Supporting Information

$A_2Zn_3P_4S_{13}$ (A = Rb, Cs): First Infrared Nonlinear Optical Materials with Mixed Thiophosphate Functional Motifs PS_4 and P_2S_6

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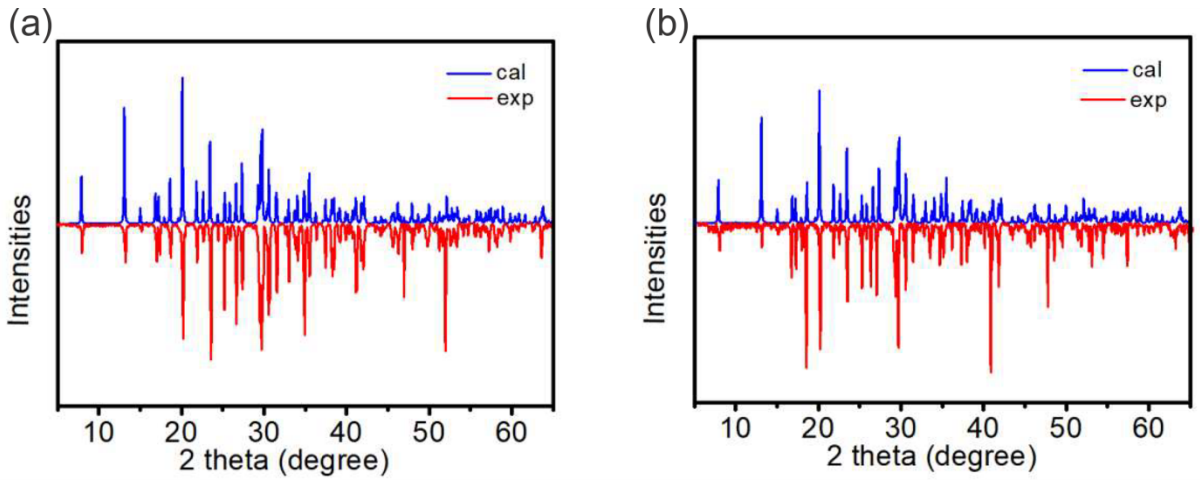

Figure S1. Experimental and simulated powder XRD patterns of **1** (a) and **2** (b).

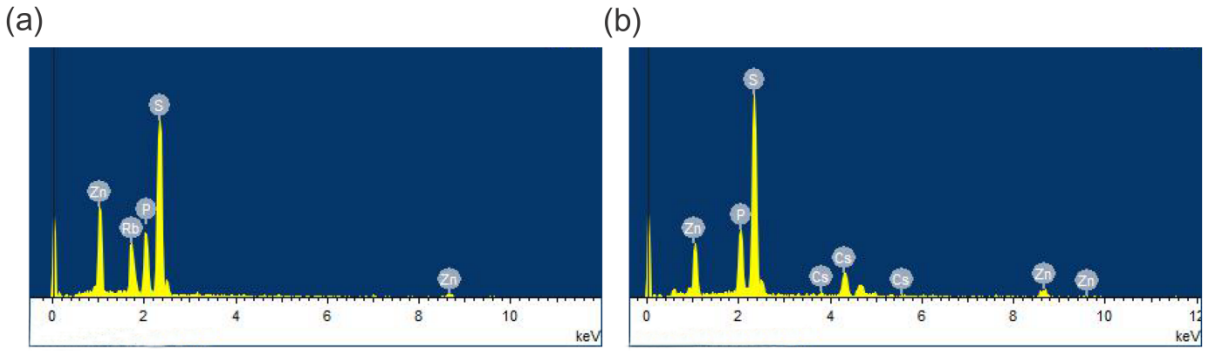

Figure. S2 Energy-dispersive X-ray spectra of single crystals of **1** (a) and **2** (b).

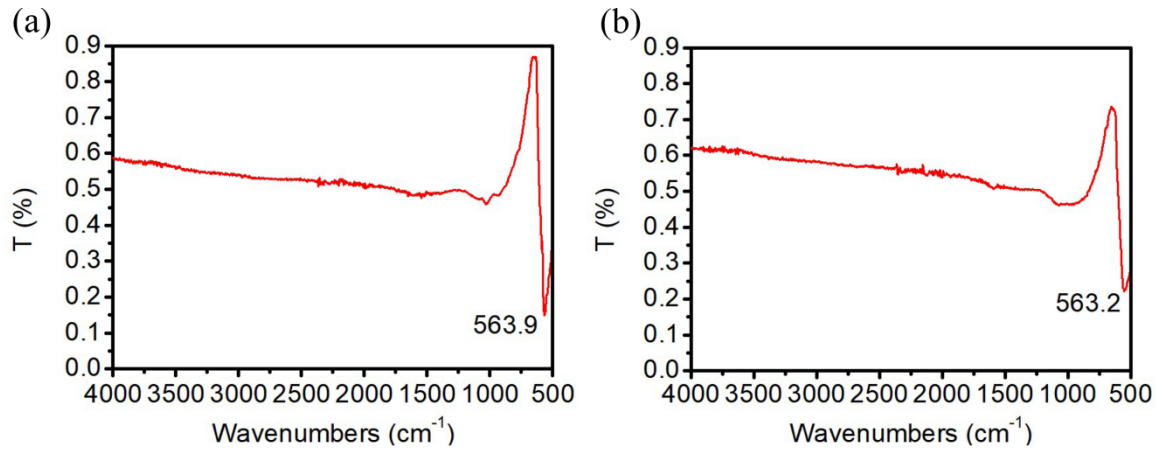

Figure S3. IR spectra of **1** (a) and **2** (b).

Table S1. NLO efficiency and LIDT of known NLO thiophosphates and their building thiophosphate units

Compounds	Thiophosphate units	NLO efficiency	LIDT
γ-Li_3PS_4[1]	$[PS_4]^{3-}$	d_{15} = -3.08 pm/V d_{24} = -4.03 pm/V d_{33} = 4.32 pm/V(cal)	d_{power} = 3.66 pm/V
$Hg_3P_2S_8$[2]	$[PS_4]^{3-}$	3.6×AGS@2.05 μm(exp)	3.0×AGS(exp.)
$Cu_5Hg_{0.5}P_2S_8$[3]	$[PS_4]^{3-}$	0.8×AGS@2.05 μm(exp)	/
$AgHg_3PS_6$[3]	$[PS_4]^{3-}$	0.5×AGS@2.05 μm(exp)	/
$CsBrHg_3P_2S_8$[4]	$[PS_4]^{3-}$	1.2×AGS@2.09 μm(exp)	5.0×AGS(exp)
$RbBrHg_3P_2S_8$[4]	$[PS_4]^{3-}$	1.05×AGS@2.09μm(exp)	4.5×AGS(exp)
$CsClHg_3P_2S_8$[4]	$[PS_4]^{3-}$	0.8×AGS@2.09 μm(exp)	6.0×AGS(exp)
$Ag_5PS_4Cl_2$[5]	$[PS_4]^{3-}$	2.5×AGS@2.09 μm(exp)	1.7×AGS(exp)
Ag_3PS_4[5]	$[PS_4]^{3-}$	1.3×AGS@2.09 μm(exp)	1.0×AGS(exp)
Cu_3PS_4[6]	$[PS_4]^{3-}$	0.8×AGS@2.09 μm(exp)	/
$Ag_{1.5}Cu_{1.5}PS4$[7]	$[PS_4]^{3-}$	0.5×AGS@2.09 μm(exp)	/
Ag_6PS_5Br[8]	$[PS_4]^{3-}$	2.7×AGS@2.09 μm(exp)	1.7×AGS(exp)
Cu_6PS_5Cl[8]	$[PS_4]^{3-}$	2.0×AGS@2.09 μm(exp)	2.3×AGS(exp)
Cu_6PS_5Br[8]	$[PS_4]^{3-}$	2.0×AGS@2.09 μm(exp)	2.3×AGS(exp)
$Cu_5Zn_{0.5}P_2S_8$[6]	$[PS_4]^{3-}$	0.3×AGS@2.05 μm(exp)	3.2×AGS(exp)
$AgHgPS_4$[9]	$[PS_4]^{3-}$	5.09×AGS@2.09	/
α-Na_3PS_4[1]	$[PS_4]^{3-}$	d_{14} = 9.64 pm/V (cal)	d_{power} = 8.15 pm/V(cal)
$Zn_3P_2S_8$[10]	$[PS_4]^{3-}$	2.6×AGS@2.09 μm(exp)	/
$LiZnPS_4$[11]	$[PS_4]^{3-}$	0.8×AGS@2.09 μm(exp)	/
$AgZnPS_4$[11]	$[PS_4]^{3-}$	1.8×AGS@2.09 μm(exp)	/

$CuZnPS_4$[12]	$[PS_4]^{3-}$	3.0×AGS@2.09 μm(exp)	6.0×AGS(exp)
$CuHgPS_4$[13]	$[PS_4]^{3-}$	6.5×AGS@2.05 μm(exp)	4.2×AGS(exp)
$AgGa_2PS_6$[14]	$[PS_4]^{3-}$	1.0×AGS@2.05 μm(exp)	5.1×AGS(exp)
$LiGa_2PS_6$[15]	$[PS_4]^{3-}$	0.5×AGS@1.91 μm(exp)	10.4×AGS(exp)
$AgCd_3PS_6$[16]	$[PS_4]^{3-}$	0.45×AGS@2.09	/
$LiCd_3PS_6$[15]	$[PS_4]^{3-}$	0.8×AGS@1.91 μm(exp)	5.5×AGS(exp)
$CuCd_3PS_6$[17]	$[PS_4]^{3-}$	0.9×AGS@2.09 μm(exp)	4.1×AGS(exp)
$[K_3Cl][Ga_3PS_8]$[18]	$[PS_4]^{3-}$	1.0×AGS@1.95 μm(exp)	39.0×AGS(exp)
$[Rb_3Cl][Ga_3PS_8]$[18]	$[PS_4]^{3-}$	1.1×AGS@1.95 μm(exp)	37.0×AGS(exp)
$[K_3Br][Ga_3PS_8]$[18]	$[PS_4]^{3-}$	1.2×AGS@1.95 μm(exp)	32.0×AGS(exp)
$[Rb_3Br][Ga_3PS_8]$[18]	$[PS_4]^{3-}$	2.0×AGS@1.95 μm(exp)	31.0×AGS(exp)
$Rb_2Ga_2P_2S_9$[19]	$[PS_4]^{3-}$	0.1×AGS@2.05μm(exp)	7.0×AGS(exp)
$K_3PS_4 \cdot H2O_{3.83}$[1]	$[PS_4]^{3-}$	d_{14} = 3.06 pm/V(cal)	d_{power} = 8.15 pm/V(cal)
$Pb_3P_2S_8$[20]	$[PS_4]^{3-}$	3.5×AGS@2.09	2.6×AGS(exp)
α-$Na_6Pb_3P_4S_{16}$[1]	$[PS_4]^{3-}$	d_{11} = -d_{12} = 17.86 pm/V d_{15} = d_{24} = -3.34 pm/V d_{33} = 8.40 pm/V(cal)	d_{power} = 13.03 pm/V(cal)
$RbPbPS_4$[1]	$[PS_4]^{3-}$	d_{14} = 0.23 pm/V(cal)	d_{power} = 0.19 pm/V(cal)
$K_9BiP_4S_{16}$[1]	$[PS_4]^{3-}$	d_{14} = 5.22 pm/V(cal)	d_{power} = 4.41 pm/V(cal)
$TlSnPS_4$[1]	$[PS_4]^{3-}$	d_{15} = -9.30 pm/V d_{24} = 2.75 pm/V d_{33} = 8.14 pm/V(cal)	d_{power} = 6.20 pm/V(cal)
$KInP_2S_7$[1]	$[PS_4]^{3-}$	d_{16} = -6.85 pm/V d_{14} = -4.34 pm/V d_{22} = 1.02 pm/V d_{23} = 2.84 pm/V(cal)	d_{power} = 5.60 pm/V(cal)
lt-$AlPS_4$[1]	$[PS_4]^{3-}$	d_{14} = 4.33 pm/V(cal)	d_{power} = 3.66 pm/V(cal)
ht-$AlPS_4$[1]	$[PS_4]^{3-}$	d_{14} = 6.14 pm/V(cal)	d_{power} = 5.19 pm/V(cal)

$Al_4(P_2S_6)_3$[1]	$[P_2S_6]^{4-}$	d_{16} = 3.29 pm/V d_{14} = -4.34 pm/V d_{22} = -5.56 pm/V d_{23} = 0.47 pm/V(cal)	d_{power} = 2.99 pm/V(cal)
$NaAlP_2S_6$[1]	$[P_2S_6]^{4-}$	d_{16} = -2.72 pm/V d_{24} = -1.46 pm/V d_{33} = 4.08 pm/V(cal)	d_{power} = 2.50 pm/V(cal)
β-$NaSbP_2S_6$[1]	$[P_2S_6]^{4-}$	d_{14} = 3.13 pm/V d_{22} = -37.47 pm/V d_{23} = -4.27 pm/V(cal)	d_{power} = 16.99 pm/V(cal)
$KSbP_2S_6$[1]	$[P_2S_6]^{4-}$	d_{14} = 3.66 pm/V d_{22} = −21.39 pm/V d_{23} = −4.04 pm/V(cal)	d_{power} = 10.48 pm/V(cal)
$KBiP_2S_6$[1]	$[P_2S_6]^{4-}$	d_{16} = -5.60 pm/V d_{22} = 18.70 pm/V(cal)	d_{power} = 7.97 pm/V(cal)
$TlBiP_2S_6$[1]	$[P_2S_6]^{4-}$	d_{16} = -7.30 pm/V d_{22} = 32.73 pm/V d_{23} = -9.65 pm/V(cal)	d_{power} = 14.28 pm/V(cal)
TiP_2S_6[1]	$[P_2S_6]^{4-}$	d_{15} = 15.45 pm/V d_{24} = 3.28 pm/V(cal)	d_{power} = 10.82 pm/V(cal)
$Cd_2P_2S_6$[1]	$[P_2S_6]^{4-}$	d_{11} = -d_{12} = -0.95 pm/V(cal)	d_{power} = 0.66 pm/V(cal)
$Sn_2P_2S_6$[1]	$[P_2S_6]^{4-}$	/	/
$SnPS_{2.86}Se_{0.14}$[21]	$[P_2Q_6]^{4-}$	1.2×AGS@2.09	3.9×AGS(exp)

Table S2 Fractional atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2×10^3), formal oxidation states (FOS) and bond valence sum (BVS) of all atoms in **1** and **2**.

1

Atom	*x*	*y*	*z*	*U*(eq)	FOS	BVS
Rb1	7687.1	0	0	13.8	1	1.066
Rb2	0	7098.0	2500	20.6	1	0.565
Zn1	2165.3	4152.2	3812.9	9.0	2	2.040
Zn2	0	1910.3	2500	9.9	2	2.064

P1	1586	648.2	1776	7.0	5	5.199
P2	695	3305.7	1615	7.9	4	4.119
S1	72	3965.9	425	10.8	-2	-2.017
S2	0	69.9	2500	7.9	-2	-2.290
S3	2672	3441.3	2237	14.1	-2	-1.852
S4	1932	1320.9	3021	8.8	-2	-2.094
S5	869	921.1	63	9.4	-2	-1.941
S6	3321	140.6	1831	9.3	-2	-2.008
S7	446	2510.0	744	15.8	-2	-2.022

2

Atom	*x*	*y*	*z*	*U*(eq)	FOS	BVS
Cs1	7636.2	0	0	28.5	1	1.245
Cs2	0	7156.0	2500	45.9	1	0.725
Zn1	0	1915.2	2500	23.8	2	2.080
Zn2	2187.8	4164.6	3832.6	21.6	2	2.025
P1	1568.9	656.5	1759.2	14.7	5	5.223
P2	687.3	3318.8	1634.0	18.4	4	4.173
S1	0	84.5	2500	16.8	-2	-2.344
S2	873.9	928.7	77.6	22.1	-2	-2.026
S3	15.6	3947.9	434.2	26.3	-2	-2.096
S4	1906.5	1318.5	2981.8	21.3	-2	-2.178
S5	3288.3	155.2	1779.3	19.6	-2	-2.039
S6	2641.2	3489.7	2214.5	32.9	-2	-1.948
S7	518	2519.4	816.7	40.5	-2	-2.078

Table S3 Selected bond lengths (Å) for **1** and **2**.

1			
Bond	Length/Å	Bond	Length/Å
Rb1−S2	3.447	Zn1−S3	2.353
Rb1−S1	3.448	Zn1−S6	2.366
Rb1−S6	3.488	Zn2−S7	2.326
Rb1−S4	3.642	Zn2−S4	2.343
Rb1−S5	3.689	P1−S6	2.018
Rb1−P1	3.758	P1−S5	2.026
Rb2−S7	3.553	P1−S4	2.026
Rb2−S1	3.897	P1−S2	2.141
Rb2−S4	3.466	P2−S7	2.022
Rb2−S3	3.762	P2−S1	2.030
Zn1−S5	2.306	P2−S3	2.030
Zn1−S1	2.331	P2−P2	2.292
2			
Bond	Length/Å	Bond	Length/Å
Cs1–S3	3.507	Zn2−S2	2.314
Cs1−S1	3.534	Zn2−S3	2.325
Cs1−S5	3.593	Zn2−S6	2.355
Cs1−S4	3.712	Zn2−S5	2.378
Cs1−S2	3.771	P2−S7	2.015

Cs1−P1	3.864	P2−S3	2.026
Cs2−S4	3.579	P2−S6	2.028
Cs2−S7	3.674	P2−P2	2.288
Cs2−S6	3.793	P1−S5	2.013
Cs2−S3	4.021	P1−S4	2.018
Zn1−S7	2.321	P1−S2	2.024
Zn1−S4	2.343	P1−S1	2.147

Table S4 Partial SHG contributions of atom types and anionic groups in unit cells of **1** and **2** averaged on all nonzero independent SHG coefficient tensors at the wavelength of 1910 nm.

		1		
Atom	P	S	Zn	Rb
SHG(%)	19.8	73.3	3.0	3.9
Anionic group	P_2S_6	PS_4	ZnS_4	Rb
SHG(%)	55.1	25.0	15.6	4.2
		2		
Atom	P	S	Zn	Cs
SHG(%)	19.3	73.3	6.1	1.3
Anionic group	P_2S_6	PS_4	ZnS_4	Cs
SHG(%)	56.5	25.6	13.8	4.1

Table S5 The LIDTs of **1** and **2**, and the reference AGS.

Compounds	Damage energy (mJ)	Spot area (cm^2)	Damage threshold (MW/cm^2)	Relative values (times)
1	3.3	0.025	13.2	6.1
2	2.6	0.025	10.4	5.2
AGS	0.5	0.025	2.0	1.0

Table S6 Dipole moment of coordination sphere around each cation in **1** and **2**.

Unit	Dipole moment
1	
$Rb(1)S_8$	0.2513
$Rb(2)S_4$	0.2636
$Zn(1)S_4$	0.0679
$Zn(2)S_4$	0.0887
$P(1)S_4$	0.3643
$P(2)S_6$	2.4840
2	
$Cs(1)S_{10}$	0.2517
$Cs(2)S_6$	0.1135
$Zn(1)S_4$	0.0989
$Zn(2)S_4$	0.1359
$P(1)S_4$	0.4329
$P(2)S_6$	2.5582

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