Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$Pb_{3.5}GeS_4Br_3$: The first phase-matching thiogermanate halide IR nonlinear optical material

Jiazheng Zhou,[a,b]† Hongshan Wang,[b]† Junjie Liu,[a]†Xin Su,[b] Yu Chu,[b,*] Jiale Qu,[a,*] Xiangzhan Jiang[a,*]

a. Institute of Rehabilitation Engineering, Binzhou Medical University, Yantai, 264003, China.

b. Research Center for Crystal Materials; State Key Laboratory of Functional Materials and Devices for Special Environmental Conditions; Xinjiang Key Laboratory of Functional Crystal Materials; Xinjiang Technical Institute of Physics & Chemistry, CAS, 40-1 South Beijing Road, Urumqi 830011, China.

*Corresponding authors (E-mails: chuy@ms.xjb.ac.cn; qujiale@buaa.edu.cn; xzjiang@bzmc.edu.cn)

† These authors contributed equally to this work.

Table S1. Atomic coordinates, equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of $Pb_3GeS_4Br_2$.

Atoms	x	y	z	U_{eq}	Wyckoff positions
Pb1	8013.3(4)	6928.8(5)	6484.4(4)	38.56(14)	4*e*
Pb2	8459.7(3)	2662.5(7)	4120.2(5)	45.47(15)	4*e*
Pb3	5460.9(3)	-944.2(4)	3366.2(4)	27.99(12)	4*e*
Ge1	6254.4(7)	2948.2(10)	5160.6(8)	15.87(18)	4*e*
S1	6672.5(17)	4938(3)	4097(2)	21.1(4)	4*e*
S2	7485.3(18)	915(3)	5463(2)	23.5(4)	4*e*
S3	4500.7(16)	1914(2)	3982.2(19)	16.0(4)	4*e*
S4	6511(2)	3843(3)	7074(2)	29.0(5)	4*e*
Br1	8735.7(10)	6875.4(15)	9343.5(10)	38.8(3)	4*e*
Br2	9674.3(8)	4356.4(13)	6993.3(10)	35.8(2)	4*e*

Table S2. Atomic coordinates, equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of $Pb_{3.5}GeS_4Br_3$.

Atoms	x	y	z	U_{eq}	Wyckoff positions
Pb1	1453.8(3)	4040.6(3)	8784.7(6)	24.32(13)	6*c*
Pb2	0	0	1517(2)	22.0(2)	2*a*
Ge1	3333.33	6666.67	4759(2)	13.0(3)	2*b*
S1	3333.33	6666.67	1140(5)	19.0(7)	2*b*
S2	1230.4(19)	6000(2)	6184(3)	15.4(4)	6*c*
Br1	786.3(7)	2606.3(7)	4002.8(15)	23.33(19)	2*b*

Table S3. Selected bond lengths of $Pb_3GeS_4Br_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb1	S1	2.980(2)	Pb3	S3[1]	3.120(2)
Pb1	Br14	3.1346(11)	Pb3	S1[2]	3.030(2)
Pb1	Br1	2.9899(11)	Pb3	S2	3.046(2)
Pb1	Br2	2.8432(10)	Pb3	S4[3]	2.939(2)
Pb2	S1	2.928(2)	Ge1	S1	2.218(2)
Pb2	S2	2.760(2)	Ge1	S2	2.194(2)
Pb2	S43	2.841(2)	Ge1	S3	2.216(2)
Pb3	S3	2.8430(19)	Ge1	S4	2.193(2)

[1]1-X,-Y,1-Z; [2]1-X,-1/2+Y,1/2-Z; [3]+X,1/2-Y,-1/2+Z; [4]+X,3/2-Y,-1/2+Z

Table S4. Selected bond lengths of $Pb_{3.5}GeS_4Br_3$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb1	S1[2]	2.9490(16)	Pb2	Br1[7]	2.9613(10)
Pb1	S2[1]	2.8960(19)	Pb2	Br1[8]	2.9613(10)
Pb1	S2	2.7797(19)	Pb2	Br1[4]	2.9702(11)
Pb1	Br1	3.2024(10)	Ge1	S1	2.191(3)
Pb2	Br1	2.9613(10)	Ge1	S2	2.2243(19)
Pb2	Br1[5]	2.9702(11)	Ge1	S2[1]	2.2243(19)
Pb2	Br1[6]	2.9702(11)	Ge1	S2[9]	2.2243(19)

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

Table S5. Selected angles (°) of $Pb_3GeS_4Br_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1	Pb1	Br1	140.79(5)	S1[2]	Pb3	S3[1]	125.98(5)
S1	Pb1	Br1[4]	72.30(5)	S1[2]	Pb3	S2	136.75(6)
Br2	Pb1	Br1	85.53(3)	S2	Pb3	S3[1]	73.25(6)
Br2	Pb1	Br1[4]	86.00(3)	S4[3]	Pb3	S3[1]	145.30(6)
Br2	Pb1	S1	82.80(5)	S4[3]	Pb3	S1[2]	79.75(6)
Br1	Pb1	Br1[4]	143.89(4)	S4[3]	Pb3	S2	72.16(6)
S2	Pb2	S1	77.13(6)	S3	Ge1	S1	111.29(8)
S2	Pb2	S4[3]	78.02(7)	S2	Ge1	S3	106.52(8)
S4[3]	Pb2	S1	81.79(7)	S2	Ge1	S1	107.06(9)
S3	Pb3	S3[1]	77.44(6)	S4	Ge1	S3	113.45(9)
S3	Pb3	S1[2]	74.27(6)	S4	Ge1	S1	110.33(10)
S3	Pb3	S2	73.68(5)	S4	Ge1	S2	107.86(9)
S3	Pb3	S4[3]	90.29(7)				

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

Table S6. Selected angles (°) of $Pb_{3.5}GeS_4Br_3$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S2	Pb1	Br1	77.49(4)	Br1	Pb2	Br1[8]	83.721(9)
S2[1]	Pb1	Br1	70.33(4)	Br1[7]	Pb2	Br1[8]	179.71(6)
S2	Pb1	S2[1]	77.43(7)	Br1[3]	Pb2	Br1[5]	96.09(4)
S2	Pb1	S1[2]	78.67(6)	Br1[6]	Pb2	Br1[3]	83.722(9)
S2[1]	Pb1	S1[2]	76.87(6)	Br1[5]	Pb2	Br1[8]	96.09(4)
S1[2]	Pb1	Br1	142.78(6)	Br1[7]	Pb2	Br1[3]	83.722(9)
Br1[3]	Pb2	Br1[8]	96.09(4)	Br1	Pb2	Br1[5]	83.721(9)
Br1	Pb2	Br1[3]	179.71(6)	S2	Ge1	S2[1]	105.93(6)
Br1[6]	Pb2	Br1[8]	83.722(9)	S2[9]	Ge1	S2[1]	105.93(6)
Br1[6]	Pb2	Br1[7]	96.47(4)	S2	Ge1	S2[9]	105.93(6)
Br1[6]	Pb2	Br1[5]	179.71(6)	S1	Ge1	S2[1]	112.82(6)
Br1[7]	Pb2	Br1[5]	83.722(9)	S1	Ge1	S2[9]	112.82(6)
Br1[6]	Pb2	Br1	96.47(4)	S1	Ge1	S2	112.82(6)
Br1[7]	Pb2	Br1	96.47(4)				

[1]1-Y,1+X-Y,+Z; [2]+X,+Y,1+Z; [3]-X,-Y,-1/2+Z; [4]-X,-Y,1/2+Z; [5]-Y+X,+X,-1/2+Z; [6]+Y-X,-X,+Z; [7]-Y,+X-Y,+Z; [8]+Y,-X+Y,-1/2+Z; [9]+Y-X,1-X,+Z; [10]+Y-X,1-X,-1+Z; [11]+X,+Y,-1+Z; [12]1-Y,1+X-Y,-1+Z

Table S7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_3GeS_4Br_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	38.5(2)	48.7(3)	25.6(2)	-1.34(16)	11.60(17)	18.96(17)
Pb2	25.7(2)	74.7(3)	40.7(3)	-11.1(2)	18.88(18)	-10.34(18)
Pb3	34.3(2)	26.06(19)	27.5(2)	2.63(13)	17.18(16)	2.76(13)
Ge1	18.0(4)	18.3(4)	11.6(4)	0.2(3)	6.8(3)	0.2(3)
S1	21.1(9)	21.9(9)	16.8(10)	3.5(7)	5.3(7)	-2.0(7)
S2	20.2(9)	20.8(9)	26.7(11)	2.2(8)	7.7(8)	5.2(7)
S3	16.0(8)	18.8(9)	13.6(9)	-0.3(7)	6.9(7)	-0.1(6)
S4	30.1(11)	41.1(13)	11.7(10)	-4.4(8)	5.5(8)	15.7(9)
Br1	41.3(5)	59.5(7)	23.3(5)	-6.7(4)	21.2(4)	-14.9(5)
Br2	26.1(4)	36.5(5)	31.0(5)	-9.8(4)	0.0(4)	11.4(4)

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_{3.5}GeS_4Br_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Pb1	27.61(19)	21.53(18)	23.92(19)	4.86(17)	1.42(18)	12.36(13)
Pb2	17.6(3)	17.6(3)	30.9(6)	0	0	8.78(14)
Ge1	14.3(4)	14.3(4)	10.4(6)	0	0	7.1(2)
S1	23.3(11)	23.3(11)	10.5(17)	0	0	11.7(6)
S2	13.5(9)	16.6(10)	16.7(10)	-0.3(8)	0.4(7)	7.9(8)
Br1	22.3(4)	24.0(4)	21.5(4)	-2.1(4)	-4.3(4)	10.0(3)

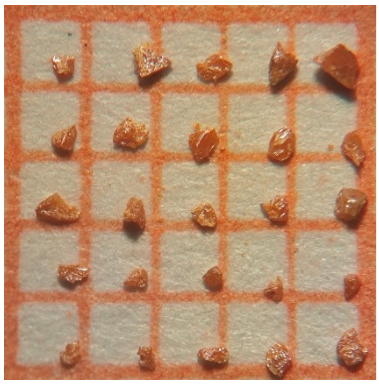

Fig. S1 The optical image of $Pb_{3.5}GeS_4Br_3$ crystals.

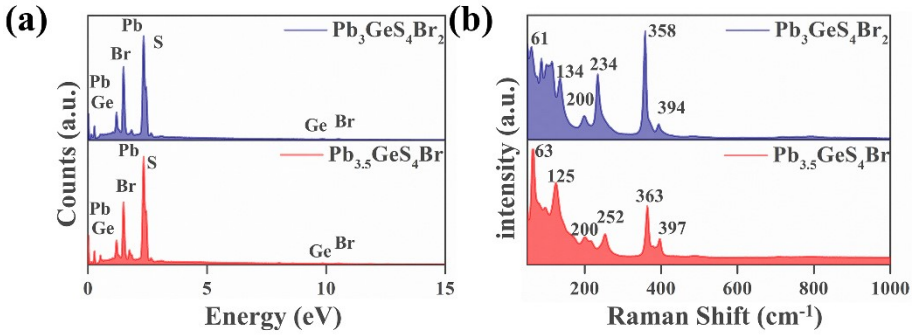

Fig. S2 The EDS (a) and Raman spectra (b) of $Pb_3GeS_4Br_2$ and $Pb_{3.5}GeS_4Br_3$.

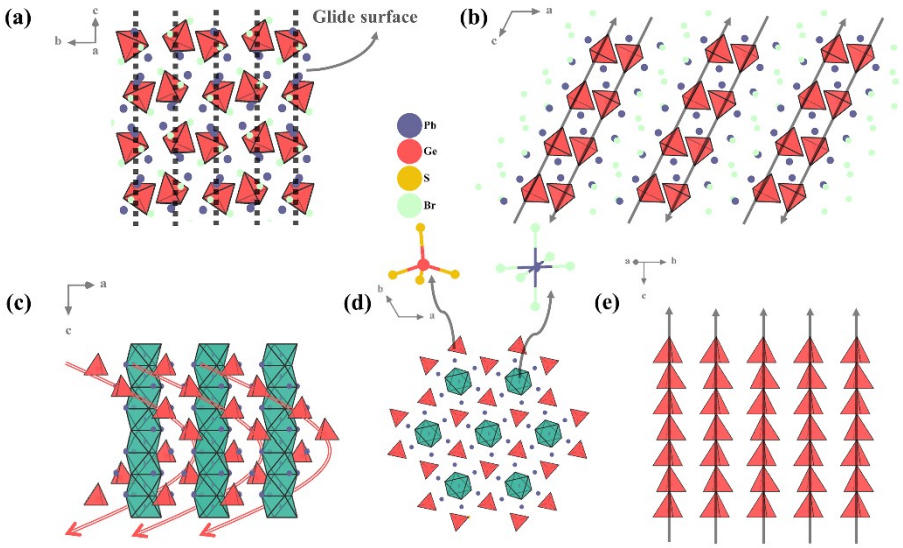

Fig. S3 The structures of $Pb_3GeS_4Br_2$ and $Pb_{3.5}GeS_4Br_3$. (a) The isolated [GeS_4] pseudo-layer structure alignment along the glide surface in $Pb_3GeS_4Br_2$; (b) The opposite-arranged [GeS_4] tetrahedra in $Pb_3GeS_4Br_2$; (c) The isolated [GeS_4] tetrahedral arranged around the [PbS_6] column configuration in $Pb_{3.5}GeS_4Br_3$; (d) The whole structure of $Pb_{3.5}GeS_4Br_3$; (e) The well-arranged [GeS_4] tetrahedra in $Pb_{3.5}GeS_4Br_3$.

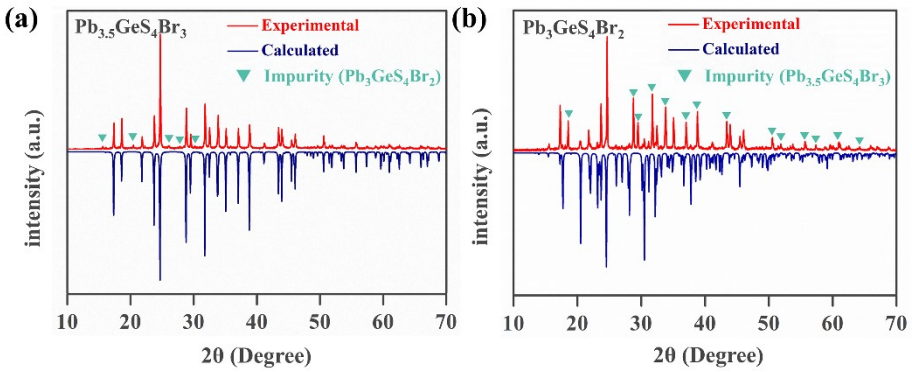

Fig. S4 The experimental and calculated XRD patterns of $Pb_{3.5}GeS_4Br_3$ (a) and $Pb_3GeS_4Br_2$ (b).

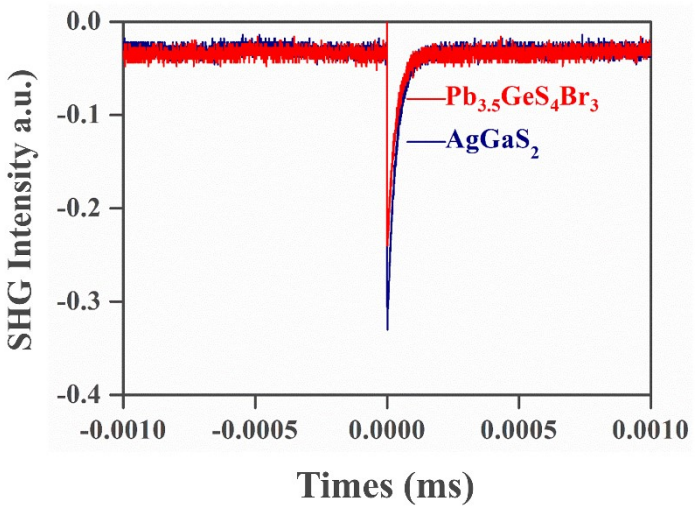

Fig. S5 Oscilloscope traces of SHG signals of $Pb_{3.5}GeS_4Br_3$ (red) with $AgGaS_2$ (blue) as a reference at a particle size of 180-212 μm.

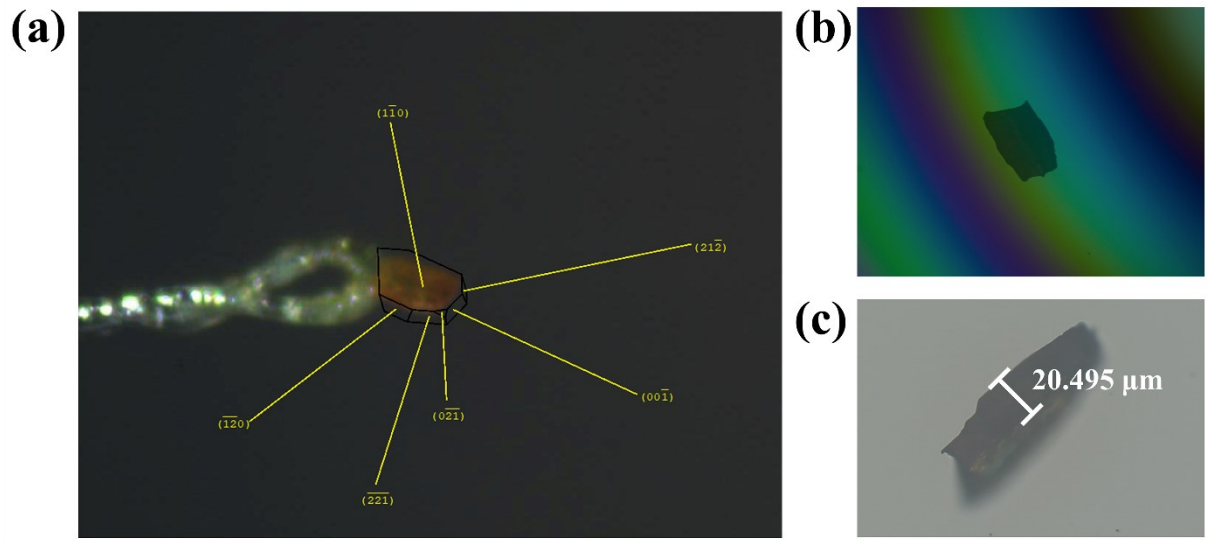

Fig. S6 The RID measurement of $Pb_{3.5}GeS_4Br_3$. (a) The plane indices determined by single crystal XRD. (b) The RID was measured to 0.05@546 nm (c) The thickness of the single crystal is 20.495 µm measured by an optical microscope.

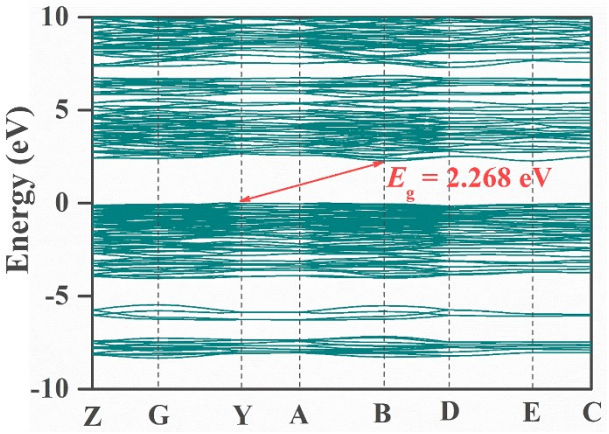

Fig. S7 The band structure of $Pb_3GeS_4Br_2$.