Supplementary Materials

Table S1. The refined unit-cell parameters for $NH_4MgCl_3 \cdot 6H_2O$ phase at different temperatures.

T, °C	*a*, Å	*b*, Å	*c*, Å	β, º	*V*, Å³
23	9.3182(7)	9.5678(6)	13.331(1)	90.098(6)	1188.5(1)
30	9.3200(7)	9.5682(6)	13.333(1)	90.079(6)	1189.0(1)
40	9.3227(7)	9.5693(7)	13.337(1)	90.086(6)	1189.8(2)
50	9.3265(7)	9.5707(6)	13.341(1)	90.086(6)	1190.8(1)
60	9.3292(7)	9.5716(6)	13.342(1)	90.081(6)	1191.4(2)
70	9.3327(7)	9.5723(7)	13.347(1)	90.081(6)	1192.4(2)
80	9.3376(7)	9.5742(7)	13.351(1)	90.073(7)	1193.6(2)

Table S2. The refined unit-cell parameters for HT phase of $NH_4MgCl_3 \cdot 2H_2O$, at different temperatures.

T, °C	*a*, Å	*b*, Å	*c*, Å	*α*, °	β, °	γ, °	*V*, Å³
100	6.558(6)	6.8957(6)	9.102(5)	91.7(1)	111.0(1)	112.4(1)	348.7(16)
110	6.567(5)	6.8976(6)	9.121(5)	91.7(1)	111.0(1)	112.3(1)	350.1(16)
120	6.578(5)	6.8987(5)	9.139(5)	91.8(1)	111.1(1)	112.2(1)	351.6(16)
130	6.593(6)	6.9110(6)	9.156(6)	91.9(1)	111.2(1)	112.2(1)	353.2(19)
140	6.605(6)	6.9439(6)	9.163(5)	91.9(1)	111.5(1)	112.4(1)	354.3(22)

Table S3. The refined unit-cell parameters for $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ phase at different temperatures.

T, °C	*a*, Å	*b*, Å	*c*, Å	*V*, Å³
24	13.763(7)	9.9434(6)	7.0416(6)	963.6(3)
30	13.769(7)	9.9380(6)	7.0433(6)	963.8(3)
40	13.769(7)	9.9438(6)	7.0452(6)	964.6(3)
50	13.780(7)	9.9486(6)	7.0489(6)	966.4(3)
60	13.790(7)	9.9541(6)	7.0520(6)	968.0(3)
70	13.792(8)	9.9591(6)	7.0583(6)	969.5(3)
80	13.791(8)	9.9660(6)	7.0588(6)	970.2(3)

Table S4. Bond-valence analysis (v.u. = valence units) for $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ phase.

Atom	NH_4	Fe	H1	Total
O1		0.39	0.80 → ×2	1.99
Cl1	0.01, 0.01 0.01, 0.01	0.45↓ × 2	0.13, 0.05 0.02, 0.01	0.58
Cl2	0.01, 0.02	0.44	0.02, 0.01	0.56
Cl3	0.01, 0.01	0.53	0.03	0.70
Cl4	0.02, 0.01	0.49	0.04	0.50
Total	0.12	2.75	1.11	

Table S5. Approximation equations for $NH_4MgCl_3 \cdot 6H_2O$ phase and its HT modification.

	*T*1	*T*2	*n*	p_0	$p_1 \times T \times 10^{-3}$	$p_2 \times T^2 \times 10^{-6}$	R^2
	$NH_4MgCl_3 \cdot 6H_2O$						
a	23	90	1	9.3099	0.0003	-	0.99
b	23	90	1	9.565	0.0001	-	0.99
c	23	90	1	13.322	0.0004	-	0.99
β	23	90	1	90.097	-0.0003	-	0.51
V	23	90	1	1186.3	0.0883	-	0.99

	HT phase						
a	100	140	1	6.436(7)	1.20(6)	-	0.99
b	100	140	2	7.5(2)	−11(3)	52(13)	0.97
c	100	140	2	8.69(8)	6(1)	−18(6)	1.00
α	100	140	2	92(1)	−5(17)	48(73)	0.97
β	100	140	2	116(2)	−91(26)	426(109)	0.98
γ	100	140	2	118(1)	−99(17)	409(72)	0.94
V	100.0	140.0	1	334.6(5)	142(4)	-	1.00

Table S6. Approximation equations for $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ phase.

	***T*1**	***T*2**	***n***	p_0	$p_1 \times T \times 10^{-3}$	R^2
a	24	80	1	13.751	0.562	0.91
b	24	80	1	9.927	0.456	0.92
c	24	80	1	7.033	0.331	0.97
V	24	80	1	960.05	129	0.98

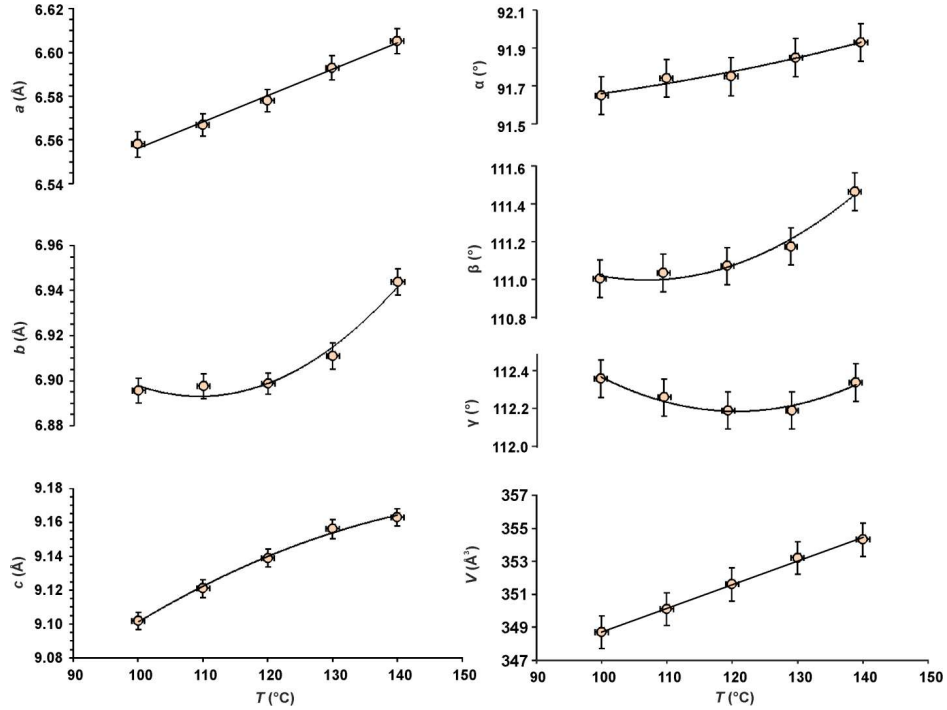

Figure S1. The dependencies of unit-cell parameters of HT modification of $NH_4MgCl_3 \cdot 2H_2O$.