

## Supporting Information

### Exploring the short and long-range order in connection with fluorine content in mixed anions copper hydroxyfluorides

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Sample	Starting NH <sub>4</sub> F/Cu ratio	Starting pH	Identified Phases	F <sup>-</sup> content *	Final Composition**
N-MW-1	0.5	7	Cu(OH) <sub>2-x</sub> F <sub>x</sub> (Structure derived from Cu-LF)	0.37(1)	Cu(OH) <sub>1.63</sub> F <sub>0.37</sub>
N-MW-2	1	7	Cu(OH) <sub>2-x</sub> F <sub>x</sub> (Structure derived from Cu-LF)	0.40(1)	Cu(OH) <sub>1.6</sub> F <sub>0.4</sub>
N-MW-3	1.5	7	Cu(OH) <sub>2-x</sub> F <sub>x</sub> (Structure derived from Cu-LF)	0.42(1)	Cu(OH) <sub>1.58</sub> F <sub>0.42</sub>
N-MW-4	2	7	Cu(OH) <sub>2-x</sub> F <sub>x</sub> (Structure derived from Cu-LF)	0.50(1)	Cu(OH) <sub>1.5</sub> F <sub>0.5</sub>

Table S1: Hydroxyl-rich phases obtained with different starting NH<sub>4</sub>F/Cu molar ratio. \*F<sup>-</sup> content determined by fluoride ion-selective electrode. \*\*Cu content determined by ICP-AES, OH content by electroneutrality

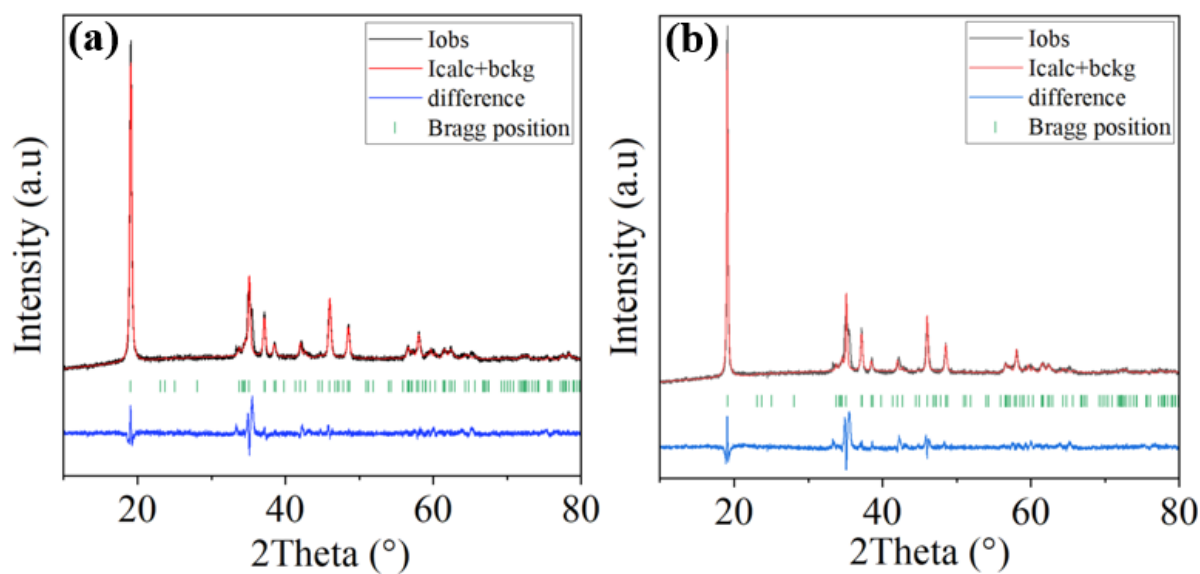


Figure S1: Full pattern profile matching refinement of two Cu-HF compositions: a) MW-2 (b) MW-3

Name	F- content	R <sub>p</sub> (%)	wR <sub>p</sub> (%)	a (Å)	b (Å)	c (Å)	B Angle
MW-2	0,95(1)	5,08	7,49	5,260(3)	6,360(4)	5,064(2)	112,92(1)
MW-3	1,46(1)	6,15	9,51	5,263(5)	6,355(2)	5,062(2)	113,09(1)

Table S2: Full pattern profile matching refinement parameters of two Cu-HF compositions corresponding to figure S1

**Cu-HF  $P2_1/a$** 

Atom	x	y	z	B <sub>iso</sub>
Cu	0.2597	0.1225	0.0039	0.7
O	0.1611	0.3640	0.1700	0.7
F	0.3720	0.3836	0.7380	0.7

**Cu-LF  $P-3m1$** 

Atom	x	y	z	B <sub>iso</sub>
Cu	0	0	0	0.7
O/F	0.3333	0.6667	0.328(4)	0.7

*Table S3: Atomic positions of Cu-LF and Cu-HF phases, refined from X-ray diffraction for Cu-LF, fixed from literature <sup>16</sup> for  $P2_1/a$*