

# LDH-mediated interfacial redox formation of phylломanganate from $\text{KMnO}_4$ : mechanistic insights and subsequent fluorination pathways

Abderraouf Rouag<sup>a</sup>, Sarah Hennequart<sup>a</sup>, Régis Porhiel<sup>a</sup>, Jean-Marc, Grenèche<sup>b</sup>, Kevin  
Lemoine<sup>a</sup>, Katia Guérin<sup>a</sup>, Diane Delbègue<sup>c</sup>, Fabrice Leroux<sup>a\*</sup>

- a. Université Clermont Auvergne, INP Clermont, CNRS, ICCF, 24, Avenue Blaise Pascal, 63178 Aubière, France.
- b. Institut des Molécules et des Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France
- c. Centre National des Etudes Spatiales, 18 avenue Edouard Belin 31 401 Toulouse Cedex 9, France.

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## Supplementary Information

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		$\text{Fe}^{n+}$	$\delta$	$\Delta E_Q$	$\tau$
<b>CCF-NO3</b>					
300 K	3 quadrupolar doublets	$\text{Fe}^{3+}$	0.35	0.68	0.51
		$\text{Fe}^{3+}$	0.35	0.37	0.20
		$\text{Fe}^{3+}$	0.36	1.12	0.29
<b>CCF-Mn</b>					
300 K	2 quadrupolar doublets	$\text{Fe}^{3+}$	0.35	0.63	0.60
		$\text{Fe}^{3+}$	0.35	1.00	0.40

**Table S1** Refined values of the hyperfine parameters of LDH phases at 300 K.

**Table S2.** Summary of cell parameters of CCF-NO<sub>3</sub>-F<sub>2</sub> and CCF-Mn-F<sub>2</sub>

Sample	CCF-NO <sub>3</sub> F <sub>2</sub>		CCF-Mn F <sub>2</sub>		
	CuF <sub>2</sub>	FeF <sub>3</sub>	CuF <sub>2</sub>	FeF <sub>3</sub>	Mn <sub>2</sub> O <sub>2</sub> F <sub>9</sub>
Phase					
Space group	<i>P2<sub>1</sub>/n</i>	<i>R-3c</i>	<i>P2<sub>1</sub>/n</i>	<i>R-3c</i>	<i>C2/c</i>
<i>a</i> (Å)	3.318(1)	5.166(1)	3.325(1)	5.089(1)	17.537(1)
<i>b</i> (Å)	4.517(1)	5.166(1)	4.528(1)	5.089(1)	8.397(1)
<i>c</i> (Å)	4.591(1)	13.356(1)	4.578(1)	13.265(1)	9.150(1)
$\beta$ (°)	83.71(1)	90.00	84.44(1)	90.00	102.39(1)
<i>V</i> (Å <sup>3</sup> )	68.37(1)	308.68(1)	68.60(1)	297.42(1)	1316.03(1)
2 $\theta$ range (°)	10–70				
Uni. reflec.	56	28	56	28	560
Ref. para.	66	58	72	66	69
$\chi^2$	3.5		7.3		
<i>R<sub>p</sub></i> / <i>R<sub>wp</sub></i>	0.08/0.09		0.15/0.16		

**Table S3** Refined values of the hyperfine parameters of fluorinated phases at 300 K and 77 K.

		$\text{Fe}^{n+}$	$\delta$	$\Delta E_Q/2\varepsilon$	$B_{\text{hf}}$	$\tau$
<b>CCF-NO3 - F2</b>						
300 K	1 quadrupolar doublet	$\text{Fe}^{3+}$	0.45	0.51	-	0.21
	2 magnetic sextets	$\text{Fe}^{3+}$	0.49	-0.06	46.5	0.43
		$\text{Fe}^{3+}$	0.49	0.00	40.5	0.36
77 K	1 quadrupolar doublet	$\text{Fe}^{3+}$	0.55	0.58	-	32
	1 magnetic sextet	$\text{Fe}^{3+}$	0.59	-0.045	61.3	68
<b>CCF - Mn - F2</b>						
300 K	2 quadrupolar doublets	$\text{Fe}^{3+}$	0.50	1.19	-	0.15
		$\text{Fe}^{3+}$	0.44	0.37	-	0.53
	2 magnetic sextets	$\text{Fe}^{3+}$	0.49	0.00	42.0	0.24
		$\text{Fe}^{3+}$	0.54	0.00	37.9	0.08
77 K	1 quadrupolar doublet	$\text{Fe}^{3+}$	0.53	0.48	-	0.38
	2 magnetic sextets	$\text{Fe}^{3+}$	0.59	0.00	60.7	0.24
		$\text{Fe}^{3+}$	0.64	0.01	58.7	0.38

$\delta$  ( $\pm 0.02$ ),  $\Delta E_Q$  ( $\pm 0.02$ ) and  $2\varepsilon$  ( $\pm 0.02$ ) are given in  $\text{mm}\cdot\text{s}^{-1}$ ,  $B_{\text{hf}}$  in T ( $\pm 0.5$ ),  $\tau$  ( $\pm 0.02$ ).