Electronic Supplement Information (ESI) for

Hexagonal tungsten oxides with large band gaps synthesized by a chemical substitution method

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Table S1. Selected bond distances (Å) for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

$K(GaF_2)_3(SeO_3)_2$			
Se(1)-O(1)#1	1.689(5)	K(1)-O(1)#3	2.834(5)
Se(1)-O(1)#2	1.689(5)	K(1)-O(1)#8	2.834(5)
Se(1)-O(1)	1.689(5)	K(1)-O(1)#9	2.834(5)
Ga(1)-O(1)	1.916(4)	K(1)-O(1)#10	2.835(5)
Ga(1)-O(1)#3	1.916(4)	K(1)-F(1)#11	2.926(4)
Ga(1)-F(1)#3	1.9257(14)	K(1)-F(1)#12	2.926(4)
Ga(1)-F(1)	1.9257(14)	K(1)-F(1)#13	2.926(4)
Ga(1)-F(1)#1	1.9258(14)	K(1)-F(1)	2.926(4)
Ga(1)-F(1)#4	1.9258(14)	K(1)-F(1)#2	2.926(4)
K(1)-O(1)#6	2.834(5)	K(1)-F(1)#1	2.926(4)
K(1)-O(1)#7	2.834(5)		

#1 -x+y,-x+1,z #2 -y+1,x-y+1,z #3 -x+1/3,-y+2/3,-z+2/3 #4 x-y+1/3,x-1/3,-z+2/3 #5 x-1/3,y-2/3,z+1/3 #6 x-y+1/3,x+2/3,-z+2/3 #7 y+1/3,-x+y+2/3,-z+2/3 #8 -y+1/3,x-y+2/3,z-1/3 #9 x+1/3,y+2/3,z-1/3 #10 -x+y+1/3,-x+2/3,z-1/3 #11 -x+2/3,-y+4/3,-z+1/3 #12 y-1/3,-x+y+1/3,-z+1/3 #13 x-y+2/3,x+1/3,-z+1/3

$NH_4(GaF_2)_3(SeO_3)_2$			
Se(1)-O(1)#1	1.689(5)	Ga(1)-F(2)	1.9218(16)
Se(1)-O(1)	1.689(5)	Ga(1)-F(2)#2	1.9218(16)
Se(1)-O(1)#2	1.689(5)	Ga(1)-F(1)#4	1.9275(15)
Se(2)-O(2)	1.704(5)	Ga(1)-F(1)	1.9275(15)
Se(2)-O(2)#3	1.704(5)	N(1)-H(1)	0.99(3)
Se(2)-O(2)#4	1.704(5)	N(1)-H(2)	0.98(3)
Ga(1)-O(2)	1.913(5)	N(1)-H(1)#1	0.99(3)
Ga(1)-O(1)	1.919(5)	N(1)-H(1)#2	0.99(3)

#1 -y+1,x-y+1,z #2 -x+y,-x+1,z #3 -y,x-y,z #4 -x+y,-x,z

Table S2. Bond valence sum calculations for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

$K(GaF_2)_3(SeO_3)_2$		$NH_4(GaF_2)_3(SeO_3)_2$	
Se(1)	4.17	Se(1)	4.17
Ga(1)	2.96	Se(2)	4.00
K(1)	1.38	Ga(1)	2.97
F(1)	0.96	F(1)	0.87
O(1)	2.14	F(2)	0.88
		O(1)	1.99
		O(2)	1.95

Table S3. Atomic ratios for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4) determined by EDX analyses.

Compounds	$K(GaF_2)_3(SeO_3)_2$	$NH_4(GaF_2)_3(SeO_3)_2$
A	1.13	0
Ga	3.00	3.00
Se	2.14	2.19
O	8.49	5.77
F	8.36	6.83

Table S4. Calculated local dipole moments for GaO_2F_4 and SeO_3 polyhedra in $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

Compounds	$K(GaF_2)_3(SeO_3)_2$	$NH_4(GaF_2)_3(SeO_3)_2$
$Ga(1)O_2F_4$	0	0.20
$Se(1)O_3$	6.75	6.92
$Se(2)O_3$		7.21

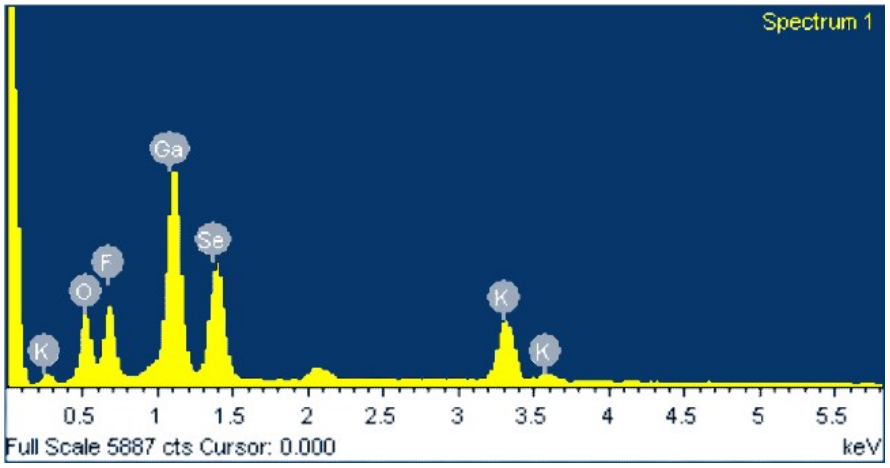
Table S5. Hydrogen bond distances for $NH_4(GaF_2)_3(SeO_3)_2$.

D-H...A	d(D-H)	d(H...A)	d(D...A)
N(1)-H(1)...O(2)	0.99(3)	2.04(3)	3.006(9)
N(1)-H(2)...F(1)#1	0.98(3)	2.790(13)	3.303(10)
N(1)-H(2)...F(1)#2	0.98(3)	2.790(13)	3.303(10)
N(1)-H(2)...F(1)#3	0.98(3)	2.790(13)	3.303(10)

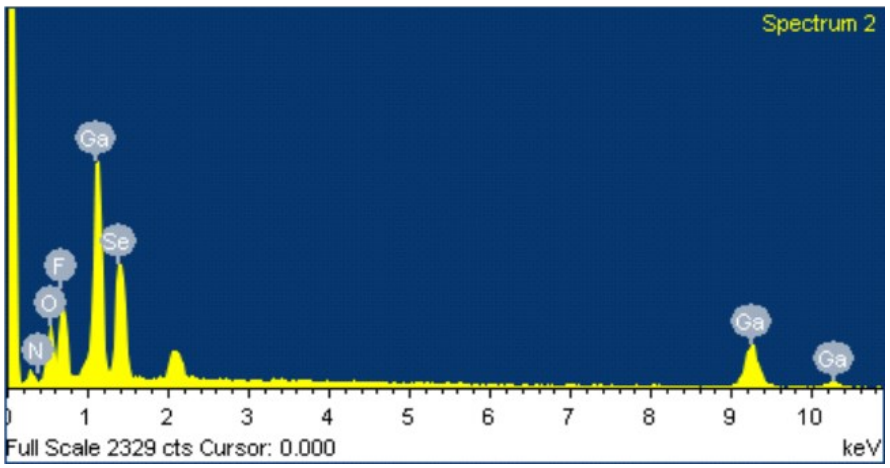
#1 -x,-y+1,z-1/2 #2 y,-x+y,z-1/2 #3 x-y+1,x+1,z-1/2

Figure S1. EDX spectra for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

(a) $K(GaF_2)_3(SeO_3)_2$



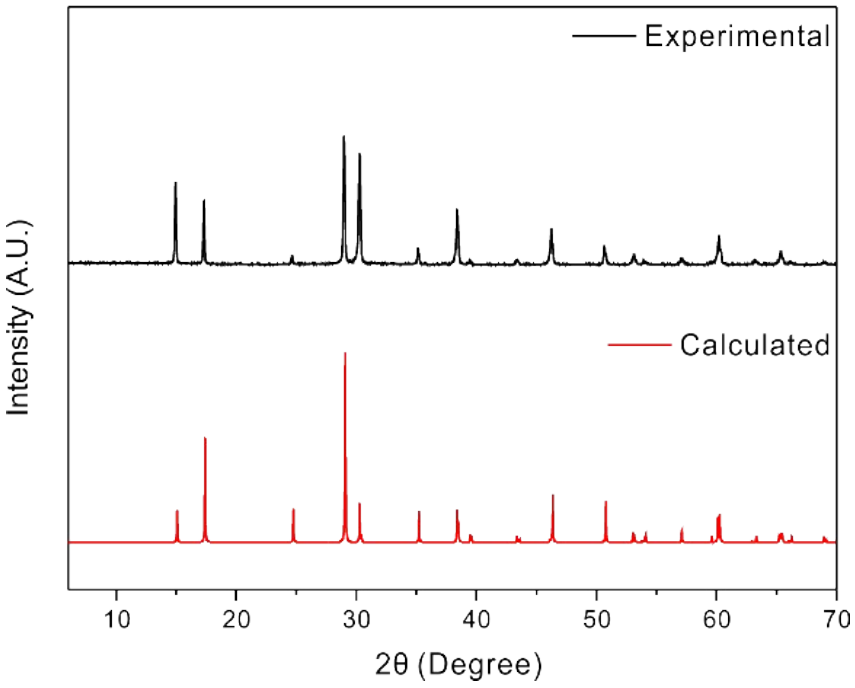
(b) $NH_4(GaF_2)_3(SeO_3)_2$



Elemental analysis for $NH_4(GaF_2)_3(SeO_3)_2$ observed (calculated): N, 2.2915% (2.35%); H, 0.9486% (0.68%).

Figure S2. Experimental and calculated powder X-ray diffraction patterns for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

(a) $K(GaF_2)_3(SeO_3)_2$



(b) $NH_4(GaF_2)_3(SeO_3)_2$

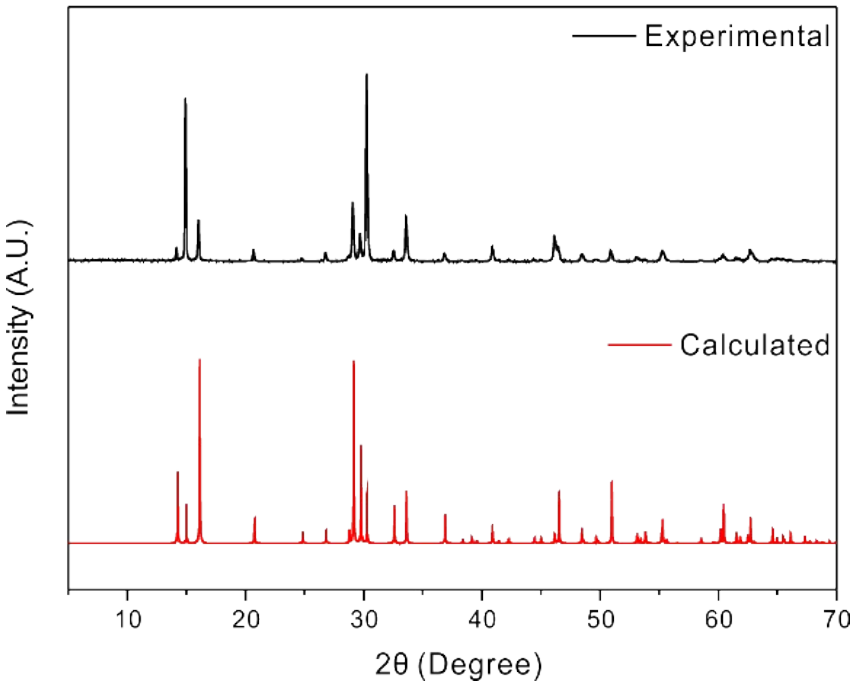


Figure S3. IR spectra for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

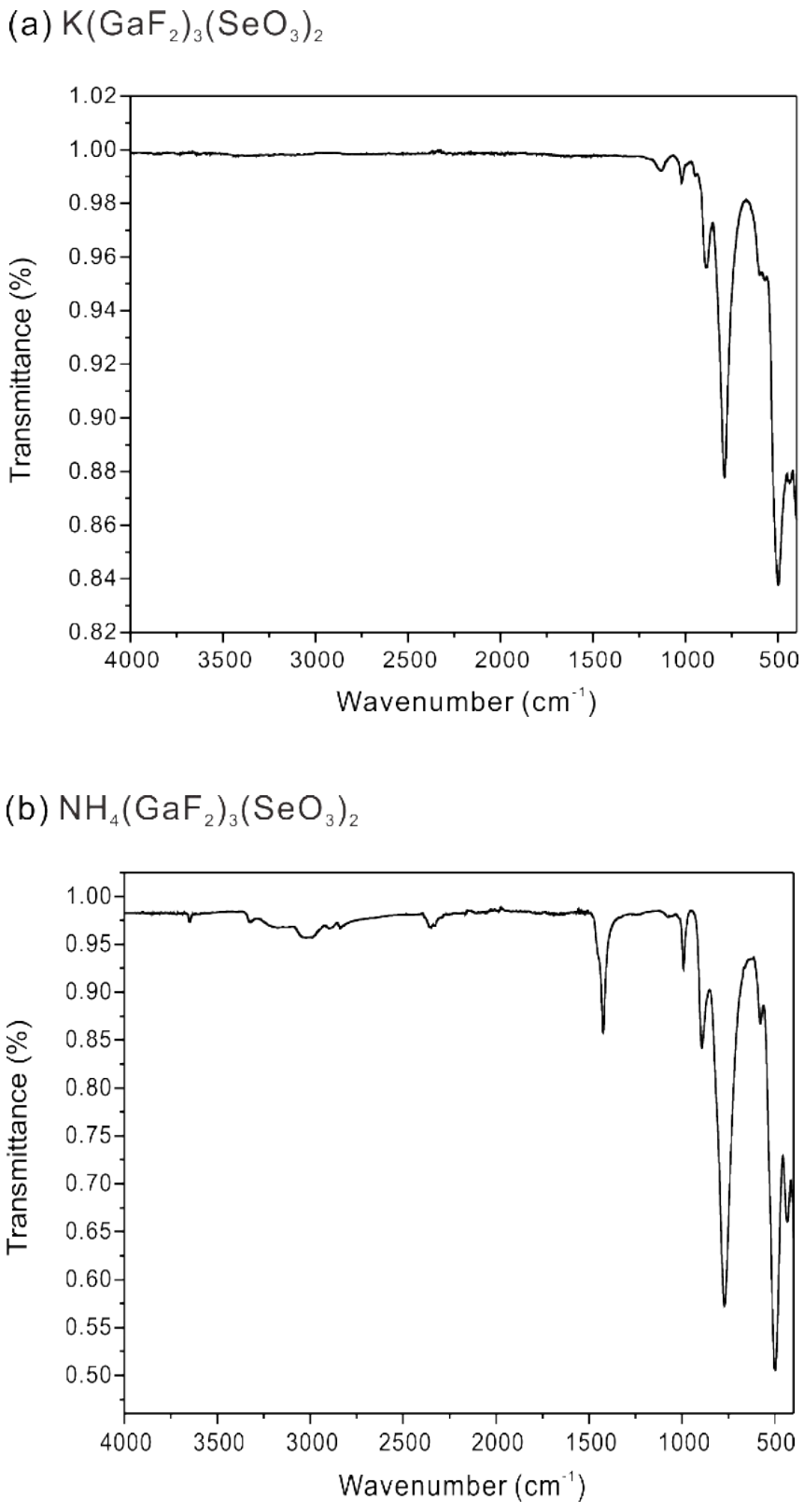


Figure S4. TGA diagrams for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

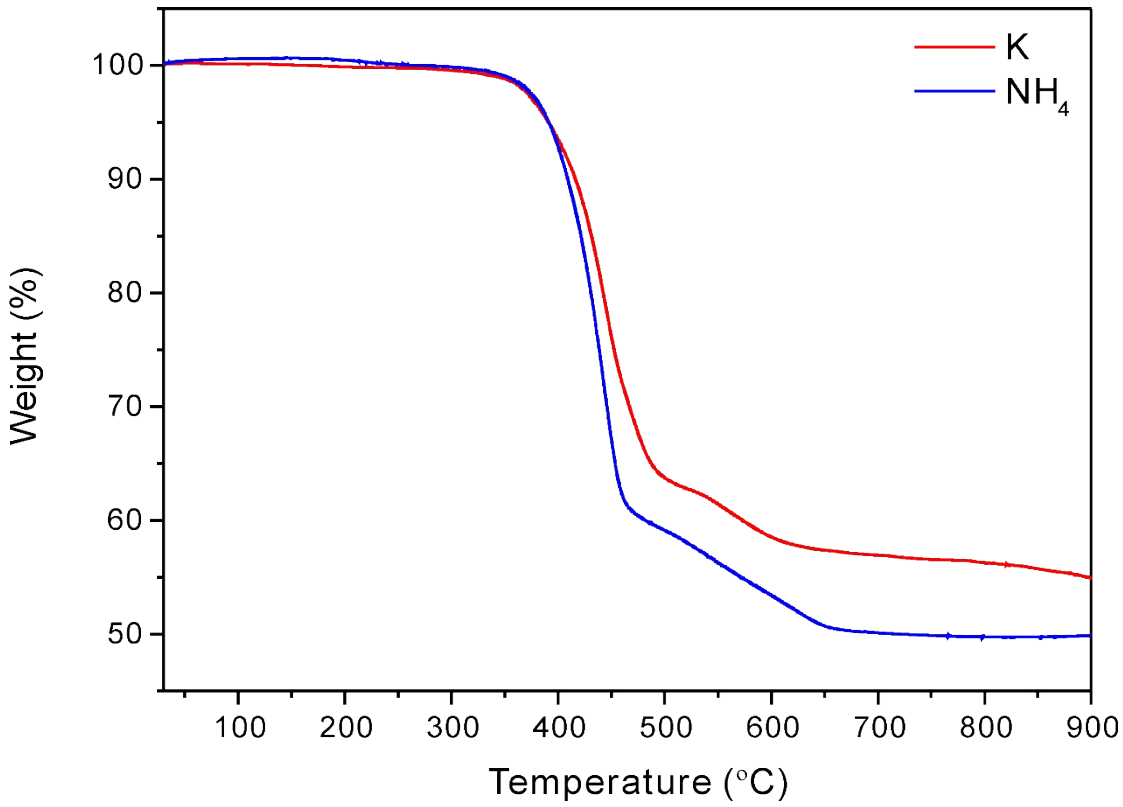


Figure S5. PXRD patterns for calcined products of $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

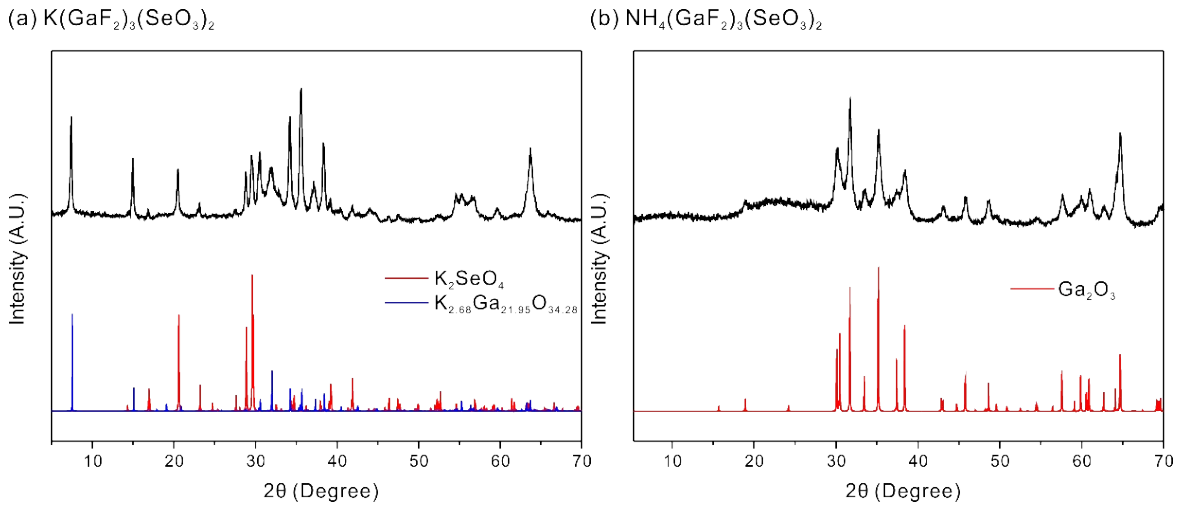
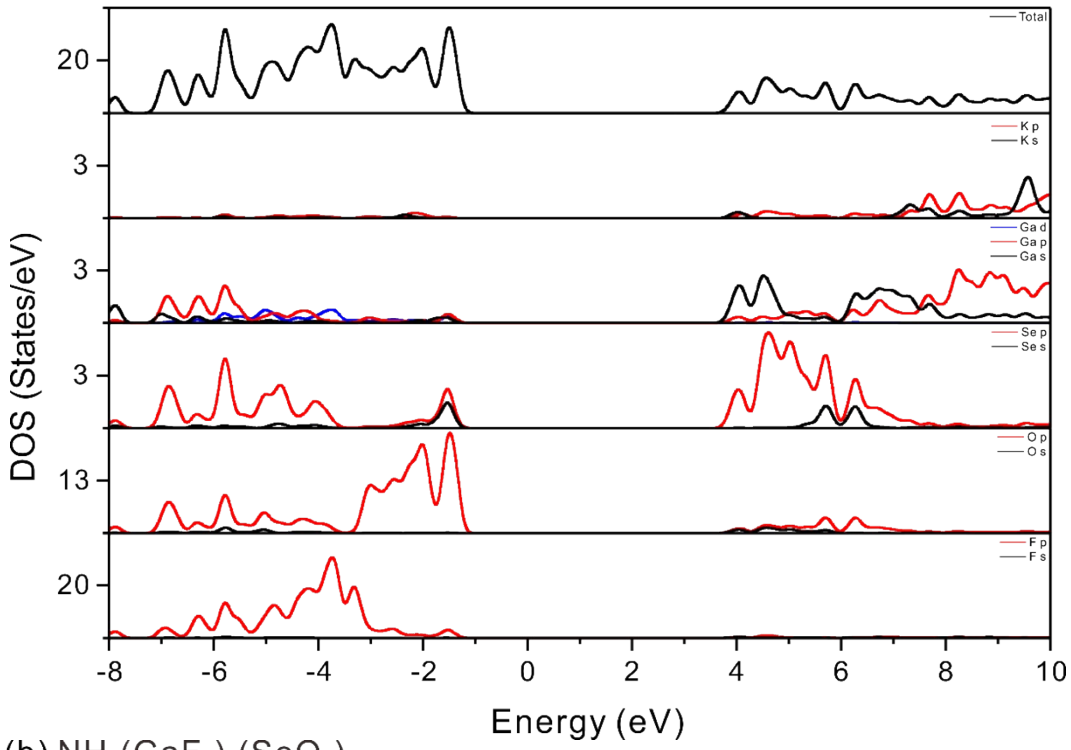


Figure S6. Total and partial density of states for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

(a) $K(GaF_2)_3(SeO_3)_2$



(b) $NH_4(GaF_2)_3(SeO_3)_2$

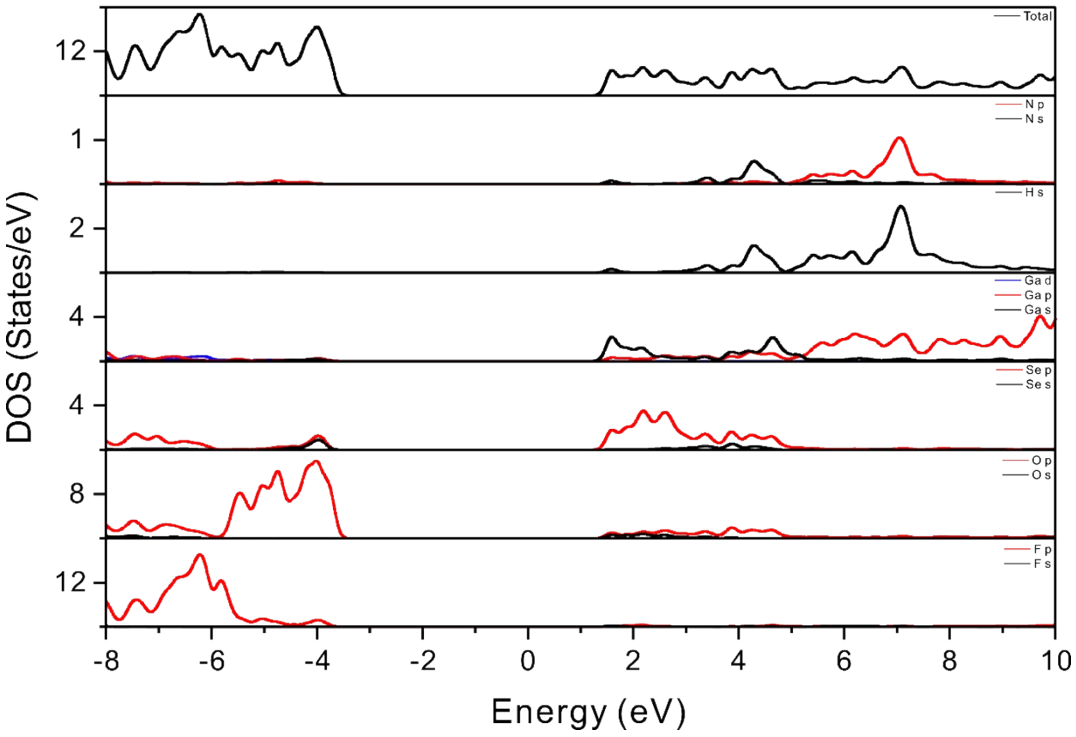
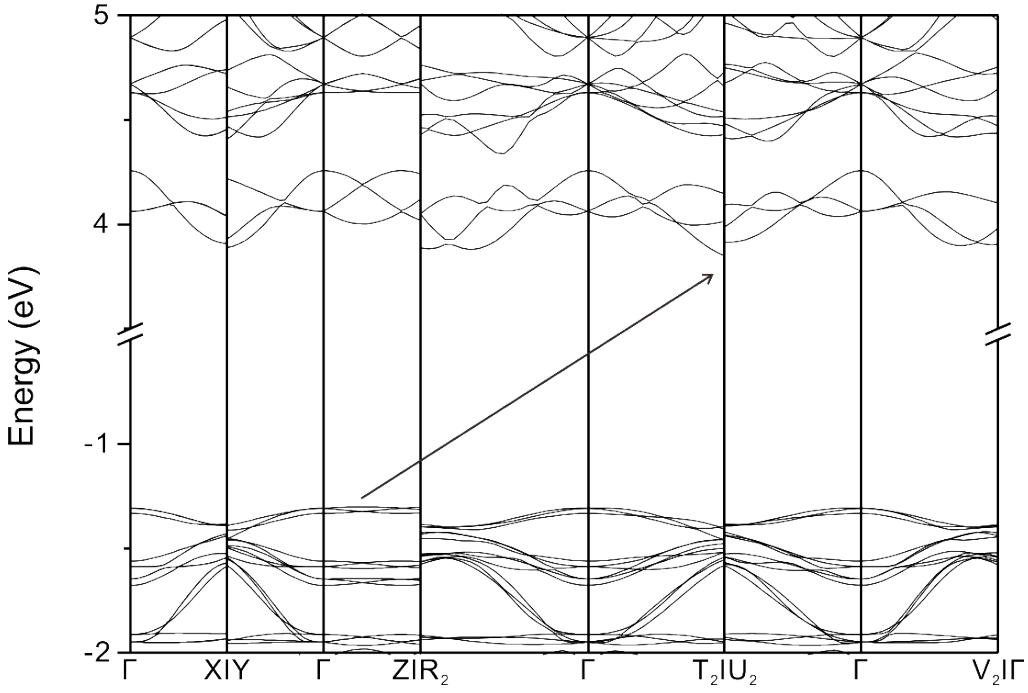


Figure S7. Band structures for $A(GaF_2)_3(SeO_3)_2$ (A = K and NH_4).

(a) $K(GaF_2)_3(SeO_3)_2$



(b) $NH_4(GaF_2)_3(SeO_3)_2$