

Electronic Supplementary Information

**Hydrogen bond-assisted crystallization: structure, growth
and characterization of a new mixed-anion transition metal
fluoride $\text{Na}_3\text{NH}_4(\text{TiF}_6)(\text{SO}_4) \cdot \text{H}_2\text{O}$**

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Table S1. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for NTS.

Atoms	U11	U22	U33	U23	U13	U12
Ti(1)	14(1)	15(1)	13(1)	0	-1(1)	0
Na(1)	50(1)	24(1)	23(1)	-4(1)	8(1)	-11(1)
Na(2)	22(1)	22(1)	20(1)	-1(1)	-2(1)	2(1)
S(1)	12(1)	14(1)	14(1)	0	0(1)	0
F(1)	33(1)	25(1)	23(1)	7(1)	-4(1)	5(1)
F(2)	33(1)	24(1)	21(1)	-7(1)	-1(1)	-1(1)
F(3)	15(1)	43(1)	34(1)	0	0(1)	0
F(4)	14(1)	29(1)	24(1)	0	0(1)	0
O(1)	26(1)	22(1)	29(1)	2(1)	2(1)	11(1)
O(2)	16(1)	36(2)	17(1)	0	5(1)	0
O(3)	23(1)	28(1)	16(1)	0	-6(1)	0
O(4)	23(1)	30(1)	21(1)	0	1(1)	0
N(5)	39(1)	39(2)	21(2)	0	2(1)	0

Table S2. Summary of hydrothermal conditions for the Tests 1 - 6.

Test	Autoclave (mL)	Na ₂ SO ₄ /(NH ₄) ₂ TiF ₆ / NaF (mmol)	H ₂ O (mL)
1	23	12 / 4 / 4	1
2	23	12 / 4 / 4	2
3	23	12 / 4 / 4	3
4	23	12 / 4 / 4	4
5	100	36 / 12 / 12	3
6	100	120 / 40 / 40	10

Table S3. Selected bond lengths (Å) and angles (deg.) for NTS.

Ti-F (Å)		S-O (Å)	
Ti(1)-F(1)	1.8445(19)×2	S(1)-O(1)	1.464(2)×2
Ti(1)-F(2)	1.8569(19)×2	S(1)-O(2)	1.482(3)
Ti(1)-F(3)	1.848(3)	S(1)-O(3)	1.465(3)
Ti(1)-F(4)	1.881(3)	average value	1.468
average value	1.855		
F-Ti-F (deg.)		O-S-O (deg.)	
F(1)#1-Ti(1)-F(1)	93.06(12)	O(1)#1-S(1)-O(1)	110.387(17)
F(1)-Ti(1)-F(2)	89.38(11)×2	O(1)-S(1)-O(2)	107.83(9)×2
F(1)-Ti(1)-F(3)	91.48(7)×2	O(1)-S(1)-O(3)	110.66(9)×2
F(1)-Ti(1)-F(4)	86.84(7)×2	O(3)-S(1)-O(2)	109.39(16)
F(2)-Ti(1)-F(4)	91.01(7)×2	average value	109.45
F(2)-Ti(1)-F(2)#2	88.08(12)		
F(3)-Ti(1)-F(2)	90.75(7)×2		
average value	90		

Note. Symmetry transformations used to generate equivalent atoms:

$$\#1 \ x, -y + 3/2, z \quad \#2 \ -x + 1/2, -y + 2, z - 1/2$$

Table S4. Hydrogen bond lengths (Å) and angles (deg.) for NTS.

Hydrogen bonds	Length (Å) (H ··· O/F)	Angle (deg.)
N(5)-H(5A) ··· O(2)	2.0941(756)	168.797(7768)
N(5)-H(5B) ··· O(1)	2.2633(430)×2	140.054(145)×2
N(5)-H(5C) ··· F(2)	2.3821(508)×2	133.997(4678)×2
O(4)-H(4A) ··· F(4)	2.0270(427)	165.410(4275)
O(4)-H(4B) ··· O(2)	2.1401(495)	176.569(5764)

Figure S1. Powder XRD of NTS.

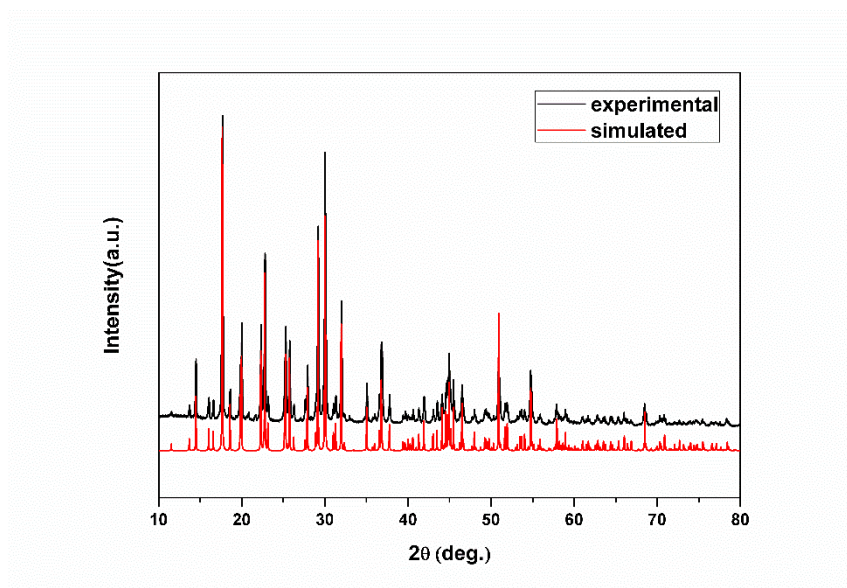
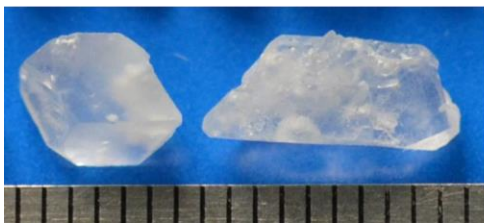


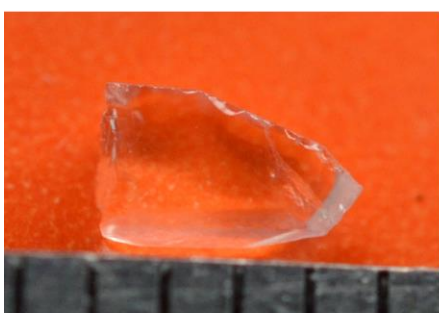
Figure S2. Photographs of representative crystals prepared in Tests 1 - 6. The length scale is 1 mm.



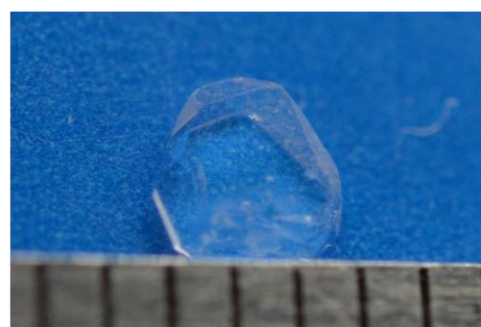
Test 1
average size, ca. $6.0 \times 5.0 \times 4.0 \text{ mm}^3$



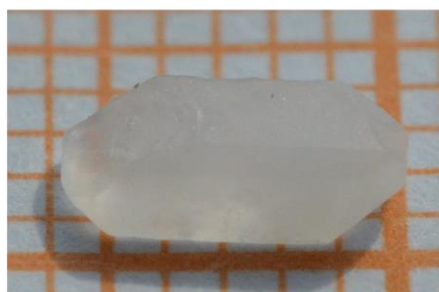
Test 2
average size, ca. $5.0 \times 2.5 \times 1.0 \text{ mm}^3$



Test 3
average size, ca. $3.5 \times 2.0 \times 1.0 \text{ mm}^3$



Test 4
average size, ca. $2.5 \times 2.0 \times 0.5 \text{ mm}^3$



Test 5
average size, ca. $6.0 \times 3.0 \times 2.0 \text{ mm}^3$



Test 6
average size, ca. $6.0 \times 2.0 \times 2.0 \text{ mm}^3$

Figure S3. The asymmetric unit and selected symmetry-equivalent atoms in NTS, showing the linkages and coordination spheres with thermal ellipsoids and atom labels. Symmetry codes: (#1) $x, -1/2 + y, -z$; (#2) $1/2 - x, 2 - y, -1/2 + z$; (#3) $1/2 + x, 1/2 - y, 1/2 - z$; (#4) $1/2 - x, 2 - y, 1/2 + z$; (#5) $-x, -1/2 + y, -z$; (#6) $-x, 2 - y, -z$.

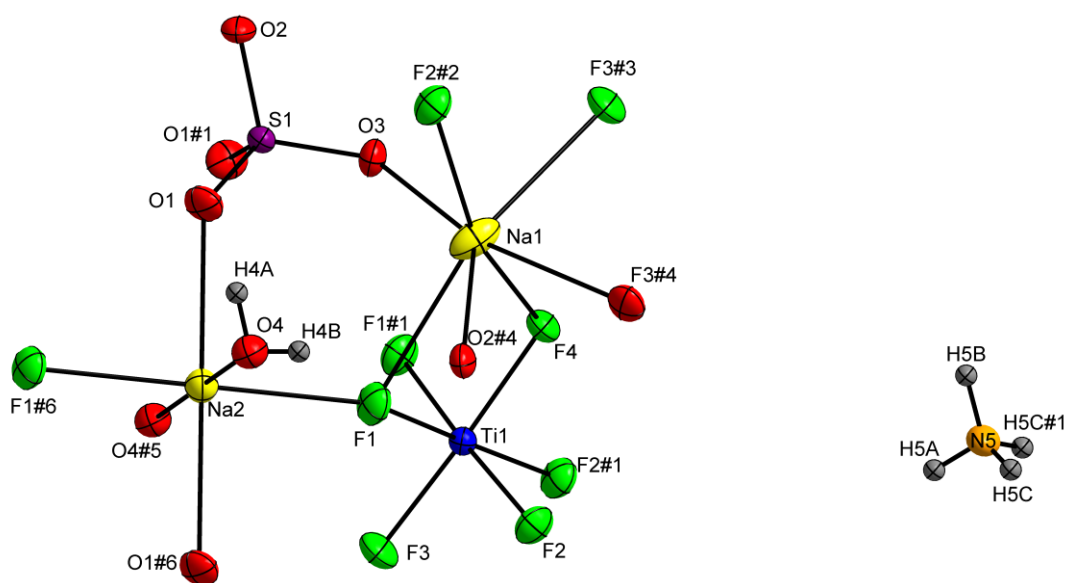
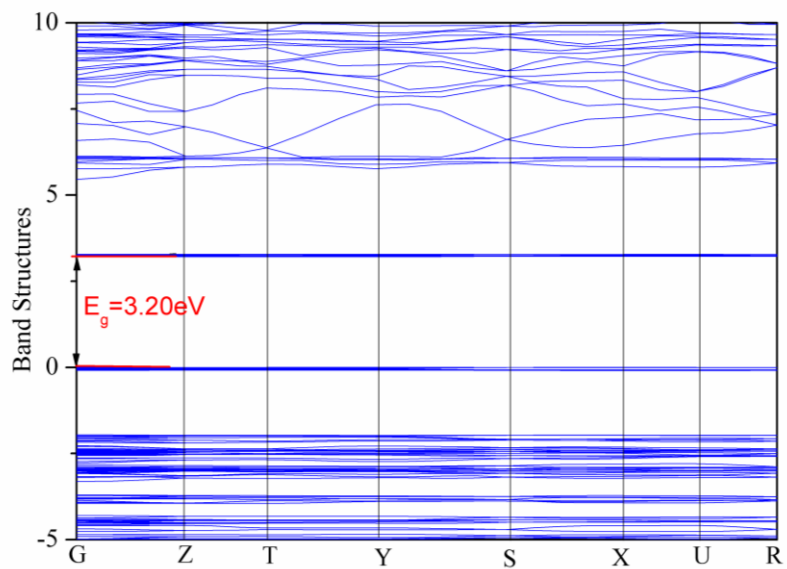
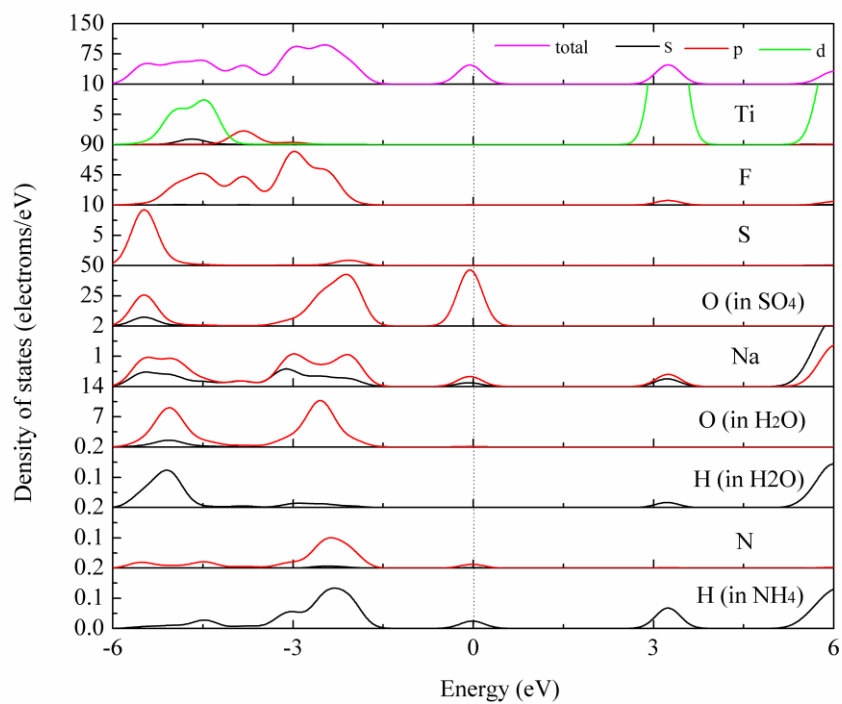


Figure S4. Calculated band structure (a) and density of states of NTS (b).



(a)



(b)