Supporting Information

$Ba_4Ni_3F_{14}·H_2O$: A ferrimagnetic compound with a staircase kagomé lattice

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Experimental details:

1. Synthesis

In hydrothermal synthesis, HF has proven to be wonderful reaction media for the synthesis of crystalline metal fluoride.[1, 2] $Ba_4Ni_3F_{14}·H_2O$ was obtained via a fluoride-rich hydrofluorothermal synthesis method. A mixture of 2.0 mmol NiF_2 (AR, 0.1934 g), 1.2 mmol BaF_2 (AR, 0.2104 g), and 1 mmol NaF (AR, 0.0420 g) was put into 20 mL Teflon-lined steel autoclave with 2 mL of deionized water, while 1.0 mL of NaOH (2 M) solution, and 0.40 mL of HF (AR, ≥ 40%, HF is a highly corrosive liquid with smoke, be careful!) were added in turn. Autoclave was heated to 180°C within 3 hours and kept at four days, and then cooled to room temperature within 2 days. Finally, green hexagonal prism crystals were obtained by washing several times with deionized water, and the yield is about 18% (based on Ni). On the other hand, we propose the following reaction mechanism for the formation of $Ba_4Ni_3F_{14}·H_2O$:

$$4BaF_2 + NaOH + HF + 3NiF_2 \rightarrow Ba_4Ni_3F_{14}·H_2O + NaF.$$

The addition of NaF may be considered to serve as a mineralizer to promote crystallization. For the crystallization of fluoride, HF not only effectively regulate PH, but also a beneficial solvent, which is conducive to the dissolution of reactants. Furthermore, excessive HF provides a fluorine-rich environment, which is more conducive to the crystallization of $Ba_4Ni_3F_{14}·H_2O$. In addition, the temperature has a great effect on the growth of crystals. The crystals of $Ba_4Ni_3F_{14}·H_2O$ can be synthesized in a wide temperature area of 170 - 230 ℃ with different quality, while the optimal growth condition is kept at 180 ℃, and then slow cooling for 2 days at least. The purity was checked by powder X-ray diffraction (XRD), which was collected on a Miniflex-600 diffractometer with Cu *Kα* radiation (λ = 1.54178 Å) (Fig. S1).

2. Single Crystal X-ray diffraction

Single-crystal X-ray diffraction data of $Ba_4Ni_3F_{14}·H_2O$ was collected on a Rigaku Mercury CCD diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) at 298 K. The structure was solved by direct methods and refined by

full-matrix least-squares on F^2 using the SHELX-2018 program package.[3] The optimized structural parameters were checked by the PLATON program.[4] The crystallographic data and structural refinement are shown in Table S1. The detailed atomic coordinates, displacement parameters, and anisotropic displacement parameters are presented in Table S2 and Table S5. The bond lengths and angles are illustrated in Tables S3-S4. Elemental analysis (Fig. S2) using energy dispersive spectrometry (EDS) confirmed only Ba, Ni, F and O elements in the system, where the average molar ratios of Ba: Ni were found to be ~1.38 : 1, agreeing with the results determined from single-crystal X-ray structural studies.

3. Magnetic Measurements.

Magnetic and specific heat measurements were measured on a commercial Quantum Design Physical Property Measurement System (PPMS). Powdered sample (16.80 mg) of $Ba_4Ni_3F_{14}\cdot H_2O$ was placed in a gel capsule sample holder suspended in a plastic drinking straw. Magnetic susceptibility was measured from 2 to 300 K with an applied field of 0.1 T. Isothermal magnetization was tested at 2 K in applied field from 0 to 8 T (field scan of 0.1 T/step). Heat capacity was obtained from 2 to 100 K under zero field by a relaxation method using a sample in pellet (~2.0 × 2.0 mm^2, 3.8 mg).

4. Infrared (IR) spectra.

Fourier transform infrared (FT-IR) spectroscopy was measured on the Bruker VERTEX70 spectrometer in the 400 - 4000 cm^{-1}. The IR (Fig. S3) absorption peak around 3419 cm^{-1} can be assigned to the O-H stretching vibrations of water molecules, while the band around 3091 cm^{-1} may be from O-H···F hydrogen bonding. The peaks at 1626-1383 cm^{-1} may originate from the H-O-H bending vibrations.[5, 6] The splitting peaks around 825-400 cm^{-1} can be assigned to stretching vibrations of ν(Ni-F).

References:

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6. E. C. Gonzalo, M. L. Sanjuan, M. Hoelzel, M. T. Azcondo, U. Amador, I. Sobrados, J. Sanz, F. Garcia-Alvarado and A. Kuhn, *Inorg. Chem.*, 2015, 54, 3172-3182.

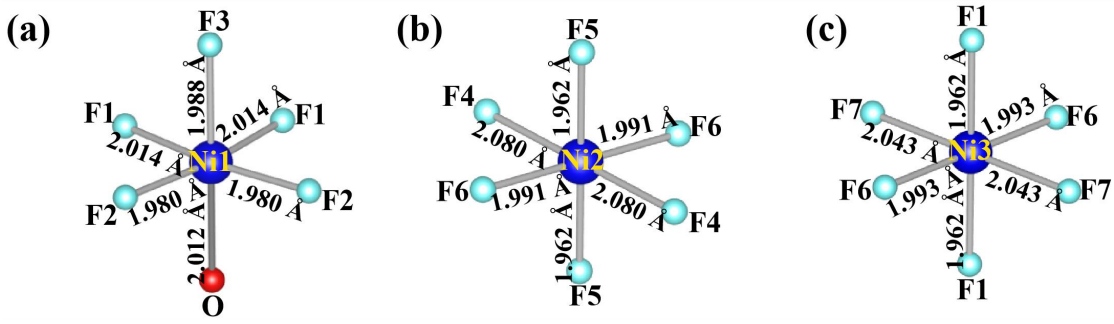

Fig. S1. Views of the coordination geometry for (a) Ni1, (b)Ni2, (c) Ni3 atoms in $Ba_4Ni_3F_{14}·H_2O$.

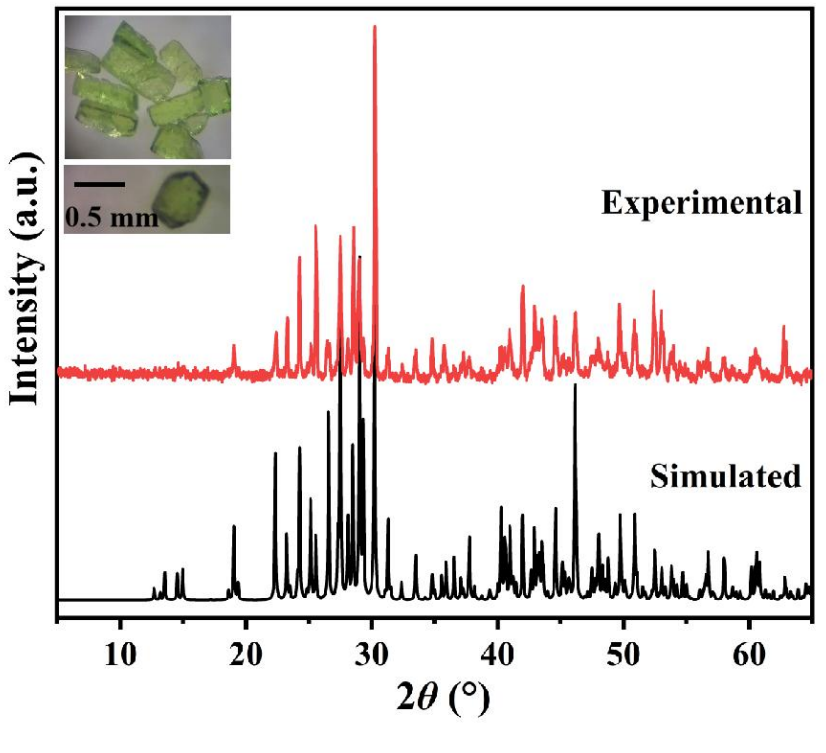

Fig. S2. Simulated and experimental powder X-ray (Cu *Kα*) diffraction patterns for $Ba_4Ni_3F_{14}·H_2O$. Inset: the single crystals of $Ba_4Ni_3F_{14}·H_2O$.

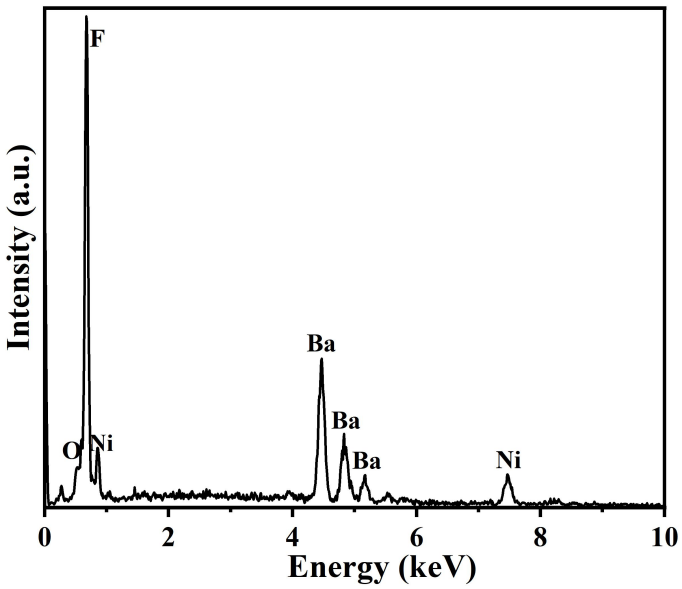

Fig. S3. The energy-dispersive spectrometry (EDS) elemental analyses of $Ba_4Ni_3F_{14}·H_2O$.

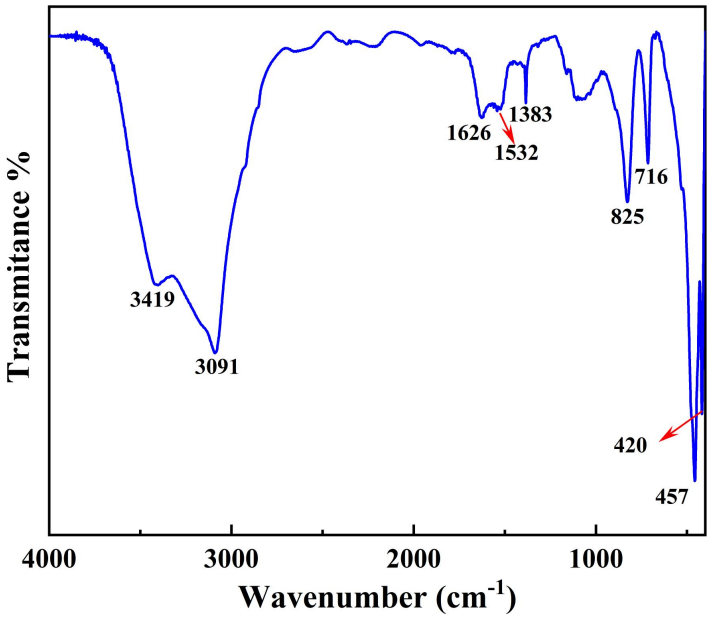

Fig. S4. FT-IR spectra of $Ba_4Ni_3F_{14}·H_2O$.

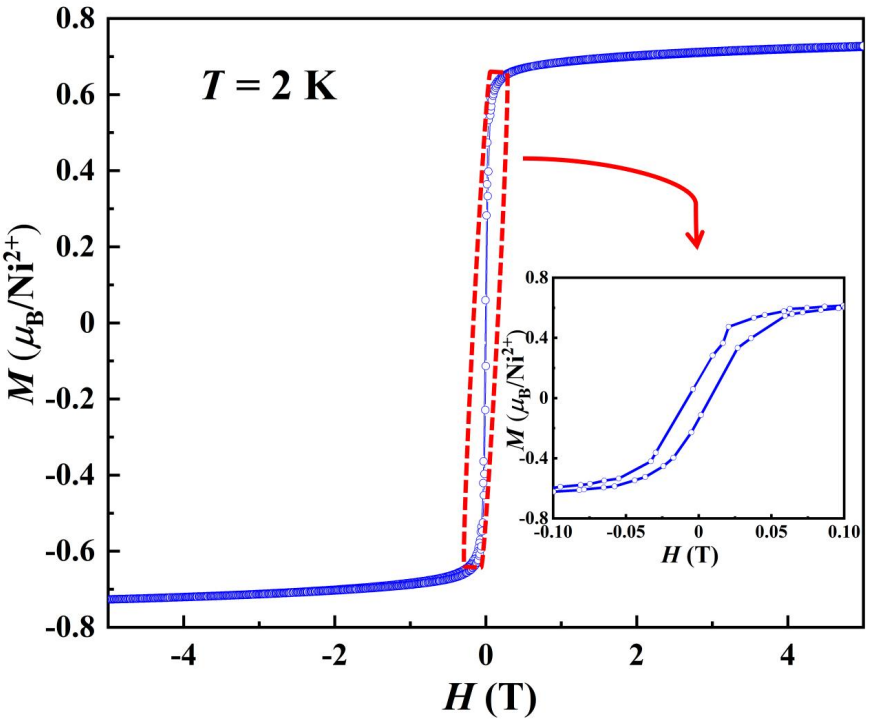

Fig. S5 The hysteresis loop with the field range from −5 to +5 T at 2 K. The inset shows an enlarged view in the −0.10 to 0.10 T.

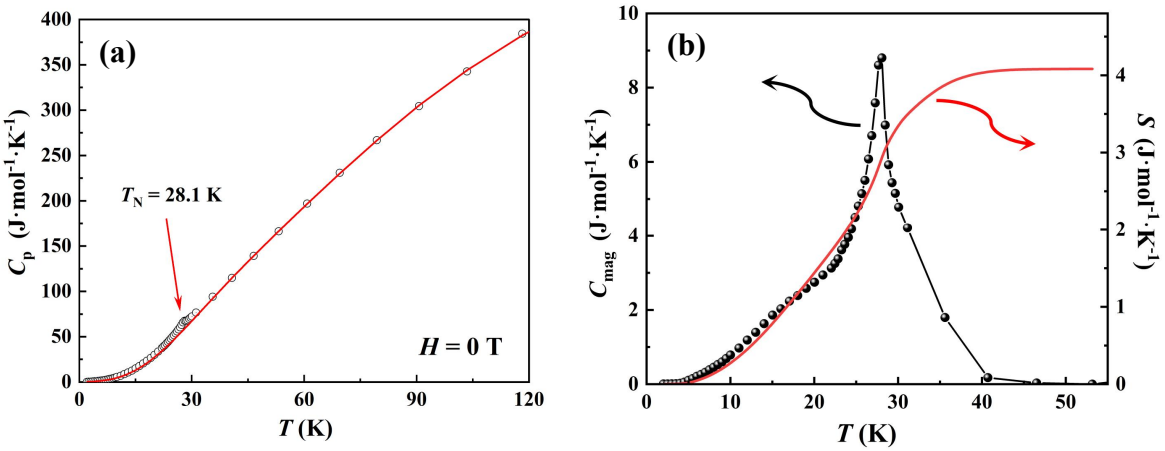

Fig. S6 (a) Temperature dependence of the specific heat at zero field. The red line shows the lattice contribution. (b) Magnetic specific heat and corresponding magnetic entropy from 2 to 55 K.

Table S1 Crystal data and structure refinement for $Ba_4Ni_3F_{14}·H_2O$.

Compound	$Ba_4Ni_3F_{14}·H_2O$
CCDC	2130595
Crystal system	Orthorhombic
Space group	*Pnma*
Fw	1009.51
T, K	298(2) K
λ, Å	0.71073
a, Å	13.9284(2)
b, Å	12.5175(2)
c, Å	7.65000(10)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1333.77(3)
Z	4
F(000)	1776
D_{calcd}, g cm^{-3}	5.027
μ, cm^{-1}	1.5914
GOF on F^2	1.370
R_1,wR_2 [$I>2\sigma(I)$][a]	0.0248, 0.0589
R_1,wR_2 (all data)	0.0257, 0.0593

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ba_4Ni_3F_{14}·H_2O$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Ba(1)	2234(1)	4370(1)	2874(1)	10(1)
Ba(2)	3823(1)	7500	3036(1)	9(1)
Ba(3)	4851(1)	2500	2098(1)	10(1)
Ni(1)	3546(1)	2500	5938(1)	8(1)
Ni(2)	5000	5000	0	8(1)
Ni(3)	5000	5000	5000	6(1)
F(1)	4618(2)	3501(2)	5283(3)	12(1)
F(2)	2628(2)	1335(2)	6461(3)	15(1)
F(3)	3152(2)	2500	3440(4)	13(1)
F(4)	6291(2)	5810(2)	-327(3)	15(1)
F(5)	4274(2)	6332(2)	284(3)	13(1)
F(6)	5298(2)	4702(2)	2499(3)	13(1)
F(7)	3621(2)	5460(2)	4486(3)	13(1)
F(8)	6508(2)	2500	3481(5)	14(1)
O(1)	3983(4)	2500	8444(5)	18(1)

Table S3. The bond lengths (Å) of $Ba_4Ni_3F_{14}·H_2O$

Bond	Dist.	Bond	Dist.
Ni(1)-F(2)	1.980(2)	Ba(1)-F(4)#2	2.915(3)
Ni(1)-F(2)#6	1.980(2)	Ba(1)-F(5)#5	2.929(2)
Ni(1)-F(3)	1.988(3)	Ba(1)-F(2)#6	2.934(3)
Ni(1)-O(1)	2.012(4)	Ba(2)-F(5)#7	2.639(2)
Ni(1)-F(1)#6	2.014(2)	Ba(2)-F(5)	2.639(2)
Ni(1)-F(1)	2.014(2)	Ba(2)-F(8)#8	2.704(3)
Ni(2)-F(5)	1.962(2)	Ba(2)-F(2)#1	2.769(2)
Ni(2)-F(5)#3	1.962(2)	Ba(2)-F(2)#4	2.769(2)
Ni(2)-F(6)#3	1.991(2)	Ba(2)-F(7)	2.798(2)
Ni(2)-F(6)	1.991(2)	Ba(2)-F(7)#7	2.798(2)
Ni(2)-F(4)#3	2.080(2)	Ba(2)-F(1)#9	2.817(2)
Ni(2)-F(4)	2.080(2)	Ba(2)-F(1)#8	2.817(2)
Ni(3)-F(1)	1.962(2)	Ba(2)-O(1)#8	3.258(5)
Ni(3)-F(1)#8	1.962(2)	Ba(3)-F(8)	2.540(3)
Ni(3)-F(6)	1.993(2)	Ba(3)-F(3)	2.579(3)
Ni(3)-F(6)#8	1.993(2)	Ba(3)-F(5)#10	2.635(2)
Ni(3)-F(7)#8	2.043(2)	Ba(3)-F(5)#3	2.635(2)
Ni(3)-F(7)	2.043(2)	Ba(3)-F(1)#6	2.759(2)
Ba(1)-F(7)	2.668(2)	Ba(3)-F(1)	2.759(2)
Ba(1)-F(2)#1	2.694(2)	Ba(3)-F(6)	2.843(3)
Ba(1)-F(3)	2.7019(17)	Ba(3)-F(6)#6	2.843(3)

Ba(1)-F(6)#2	2.743(2)	Ba(3)-F(4)#10	2.973(3)
Ba(1)-F(8)#2	2.7517(18)	Ba(3)-F(4)#3	2.973(3)
Ba(1)-F(4)#3	2.840(2)	Ba(3)-O(1)#11	3.045(4)
Ba(1)-F(7)#4	2.860(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,z-1/2 #2 x-1/2,y,-z+1/2 #3 -x+1,-y+1,-z

#4 -x+1/2,-y+1,z-1/2 #5 -x+1/2,-y+1,z+1/2 #6 x,-y+1/2,z

#7 x,-y+3/2,z #8 -x+1,-y+1,-z+1 #9 -x+1,y+1/2,-z+1

#10 -x+1,y-1/2,-z #11 x,y,z-1 #12 x+1/2,y,-z+1/2

#13 -x+1/2,y-1/2,z+1/2 #14 x+1/2,-y+1/2,-z+1/2

#15 x,y,z+1

Table S4. The bond angles (°) of $Ba_4Ni_3F_{14}\cdot H_2O$

Angle	(°)	Angle	(°)
F(2)-Ni(1)-F(2)#6	94.92(15)	F(8)#2-Ba(1)-F(4)#2	127.12(9)
F(2)-Ni(1)-F(3)	90.94(10)	F(4)#3-Ba(1)-F(4)#2	144.72(2)
F(2)#6-Ni(1)-F(3)	90.94(10)	F(7)#4-Ba(1)-F(4)#2	110.47(7)
F(2)-Ni(1)-O(1)	90.19(13)	F(7)-Ba(1)-F(5)#5	112.45(7)
F(2)#6-Ni(1)-O(1)	90.19(13)	F(2)#1-Ba(1)-F(5)#5	125.27(7)
F(3)-Ni(1)-O(1)	178.34(18)	F(3)-Ba(1)-F(5)#5	88.79(8)
F(2)-Ni(1)-F(1)#6	94.04(10)	F(6)#2-Ba(1)-F(5)#5	53.58(7)
F(2)#6-Ni(1)-F(1)#6	171.00(10)	F(8)#2-Ba(1)-F(5)#5	73.68(9)
F(3)-Ni(1)-F(1)#6	87.98(10)	F(4)#3-Ba(1)-F(5)#5	157.90(7)
O(1)-Ni(1)-F(1)#6	90.71(14)	F(7)#4-Ba(1)-F(5)#5	107.10(6)
F(2)-Ni(1)-F(1)	171.00(10)	F(4)#2-Ba(1)-F(5)#5	57.15(7)
F(2)#6-Ni(1)-F(1)	94.04(10)	F(7)-Ba(1)-F(2)#6	65.54(7)
F(3)-Ni(1)-F(1)	87.98(10)	F(2)#1-Ba(1)-F(2)#6	129.52(7)
O(1)-Ni(1)-F(1)	90.72(14)	F(3)-Ba(1)-F(2)#6	60.08(9)
F(1)#6-Ni(1)-F(1)	76.99(14)	F(6)#2-Ba(1)-F(2)#6	109.09(7)
F(5)-Ni(2)-F(5)#3	180	F(8)#2-Ba(1)-F(2)#6	99.53(8)
F(5)-Ni(2)-F(6)#3	80.77(10)	F(4)#3-Ba(1)-F(2)#6	118.84(7)
F(5)#3-Ni(2)-F(6)#3	99.23(10)	F(7)#4-Ba(1)-F(2)#6	161.40(7)
F(5)-Ni(2)-F(6)	99.23(10)	F(4)#2-Ba(1)-F(2)#6	70.62(7)
F(5)#3-Ni(2)-F(6)	80.77(10)	F(5)#5-Ba(1)-F(2)#6	57.02(6)
F(6)#3-Ni(2)-F(6)	180	F(5)#7-Ba(2)-F(5)	67.28(10)
F(5)-Ni(2)-F(4)#3	87.44(10)	F(5)#7-Ba(2)-F(8)#8	145.77(5)
F(5)#3-Ni(2)-F(4)#3	92.56(10)	F(5)-Ba(2)-F(8)#8	145.77(5)
F(6)#3-Ni(2)-F(4)#3	91.50(10)	F(5)#7-Ba(2)-F(2)#1	96.79(7)
F(6)-Ni(2)-F(4)#3	88.50(10)	F(5)-Ba(2)-F(2)#1	62.27(7)

F(5)-Ni(2)-F(4)	92.56(10)	F(8)#8-Ba(2)-F(2)#1	107.69(8)
F(5)#3-Ni(2)-F(4)	87.44(10)	F(5)#7-Ba(2)-F(2)#4	62.27(7)
F(6)#3-Ni(2)-F(4)	88.50(10)	F(5)-Ba(2)-F(2)#4	96.79(7)
F(6)-Ni(2)-F(4)	91.50(10)	F(8)#8-Ba(2)-F(2)#4	107.69(8)
F(4)#3-Ni(2)-F(4)	180	F(2)#1-Ba(2)-F(2)#4	63.57(10)
F(1)-Ni(3)-F(1)#8	180	F(5)#7-Ba(2)-F(7)	147.75(7)
F(1)-Ni(3)-F(6)	89.06(10)	F(5)-Ba(2)-F(7)	80.49(7)
F(1)#8-Ni(3)-F(6)	90.94(10)	F(8)#8-Ba(2)-F(7)	65.93(5)
F(1)-Ni(3)-F(6)#8	90.94(10)	F(2)#1-Ba(2)-F(7)	67.57(7)
F(1)#8-Ni(3)-F(6)#8	89.06(10)	F(2)#4-Ba(2)-F(7)	125.43(7)
F(6)-Ni(3)-F(6)#8	180	F(5)#7-Ba(2)-F(7)#7	80.49(7)
F(1)-Ni(3)-F(7)#8	87.93(10)	F(5)-Ba(2)-F(7)#7	147.75(7)
F(1)#8-Ni(3)-F(7)#8	92.07(10)	F(8)#8-Ba(2)-F(7)#7	65.93(5)
F(6)-Ni(3)-F(7)#8	86.33(10)	F(2)#1-Ba(2)-F(7)#7	125.43(7)
F(6)#8-Ni(3)-F(7)#8	93.67(10)	F(2)#4-Ba(2)-F(7)#7	67.57(7)
F(1)-Ni(3)-F(7)	92.07(10)	F(7)-Ba(2)-F(7)#7	131.71(10)
F(1)#8-Ni(3)-F(7)	87.93(10)	F(5)#7-Ba(2)-F(1)#9	86.26(7)
F(6)-Ni(3)-F(7)	93.67(10)	F(5)-Ba(2)-F(1)#9	115.31(7)
F(6)#8-Ni(3)-F(7)	86.33(10)	F(8)#8-Ba(2)-F(1)#9	71.45(8)
F(7)#8-Ni(3)-F(7)	180.00(4)	F(2)#1-Ba(2)-F(1)#9	174.63(7)
Ni(3)-F(1)-Ni(1)	145.47(13)	F(2)#4-Ba(2)-F(1)#9	121.80(7)
Ni(3)-F(1)-Ba(3)	107.77(10)	F(7)-Ba(2)-F(1)#9	107.61(7)
Ni(1)-F(1)-Ba(3)	91.40(8)	F(7)#7-Ba(2)-F(1)#9	59.37(6)
Ni(3)-F(1)-Ba(2)#8	105.47(9)	F(5)#7-Ba(2)-F(1)#8	115.31(7)
Ni(1)-F(1)-Ba(2)#8	100.42(9)	F(5)-Ba(2)-F(1)#8	86.25(7)
Ba(3)-F(1)-Ba(2)#8	96.34(7)	F(8)#8-Ba(2)-F(1)#8	71.45(8)
Ni(1)-F(2)-Ba(1)#13	135.06(11)	F(2)#1-Ba(2)-F(1)#8	121.80(7)
Ni(1)-F(2)-Ba(2)#5	99.85(10)	F(2)#4-Ba(2)-F(1)#8	174.63(7)
Ba(1)#13-F(2)-Ba(2)#5	111.00(8)	F(7)-Ba(2)-F(1)#8	59.37(6)
Ni(1)-F(2)-Ba(1)#6	98.83(10)	F(7)#7-Ba(2)-F(1)#8	107.61(7)
Ba(1)#13-F(2)-Ba(1)#6	96.56(8)	F(1)#9-Ba(2)-F(1)#8	52.83(9)
Ba(2)#5-F(2)-Ba(1)#6	115.37(8)	F(5)#7-Ba(2)-O(1)#8	59.99(8)
Ni(1)-F(3)-Ba(3)	97.47(13)	F(5)-Ba(2)-O(1)#8	59.99(8)
Ni(1)-F(3)-Ba(1)#6	106.52(9)	F(8)#8-Ba(2)-O(1)#8	120.18(10)
Ba(3)-F(3)-Ba(1)#6	111.75(8)	F(2)#1-Ba(2)-O(1)#8	122.24(8)
Ni(1)-F(3)-Ba(1)	106.52(9)	F(2)#4-Ba(2)-O(1)#8	122.24(8)
Ba(3)-F(3)-Ba(1)	111.75(8)	F(7)-Ba(2)-O(1)#8	103.42(6)
Ba(1)#6-F(3)-Ba(1)	120.02(12)	F(7)#7-Ba(2)-O(1)#8	103.42(6)
Ni(2)-F(4)-Ba(1)#3	132.01(11)	F(1)#9-Ba(2)-O(1)#8	55.68(8)
Ni(2)-F(4)-Ba(1)#12	90.59(9)	F(1)#8-Ba(2)-O(1)#8	55.68(8)
Ba(1)#3-F(4)-Ba(1)#12	93.84(7)	F(8)-Ba(3)-F(3)	131.92(11)
Ni(2)-F(4)-Ba(3)#3	86.50(8)	F(8)-Ba(3)-F(5)#10	82.38(8)
Ba(1)#3-F(4)-Ba(3)#3	97.51(7)	F(3)-Ba(3)-F(5)#10	134.41(7)
Ba(1)#12-F(4)-Ba(3)#3	167.01(10)	F(8)-Ba(3)-F(5)#3	82.38(8)

Ni(2)-F(5)-Ba(3)#3	99.00(9)	F(3)-Ba(3)-F(5)#3	134.41(7)
Ni(2)-F(5)-Ba(2)	132.96(11)	F(5)#10-Ba(3)-F(5)#3	67.39(10)
Ba(3)#3-F(5)-Ba(2)	110.76(9)	F(8)-Ba(3)-F(1)#6	74.86(9)
Ni(2)-F(5)-Ba(1)#4	92.59(9)	F(3)-Ba(3)-F(1)#6	62.66(8)
Ba(3)#3-F(5)-Ba(1)#4	93.61(7)	F(5)#10-Ba(3)-F(1)#6	114.39(7)
Ba(2)-F(5)-Ba(1)#4	119.86(9)	F(5)#3-Ba(3)-F(1)#6	156.49(7)
Ni(2)-F(6)-Ni(3)	147.46(14)	F(8)-Ba(3)-F(1)	74.86(9)
Ni(2)-F(6)-Ba(1)#12	97.69(9)	F(3)-Ba(3)-F(1)	62.66(8)
Ni(3)-F(6)-Ba(1)#12	109.46(10)	F(5)#10-Ba(3)-F(1)	156.49(7)
Ni(2)-F(6)-Ba(3)	91.84(9)	F(5)#3-Ba(3)-F(1)	114.39(7)
Ni(3)-F(6)-Ba(3)	103.83(10)	F(1)#6-Ba(3)-F(1)	54.04(9)
Ba(1)#12-F(6)-Ba(3)	93.27(8)	F(8)-Ba(3)-F(6)	75.86(5)
Ni(3)-F(7)-Ba(1)	128.70(11)	F(3)-Ba(3)-F(6)	99.11(5)
Ni(3)-F(7)-Ba(2)	103.84(9)	F(5)#10-Ba(3)-F(6)	120.73(7)
Ba(1)-F(7)-Ba(2)	110.90(8)	F(5)#3-Ba(3)-F(6)	55.61(7)
Ni(3)-F(7)-Ba(1)#5	103.77(9)	F(1)#6-Ba(3)-F(6)	111.78(7)
Ba(1)-F(7)-Ba(1)#5	98.93(7)	F(1)-Ba(3)-F(6)	59.33(6)
Ba(2)-F(7)-Ba(1)#5	109.47(8)	F(8)-Ba(3)-F(6)#6	75.86(5)
Ba(3)-F(8)-Ba(2)#8	104.78(12)	F(3)-Ba(3)-F(6)#6	99.11(5)
Ba(3)-F(8)-Ba(1)#12	100.18(9)	F(5)#10-Ba(3)-F(6)#6	55.61(7)
Ba(2)#8-F(8)-Ba(1)#12	115.72(7)	F(5)#3-Ba(3)-F(6)#6	120.73(7)
Ba(3)-F(8)-Ba(1)#14	100.18(9)	F(1)#6-Ba(3)-F(6)#6	59.34(6)
Ba(2)#8-F(8)-Ba(1)#14	115.72(7)	F(1)-Ba(3)-F(6)#6	111.78(7)
Ba(1)#12-F(8)-Ba(1)#14	116.51(12)	F(6)-Ba(3)-F(6)#6	151.71(10)
Ni(1)-O(1)-Ba(3)#15	174.3(2)	F(8)-Ba(3)-F(4)#10	132.56(5)
Ni(1)-O(1)-Ba(2)#8	87.31(16)	F(3)-Ba(3)-F(4)#10	71.97(7)
Ba(3)#15-O(1)-Ba(2)#8	86.96(12)	F(5)#10-Ba(3)-F(4)#10	62.48(7)
F(7)-Ba(1)-F(2)#1	70.52(7)	F(5)#3-Ba(3)-F(4)#10	109.10(7)
F(7)-Ba(1)-F(3)	91.51(8)	F(1)#6-Ba(3)-F(4)#10	90.94(7)
F(2)#1-Ba(1)-F(3)	145.23(9)	F(1)-Ba(3)-F(4)#10	131.50(7)
F(7)-Ba(1)-F(6)#2	133.01(7)	F(6)-Ba(3)-F(4)#10	148.90(7)
F(2)#1-Ba(1)-F(6)#2	83.66(7)	F(6)#6-Ba(3)-F(4)#10	58.45(7)
F(3)-Ba(1)-F(6)#2	127.85(8)	F(8)-Ba(3)-F(4)#3	132.56(5)
F(7)-Ba(1)-F(8)#2	151.08(8)	F(3)-Ba(3)-F(4)#3	71.97(7)
F(2)#1-Ba(1)-F(8)#2	130.66(9)	F(5)#10-Ba(3)-F(4)#3	109.10(7)
F(3)-Ba(1)-F(8)#2	59.84(9)	F(5)#3-Ba(3)-F(4)#3	62.48(7)
F(6)#2-Ba(1)-F(8)#2	74.28(8)	F(1)#6-Ba(3)-F(4)#3	131.50(7)
F(7)-Ba(1)-F(4)#3	80.44(7)	F(1)-Ba(3)-F(4)#3	90.93(7)
F(2)#1-Ba(1)-F(4)#3	75.26(7)	F(6)-Ba(3)-F(4)#3	58.45(7)
F(3)-Ba(1)-F(4)#3	72.47(9)	F(6)#6-Ba(3)-F(4)#3	148.90(7)
F(6)#2-Ba(1)-F(4)#3	130.66(7)	F(4)#10-Ba(3)-F(4)#3	90.69(9)
F(8)#2-Ba(1)-F(4)#3	86.54(9)	F(8)-Ba(3)-O(1)#11	138.00(13)
F(7)-Ba(1)-F(7)#4	133.02(6)	F(3)-Ba(3)-O(1)#11	90.08(12)
F(2)#1-Ba(1)-F(7)#4	66.30(7)	F(5)#10-Ba(3)-O(1)#11	63.19(9)

F(3)-Ba(1)-F(7)#4	114.00(8)	F(5)#3-Ba(3)-O(1)#11	63.19(9)
F(6)#2-Ba(1)-F(7)#4	59.01(6)	F(1)#6-Ba(3)-O(1)#11	139.82(9)
F(8)#2-Ba(1)-F(7)#4	64.47(8)	F(1)-Ba(3)-O(1)#11	139.81(9)
F(4)#3-Ba(1)-F(7)#4	71.66(7)	F(6)-Ba(3)-O(1)#11	100.72(5)
F(7)-Ba(1)-F(4)#2	73.26(7)	F(6)#6-Ba(3)-O(1)#11	100.72(5)
F(2)#1-Ba(1)-F(4)#2	74.06(7)	F(4)#10-Ba(3)-O(1)#11	50.91(6)
F(3)-Ba(1)-F(4)#2	130.24(9)	F(4)#3-Ba(3)-O(1)#11	50.91(6)
F(6)#2-Ba(1)-F(4)#2	61.99(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,z-1/2 #2 x-1/2,y,-z+1/2 #3 -x+1,-y+1,-z

#4 -x+1/2,-y+1,z-1/2 #5 -x+1/2,-y+1,z+1/2 #6 x,-y+1/2,z

#7 x,-y+3/2,z #8 -x+1,-y+1,-z+1 #9 -x+1,y+1/2,-z+1

#10 -x+1,y-1/2,-z #11 x,y,z-1 #12 x+1/2,y,-z+1/2

#13 -x+1/2,y-1/2,z+1/2 #14 x+1/2,-y+1/2,-z+1/2

#15 x,y,z+1

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3) for $Ba_4Ni_3F_{14}·H_2O$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka^*b^*U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
Ba(1)	8(1)	11(1)	10(1)	0(1)	-1(1)	0(1)
Ba(2)	10(1)	11(1)	7(1)	0	-1(1)	0
Ba(3)	9(1)	13(1)	8(1)	0	1(1)	0
Ni(1)	6(1)	9(1)	8(1)	0	0(1)	0
Ni(2)	7(1)	9(1)	6(1)	0(1)	0(1)	1(1)
Ni(3)	6(1)	8(1)	5(1)	0(1)	0(1)	0(1)
F(1)	12(1)	8(1)	17(1)	0(1)	2(1)	-2(1)
F(2)	11(1)	13(1)	21(1)	4(1)	2(1)	-3(1)
F(3)	11(1)	16(2)	12(1)	0	-4(1)	0
F(4)	11(1)	17(1)	17(1)	-1(1)	2(1)	-3(1)
F(5)	15(1)	13(1)	12(1)	-1(1)	4(1)	3(1)
F(6)	15(1)	19(1)	5(1)	0(1)	0(1)	2(1)
F(7)	9(1)	16(1)	13(1)	1(1)	-3(1)	-1(1)
F(8)	10(1)	17(2)	14(1)	0	1(1)	0
O(1)	31(2)	14(2)	9(2)	0	-6(2)	0