$ZnGa(SeO_3)_2F$: A UV Transparent Birefringent Crystal Explored in M(II)-IIIA-Selenite-F System

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S1. Computational method

Single-crystal structural data of $SrAl(SeO_3)F_3$ (**1**), $BaAl(SeO_3)F_3•(H_2O)_{0.25}$ (**2**) and $ZnGa(SeO_3)_2F$ (**3**), were directly used for the theoretical calculations. The electronic structures and optical properties were calculated by using a plane-wave pseudo-potentials method within density functional theory (DFT) implemented in the total energy code of CASTEP.[1] For the exchange and correlation functional, we chose Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA).[2] The interactions between the ionic cores and the electrons were described by the Norm conserving pseudopotential.[3] The following valence-electron configurations were considered in the computation: Se-$4s^24p^4$, O-$2s^22p^4$, F-$2s^22p^5$, Al-$3s^23p^1$, Ga-$3d^{10}4s^24p^1$, Sr-$4s^24p^65s^2$, Ba-$5s^25p^66s^2$, Zn-$3d^{10}4s^2$ and H-$1s^1$. The number of plane waves incorporated into the basis sets was determined by a cutoff energy of 850 eV. The numerical integration of the Brillouin zone was performed using Monkhorst-Pack k-point sampling of 2×2×6, 2×5×2 and 4×2×4 for $SrAl(SeO_3)F_3$ (**1**), $BaAl(SeO_3)F_3•(H_2O)_{0.25}$ (**2**) and $ZnGa(SeO_3)_2F$ (**3**).

Table S1. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $SrAl(SeO_3)F_3$(1), $BaAl(SeO_3)F_3(H_2O)_{0.25}$(2) and $ZnGa(SeO_3)_2F$(3). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

$SrAl(SeO_3)F_3$				
Atom	***x***	***y***	***z***	**U(eq)**
Sr1	1269.0(4)	5365.1(4)	7500	9.09(18)
Se1	73.7(4)	7441.8(4)	7500	7.40(18)
Al1	1371.3(13)	7160.6(13)	2500	7.7(3)
F1	917(2)	5606(2)	2500	12.8(7)
F2	2385.0(19)	7359.4(19)	4979(4)	19.5(5)
O1	-1339(3)	7053(3)	7500	16.2(9)
O4	156(2)	6657(2)	5022(5)	19.4(7)
$BaAl(SeO_3)F_3(H_2O)_{0.25}$				
Atom	***x***	***y***	***z***	**U(eq)**
Ba1	3766.27(16)	4414.60(16)	2032.8(5)	13.75(10)
Al1	4920.2(8)	6752.5(8)	2596(2)	9.3(3)
Se1	3559.7(3)	6521.4(2)	-2385.9(7)	9.98(12)
F1	4108.3(14)	2851.4(14)	-752(4)	15.5(5)
F2	4504.3(15)	4321.6(14)	-3099(4)	15.6(5)
F3	4633.2(15)	2804.7(15)	4449(4)	18.8(5)
O1	4443.8(16)	6151.8(17)	-488(5)	10.6(6)
O2	3867.9(18)	6256.5(18)	-5509(5)	15.7(6)
O3	2849.2(17)	5650(2)	-1641(5)	19.1(7)
O1W	2500	2500	4935(17)	108(4)
$ZnGa(SeO_3)_2F$				
Atom	***x***	***y***	***z***	**U(eq)**
Zn1	-7129.2(16)	-4923.6(8)	-5014.6(15)	8.8(2)
Ga1	-373.8(14)	-2504.3(7)	-2250.1(14)	5.4(2)
Se1	-5370.9(13)	-2645.8(7)	-5958.1(13)	7.0(2)
Se2	1606.2(13)	-4949.1(7)	-1567.5(13)	6.9(2)
F1	-398(9)	-2245(4)	-4760(8)	12.3(11)
O1	-5354(10)	-4038(5)	-5784(10)	11.4(13)
O2	-3352(10)	-2298(5)	-3592(10)	11.4(13)
O3	-7339(10)	-2351(5)	-5516(9)	10.4(13)
O4	3246(10)	-4599(5)	-2358(10)	12.0(13)
O6	-50(10)	-937(5)	-1733(9)	8.8(12)
O5	-565(10)	-4070(5)	-2767(9)	9.3(12)

Table S2. The bond lengths (Å) and calculated bond valences for compounds **1-3**.

Componud	Bond	Bond lengths	Band-valence	BVS
$SrAl(SeO_3)F_3$ (**1**)	Se1-O1	1.671(6)	1.46	4.23
	Se1-O2	1.689(9)	1.39	
	Se1-O2	1.690(1)	1.39	
	Al1-O1	1.851(9)	0.57	3.11
	Al1-O2	1.914(6)	0.48	
	Al1-O2#1	1.914(8)	0.48	
	Al1-F1	1.779(6)	0.53	
	Al1-F2	1.779(8)	0.53	
	Al1-F2#2	1.779(8)	0.53	
$BaAl(SeO_3)F_3•(H_2O)_{0.25}$ (**2**)	Se1-O1	1.697(2)	1.36	4.16
	Se1-O2	1.692(2)	1.38	
	Se1-O3	1.681(6)	1.42	
	Al1-O1	1.923(2)	0.47	3.08
	Al1-O2	1.950(5)	0.43	
	Al1-O3	1.865(2)	0.55	
	Al1-F1	1.794(4)	0.51	
	Al1-F2	1.757(7)	0.56	
	Al1-F3	1.757(7)	0.56	
$ZnGa(SeO_3)_2F$ (**3**)	Se1-O1	1.724(3)	1.26	3.95
	Se1-O2	1.707(0)	1.32	
	Se1-O3	1.696(8)	1.36	
	Se2-O4	1.669(4)	1.47	3.92
	Se2-O5	1.751(4)	1.18	
	Se2-O6	1.720(9)	1.28	
	Ga1-O2	1.901(9)	0.63	3.25
	Ga1-O3	1.931(5)	0.58	
	Ga1-O5	1.964(0)	0.53	
	Ga1-O6	1.967(0)	0.53	
	Ga1-F1#1	1.953(8)	0.49	
	Ga1-F1	1.951(2)	0.49	
	Zn1-O1	2.053(1)	0.39	1.98
	Zn1-O1#2	2.018(4)	0.43	
	Zn1-O4	1.960(0)	0.50	
	Zn1-O5	2.084(8)	0.36	
	Zn1-O6	2.137(4)	0.31	

Symmetry transformations used to generate equivalent atoms:

For $SrAl(SeO_3)F_3$: #1 x, y, 1/2-z; #2 x, y, 1/2-z

For $ZnGa(SeO_3)_2F$: #1 x, -1/2-y, 1/2+z; #2 -1-x, -1-y, -1-z

$$V_i = \sum_j S_{ij} = \sum_j exp\{(r_0 - r_{ij})/B\}$$

The BVS were calculated via equation: , where V_i is the oxidation state of the cation, S_{ij} is the valence of the bond between the cation i and the anion j, r_0 is the default key length, r_{ij} is the actual key length, B is an empirical parameter generally assumed to be 0.37[4].

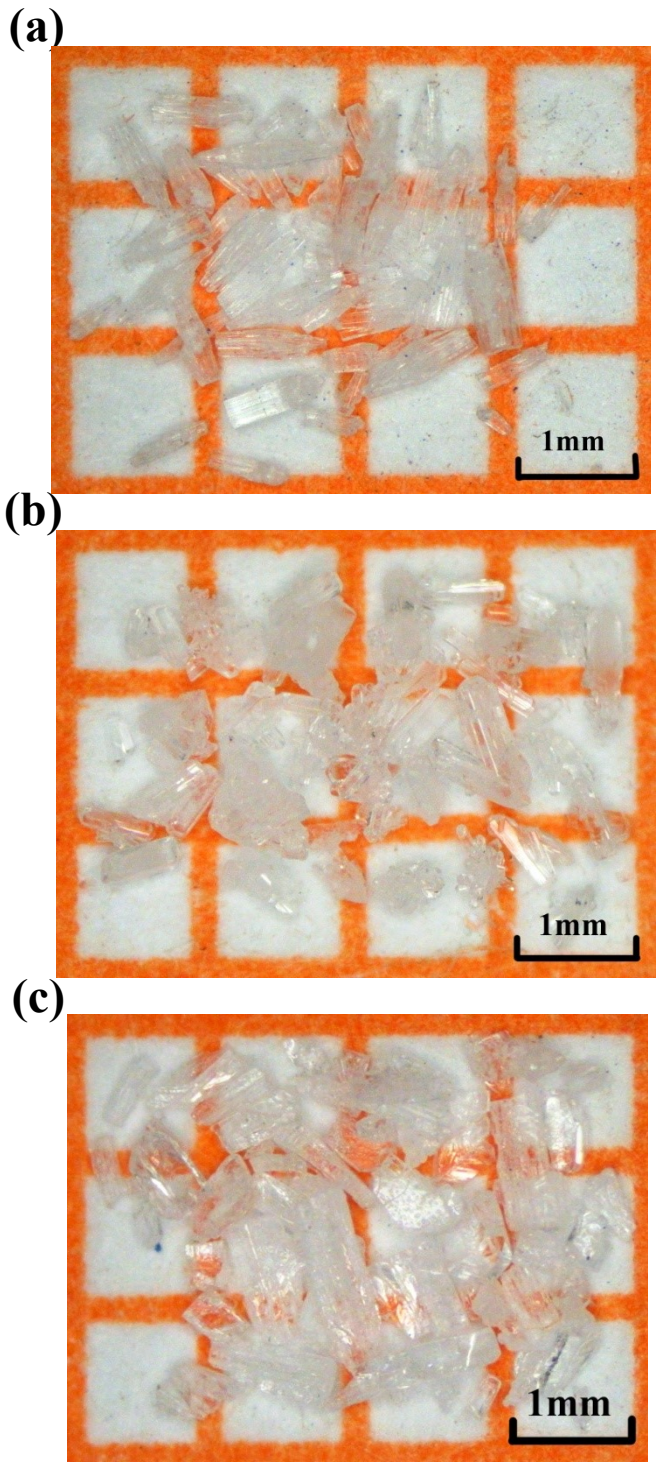


Figure S1. The photographs of crystals for compounds **1** (a), **2** (b) and **3** (c)

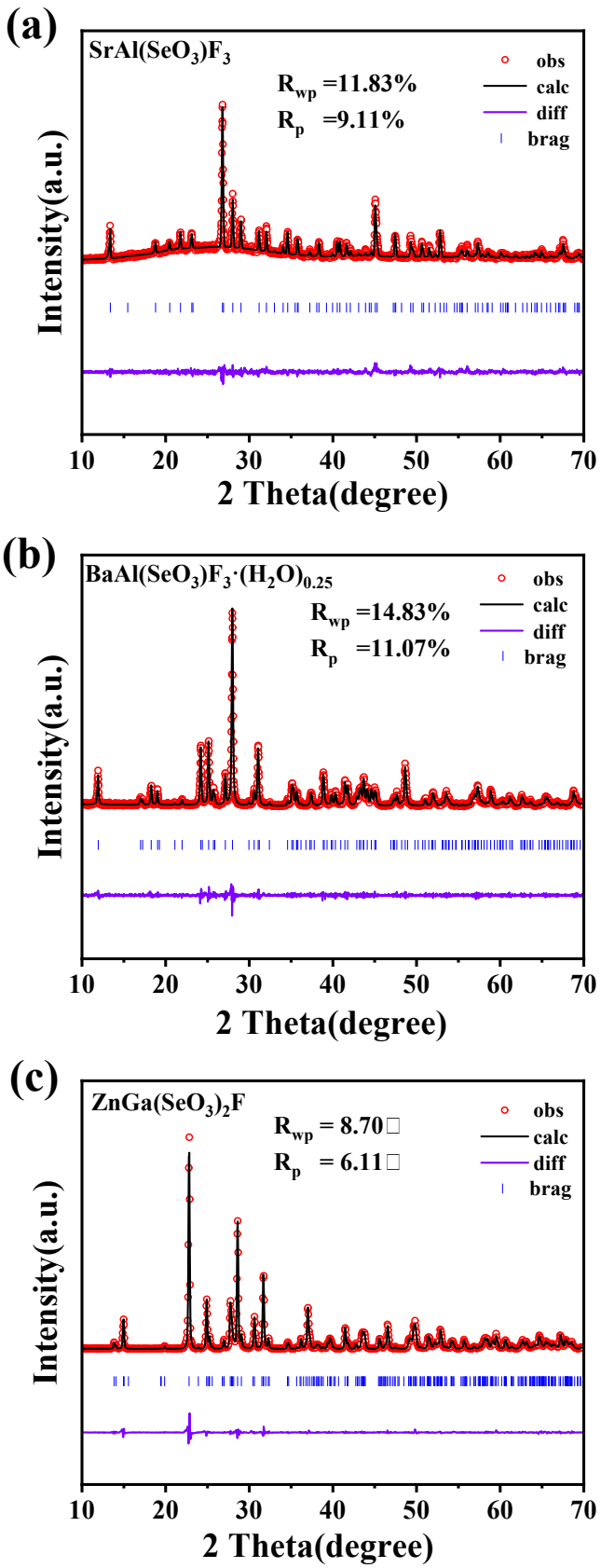


Figure S2. Rietveld refinement plot of the powder XRD patterns for compounds **1-3**.

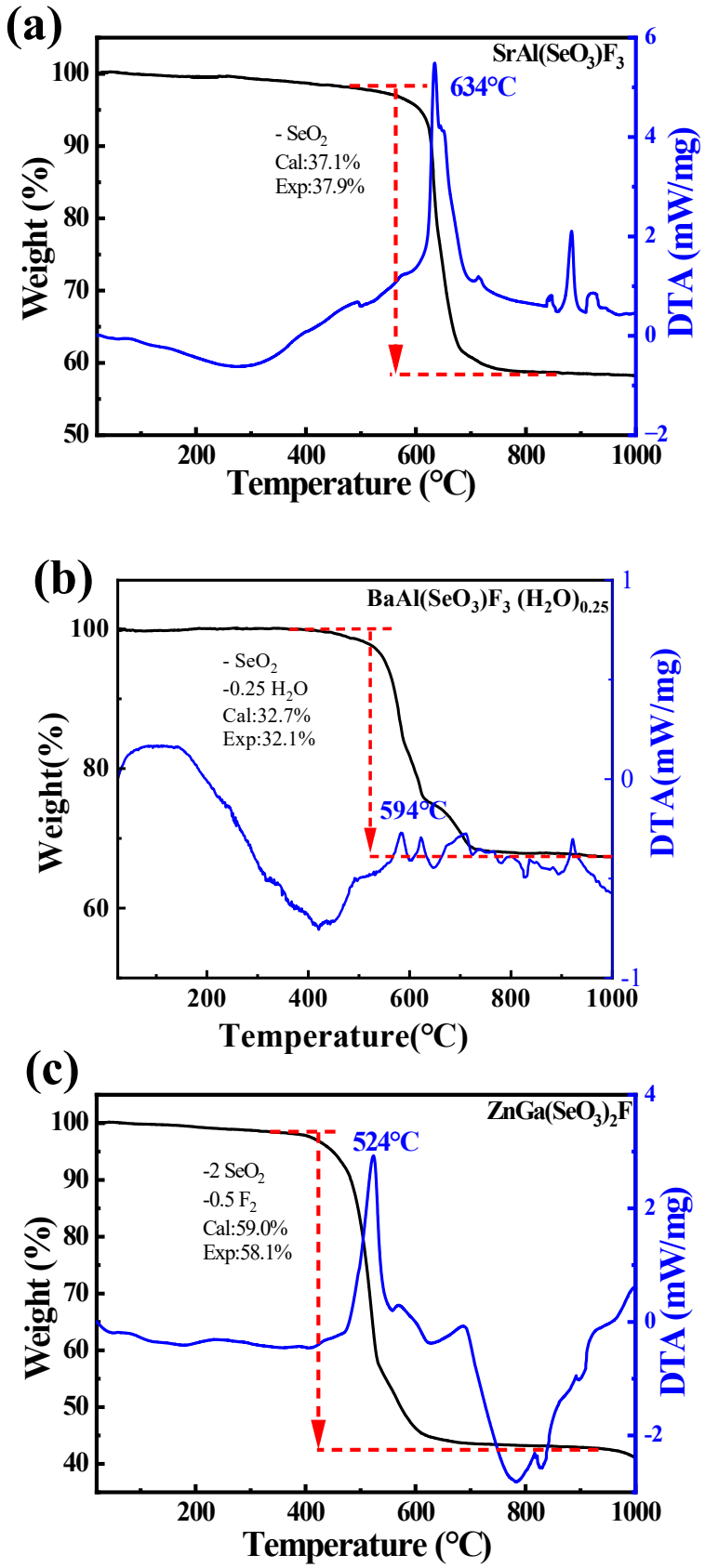


Figure S3. TGA results of compounds **1-3**.

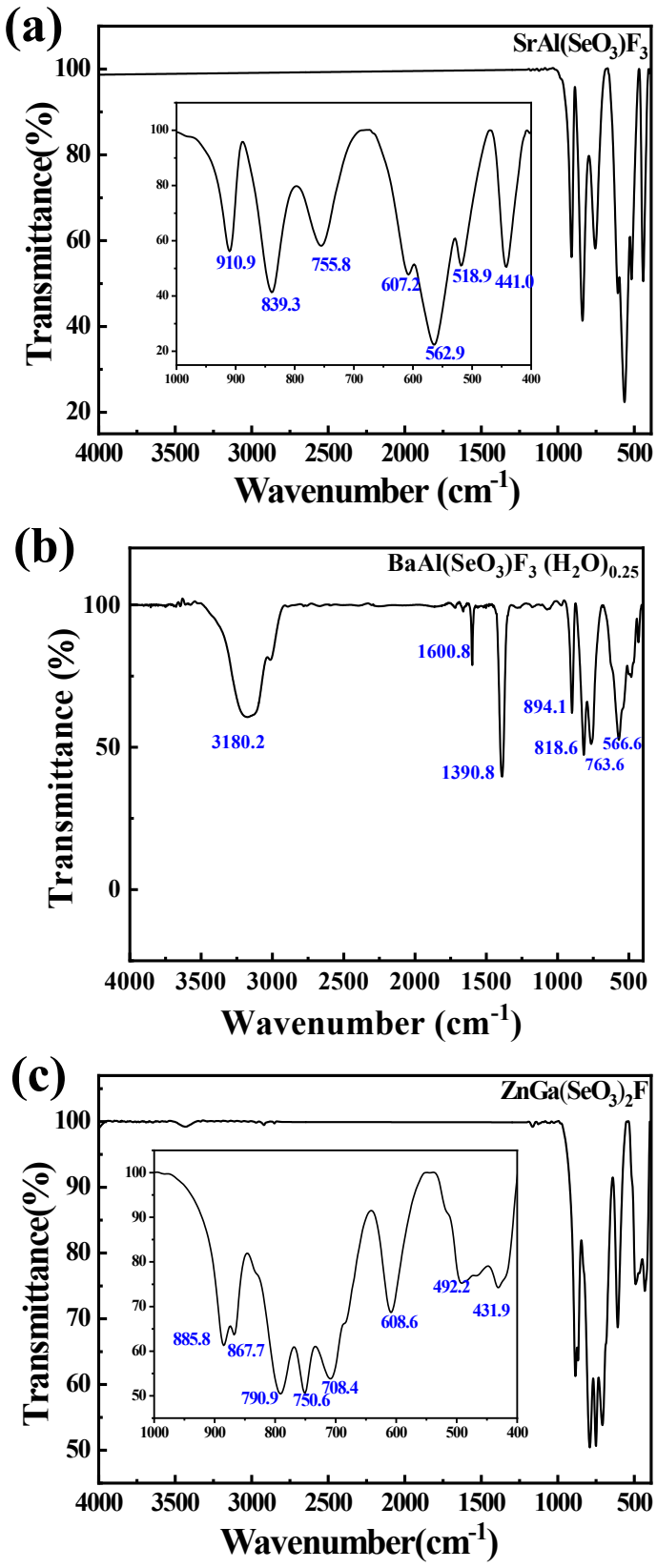


Figure S4. IR spectra of compounds **1-3.**

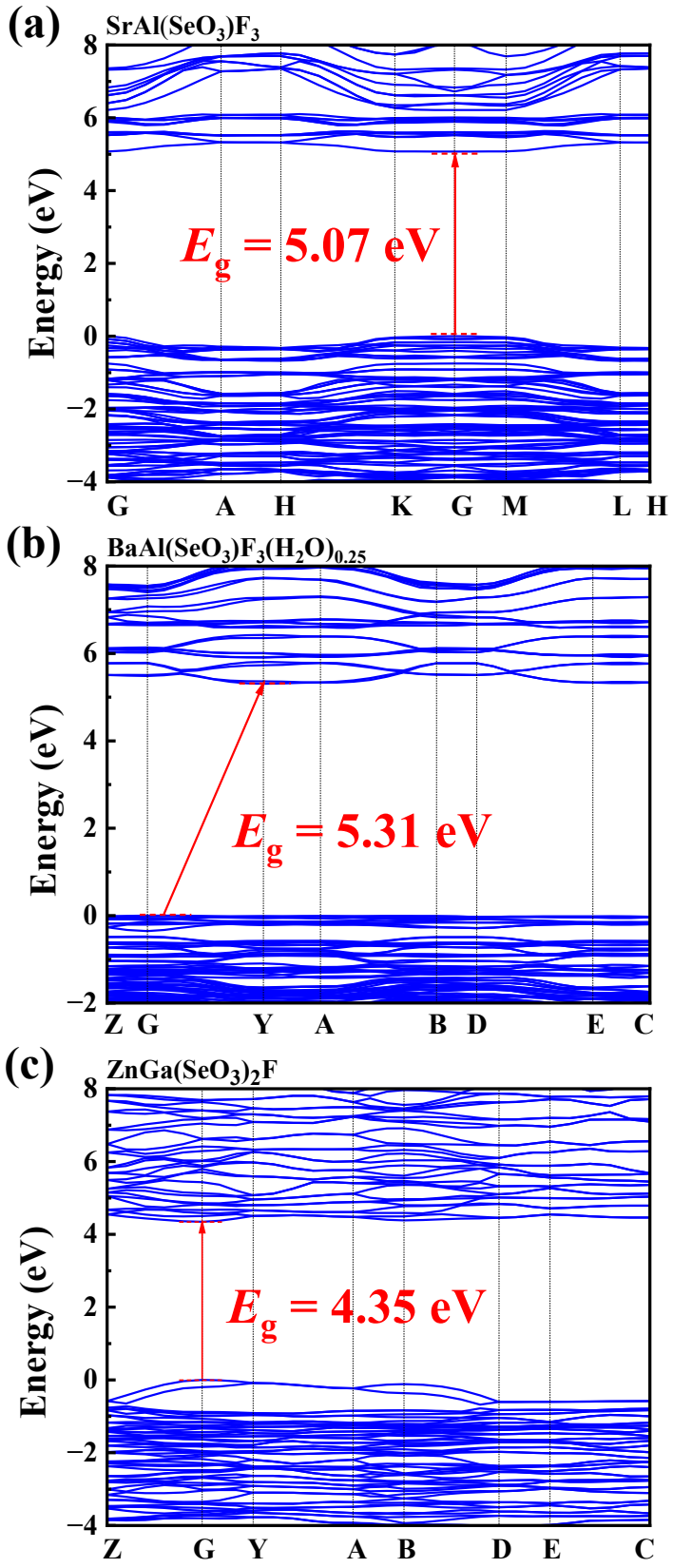
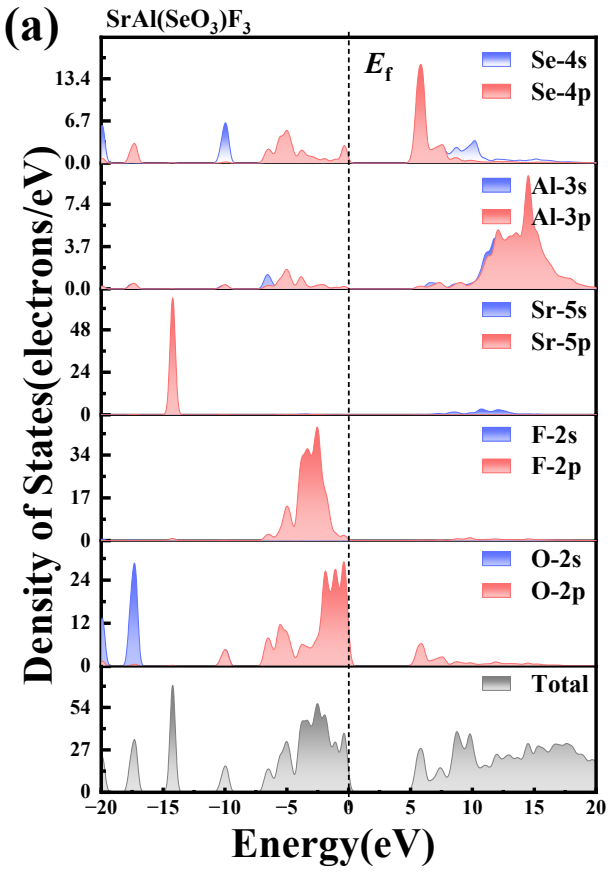
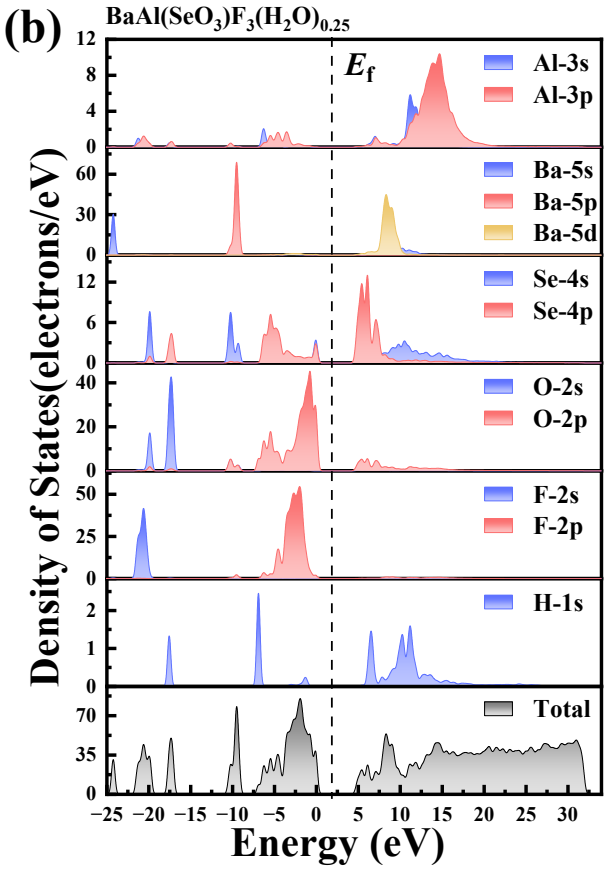


Figure S5. Band structures of compounds **1-3**.


(a)
SrAl(SeO3)F3
Ef
Se-4s
Se-4p
Al-3s
Al-3p
Sr-5s
Sr-5p
F-2s
F-2p
O-2s
O-2p
Total
Density of States(electrons/eV)
Energy(eV)


(b)
BaAl(SeO3)F3(H2O)0.25
Ef
Al-3s
Al-3p
Ba-5s
Ba-5p
Ba-5d
Se-4s
Se-4p
O-2s
O-2p
F-2s
F-2p
H-1s
Total
Density of States(electrons/eV)
Energy (eV)

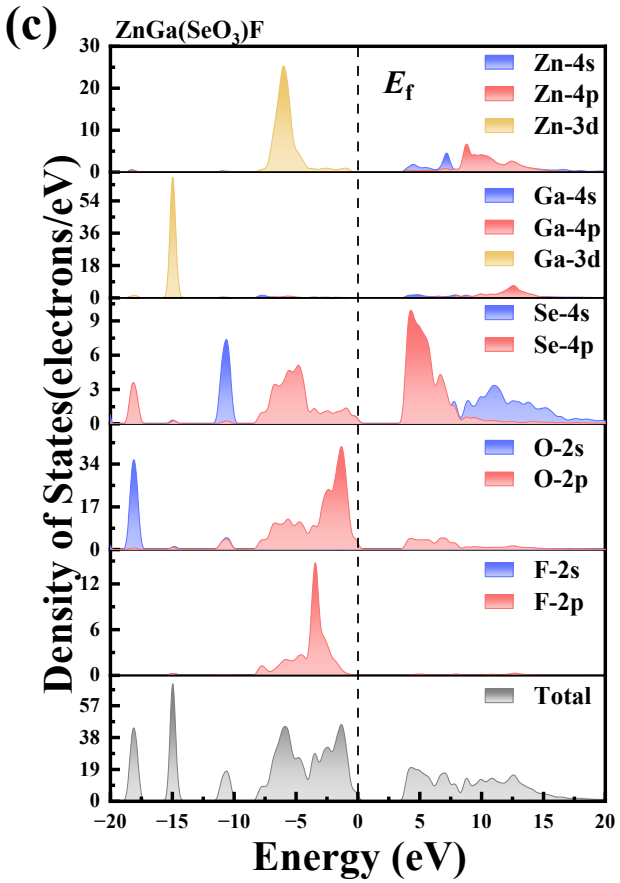


Figure S6. Total and partial density of states of compounds **1-3**.

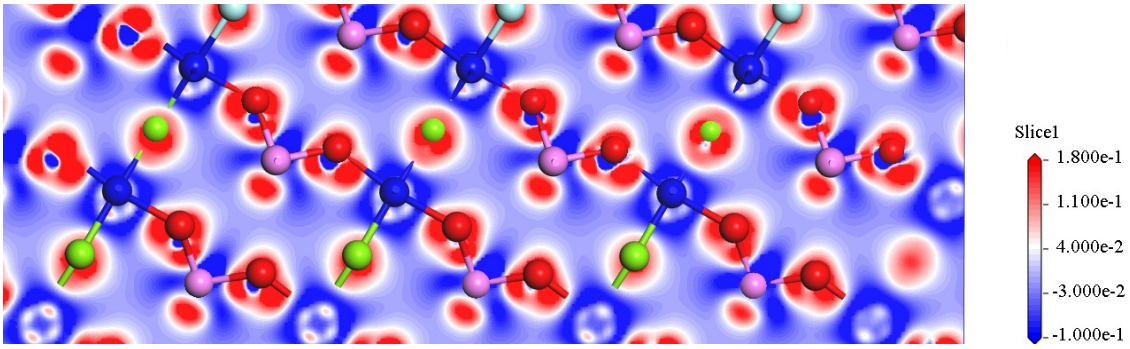


Figure S7. The electron density difference (EDD) map of $ZnGa(SeO_3)_2F$.

References

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