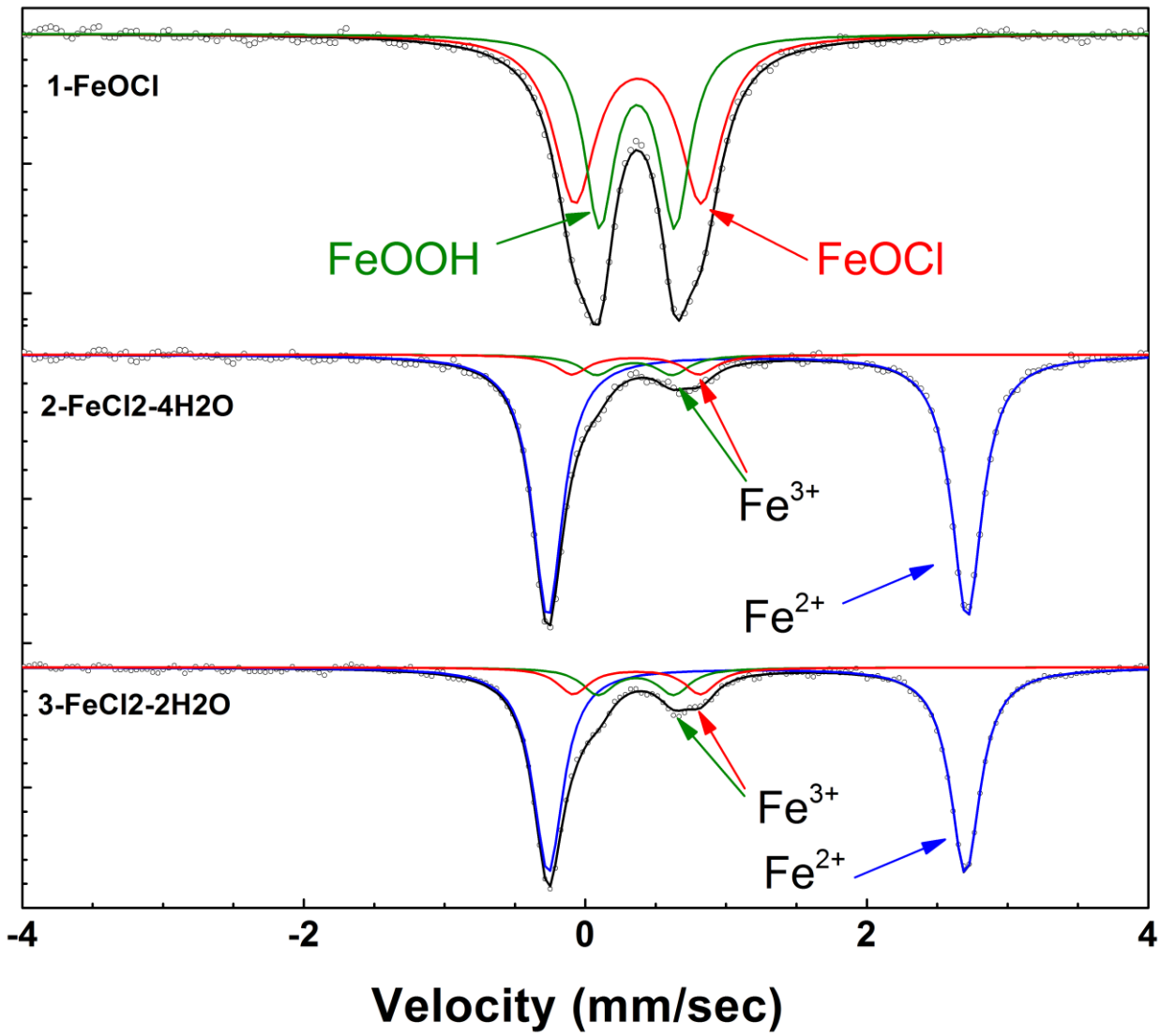

Fig. S18 Mössbauer spectra of the iron chloride precursors

Comments on the Mössbauer spectroscopy of the iron chloride precursors

The Mössbauer spectra of $FeCl_2 \cdot 4H_2O$ and $FeCl_2 \cdot 2H_2O$ are similar: the re-hydration of the dihydrate phase can occur rather quickly after being exposed to air.

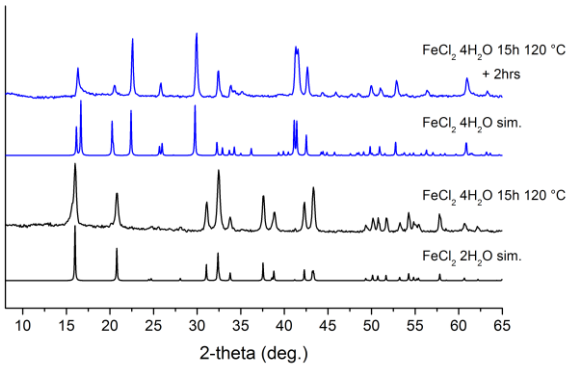

Fig. S19 XRD patterns of $FeCl_2 \cdot 4H_2O$ thermally treated under vacuum at 120 °C for 15 hrs, and the simulation of $FeCl_2 \cdot 2H_2O$ (black line); the same powder exposed to air humidity for 2 hrs, and the simulation of $FeCl_2 \cdot 4H_2O$ (blue line)

Iron fluoride products

Mössbauer spectra

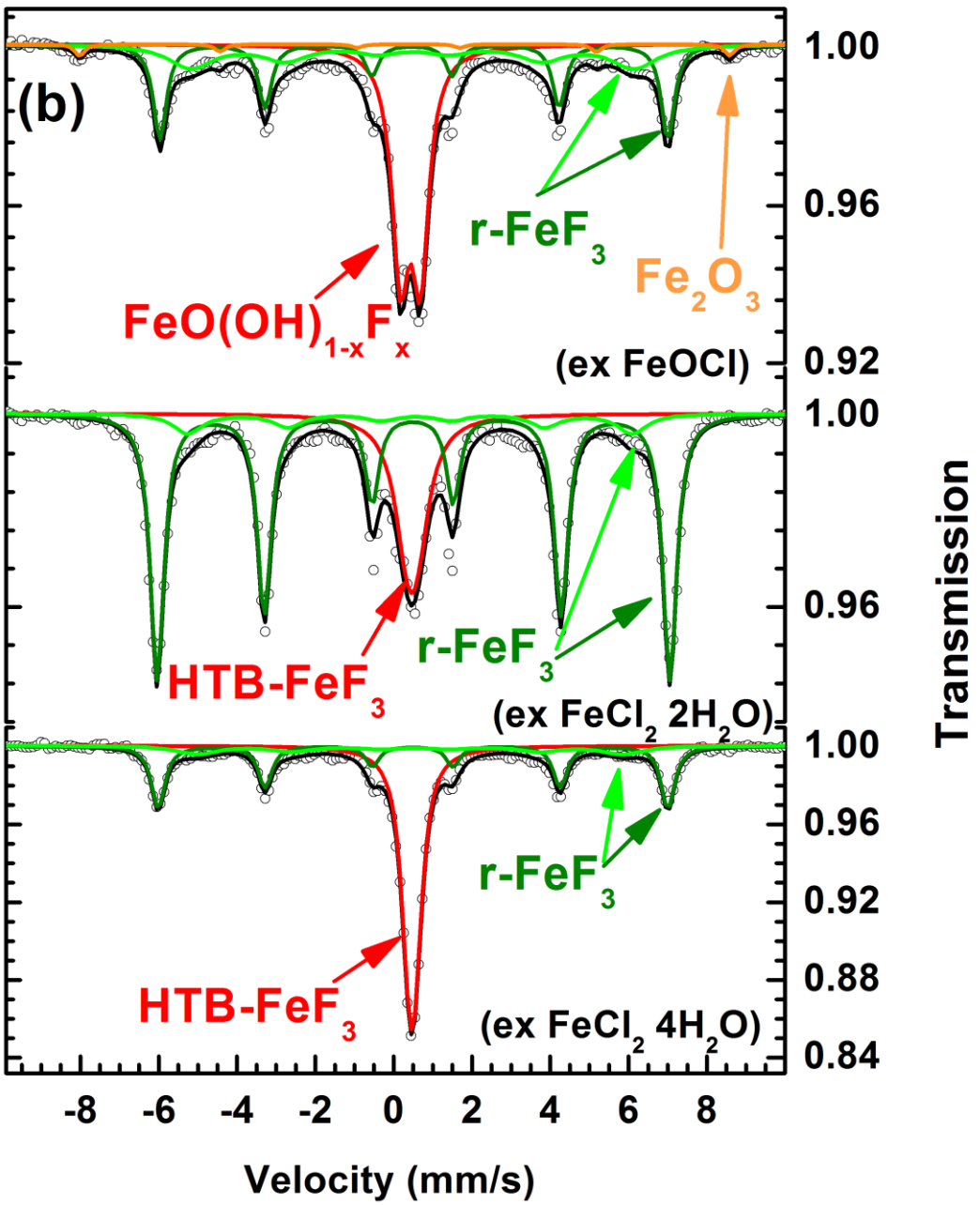

Fig. S20 Mössbauer spectra of the iron chloride precursors

Fitting parameters

Table S1: Room-temperature Mössbauer parameters for the iron chlorides precursors and their corresponding fluorinated samples; as extracted from the previous Figures S22 and S23.

	***δ, mm/s*[a]**	***Δ, mm/s*[b]**	***FWHM, mm/s***	***H, Tesla***	***%***	***Attribution***
Spectra with magnetic components						
FeOCl	0.37	0.90	0.36	-	55	FeOCl
	0.26	0.54	0.26	-	45	FeOOH
$FeCl_2·4H_2O$	1.22	2.98	0.26	-	86	$FeCl_2·4H_2O$
	0.35	0.54	0.28	-	7	FeOOH
	0.36	0.90	0.28	-	7	FeOCl
$FeCl_2·2H_2O$	1.22	2.96	0.26	-	78	$FeCl_2·4H_2O$
	0.36	0.54	0.27	-	10	FeOOH
	0.37	0.90	0.27	-	10	FeOCl
Spectra with magnetically-ordered components						
ex $FeCl_2·4H_2O$	0.46	0.17	0.47	0	50	HTB- FeF_3
	0.49	0.01	0.43	40.4	35	r-FeF_3
	0.49	-0.15	1.3	33.8	15	am-FeF_3
ex $FeCl_2·2H_2O$	0.46	0.25	0.77	0	22	HTB- FeF_3
	0.49	0.02	0.42	40.6	67	r-FeF_3
	0.49	-0.16	0.92	35.2	11	am-FeF_3
ex FeOCl	0.43	0.51	0.52	0	42.6	$FeO(OH)_{1-x}F_x$
	0.49	0.05	0.41	40.3	29.4	r-FeF_3
	0.49	-0.02	0.41	35.1	25.1	am-FeF_3
	0.32	-0.09	0.31	51.5	2.8	Fe_2O_3

[a] Isomeric shift; [b] Quadrupole splitting