Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

$Pb_2Ga_3F_6(SeO_3)_2X_3 \cdot 2H_2O$ (X=Cl, Br): Two New HTO-Type Members Exhibiting Large NLO Effect Mediated by Ionic Mixing and Substitution Strategy

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Table S1. HTO-type selenite.

	Molecule	Space group	SHG effect ×KDP	Band gap (eV)	Phase matchability
1	$NH_4(VO_2)_3(SeO_3)_2$	$P6_3$	1.0	N/A	NPM
2	$K(VO_2)_3(SeO_3)_2$	$P6_3$	1.1	2.43	NPM
3	$Rb(VO_2)_3(SeO_3)_2$	$P6_3$	1.0	2.39	NPM
4	$Cs(VO_2)_3(SeO_3)_2$	$P6_3$	1.0	2.4	NPM
5	$Tl(VO_2)_3(SeO_3)_2$	$P6_3$	1.2	2.44	NPM
6	$(NH_4)_2(MoO_3)_3SeO_3$	$P6_3$	10.0	N/A	NPM
7	$Rb_2(MoO_3)_3SeO_3$	$P6_3$	7.5	3.2	NPM
8	$Cs_2(MoO_3)_3SeO_3$	$P6_3$	8.7	3.1	NPM
9	$Tl_2(MoO_3)_3SeO_3$	P31c	10.0	3.0	NPM
10	$Na_2(WO_3)_3(SeO_3)\cdot 2H_2O$	P31c	11.2	3.2	NPM
11	$Na_6(W_6O_{19})(SeO_3)_2$	C2	0.5	2.9	NPM
12	$(NH_4)_2(WO_3)_3SeO_3$	$P6_3$	5.0	N/A	PM
13	$Rb_2(WO_3)_3SeO_3$	$P6_3$	N/A	3.2	N/A
14	$Cs_2(WO_3)_3SeO_3$	$P6_3$	5.0	3.2	PM
15	$K_2(WO_3)_3SeO_3$	$P6_3$	N/A	3.1	N/A
16	$Tl_2(WO_3)_3SeO_3$	Unstable	N/A	2.0	N/A
17	$Cs(TiOF)_3(SeO_3)_2$	$P6_3mc$	5.0	3.5	PM
18	$RbGa_3F_6(SeO_3)_2$	$P6_3mc$	5.6	3.57	PM
19	$CsGa_3F_6(SeO_3)_2$	$P6_3mc$	5.4	3.65	PM
20	$K(GaF_2)_3(SeO_3)_2$	R-3m	-	5.62	-
21	$NH_4(GaF_2)_3(SeO_3)_2$	$P6_3mc$	1.1	5.77	PM

N/A: not available

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $Pb_2Ga_3F_6(SeO_3)_2Br_3 \cdot 2H_2O$ and $Pb_2Ga_3F_6(SeO_3)_2Br_3 \cdot 2H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$Pb_2Ga_3F_6(SeO_3)_2Cl_3 \cdot 2H_2O$					
	x	y	z	U(eq)	BVS
Pb(1)	3333	6667	4386(1)	19(1)	2.14
Cl(1)	4057(8)	4057(8)	5000	39(1)	0.99
Se(1)	10000	10000	5742(1)	7(1)	4.12
Ga(1)	8278(4)	6667	6667	7(1)	2.74
F(1)	5380(15)	4547(16)	6488(2)	19(1)	0.93
O(1)	8610(16)	7561(10)	6001(2)	12(1)	1.91
O(2)	3333	6667	6051(4)	30(3)	1.78
H2(A)	3460	5960	5785	45	0.92
H2(B)	2655	5521	6272	45	0.86
$Pb_2Ga_3F_6(SeO_3)_2Br_3 \cdot 2H_2O$					
	x	y	z	U(eq)	BVS
Pb(1)	6667	3333	5638(1)	22(1)	2.24
Br(1)	6160(2)	6160(2)	5000	42(1)	1.06
Se(1)	0	0	4230(1)	9(1)	3.99
Ga(1)	1721(2)	3333	3333	9(1)	2.73
F(1)	4629(9)	5448(9)	3508(1)	22(1)	0.90
O(1)	1373(10)	2451(6)	3977(1)	14(1)	1.88
O(2)	6667	3333	3935(3)	34(2)	1.69
H(2A)	6540	4040	4202	51	0.86
H(2B)	7345	4479	3714	51	0.83

Table S3. Bond lengths [Å] and angles [deg] for $Pb_2Ga_3F_6(SeO_3)_2Cl_3·2H_2O$ and $Pb_2Ga_3F_6(SeO_3)_2Br_3·2H_2O$.

$Pb_2Ga_3F_6(SeO_3)_2Cl_3·2H_2O$			
Pb(1)-O(1)	2.860(7)	O(1)#4-Se(1)-O(1)	102.7(2)
Pb(1)-Cl(1)#1	2.7922(14)	O(1)#5-Se(1)-O(1)	102.7(2)
Pb(1)-Cl(1)#2	2.7922(14)	F(1)#6-Ga(1)-F(1)	93.8(4)
Pb(1)-Cl(1)	2.7922(14)	F(1)#6-Ga(1)-F(1)#7	88.2(3)
Se(1)-O(1)#4	1.694(6)	F(1)-Ga(1)-F(1)#7	177.9(2)
Se(1)-O(1)#5	1.694(6)	F(1)#6-Ga(1)-F(1)#8	177.9(2)
Se(1)-O(1)	1.694(6)	F(1)-Ga(1)-F(1)#8	88.2(3)
Ga(1)-F(1)#6	1.940(10)	F(1)#7-Ga(1)-F(1)#8	89.8(3)
Ga(1)-F(1)	1.940(11)	F(1)#6-Ga(1)-O(1)#6	85.2(3)
Ga(1)-F(1)#7	1.946(11)	F(1)-Ga(1)-O(1)#6	91.4(3)
Ga(1)-F(1)#8	1.946(11)	F(1)#7-Ga(1)-O(1)#6	88.2(4)
Ga(1)-O(1)#6	1.963(6)	F(1)#8-Ga(1)-O(1)#6	95.2(3)
Ga(1)-O(1)	1.963(6)	F(1)#6-Ga(1)-O(1)	91.4(3)
Cl(1)#1-Pb(1)-Cl(1)#2	85.55(3)	F(1)-Ga(1)-O(1)	85.2(4)
Cl(1)#1-Pb(1)-Cl(1)	85.55(3)	F(1)#7-Ga(1)-O(1)	95.2(3)
Cl(1)#2-Pb(1)-Cl(1)	85.55(3)	F(1)#8-Ga(1)-O(1)	88.2(3)
O(1)#4-Se(1)-O(1)#5	102.7(2)	O(1)#6-Ga(1)-O(1)	175.1(7)
Symmetry transformations used to generate equivalent atoms: #1 -y+1,x-y+1,z #2 -x+y,-x+1,z #3 y,x,-z+1 #4 -x+y+1,-x+2,z #5 -y+2,x-y+1,z #6 x-y+2/3,-y+4/3,-z+4/3 #7 y+2/3,x+1/3,-z+4/3 #8 -x+y+1,-x+1,z #9 -y+1,x-y,z			

$Pb_2Ga_3F_6(SeO_3)_2Br_3·2H_2O$			
Pb(1)-O(1)	2.870(4)	O(1)-Se(1)-O(1)#5	102.74(17)

Pb(1)-Br(1)#1	2.9153(6)	O(1)#4-Se(1)-O(1)#5	102.74(17)
Pb(1)-Br(1)#2	2.9153(6)	F(1)-Ga(1)-F(1)#6	93.3(2)
Pb(1)-Br(1)	2.9153(5)	F(1)-Ga(1)-O(1)#6	91.9(2)
Se(1)-O(1)	1.706(4)	F(1)#6-Ga(1)-O(1)#6	85.3(2)
Se(1)-O(1)#4	1.706(4)	F(1)-Ga(1)-O(1)	85.3(2)
Se(1)-O(1)#5	1.706(4)	F(1)#6-Ga(1)-O(1)	91.9(2)
Ga(1)-F(1)	1.950(7)	O(1)#6-Ga(1)-O(1)	176.0(4)
Ga(1)-F(1)#6	1.950(6)	F(1)-Ga(1)-F(1)#7	88.7(2)
Ga(1)-O(1)#6	1.951(4)	F(1)#6-Ga(1)-F(1)#7	177.95(11)
Ga(1)-O(1)	1.951(4)	O(1)#6-Ga(1)-F(1)#7	95.1(2)
Ga(1)-F(1)#7	1.953(6)	O(1)-Ga(1)-F(1)#7	87.7(2)
Ga(1)-F(1)#8	1.953(6)	F(1)-Ga(1)-F(1)#8	177.95(11)
Br(1)#1-Pb(1)-Br(1)#2	83.862(16)	F(1)#6-Ga(1)-F(1)#8	88.7(2)
Br(1)#1-Pb(1)-Br(1)	83.862(16)	O(1)#6-Ga(1)-F(1)#8	87.7(2)
Br(1)#2-Pb(1)-Br(1)	83.862(16)	O(1)-Ga(1)-F(1)#8	95.1(2)
O(1)-Se(1)-O(1)#4	102.74(17)	F(1)#7-Ga(1)-F(1)#8	89.4(2)

Symmetry transformations used to generate equivalent atoms:

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

#4 -y,x-y,z #5 -x+y,-x,z #6 x-y+1/3,-y+2/3,-z+2/3

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

Figure S1. Calculated and experimental powder XRD patterns for $Pb_2Ga_3F_6(SeO_3)_2Cl_3·2H_2O$ (a) and $Pb_2Ga_3F_6(SeO_3)_2Br_3·2H_2O$ (b).

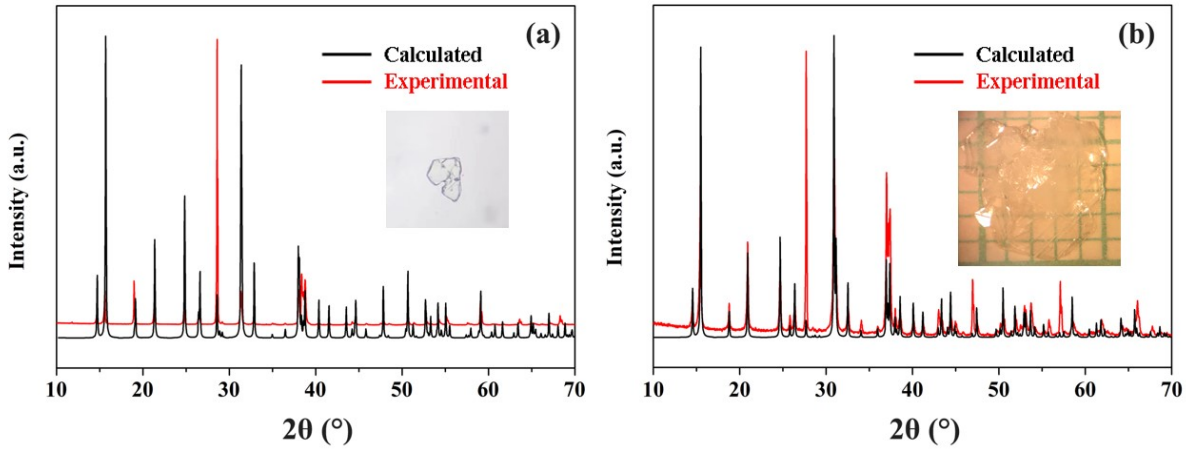

Figure S2. Unit cell of $Pb_2Ga_3F_6(SeO_3)_2Br_3·2H_2O$

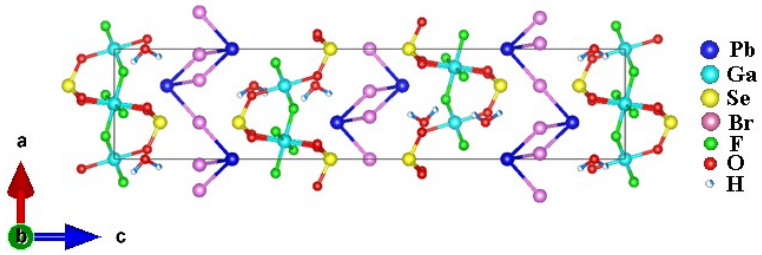

Figure S3. Coordination environments of cations in $Pb_2Ga_3F_6(SeO_3)_2Br_3 \cdot 2H_2O$.

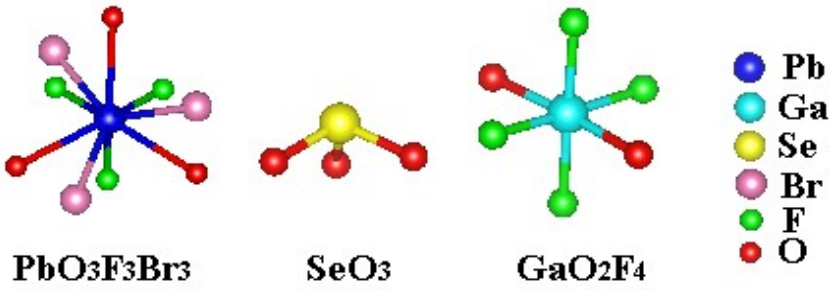

Figure S4. IR spectra of (a) $Pb_2Ga_3F_6(SeO_3)_2Cl_3 \cdot 2H_2O$ and (b) $Pb_2Ga_3F_6(SeO_3)_2Br_3 \cdot 2H_2O$.

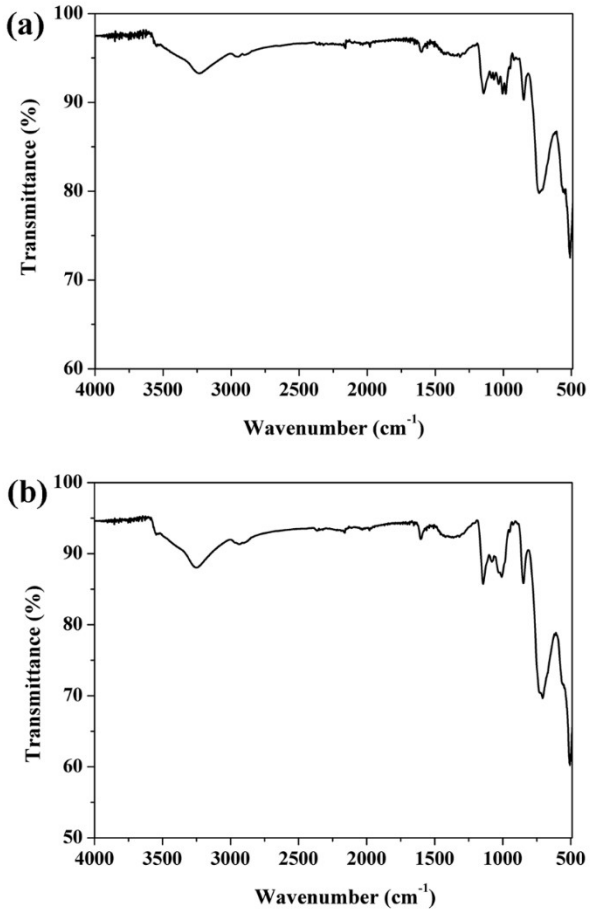

Figure S5. The TG curves of (a) $Pb_2Ga_3F_6(SeO_3)_2Cl_3·2H_2O$ and (b) $Pb_2Ga_3F_6(SeO_3)_2Br_3·2H_2O$.

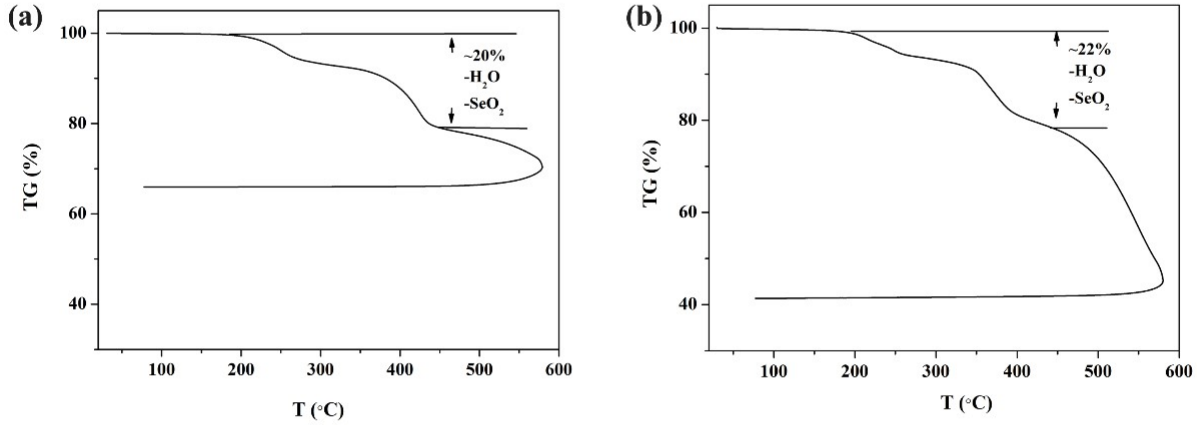

Figure S6. The band structure of (a) $Pb_2Ga_3F_6(SeO_3)_2Cl_3·2H_2O$ and (b) $Pb_2Ga_3F_6(SeO_3)_2Br_3·2H_2O$.

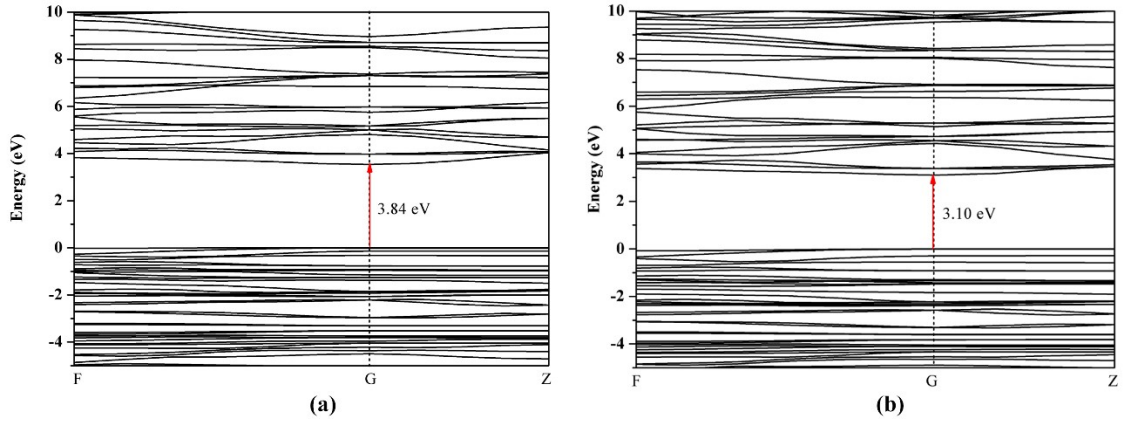

Figure S7 The calculated refractive index and birefringence curves of (a) $Pb_2Ga_3F_6(SeO_3)_2Cl_3{\cdot}2H_2O$ and (b) $Pb_2Ga_3F_6(SeO_3)_2Br_3{\cdot}2H_2O$.