Supplementary Information for

$Na_nMTh_6F_{30}$ – a Large Family of Quaternary Thorium Fluorides

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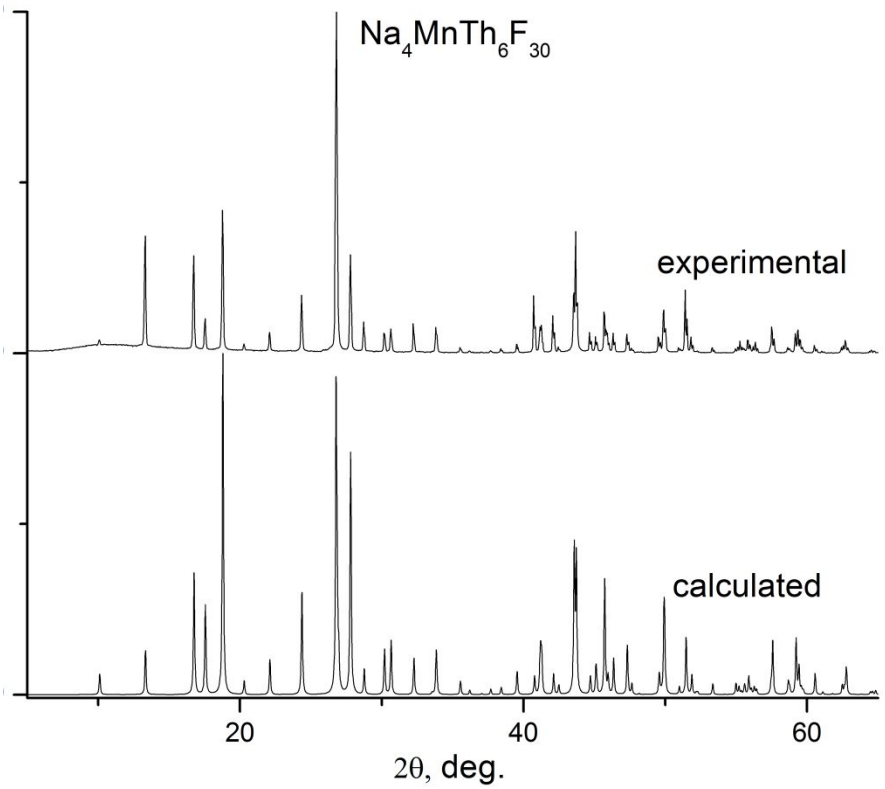

Figure S1. Experimental and calculated powder diffraction patterns of $Na_4MnTh_6F_{30}$.

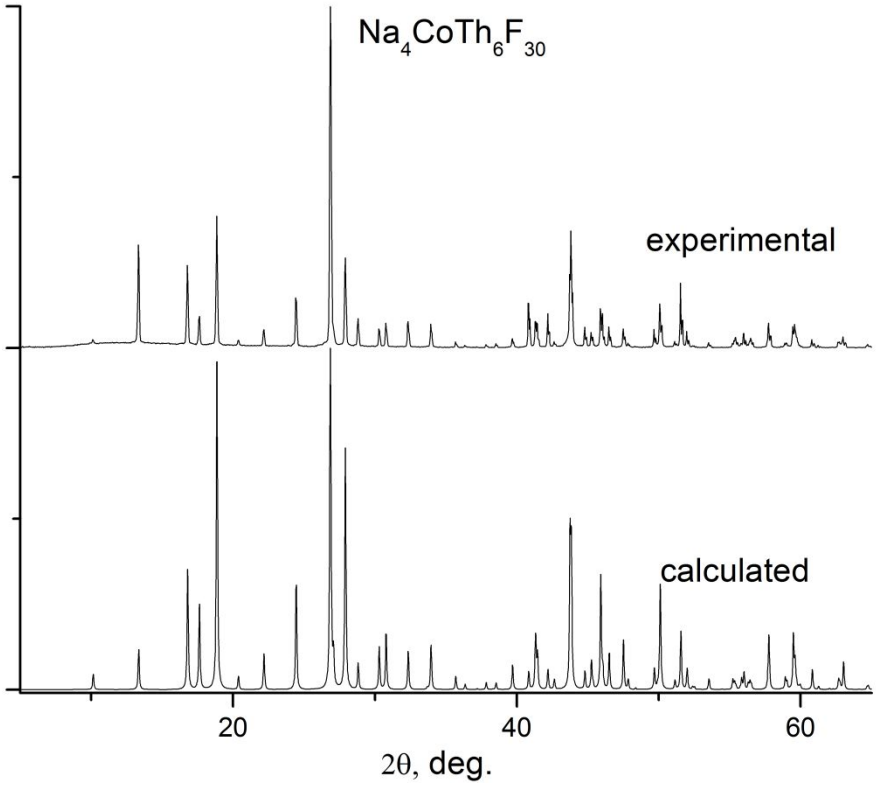

Figure S2. Experimental and calculated PXRD patterns of $Na_4CoTh_6F_{30}$.

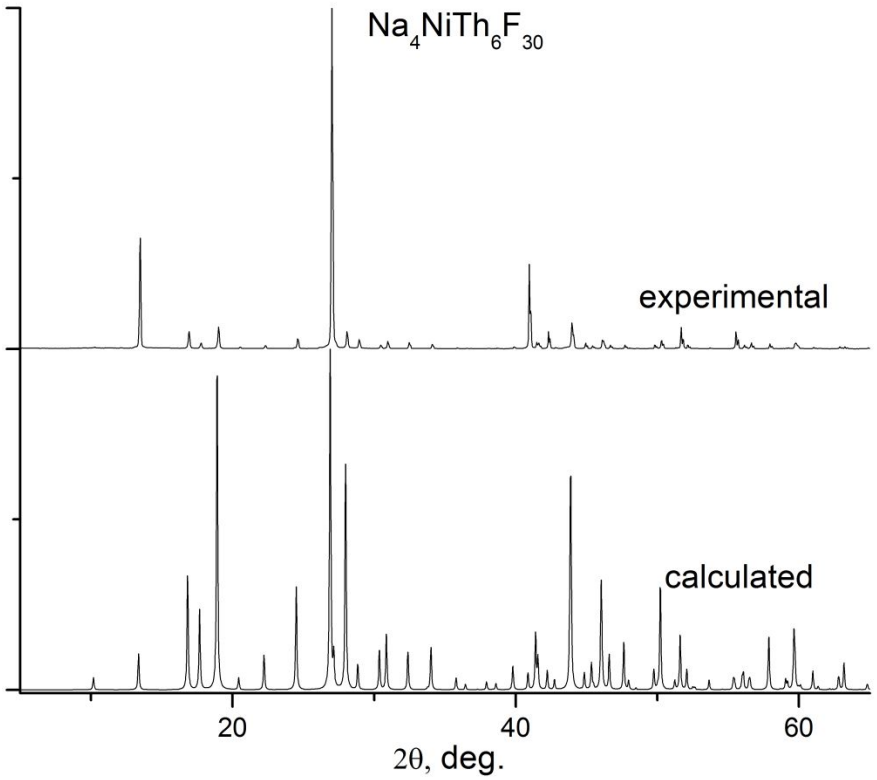

Figure S3. Experimental and calculated PXRD patterns of $Na_4NiTh_6F_{30}$.

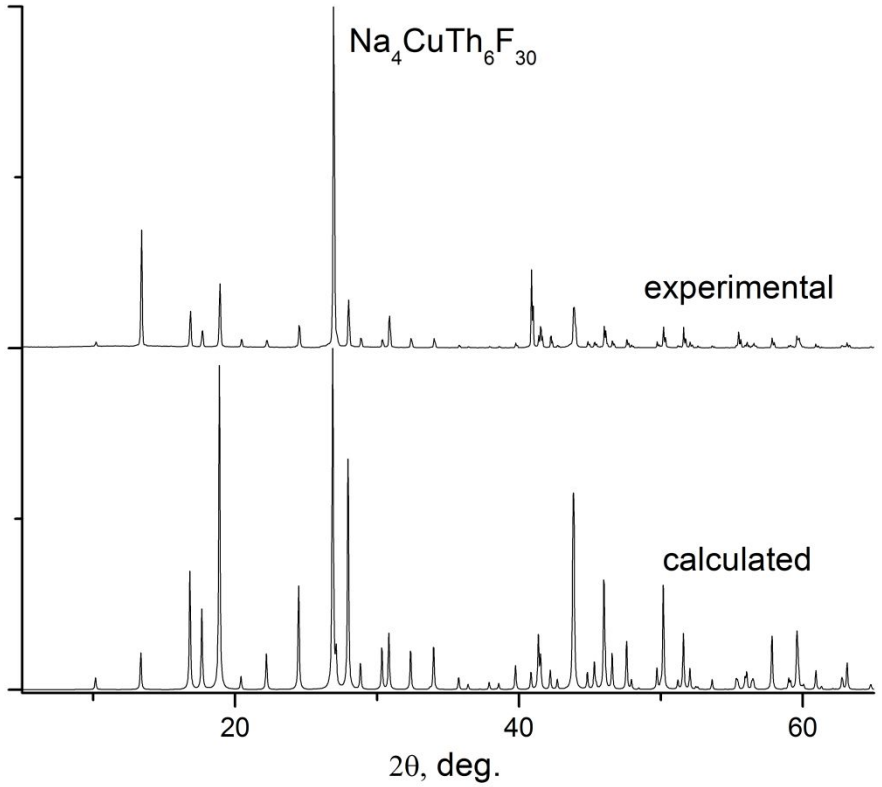

Figure S4. Experimental and calculated PXRD patterns of $Na_4CuTh_6F_{30}$.

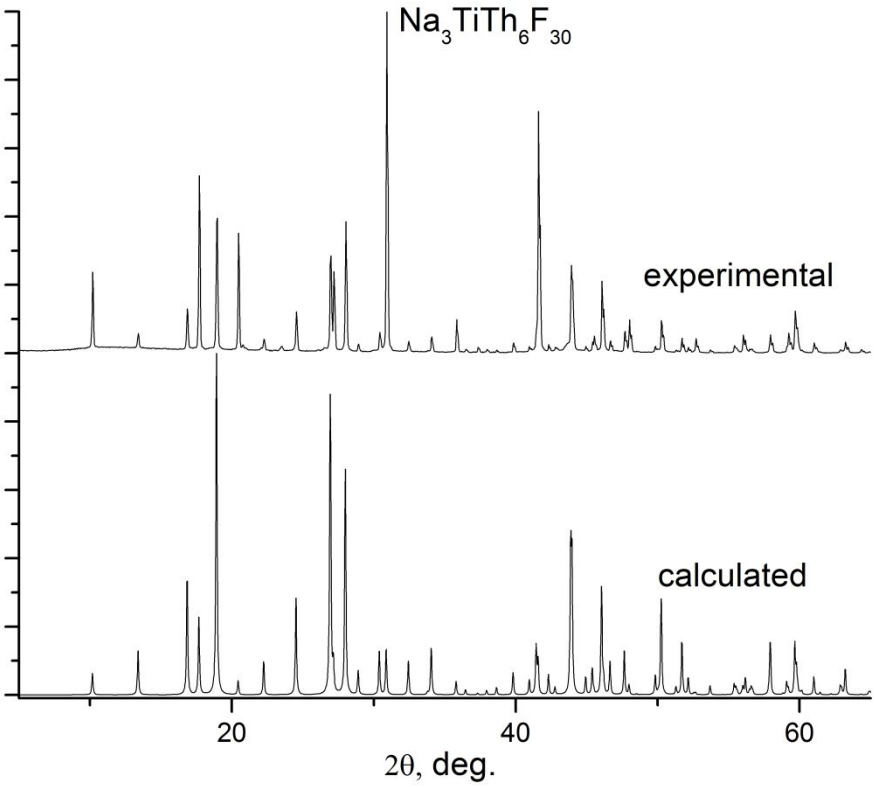

Figure S5. Experimental and calculated PXRD patterns of $Na_3TiTh_6F_{30}$.

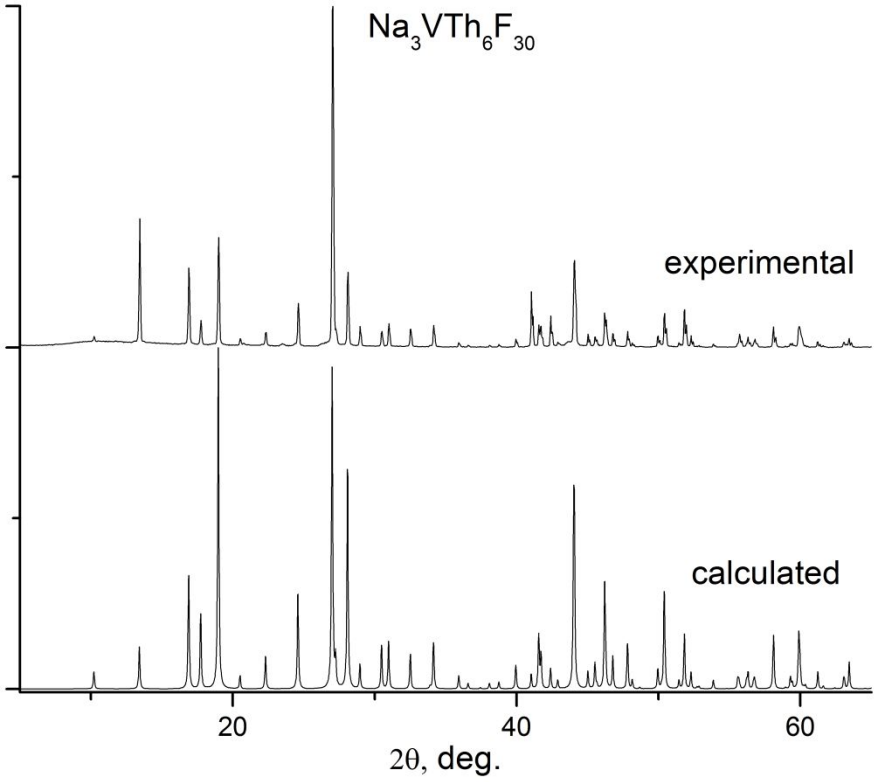

Figure S6. Experimental and calculated PXRD patterns of $Na_3VTh_6F_{30}$.

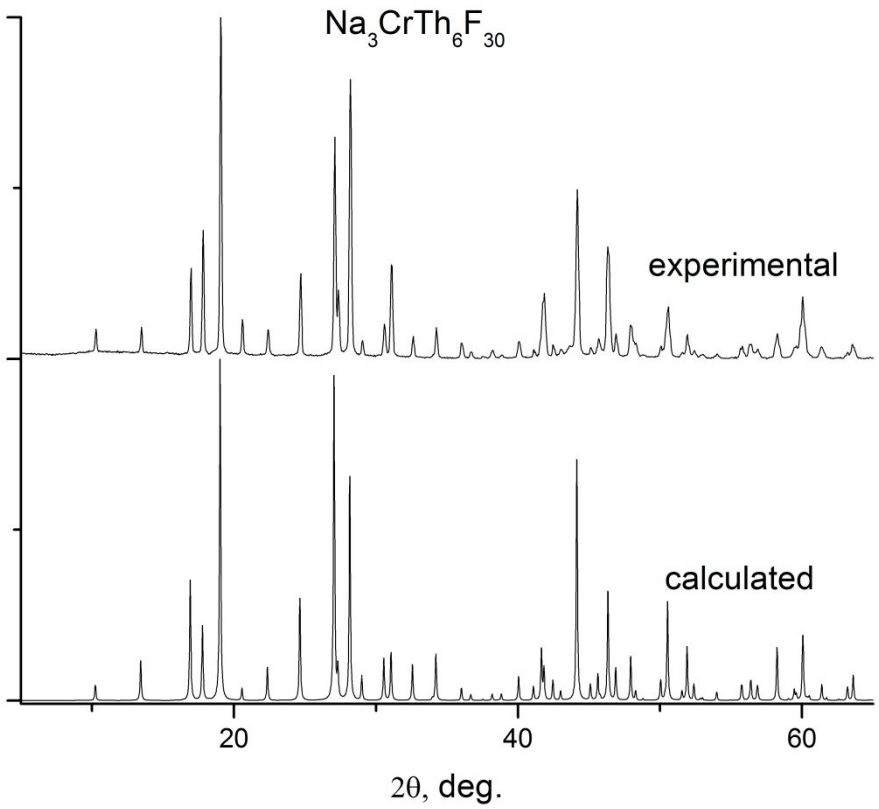

Figure S7. Experimental and calculated PXRD patterns of $Na_3CrTh_6F_{30}$.

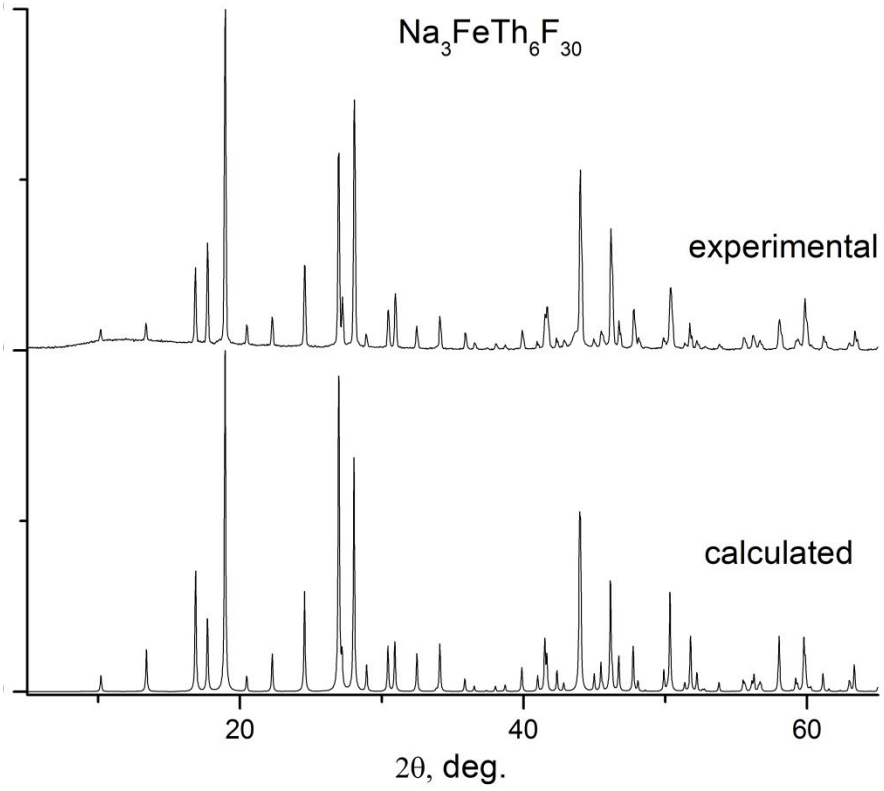

Figure S8. Experimental and calculated PXRD patterns of $Na_3FeTh_6F_{30}$.

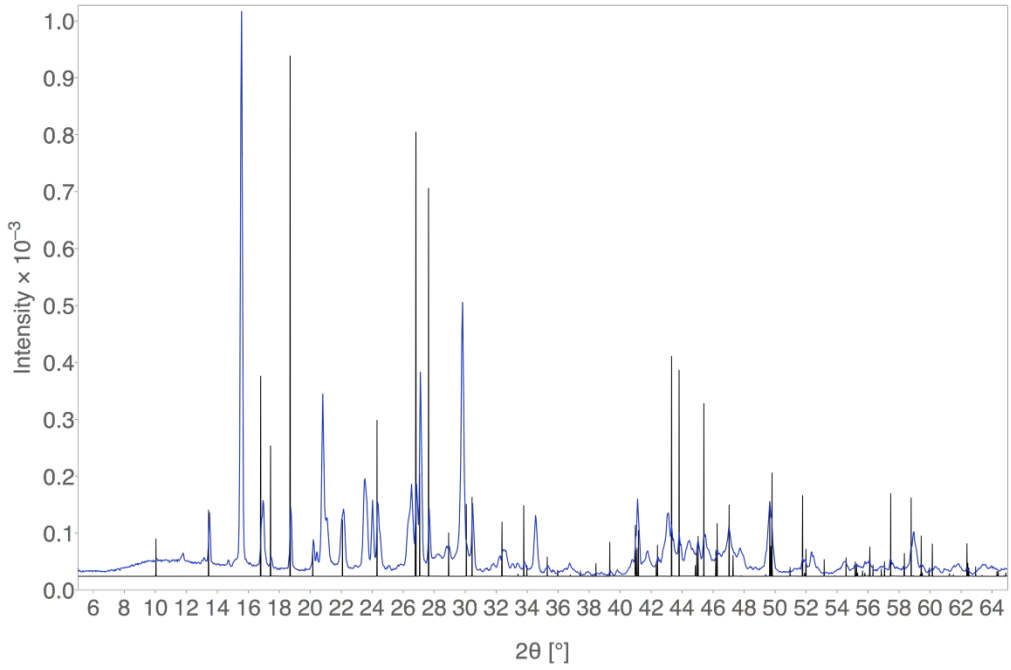

Figure S9. Experimental and calculated PXRD patterns of $Na_{4.39}Lu_{0.54}Th_6F_{30}$.

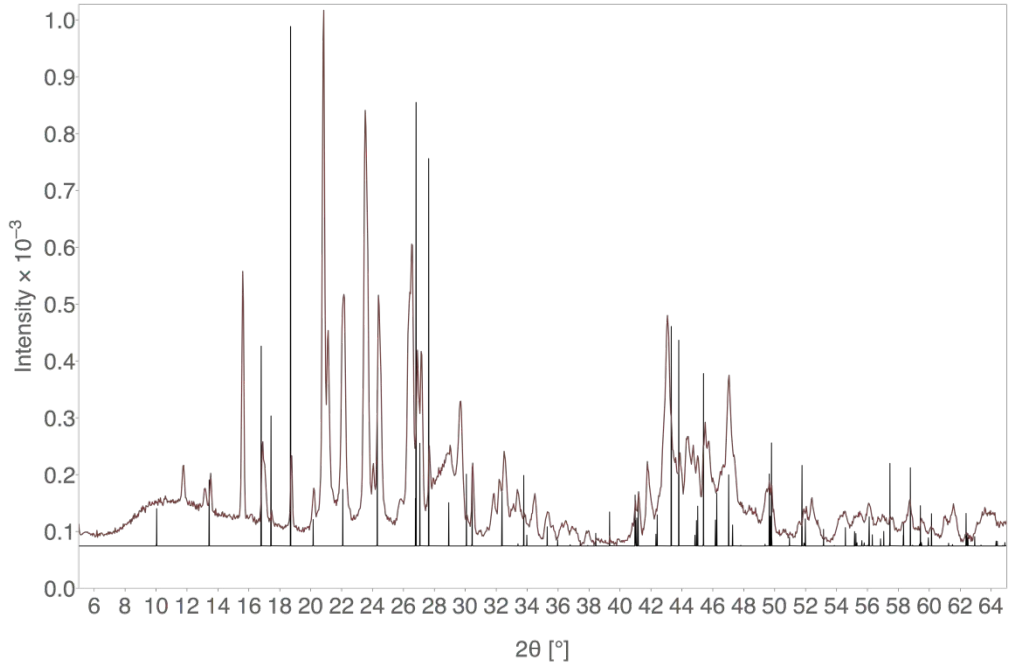

Figure S10. Experimental PXRD pattern of the product of the reaction with Yb_2O_3 and calculated pattern of $Na_{4.39}Lu_{0.54}Th_6F_{30}$.

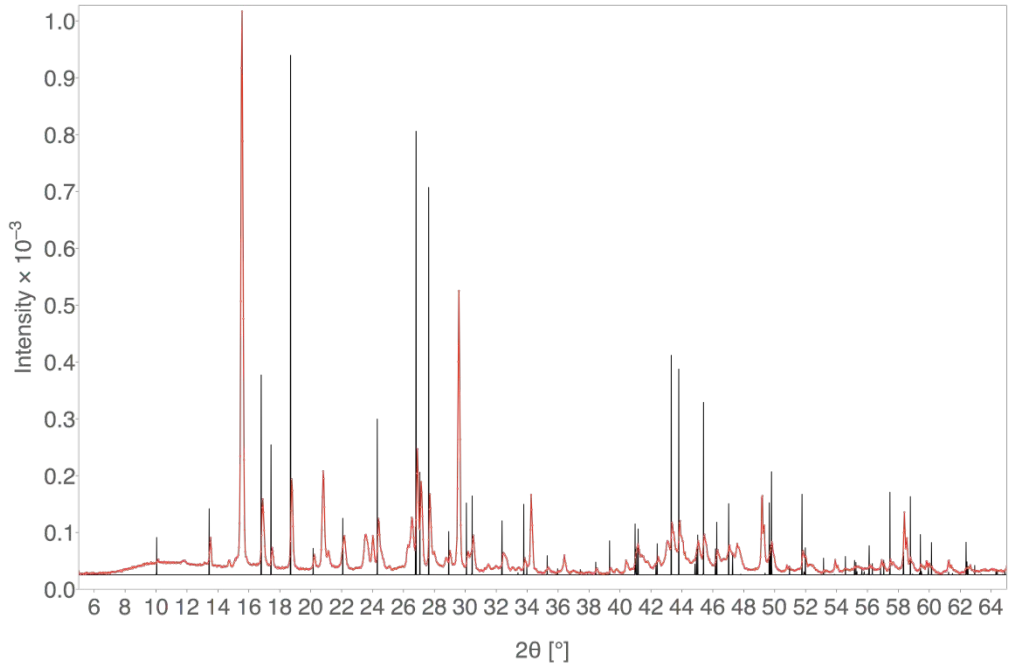

Figure S11. Experimental and calculated PXRD patterns of $Na_{4.11}Tm_{0.63}Th_6F_{30}$.

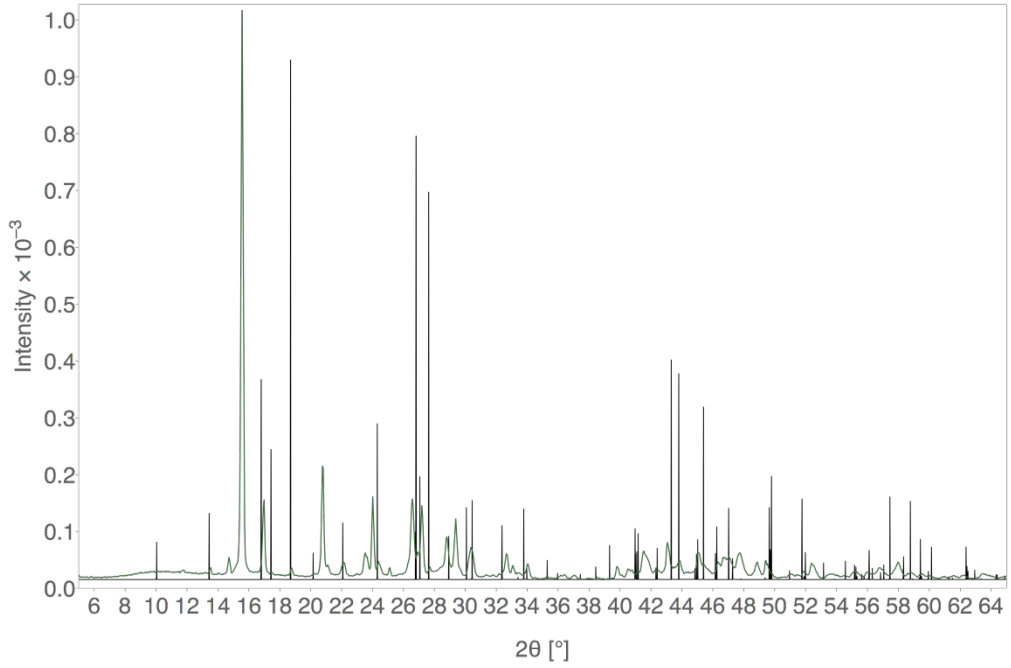

Figure S12. Experimental PXRD pattern of the product of the reaction with Er_2O_3 and calculated pattern of $Na_{4.39}Lu_{0.54}Th_6F_{30}$.

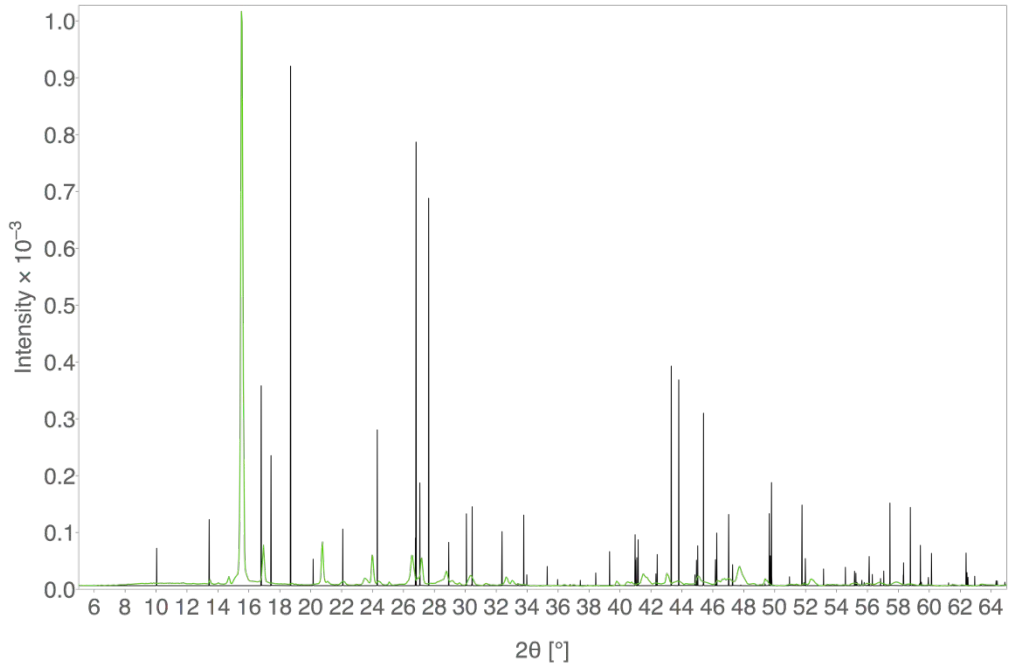

Figure S13. Experimental PXRD pattern of the product of the reaction with Ho_2O_3 and calculated pattern of $Na_{4.39}Lu_{0.54}Th_6F_{30}$.

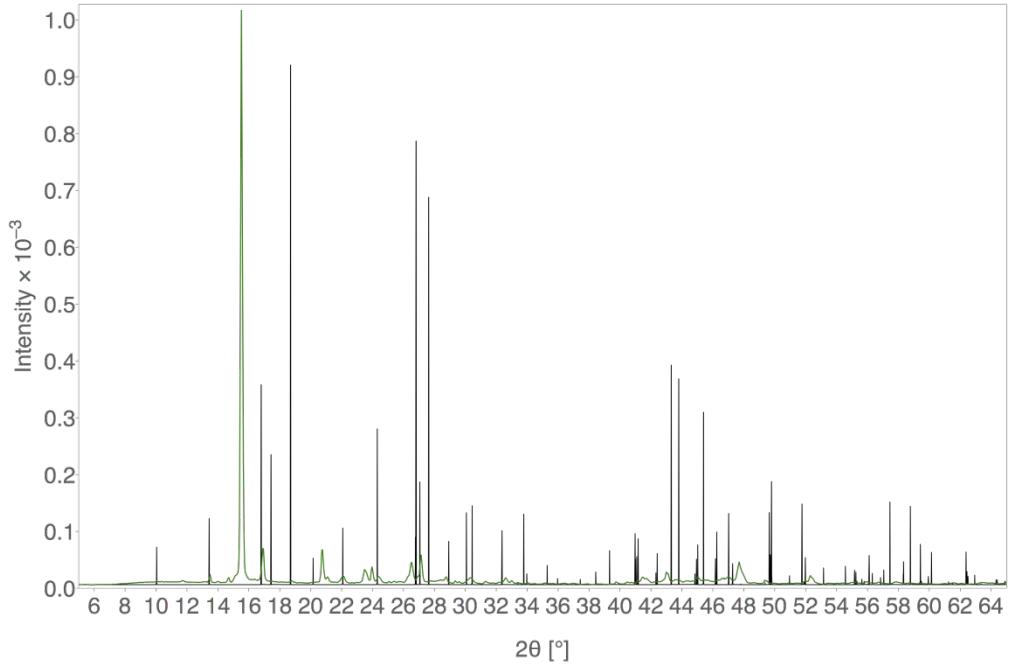

Figure S14. Experimental PXRD pattern of the product of the reaction with Dy_2O_3 and calculated pattern of $Na_{4.39}Lu_{0.54}Th_6F_{30}$.

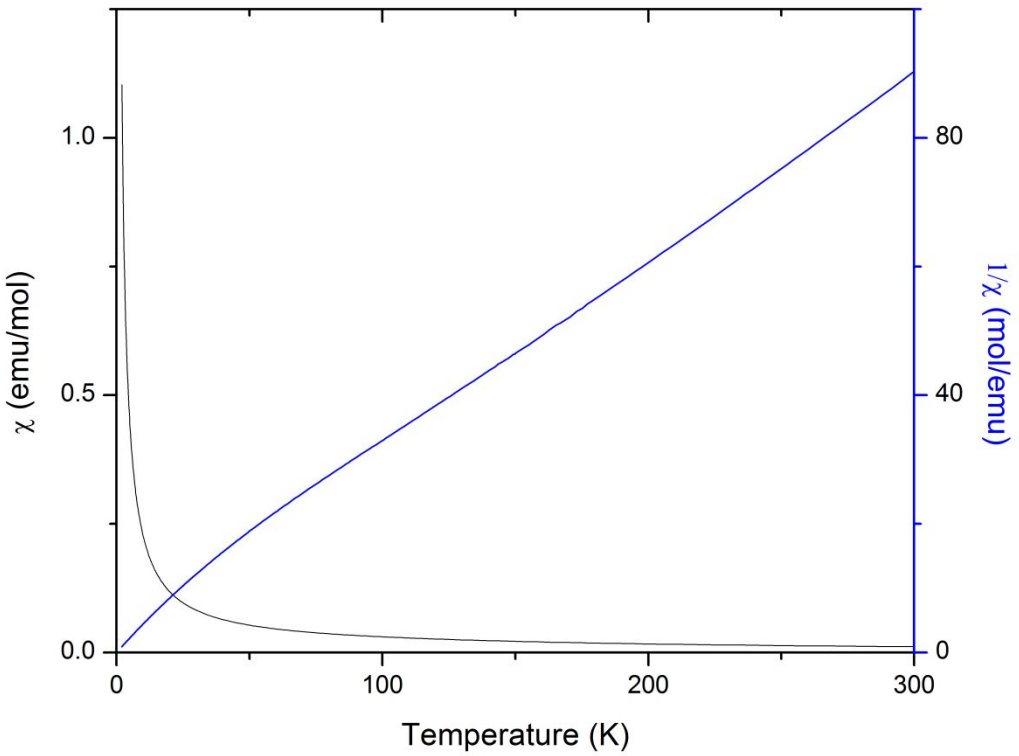

Figure S15. Temperature dependence of the molar and inverse molar susceptibility for $Na_4CoTh_6F_{30}$.

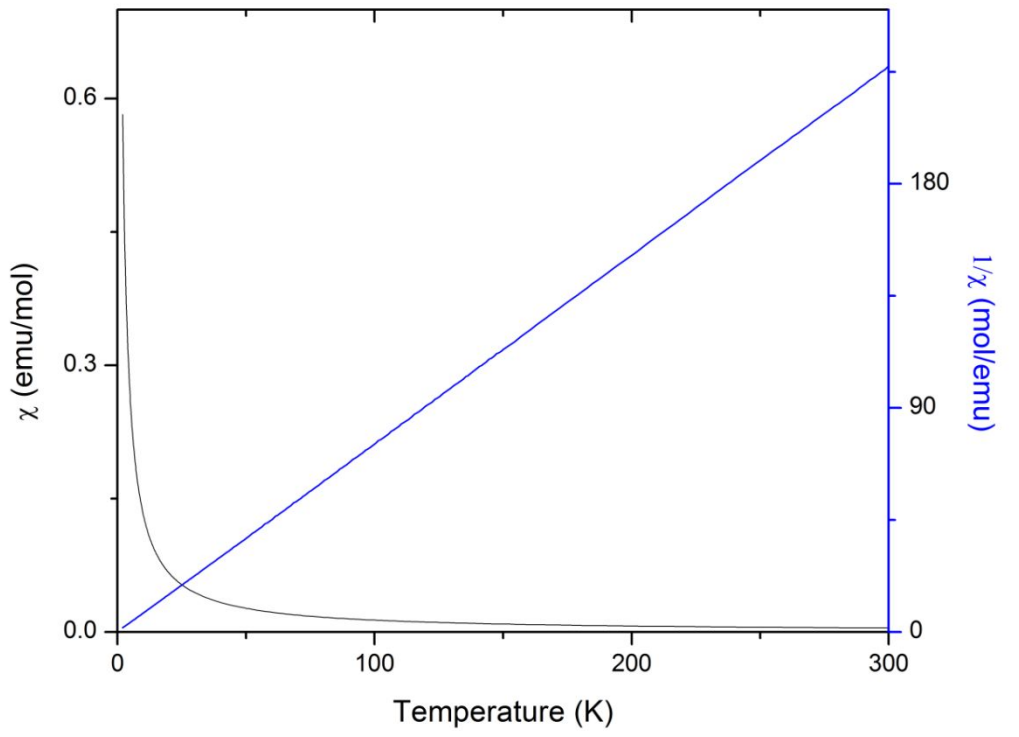

Figure S16. Temperature dependence of the molar and inverse molar susceptibility for $Na_4NiTh_6F_{30}$.

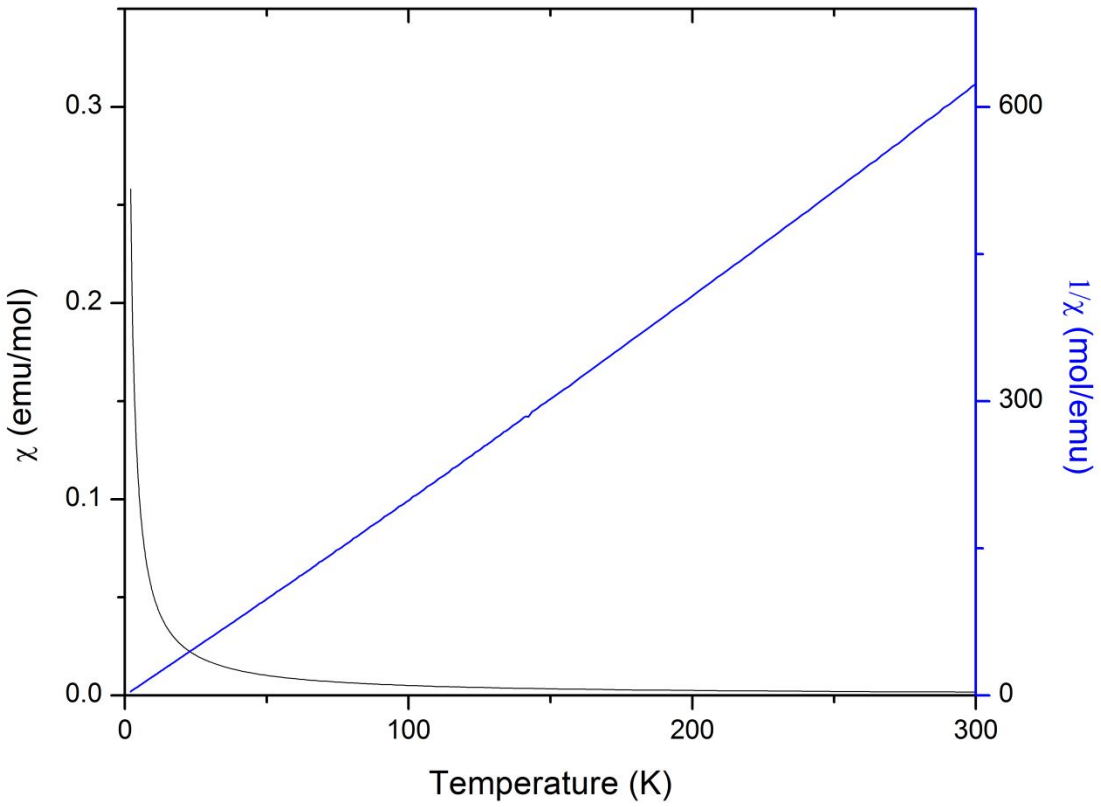

Figure S17. Temperature dependence of the molar and inverse molar susceptibility for $Na_4CuTh_6F_{30}$.

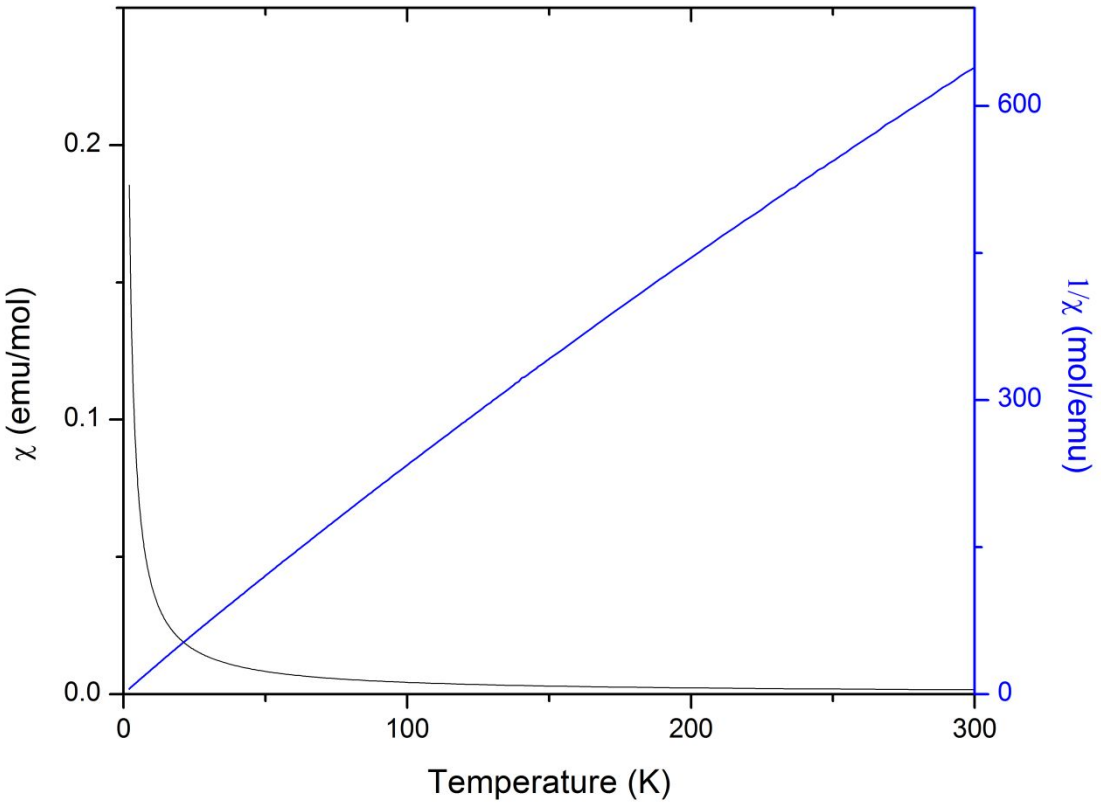

Figure S18. Temperature dependence of the molar and inverse molar susceptibility for $Na_3VTh_6F_{30}$.

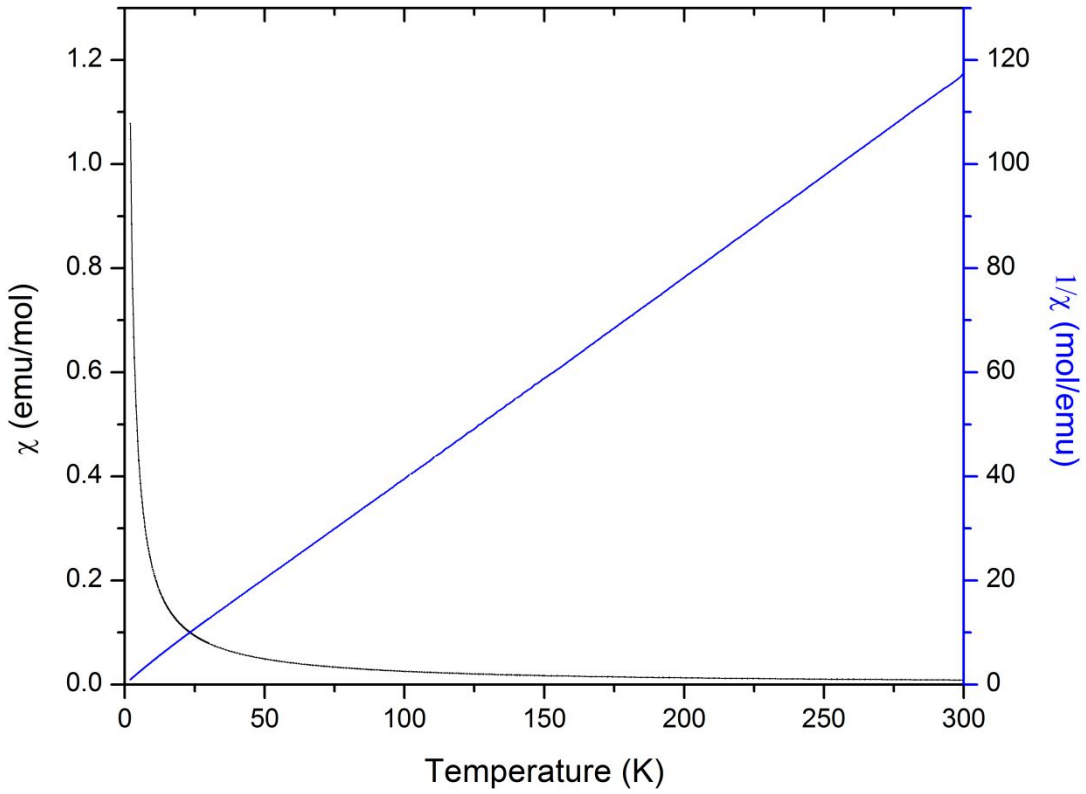

Figure S19. Temperature dependence of the molar and inverse molar susceptibility for $Na_3CrTh_6F_{30}$.

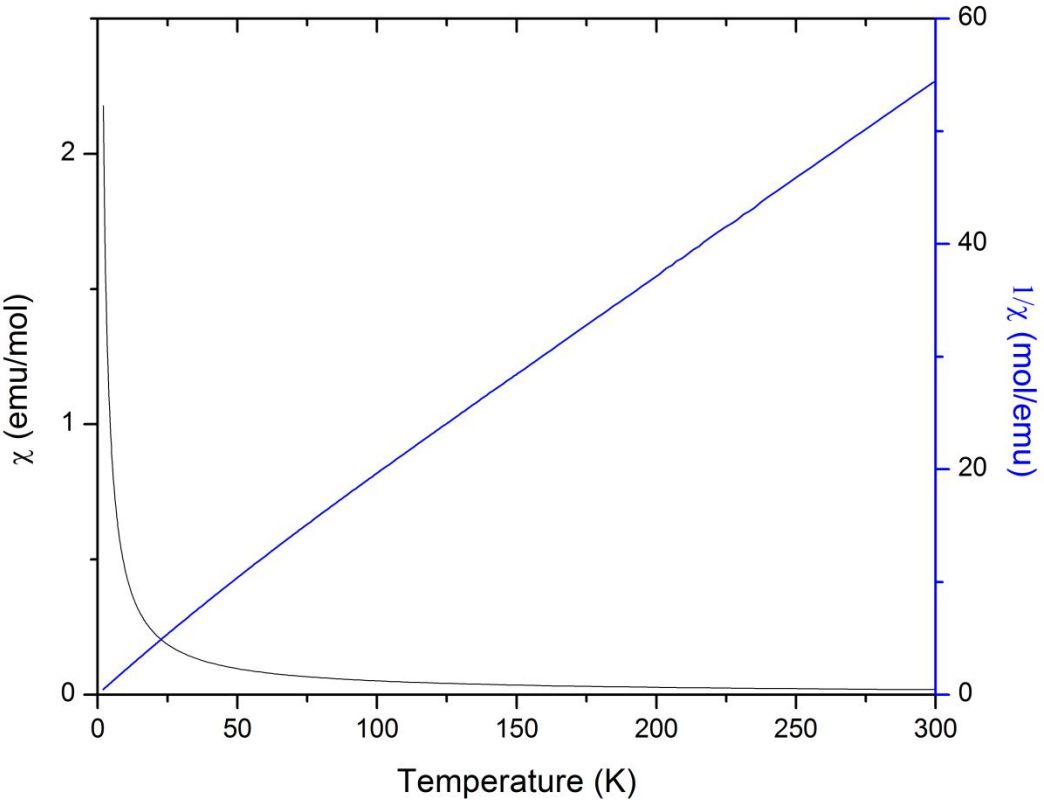

Figure S20. Temperature dependence of the molar and inverse molar susceptibility for $Na_3FeTh_6F_{30}$.

Table S1. Elemental compositions of the quaternary fluorides determined by EDS.

Mg (**1**)		Mn (**2**)		Co (**3**)	
Element	Atom %	Element	Atom %	Element	Atom %
Mg	4.58	Mn	4.92	Co	4.67
Na	15.55	Na	13.91	Na	12.43
Th	11.76	Th	15.46	Th	15.61
F	68.11	F	65.71	F	67.29
Ni (**4**)		Cu (**5**)		Zn (**6**)	
Element	Atom %	Element	Atom %	Element	Atom %
Ni	4.36	Cu	4.12	Zn	5.16
Na	13.12	Na	12.65	Na	n.d./overlap
Th	16.68	Th	15.54	Th	16.91
F	65.76	F	67.69	F	77.92
Al (**7**)		Sc (**8**)		Ti (**9**)	
Element	Atom %	Element	Atom %	Element	Atom %
Al	3.96	Sc	6.25	Ti	4.54
Na	12.08	Na	9.14	Na	11.94
Th	17.02	Th	10.34	Th	17.86
F	66.94	F	74.27	F	65.66
V (**10**)		Cr (**11**)		Fe (**12**)	
Element	Atom %	Element	Atom %	Element	Atom %
V	3.72	Cr	5.84	Fe	4.29
Na	12.96	Na	13.83	Na	14.42
Th	17.64	Th	17.15	Th	18.37
F	65.68	F	66.94	F	62.92
Ga (**13**)		In (**14**)		$Na_{3.87}Y_{0.71}$ (**15**)	
Element	Atom %	Element	Atom %	Element	Atom %
Ga	6.06	In	3.58	Y	1.79
Na	9.30	Na	6.89	Na	13.58
Th	15.31	Th	19.44	Th	18.50
F	69.32	F	70.10	F	66.13
$Na_{4.39}Lu_{0.54}$ (**16**)		$Na_{4.11}Tm_{0.63}$ (**17**)		$Na_3ScU_6F_{30}$ (**18**)	
Element	Atom %	Element	Atom %	Element	Atom %
Lu	1.74	Tm	1.15	Sc	1.58
Na	14.13	Na	15.94	Na	12.10
Th	13.39	Th	11.35	Th	12.81
F	70.73	F	71.57	F	73.51
$Na_{3.84}In_{0.72}U_6F_{30}$ (**19**)					
Element	Atom %				
In	2.45				
Na	13.56				
Th	11.51				
F	72.49				

Table S2. Comparison of the atomic coordinates obtained from the structural model for $Na_4ZnTh_6F_{30}$ in the $P\bar{3}c1$ space group and the previously reported $Na_3ZnTh_6F_{29}$.[43]

Basis atoms in $P\bar{3}c1$ sp. gr.	Atomic coordinates in the $P\bar{3}c1$ sp. gr.	Origin shift	Atomic coordinates in the $P321$ sp. gr.	Basis atoms in $P321$ sp. gr. reported in ref.[43]
Th1 (0.39797 0.32305 0.39825)	Th1 (0.39797 0.32305 0.39825) Th1a (0.39797 0.07492 0.89825)	(0 0 ¼)	Th1 (0.39797 0.32305 0.64825) Th2 (0.39797 0.07492 0.14825)	Th2 (0.4007 0.3235 0.6484) Th1 (0.4028 0.0794 0.1491)
Zn1 (0 0 ¼)	Zn1 (0 0 ¼) Zn1a (0 0 ¾)		Zn1 (0 0 ½) Zn2 (0 0 0)	Zn2 (0 0 ½) Zn1 (0 0 0)
Na1 (⅓ ⅔ 0.3415)	Na1 (⅓ ⅔ 0.3415) Na1b (⅓ ⅔ 0.8415)		Na1 (⅓ ⅔ 0.5915) Na2 (⅓ ⅔ 0.0915)	Na3 (⅓ ⅔ 0.6012) Na2 (⅓ ⅔ 0.0893)
Na2 (0 0 ½)	Na2 (0 0 0)		Na3 (0 0 0)	Na1 (0 0 0.2624)
Na3 (0.0382 0.3320.2849) 0.1667 occupancy	Na3 (0.0382 0.3320.2849) Na3b (0.2938 0.3320 0.7849)		Na4 (0.0382 0.3320.5349) Na5 (0.2938 0.3320 0.0349)	– –
F1 (0.3083 0.4405 0.2821)	F1c (0.4405 0.3083 0.2179) F1b (0.1322 0.4405 0.7821)		F1 (0.4405 0.3083 0.4679) F2 (0.1322 0.4405 0.0321)	F10 (0.4433 0.3134 0.4661) F1 (0.1315 0.4369 0.0348)
F2 (0.1881 0.3108 0.4807)	F2c (0.3108 0.1881 0.0193) F2b (0.1227 0.3108 0.9807)		F3 (0.3108 0.1881 0.2693) F4 (0.1227 0.3108 0.2307)	F7 (0.3142 0.1933 0.2652) F5 (0.1229 0.3166 0.2231)
F3 (0.5343 0.4153 0.5524)	F3d (0.1190 0.5847 -0.0524) F3a (0.5343 0.1190 0.0524)		F5 (0.1190 0.5847 0.1976) F6 (0.5343 0.1190 0.3024)	F4 (0.1195 0.5861 0.2005) F6 (0.5244 0.1111 0.3086)
F4 (0.1863 0.1061 0.3397)	F4d (0.0802 0.8939 0.1603) F4a (0.1863 0.0802 0.8397)		F7 (0.0802 0.8939 0.4103) F8 (0.1863 0.0802 0.0897)	F9 (0.0840 0.8949 0.4104) F2 (0.2040 0.0898 0.0927) 0.667 occupancy
F5 (0.5098 0.1693 0.3629)	F5c (0.1693 0.5098 0.1371) F5a (0.5098 0.3405 0.8629)		F9 (0.1693 0.5098 0.3871) F10 (0.5098 0.3405 0.1129)	F8 (0.1510 0.4948 0.3989) F3 (0.5228 0.3404 0.1178)

*Symmetry codes: **a** (x, x-y, z+½), **b** ($\bar{x}$+y,y,z+½), **c** (y,x,$\bar{z}$+½), **d** (x-y,$\bar{y}$+1,$\bar{z}$+½)