Supporting Information

Selenite Bromides Nonlinear Optical Materials $Pb_2GaF_2(SeO_3)_2Br$ and $Pb_2NbO_2(SeO_3)_2Br$: Synthesis and Characterization

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1. Tables

Table S1. Bond Lengths and Bond Angles for $Pb_2GaF_2(SeO_3)_2Br$.

$Pb_2GaF_2(SeO_3)_2Br$			
Pb1-Br1[1]	3.1407(18)	Se1-O5	1.717(13)
Pb1-Br1	3.0065(18)	Br1-Pb1[4]	3.1407(18)
Pb1-O1	2.567(15)	Ga1-F2	1.837(10)
Pb1-O1[2]	2.565(13)	Ga1-O6	1.974(12)
Pb1-O2[3]	2.669(13)	Ga1-F1[5]	1.995(9)
Pb1-O4[1]	2.596(12)	Ga1-F1	1.962(9)
Pb2-Br1	3.095(2)	Ga1-O5[4]	1.985(12)
Pb2-O1[4]	2.650(14)	Ga1-O3[6]	1.911(13)
Pb2-O2	2.686(13)	Se2-O2	1.696(13)
Pb2-O4	2.573(11)	Se2-O3	1.721(12)
Pb2-O3[4]	2.649(12)	Se1-O6	1.730(12)
Se2-O1	1.711(14)	Se1-O4	1.672(10)
Br1-Pb1-Br1[1]	123.27(6)	F1-Ga1-O6	171.2(5)
F2-Ga1-O6	96.7(5)	F1-Ga1-F1[5]	88.68(12)
F2-Ga1-F1[5]	88.3(5)	F1-Ga1-O5[4]	91.0(5)
F2-Ga1-F1	91.7(5)	O5[4]-Ga1-F1[5]	177.7(5)
F2-Ga1-O5[4]	94.0(5)	O3[6]-Ga1-O6	83.3(5)
F2-Ga1-O3[6]	176.7(5)	O3[6]-Ga1-F1	88.2(5)
O6-Ga1-F1[5]	89.0(5)	O3[6]-Ga1-F1[5]	88.4(5)
O6-Ga1-O5[4]	91.0(5)	O3[6]-Ga1-O5[4]	89.3(6)
O1-Se2-O3	96.2(6)	Se2-O1-Pb1[3]	112.3(6)
O2-Se2-O1	99.0(6)	Se2-O1-Pb1	105.1(6)
O2-Se2-O3	103.1(6)	Se2-O1-Pb2[1]	103.1(7)
O4-Se1-O6	100.1(6)	Pb1[2]-O2-Pb2	112.0(5)
O4-Se1-O5	98.6(6)	Se2-O2-Pb1[2]	108.6(6)
O5-Se1-O6	100.4(6)	Se2-O2-Pb2	122.3(7)
Pb1-Br1-Pb1[4]	123.27(6)	Se1-O6-Ga1	122.0(7)
Pb1-Br1-Pb2	92.27(5)	Pb2-O4-Pb1[4]	103.4(4)
Pb2-Br1-Pb1[4]	81.17(4)	Se1-O4-Pb1[4]	132.5(7)
Se2-O3-Pb2[1]	102.9(5)	Se1-O4-Pb2	111.0(5)
Se2-O3-Ga1[8]	125.9(6)	Ga1-F1-Ga1[7]	159.2(5)
Ga1[8]-O3-Pb2[1]	122.0(6)	Se1-O5-Ga1[1]	123.5(7)

[1]+X,-1+Y,+Z; [2]2-X,1/2+Y,2-Z; [3]2-X,-1/2+Y,2-Z; [4]+X,1+Y,+Z; [5]-X,-1/2+Y,1-Z; [6]1-X,3/2+Y,1-Z; [7]-X,1/2+Y,1-Z; [8]1-X,-3/2+Y,1-Z

[1]+X,-1+Y,+Z; [2]2-X,1/2+Y,2-Z; [3]2-X,-1/2+Y,2-Z; [4]+X,1+Y,+Z; [5]-X,-1/2+Y,1-Z; [6]1-X,3/2+Y,1-Z; [7]-X,1/2+Y,1-Z; [8]1-X,-3/2+Y,1-Z

Table S2. Bond Lengths and Bond Angles for $Pb_2NbO_2(SeO_3)_2Br$.

$Pb_2NbO_2(SeO_3)_2Br$			
Pb1-Br1[1]	3.2051(14)	Nb1-O2[6]	2.220(8)
Pb1-Br1	3.0263(13)	Se1-O3	1.698(9)
Pb1-O3[1]	2.664(9)	Se1-O1	1.731(9)
Pb1-O1	2.525(9)	Se1-O2	1.707(8)
Pb1-O1[2]	2.608(9)	Se2-O4	1.673(8)
Pb1-O4[2]	2.700(8)	Se2-O6	1.721(9)
Pb1-O8[3]	2.672(8)	Se2-O5	1.738(9)
Pb2-Br1[2]	3.0725(13)	Nb1-O6	2.144(9)
Pb2-O3[1]	2.639(9)	Nb1-O7	1.938(8)
Pb2-O1	2.603(9)	Nb1-O7[4]	1.920(8)
Pb2-O4	2.524(9)	Nb1-O8	1.763(8)
Pb2-O2	2.594(9)	Nb1-O5[5]	2.110(9)
Br1-Pb1-Br1[1]	122.17(4)	Pb2-O4-Pb1[7]	102.6(3)
O7-Nb1-O2[4]	86.4(3)	O2-Pb2-O3[1]	108.9(3)
O75-Nb1-O2[4]	83.8(3)	O2-Pb2-O1	58.9(3)
O8-Nb1-O6	98.3(4)	O6-Nb1-O2[4]	75.1(3)
O8-Nb1-O7	98.6(4)	O7[5]-Nb1-O6	158.9(4)
O8-Nb1-O7[5]	102.6(4)	O7-Nb1-O6	85.6(3)
O8-Nb1-O5[6]	92.6(4)	O7[5]-Nb1-O7	94.32(12)
O8-Nb1-O2[4]	171.4(3)	O7[5]-Nb1-O5[6]	91.5(4)
O5[6]-Nb1-O6	84.4(3)	O7-Nb1-O5[6]	166.0(4)
O5[6]-Nb1-O2[4]	81.5(3)	Se2-O4-Pb1[7]	127.8(5)
O3-Se1-O1	99.4(4)	Se2-O4-Pb2	114.2(4)
O3-Se1-O2	103.6(4)	Se2-O6-Nb1	119.2(5)
O2-Se1-O1	96.0(4)	Nb1[8]-O7-Nb1	151.9(5)
O4-Se2-O6	100.5(4)	Nb1-O8-Pb1[9]	163.7(6)
O4-Se2-O5	99.2(4)	Se2-O5-Nb1[1]	121.3(5)
O6-Se2-O5	101.0(4)	Nb1[10]-O2-Pb2	126.2(3)
Pb1-Br1-Pb1[6]	122.17(4)	Se1-O2-Pb2	103.0(4)
Pb1-Br1-Pb2	793.61(4)	Se1-O2-Nb1[10]	120.0(4)
Pb2[7]-Br1-Pb1	681.01(3)	Pb1-O1-Pb2	115.1(3)
Pb2[6]-O3-Pb1[6]	109.4(3)	Pb2-O1-Pb1[7]	103.0(3)
Se1-O3-Pb1[6]	108.6(5)	Se1-O1-Pb1[7]	106.2(4)
Se1-O3-Pb2[6]	125.9(4)	Se1-O1-Pb1	111.3(4)
Pb1-O1-Pb1[7]	117.6(3)	Se1-O1-Pb2	102.0(4)

[1]+X,-1+Y,+Z; [2]-X,-1/2+Y,1-Z; [3]-1+X,-1+Y,+Z; [4]2-X,1/2+Y,2-Z; [5]+X,1+Y,+Z; [6]1-X,1/2+Y,2-Z; [7]-X,1/2+Y,1-Z; [8]2-X,-1/2+Y,2-Z; [9]1+X,1+Y,+Z; [10]1-X,-1/2+Y,2-Z

[1]+X,-1+Y,+Z; [2]-X,-1/2+Y,1-Z; [3]-1+X,-1+Y,+Z; [4]1-X,1/2+Y,2-Z; [5]2-X,1/2+Y,2-Z; [6]+X,1+Y,+Z; [7]-X,1/2+Y,1-Z; [8]2-X,-1/2+Y,2-Z; [9]1+X,1+Y,+Z; [10]1-X,-1/2+Y,2-Z

Table S3. The calculated SHG coefficients of $Pb_2GaF_2(SeO_3)_2Br$ and $Pb_2NbO_2(SeO_3)_2Br$.

	d_{16}	d_{14}	d_{22}	d_{33}	d_{powder}
$Pb_2GaF_2(SeO_3)_2Br$	-0.55	-1.17	5.37	-2.08	2.58
$Pb_2NbO_2(SeO_3)_2Br$	0.47	-0.08	1.95	-0.55	0.91

2. Figures

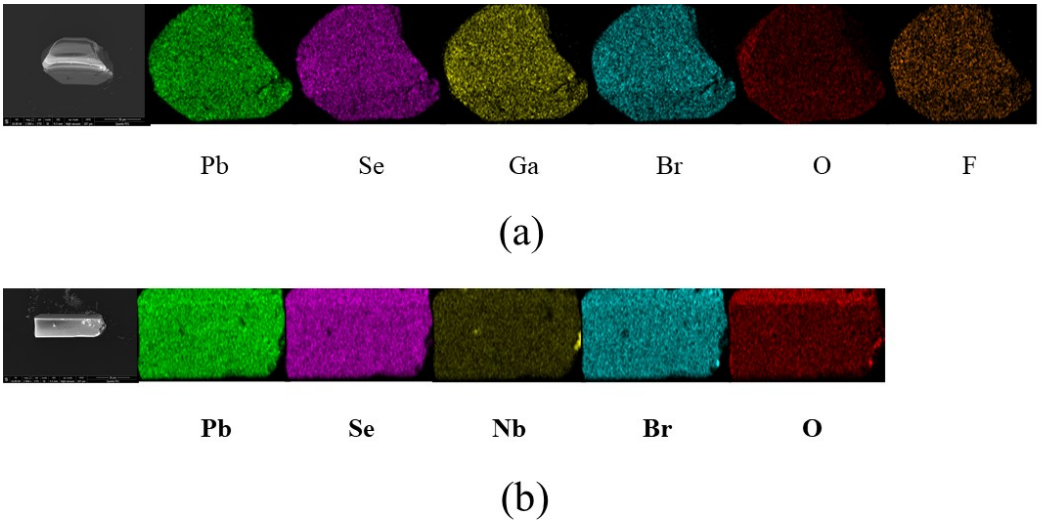
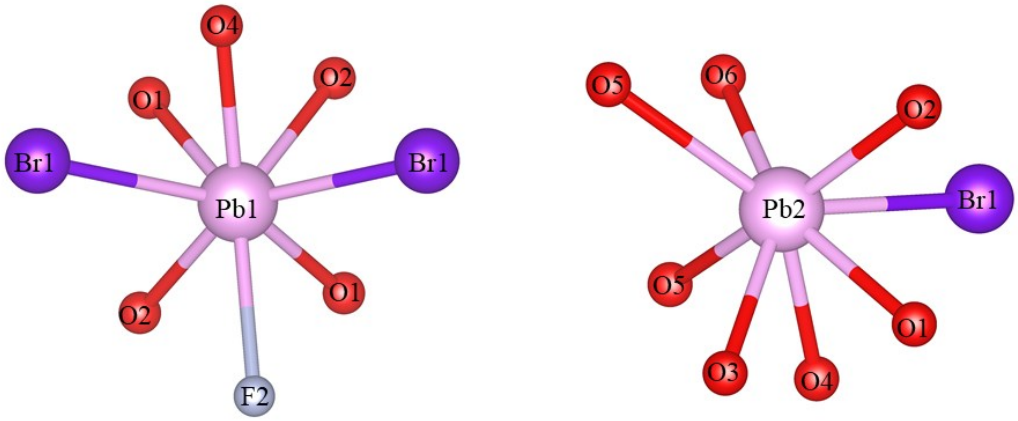


Figure S1. SEM images of $Pb_2GaF_2(SeO_3)_2Br$(a) and $Pb_2NbO_2(SeO_3)_2Br$ (b).



(a) (b)

Figure S2. The coordination geometries around the Pb(1) (a) and Pb(2) (b) atoms in $Pb_2GaF_2(SeO_3)_2Br$.

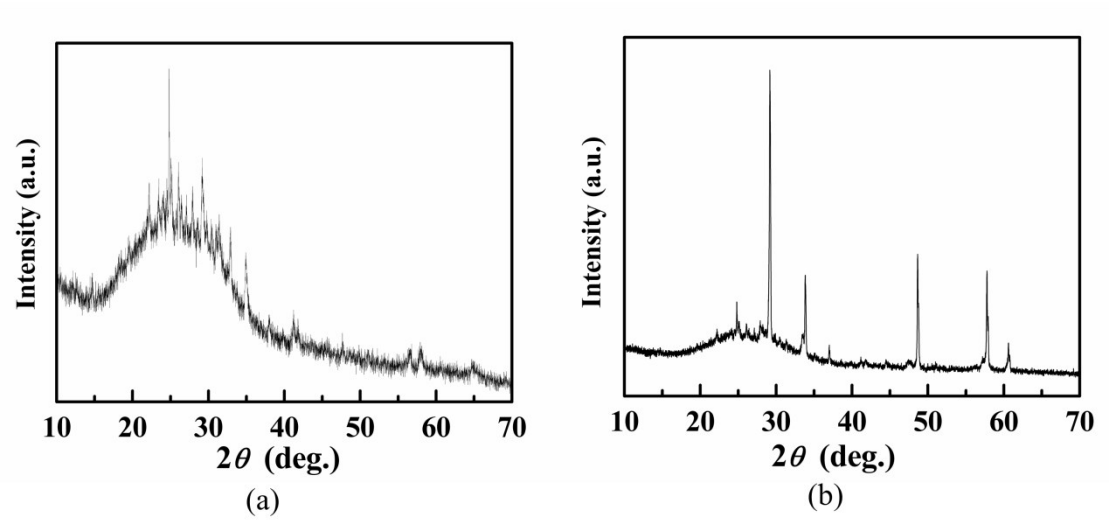


Figure S3. Powder XRD patterns for calcined products of $Pb_2GaF_2(SeO_3)_2Br$ (a), $Pb_2NbO_2(SeO_3)_2Br$ (b).

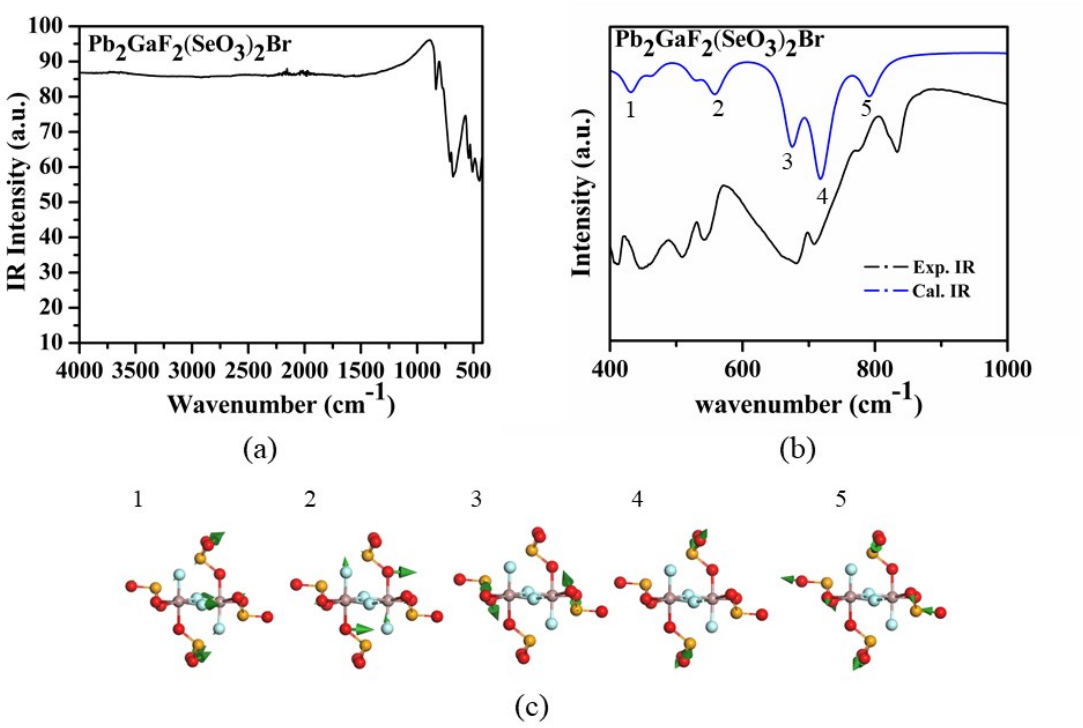


Figure S4. The experimental and simulated IR spectrum of $Pb_2GaF_2(SeO_3)_2Br$ (a, b); Assignments of peaks and the corresponding vibrational mode in the range of 400-1000 cm^{-1} in the IR spectrum for $Pb_2GaF_2(SeO_3)_2Br$ (c).

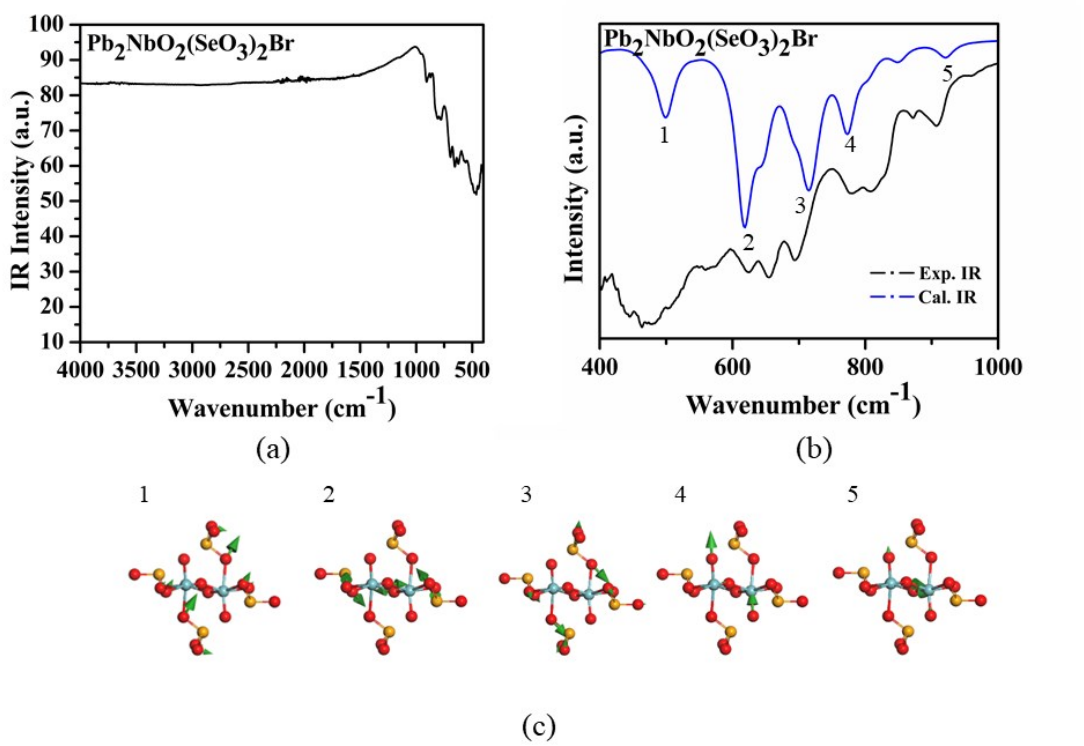


Figure S5. The experimental and simulated IR spectrum of $Pb_2NbO_2(SeO_3)_2Br$ (a, b); Assignments of peaks and the corresponding vibrational mode in the range of 400-1000 cm^{-1} in the IR spectrum for $Pb_2NbO_2(SeO_3)_2Br$ (c).

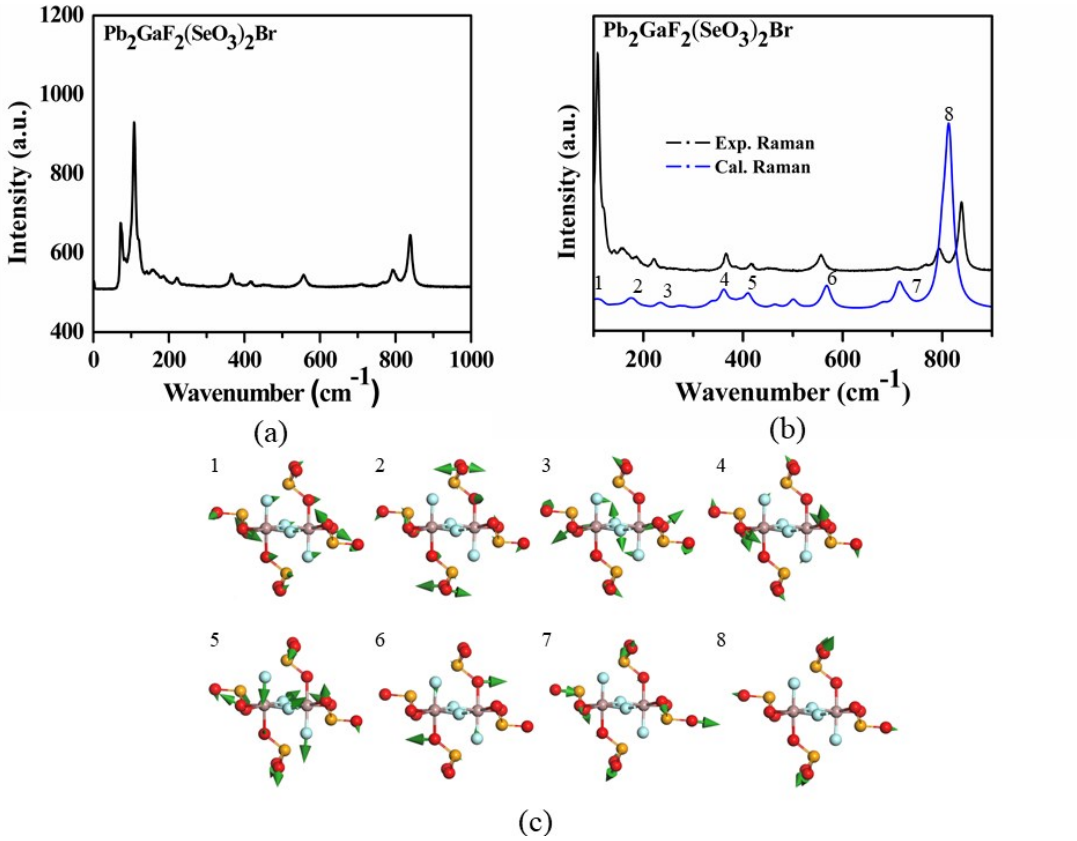


Figure S6. The experimental and simulated Raman spectrum of $Pb_2GaF_2(SeO_3)_2Br$ (a, b); Assignments of peaks and the corresponding vibrational mode in the range of 100-900 cm^{-1} in the Raman spectrum for $Pb_2GaF_2(SeO_3)_2Br$ (c).

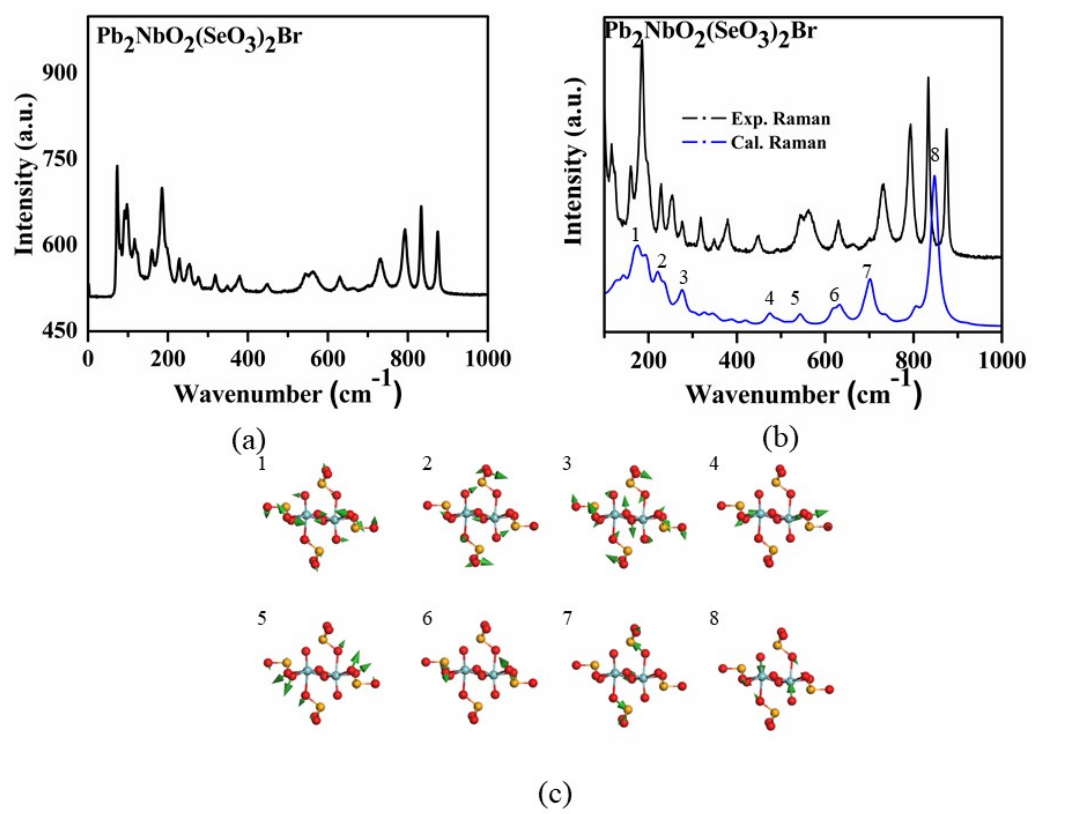


Figure S7. The experimental and simulated Raman spectrum of $Pb_2NbO_2(SeO_3)_2Br$ (a, b); Assignments of peaks and the corresponding vibrational mode in the range of 100-1000 cm^{-1} in the Raman spectrum for $Pb_2NbO_2(SeO_3)_2Br$ (c).

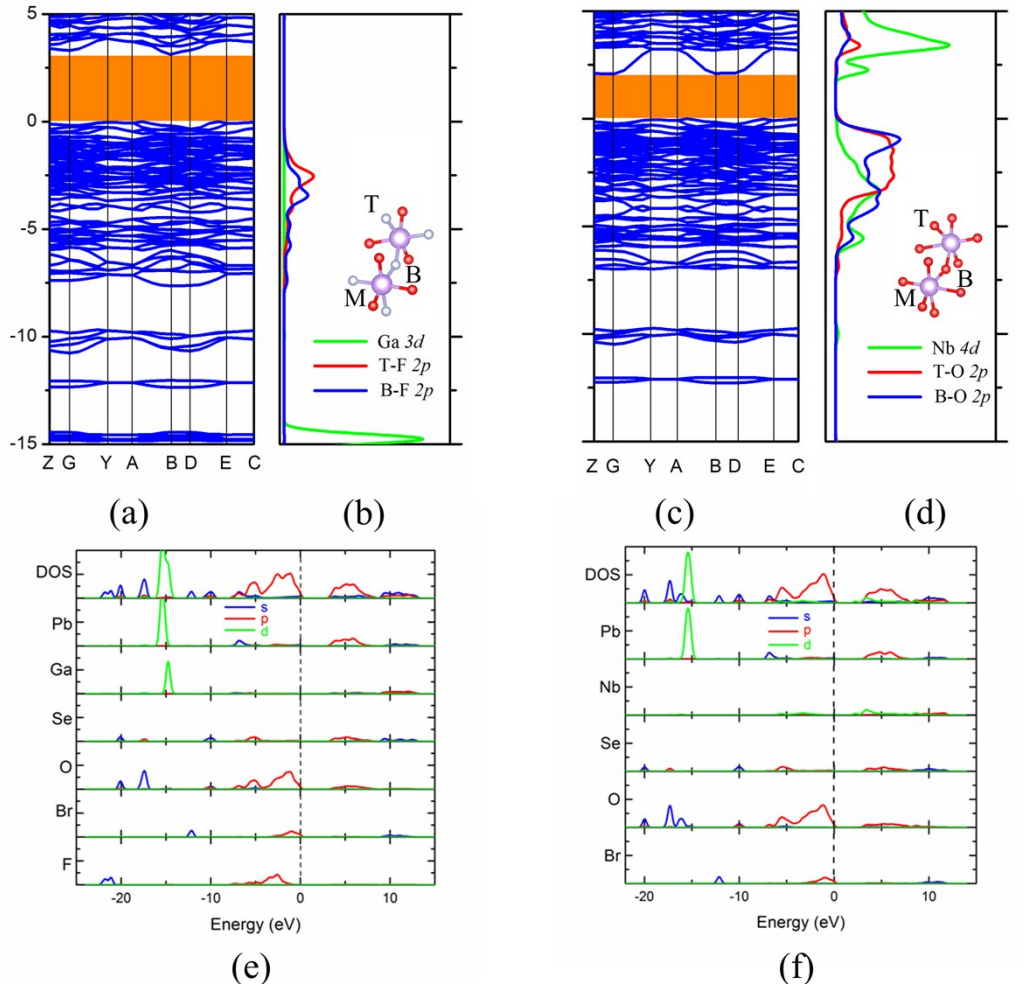


Figure S8. Band structures of (a) $Pb_2GaF_2(SeO_3)_2Br$ and (c) $Pb_2NbO_2(SeO_3)_2Br$; PDOS for (b) $(GaO_3F_3)^{6-}$ and (d) $(NbO_6)^{7-}$ groups. Three crucial atomic sites were highlighted, namely, metal cations (M site), terminal O/F (T site), and bridge O/F (B site). T-F and T-O indicate terminal F and O atoms, while B-F and B-O indicate bridged F and O atoms, respectively. The orange regions represent forbidden gap. The PDOS for all constituent ions of $Pb_2GaF_2(SeO_3)_2Br$ (e) and $Pb_2NbO_2(SeO_3)_2Br$ (f).

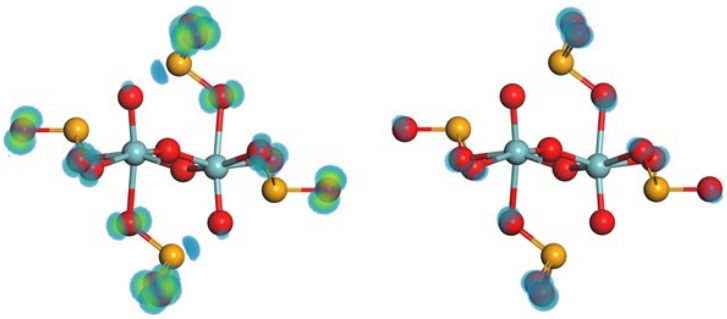


Figure S9. SHG-weighted electron density maps of the occupied and unoccupied states of $[Nb_2O_2(SeO_3)_4]^{6-}$ building blocks of $Pb_2NbO_2(SeO_3)_2Br$. The blue, red, and orange balls represent Nb, O, and Se, respectively.