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Supporting Information

Synthesis and Characterization of the Crystal Structure and Magnetic Properties of the Hydroxyfluorides $MnF_{2-x}(OH)_x$ (x ~ 0.8)

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Electronic Supplementary Information (ESI)

Table S1. Crystal structural parameters for $MnF_{1.20(1)}(OH)_{0.80(1)}$ at 3 K based on Rietveld refinement against NPD data. Space group *Pnn*2 (No 34), a = 4.71143(10) Å, b = 5.24377(11) Å, c = 3.24834(6) Å, V = 80.252(3) Å^3.

Atom	Wyck.	x	y	z	Occupancy	B_{iso}, Å^2
Mn	2*a**	0	0	0	1	0.21(6)
O/F	4*c*	0.2511(6)	0.1533(3)	0.504(5)	0.399(8)/0.601(8)	0.49(3)
H	4*c*	0.4250(11)	0.0287(13)	0.543(5)	0.399(8)	0.49(3)

* z(Mn) was kept at 0 to fix the unit cell origin as all the sites in the *Pnn*2 space group have variable *z*-coordinates

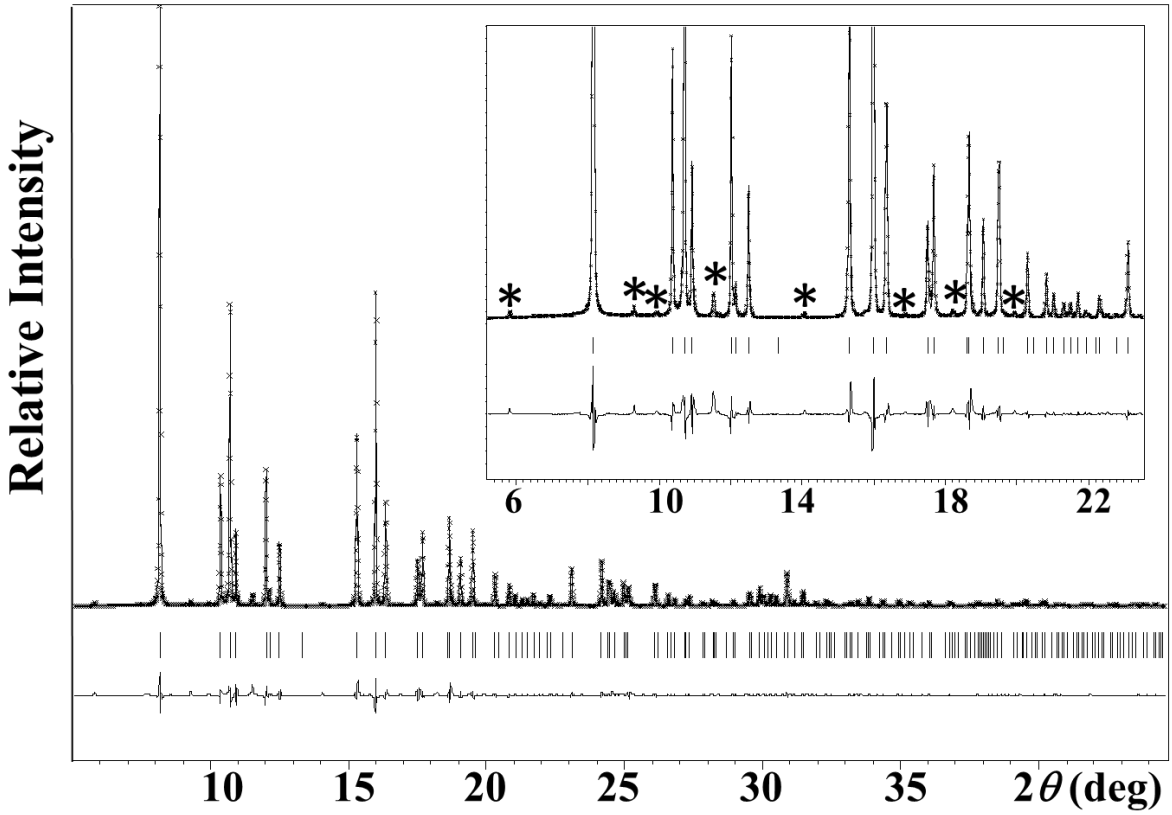

Figure S1. Final observed, calculated and difference plots for synchrotron X-ray powder diffraction refinement (λ = 0.5001 Å) of $MnF_{2-x}(OH)_x$ (x ~ 0.8). The asterisk in the inset corresponds to Mn_3O_4.

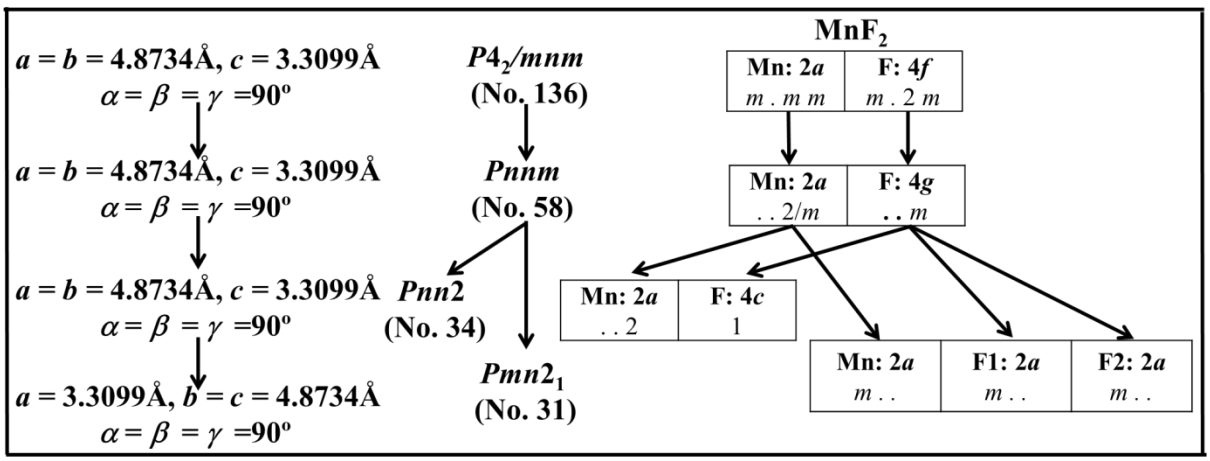

Figure S2. Group-subgroup transformation from tetragonal $P4_2/mnm$ to orthorhombic *Pnnm, Pnn*2, *and* $Pmn2_1$, for MnF_2 structure.

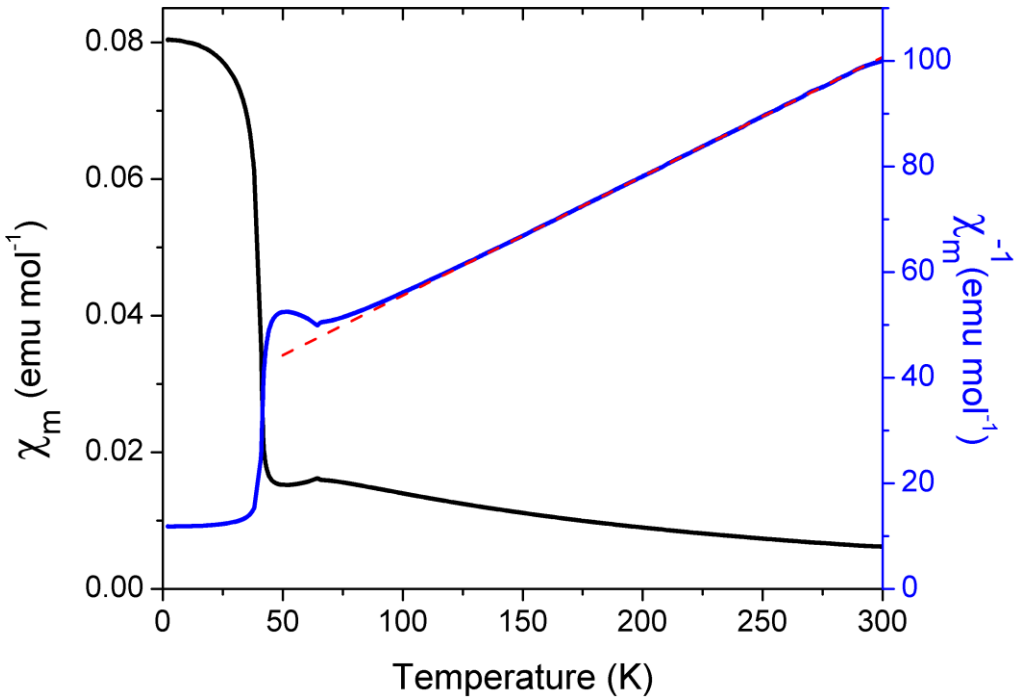

Figure S3. Magnetic susceptibility χ_m and the corresponding χ_m^{-1} as a function of temperature under 0.1 T field for $MnF_{1.20(1)}(OH)_{0.80(1)}$. The signature of the AFM transition can be seen at ~70 K. The anomaly at ~40 K is due to a ferrimagnetic transition in the minor impurity phase Mn_3O_4. Red dashed line shows the Curie-Weiss fit done in the range 200-300K and yielding Θ=-146(1) K and the effective moment 5.95(1) μ_B consistent with the spin-only value for S=5/2 Mn^{2+}.

Thermal analyses

Thermal analyses (TG-DTA-MS) were carried out on the $MnF_{2-x}(OH)_x$ (x ~ 0.8) sample using a Rigaku TG-DTA-PIMS410/s instrument. The measurements were done between 25 ºC and 600 ºC at a heating rate of 5 ºC/min. The experiment was performed in alumina crucible under helium atmosphere. We clearly observe 7.7% of weight loss. Based on the mass spectrometer analysis, this loss corresponds to water molecules (18g/mol). Furthermore, the examination using X-ray diffraction of the powder collected after the thermal analysis shows a decomposition of the sample to a mixture of MnO and MnF_2. Therefore, the decomposition mechanism is as follow:

$$2MnF_{2-x}(OH)_x = (2-x)\ MnF_2 + x\ MnO + x\ H_2O \quad \text{(eq. 1)}$$

If we consider y the % of H_2O weight loss then: $y = \frac{x \times M(H2O)}{2 \times [M(Mn) + (2-x) \times M(F) + x \times M(OH)]} \times 100$ (eq. 2)

We then deduce from eq. 2: $x = \frac{M(MnF2)}{\left(\frac{50}{y}\right) \times [M(H2O)] + [M(F) - M(OH)]}$ (eq. 3)

For y = 7.7%, x would be equal to 0.782. This is in very good agreement with the composition x = 0.8 determined from Rietveld refinement.

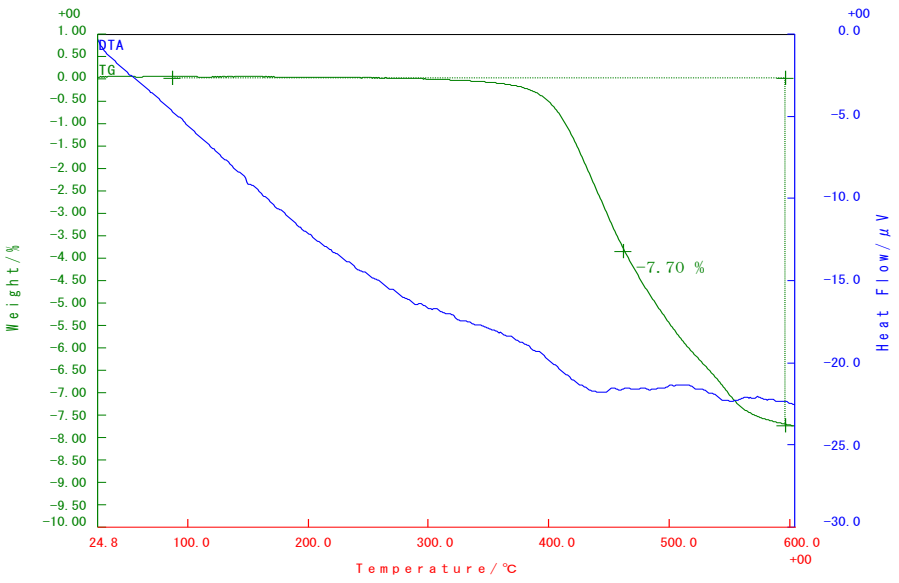

Figure S4. DT and TG thermal analyses for $MnF_{2-x}(OH)_x$ (x ~ 0.8) sample.