Electronic Supplementary Information

$Na_6Mg_3P_4S_{16}$ and $RbMg_2PS_4Cl_2$: Two Mg-Based Thiophosphates with Ultrawide Bandgap Induced by $[MgS_6]$ and $[MgS_xCl_{6-x}]$ Octahedra

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CONTENTS

1. Synthesis of Title Compounds

High-purity chemicals such as the Na_2S powder (99%), RbCl powder (99.9%), Mg powder (99.9%), P_2S_5 powder (99.9%) and S powder (99.99%) were used as purchased from Shanghai Aladdin Biochemistry Technology Co., Ltd. To better ensure the reliability of the raw material ratio, vacuum glove box was chosen to complete the preparation process and avoid the effect of air oxidation.

First, Raw mixture (Na_2S:Mg:P_2S_5:S) with stoichiometric proportion of 3:3:2:3 for $Na_6Mg_3P_4S_{16}$ (NMPS). Raw mixture (RbCl:Mg:P_2S_5:S) with 2:2:1:3 for $RbMg_2PS_4Cl_2$ (RMPSC). Then the mixture was loaded into the graphite crucible and then put it into silica tubes. Using the flame gun and air extractor, silica tube was carefully vacuum-sealed with the internal vacuum degree about 10^{-3} Pa. Muffle furnace was used to complete the crystallization reaction, NMPS and RMPSC have the same temperature process as follows:

30℃ (1000 min) →850℃ (500 min) →850℃ (10000 min) → 550℃ (2500 min) → 450 ℃ (2500 min) → 50℃ (natural cooling) → 30℃.

Carefully ground microcrystal powders were used for powder X-ray diffraction (PXRD) measurement by an automated Bruker D2 X-ray diffractometer at room temperature. After test, experimental results are essentially in accordance with the calculated ones from the single-crystal data, respectively. The synthesis of other alkali metals-contained compounds (Li, K, and Cs) in this system has been attempted by adjusting the different ratios of reagents or reaction temperatures, unfortunately, failed.

2. Structural Refinement and Crystal Data

A Bruker SMART APEX III 4K CCD diffractometer with Mo Ka radiation (λ = 0.71073 Å) was used to complete the crystal data collection at room temperature. Multi-scan method was used for absorption correction. The crystal structure was solved by the direct method and refined using the SHELXTL program package[1]. Note that all atom sites are completely occupied by each atom in NMPS and RMPSC. Crystal data and structure refinements of title compounds are given in Table S1. Table S2 and Table S3 summarize the atomic coordinates, isotropic displacement parameters and bond valences of title compounds. Bond lengths and angles for NMPS and RMPSC are

provided in Tables S4-S5.

3. Property Characterization

Powder X-ray Diffraction Measurement. An automated Bruker D2 X-ray diffractometer was used to carry out the powder X-ray diffraction (XRD) characterization for the NMPS and RMPSC, the 2θ range was from 5 to 70 ° with a step rate of 0.02 °/s.

UV–Vis–NIR Diffuse-reflectance Spectroscopy. Shimadzu SolidSpec-3700 DUV spectrophotometer was used to measure the diffuse-reflectance spectra within the wavelength range from 200 to 2600 nm. The absorption spectra were converted from the reflection spectra via the Kubelka-Munk function. The reflectance data were recorded and converted to absorbance by the Kubelka-Munk function. The direct and indirect bandgap were estimated by Tauc plots method.

Laser Induced Damage Threshold (LIDT) Measurements. The NMPS and RMPSC powder samples (~45 μm) were evaluated by the pulsed laser beam (2090 nm, 1 ms, 3 Hz). The AGS sample with similar size distribution was utilized as the reference. The laser output energy was gradually increased until visible damage is noticed on the surface of the samples under the microscope. Because the damage energy of AGS is relatively low, so the attenuator filter was used to reduce the energy of light irradiated on the sample of AGS. The damaged energies before the attenuator filter were measured to be ~57.8 mJ and ~76.6 mJ for NMPS and RMPSC, and 9.6 mJ for AGS. It is indicated that NMPS and RMPSC have about six and eight times higher LIDT than AGS.

Infrared Spectroscopy. Ground micro-crystals mixed with KBr powder in the molar ratio of about 1:100, was dried and ground into fine powder, and then pressed into a transparent sheet on the tablet machine. The sheet was loaded in the sample chamber and were used to complete the IR spectroscopy measurement on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer within the range from 400 to 4000 cm^{-1}.

Energy Dispersive X-ray Spectroscopy. Elemental analysis was carried on clean single crystal surfaces with the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscope (EDX,

BRUKER x-flash-sdd-5010).

Computational Description

The band structures and optical properties of title compounds were calculated by density functional theory (DFT) based on first-principles calculations implemented in the CASTEP package[2]. The generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) and norm-conserving pseudo-potentials (NCP) were employed[3-5]. During the calculation, the plane-wave cut-off energy was set as 900 eV for NMPS and RMPSC. The k-points sampling of 4 × 4 × 2 for NMPS, 2 × 5 × 4 for RMPSC was chosen to ensure the convergence for all computations. Na-$2s^2 2p^6 3s^1$, Rb-$4s^2 4p^6 5s^1$, Mg-$2s^2 2p^6 3s^2$, P-$3s^2 3p^3$, S-$3s^2 3p^4$ and Cl-$3s^2 3p^5$ were treated as the valence electrons, respectively. The other calculated parameters used and convergent criteria were in line with the default values of the CASTEP code.

4. Tables

Table S1 Crystal Data and Structure Refinement for NMPS and RMPSC.

Empirical formula	**$Na_6Mg_3P_4S_{16}$**	**$RbMg_2PS_4Cl_2$**
Formula weight	847.71	364.20
Crystal system	Monoclinic	Monoclinic
Space group	*P2/n* (13)	*C2/m* (12)
Unit cell dimensions (Å)	a=8.6754(3)	a=17.2779(7)
	b=8.3180(2)	b=7.2426(4)
	c=18.2658(6)	c=8.8927(4)
	β=95.7220(10)°	β=118.839(2)°
Z/V ($Å^3$)	2/1311.53(7)	4/974.79(8)
Density (g/cm^3)	2.147	2.482
Absorption coefficient (mm^{-1})	1.730	6.698
F (000)	836	696
Completeness to theta (%)	99.6	99.9
Goodness-of-fit on F^2	1.082	1.084
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0307, 0.0731	0.0260, 0.0563
R_1, wR_2 (all data)[a]	0.0364, 0.0775	0.0298, 0.0583
Largest diff. peak and hole ($eÅ^{-3}$)	1.290 and -0.638	0.834 and -0.555

[a] $R_1 = F_0 - F_c/F_0$ and $wR_2 = [w(F_0^2 - F_c^2)^2/wF_o^4]^{1/2}$ for $F_0^2 > 2\sigma(F_0^2)$

Table S2 Atomic coordinates, equivalent isotropic displacement parameters and bond valences for NMPS.

Atom	x	y	z	Ueq	Occupancy	Bond valence
Na (1)	0.29521(19)	0.6078(2)	0.51159(10)	0.0598(5)	1	0.80
Na (2)	0.750000	0.3764(2)	0.250000	0.0472(5)	1	0.90
Na (3)	0.250000	0.5482(3)	0.250000	0.0598(7)	1	1.18
Na (4)	0.39274(19)	1.0955(2)	0.35367(9)	0.0536(4)	1	0.85
Mg (1)	0.84109(11)	0.86895(11)	0.45685(5)	0.0219(2)	1	1.89
Mg (2)	0.750000	0.86783(17)	0.250000	0.0243(3)	1	1.60
P (1)	1.00020(8)	0.82970(8)	0.62266(4)	0.01788(14)	1	5.03
P (2)	0.55089(8)	0.69132(8)	0.36968(4)	0.01855(14)	1	4.97
S (1)	1.22756(8)	0.90384(9)	0.64107(4)	0.02455(16)	1	1.88
S (2)	0.92743(10)	0.74321(10)	0.71489(4)	0.03278(19)	1	2.01
S (3)	0.97798(9)	0.66371(8)	0.54121(4)	0.02423(15)	1	1.95
S (4)	0.88190(8)	1.03082(8)	0.58103(4)	0.02342(15)	1	1.86
S (5)	0.78067(8)	0.64524(9)	0.35763(4)	0.02340(15)	1	1.96
S (6)	0.54665(8)	0.83561(8)	0.45979(4)	0.02308(15)	1	1.81
S (7)	0.43294(10)	0.48779(9)	0.38492(4)	0.03303(18)	1	2.00
S (8)	0.46728(8)	0.81241(10)	0.27656(4)	0.02792(17)	1	1.97
						G[a]=0.148

[a] The global instability index (G) calculated using

$$G = \sqrt{\frac{\sum_{i=1}^{n} (BVS - v_i)^2}{N}}$$

where N is the number of atoms in the formula unit. The G is calculated as 0.148, which is lower than 0.2, indicating the rationality of the structure from this side.

Table S3 Atomic coordinates, equivalent isotropic displacement parameters and bond valences for RMPSC.

Atom	x	y	z	Ueq	Occupancy	Bond valence
Rb (1)	0.12390(3)	0.500000	-0.15805(6)	0.04336(16)	1	0.81
Mg (1)	0.250000	0.750000	0.500000	0.0189(2)	1	2.06
Mg (2)	0.46168(8)	0.500000	0.78059(15)	0.0209(3)	1	1.87
P (1)	0.35337(6)	0.500000	0.36642(11)	0.01715(19)	1	4.81
S (1)	0.40358(4)	0.72877(8)	0.52386(8)	0.01825(14)	1	1.88
S (2)	0.37253(6)	0.500000	0.16168(11)	0.0230(2)	1	1.87
S (3)	0.21839(5)	0.500000	0.27723(11)	0.01822(18)	1	2.05

Cl (1)	0.20274(5)	1.000000	0.27460(10)	0.01909(18)	1	0.89
Cl (2)	0.500000	0.74029(11)	1.000000	0.02124(18)	1	0.88

Table S4 Selected bond lengths [Å] and angles [°] for NMPS.

Na1#3-S3	2.8948(17)	S2-P1-S1	110.41(4)
Na1#4-S3	3.345(2)	S2-P1-S3	111.12(4)
Na1-S6	3.1074(19)	S2-P1-S4	114.57(5)
Na1#4-S5	3.2991(18)	S6-P2-S5	106.90(4)
Na1-S7	2.8860(19)	S6-P2-S8	110.34(4)
Na1#4-S7	2.9797(19)	S8-P2-S5	105.60(4)
Na2#2-S1	3.0584(17)	S7-P2-S6	109.46(4)
Na2-S5	2.9718(16)	S7-P2-S5	111.63(5)
Na2#2-S2	2.9791(11)	S7-P2-S8	112.71(5)
Na3#6-S8	2.9046(19)	S1#1-Mg1-S4#1	75.56(3)
Na3-S8	2.9046(19)	S1#1-Mg1-S4	102.74(4)
Na3#4-S2	2.975(2)	S3-Mg1-S1#1	164.82(5)
Na3#6-S7	2.8398(9)	S3-Mg1-S6	108.82(4)
Na3-S7	2.8398(9)	S3-Mg1-S4	78.73(3)
Na4#1-S1	3.2859(18)	S3-Mg1-S4#1	89.35(4)
Na4-S6	3.1139(17)	S3-Mg1-S5	89.51(4)
Na4#5-S4	2.9614(18)	S6-Mg1-S1#1	86.20(4)
Na4-S8	2.8511(19)	S6-Mg1-S4	94.91(4)
Na4#5-S2	3.2233(19)	S6-Mg1-S4#1	161.67(5)
Na4#7-S2	2.9101(17)	S6-Mg1-S5	78.87(3)
Na4#8-S7	3.3250(19)	S4-Mg1-S4#1	90.93(3)
Mg1#3-S1	2.6292(12)	S5-Mg1-S1#1	91.37(4)
Mg1-S3	2.5168(12)	S5-Mg1-S4	164.25(5)
Mg1-S6	2.5753(12)	S5-Mg1-S4#1	99.46(4)
Mg1-S4	2.6312(11)	S1#1-Mg2-S1#9	92.38(5)
Mg1#1-S4	2.6982(12)	S5-Mg2-S1#9	178.39(2)
Mg1-S5	2.6139(11)	S5#10-Mg2-S1#1	178.39(2)
Mg2#1-S1	2.7434(13)	S5#10-Mg2-S1#9	87.24(2)
Mg2-S5	2.6943(12)	S5-Mg2-S1#1	87.24(2)
Mg2-S8	2.5886(8)	S5#10-Mg2-S5	93.18(5)
P1-S1	2.0620(9)	S8#10-Mg2-S1#1	105.02(3)
P1-S2	1.9916(10)	S8-Mg2-S1#9	105.02(3)
P1-S3	2.0248(9)	S8-Mg2-S1#1	89.28(3)
P1-S4	2.0675(10)	S8#10-Mg2-S1#9	89.28(3)
P2-S5	2.0632(10)	S8#10-Mg2-S5#10	76.55(3)
P2-S6	2.0402(9)	S8-Mg2-S5	76.55(3)
P2-S7	2.0119(10)	S8#10-Mg2-S5	89.30(4)
P2-S8	2.0465(10)	S8-Mg2-S5#10	89.30(4)

S1-P1-S4	104.46(4)	S8-Mg2-S8#10	159.48(7)
S3-P1-S1	110.07(4)	S3#13-Na1-S3#3	60.20(4)
S3-P1-S4	105.91(4)	S3#13-Na1-S6	131.93(7)
S3#13-Na1-S5#3	72.85(4)	S7#6-Na3-S8#6	72.04(3)
S3#13-Na1-S7#3	129.15(6)	S7-Na3-S8#6	125.17(6)
S6-Na1-S3#3	145.34(6)	S7#6-Na3-S8	125.17(6)
S6-Na1-S5#3	143.74(6)	S7#6-Na3-S2#3	77.68(4)
S5#3-Na1-S3#3	65.88(4)	S7-Na3-S2#11	77.68(4)
S7-Na1-S3#3	82.73(5)	S7#6-Na3-S2#11	85.71(5)
S7-Na1-S3#13	133.06(7)	S7-Na3-S2#3	85.71(5)
S7#3-Na1-S3#3	119.73(6)	S7#6-Na3-S7	159.62(10)
S7-Na1-S6	66.89(4)	S1#1-Na4-S7#12	84.59(5)
S7#3-Na1-S6	79.67(5)	S6-Na4-S1#1	67.45(4)
S7-Na1-S5#3	119.23(7)	S6-Na4-S2#5	146.12(6)
S7#3-Na1-S5#3	64.71(4)	S6-Na4-S7#12	122.91(6)
S7-Na1-S7#3	92.96(5)	S4#5-Na4-S1#1	146.44(6)
S1#11-Na2-S1#2	80.68(6)	S4#5-Na4-S6	79.36(4)
S5#10-Na2-S1#2	178.35(3)	S4#5-Na4-S2#5	66.89(4)
S5-Na2-S1#2	98.48(2)	S4#5-Na4-S7#12	110.73(5)
S5#10-Na2-S1#11	98.48(2)	S8-Na4-S1#1	74.91(4)
S5-Na2-S1#11	178.35(3)	S8-Na4-S6	68.28(4)
S5#10-Na2-S5	82.39(6)	S8-Na4-S4#5	97.88(6)
S5#10-Na2-S2#2	114.45(3)	S8-Na4-S2#5	112.39(6)
S5-Na2-S2#2	95.09(3)	S8-Na4-S2#9	84.38(5)
S5#10-Na2-S2#11	95.09(3)	S8-Na4-S7#12	150.49(6)
S5-Na2-S2#11	114.45(3)	S2#9-Na4-S1#1	80.46(4)
S2#2-Na2-S1#11	83.28(4)	S2#5-Na4-S1#1	146.43(6)
S2#11-Na2-S1#2	83.28(4)	S2#9-Na4-S6	141.91(6)
S2#11-Na2-S1#11	66.91(3)	S2#9-Na4-S4#5	132.19(7)
S2#2-Na2-S1#2	66.91(3)	S2#9-Na4-S2#5	68.26(4)
S2#11-Na2-S2#2	140.98(8)	S2#9-Na4-S7#12	71.27(4)
S8#6-Na3-S8	81.65(7)	S2#5-Na4-S7#12	74.32(4)
S8-Na3-S2#3	157.15(2)		
S8#6-Na3-S2#3	108.14(2)		
S8#6-Na3-S2#11	157.15(2)		
S8-Na3-S2#11	108.14(2)		
S2#3-Na3-S2#11	70.89(6)		
S7-Na3-S8	72.04(3)		

Symmetry transformations used to generate equivalent atoms (lengths):

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

Symmetry transformations used to generate equivalent atoms (angles):

#1 2-X, 2-Y, 1-Z; #2 2-X, 1-Y, 1-Z; #3 1-X, 1-Y, 1-Z; #4 1+X, +Y, +Z; #5 1-X, 2-Y, 1-Z; #6 1/2-X,

+Y, 1/2-Z; #7 1/2+X, 2-Y, 1/2+Z; #8 +X, -1+Y, +Z; #9, -1/2+X, 2-Y, -1/2+Z; #10, 3/2-X, +Y, 1/2-Z; #11, -1/2+X, 1-Y, -1/2+Z; #12, +X, 1+Y, +Z; #13, -1+X, +Y, +Z

Table S5 Selected bond lengths [Å] and angles [°] for RMPSC.

Rb1-S1#4	3.6300(7)	S3-Rb1-Cl1#1	108.51(2)
Rb1-S1#5	3.9955(7)	S3-Rb1-Cl2#3	66.760(14)
Rb1-S1#3	3.9955(7)	S3-Rb1-Cl2#6	66.760(14)
Rb1-S1#1	3.6300(7)	S3-Rb1-S1#4	125.208(17)
Rb1-S2	3.8413(10)	S3-Rb1-S1#3	125.208(17)
Rb1-S2#1	3.6222(2)	S3-Rb1-S1#1	143.507(14)
Rb1-S2#6	3.6222(2)	S3-Rb1-S1#2	143.507(14)
Rb1-S3	3.3988(10)	S3-Rb1-S2#5	90.531(16)
Rb1-Cl1#1	3.6112(9)	S3-Rb1-S2	53.54(2)
Rb1-Cl2#2	3.6053(6)	S3-Rb1-S2#1	90.531(16)
Rb1- Cl2#3	3.6053(6)	S2#5-Rb1-S12	56.386(17)
Mg1-S1	2.5625(6)	S2#1-Rb1-S1#2	121.90(2)
Mg1#2-S1	2.5625(6)	S21-Rb1-S1#3	119.98(2)
Mg1#9-S3	2.5412(6)	S2#1-Rb1-S1#1	56.386(17)
Mg1#10-S3	2.5412(6)	S2#5-Rb1-S1#1	121.90(2)
Mg1#2-S3	2.5412(6)	S2#5-Rb1-S1#4	119.98(2)
Mg1-S3	2.5412(6)	S2#5-Rb1-S1#3	61.097(17)
Mg1#7-Cl1	2.5267(6)	S2#1-Rb1-S1#4	61.097(17)
Mg1-Cl1	2.5267(6)	S2-Rb1-S1#3	150.166(9)
Mg1#2-Cl1	2.5267(6)	S2-Rb1-S1#4	150.166(10)
Mg2-S1	2.5989(11)	S2#1-Rb1-S2	89.359(17)
Mg2#11-S2	2.6552(14)	S2#1-Rb1-S2#5	177.40(3)
Mg2#2-Cl1	2.6393(14)	S2#5-Rb1-S2	89.359(17)
Mg2#8-Cl2	2.4551(10)	S1#11-P1-S1	106.32(5)
Mg2-Cl2	2.4552(10)	S3-P1-S1	106.64(3)
P1-S1	2.0703(8)	S3-P1-S1#11	106.64(3)
P1-S3	2.0696(12)	S2-P1-S1#11	114.58(3)
P1-S2	2.0016(12)	S2-P1-S1	114.58(3)
Cl1#1-Rb1-S1#2	60.714(15)	S2-P1-S3	107.56(5)
Cl1#1-Rb1-S1#1	60.714(15)	Cl1#6-Mg2-S2#12	179.62(6)
Cl1#1-Rb1-S1#3	115.831(17)	Cl2-Mg2-Cl1#6	90.07(3)
Cl1#1-Rb1-S1#4	115.831(17)	Cl2#9-Mg2-Cl1#6	90.07(4)
Cl1#1-Rb1-S2#5	88.704(15)	Cl2-Mg2-Cl2#9	90.28(5)
Cl1#1-Rb1-S2#1	88.704(15)	Cl2-Mg2-S1	95.052(19)
Cl1#1-Rb1-S2	54.980(19)	Cl2-Mg2-S1#11	172.68(5)
Cl2#6-Rb1-Cl1#1	147.408(12)	Cl2#9-Mg2-S1	172.69(5)
Cl2#3-Rb1-Cl1#1	147.408(13)	Cl2#9-Mg2-S1#11	95.052(19)
Cl2#3-Rb1-Cl2#6	62.90(2)	Cl2-Mg2-S2#12	89.66(4)
Cl2#3-Rb1-S1#4	89.451(15)	Cl2#9-Mg2-S2#12	89.66(4)
Cl2#3-Rb1-S1#1	141.824(18)	S1#11-Mg2-Cl1#6	84.93(4)
Cl2#3-Rb1-S1#2	102.793(15)	S1-Mg2-Cl1#6	84.93(4)
Cl2#6-Rb1-S1#4	58.492(11)	S1-Mg2-S1#11	79.22(4)

Cl2#6-Rb1-S1#1	102.793(14)	S1#11-Mg2-S2#12	95.36(4)
Cl2#3-Rb1-S1#3	58.492(11)	S1-Mg2-S2#12	95.36(4)
Cl2#6-Rb1-S1#3	89.451(15)	Cl1-Mg1-Cl1#6	180.0
Cl2#6-Rb1-S1#2	141.824(18)	Cl1-Mg1-S1#6	88.04(2)
Cl2#6-Rb1-S2#5	122.75(2)	Cl1#6-Mg1-S1#6	91.96(2)
Cl2#3-Rb1-S2	111.949(15)	Cl1-Mg1-S1	91.96(2)
Cl2#6-Rb1-S2#1	59.852(17)	Cl1#6-Mg1-S1	88.04(2)
Cl2#3-Rb1-S2#5	59.852(17)	Cl1-Mg1-S3	91.516(19)
Cl2#6-Rb1-S2	111.949(15)	Cl1-Mg1-S3#6	88.484(19)
Cl2#3-Rb1-S2#1	122.75(2)	Cl1#6-Mg1-S3#6	91.516(19)
S1#2-Rb1-S1#3	55.346(16)	Cl1#6-Mg1-S3	88.484(19)
S1#1-Rb1-S1#4	55.346(16)	S1-Mg1-S1#6	180.0
S1#2-Rb1-S1#1	65.53(2)	S3-Mg1-S1#6	98.84(2)
S1#3-Rb1-S1#4	58.901(18)	S3-Mg1-S1	81.16(2)
S1#2-Rb1-S1#4	87.910(16)	S3#6-Mg1-S1	98.84(2)
S1#1-Rb1-S1#3	87.910(16)	S3#6-Mg1-S1#6	81.16(2)
S1#2-Rb1-S2	106.227(17)	S3-Mg1-S3#6	180.0
S1#1-Rb1-S2	106.227(17)		

Symmetry transformations used to generate equivalent atoms (lengths):

#1 1/2-X, 3/2-Y, -Z; #2 1/2-X, 3/2-Y, 1-Z; #3 -1/2+X, -1/2+Y, -1+Z;

#4 1/2-X, -1/2+Y, -Z; #5 -1/2+X, 3/2-Y, -1+Z; #6 1/2-X, 1/2-Y, -Z;

#7 1/2-X, 1/2+Y, 1-Z; #8 1-X, 1-Y, 2-Z; #9 1/2-X, -1/2+Y, 1-Z;

#10 +X, 1-Y, +Z; #11 1-X, 1-Y, 1-Z

Symmetry transformations used to generate equivalent atoms (angles):

#1 1/2-X, 3/2-Y, -Z; #2 1/2-X, -1/2+Y, -Z; #3 -1/2+X, -1/2+Y, -1+Z;

#4 -1/2+X, 3/2-Y, -1+Z; #5 1/2-X, 1/2-Y, -Z; #6 1/2-X, 3/2-Y, 1-Z;

#7 1/2-X, 1/2+Y, 1-Z; #8 1/2+X, 1/2+Y, 1+Z; #9 1-X, 1-Y, 2-Z;

#10 1/2-X, -1/2+Y, 1-Z; #11+X, 1-Y, +Z; #12 1-X, 1-Y, 1-Z; #13 1/2+X, -1/2+Y, 1+Z

Table S6 Band gap of thiophosphate halides

Compound	Band gap (eV)	Compound	Band gap (eV)	Compound	Band gap (eV)
$Cs_2InPS_4Cl_2$	3.21	$[K_3Cl][Ga_3PS_8]$	3.60	$Cs_4Zn_5P_6S_{18}I_2$	3.75
$Cs_2InPS_4Br_2$	3.12	$[Rb_3Cl][Ga_3PS_8]$	3.65	$CsBrHg_3P_2S_8$	2.95
Ag_6PS_5Cl	2.01	$[K_3Br][Ga_3PS_8]$	3.85	$CsClHg_3P_2S_8$	3.0
Ag_6PS_5Br	1.95	$[Rb_3Br][Ga_3PS_8]$	3.50	$RbBrHg_3P_2S_8$	2.94
Cu_6PS_5Cl	2.22	$Li_4Sm[PS_4]2Cl$	2.69	$RbMg_2PS_4Cl_2$	3.93 (our work)
Cu_6PS_5Br	2.20	$Li_4Nd[PS_4]_2Cl$	3.52		
$Ag_5PS_4Cl_2$	2.71	$Li_4Pr[PS_4]_2Cl$	3.49		

5. Figures

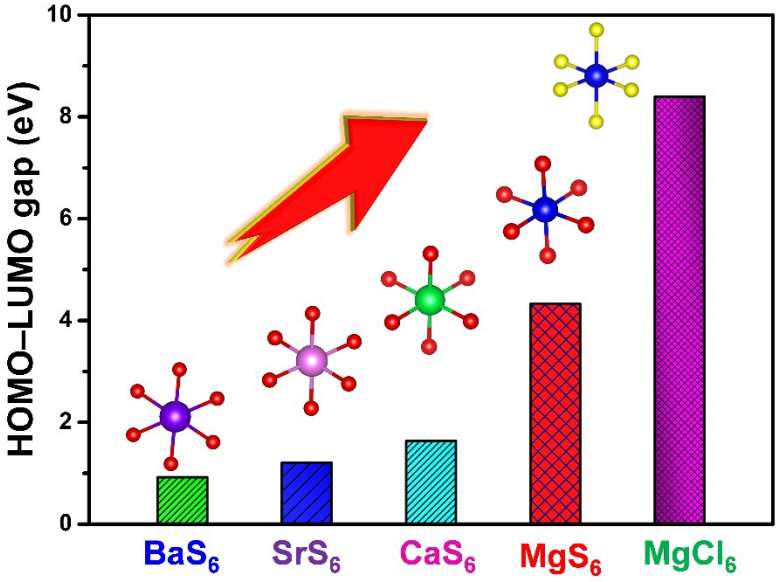

Fig. S1. HOMO-LUMO gap of the [MgS_6], [CaS_6], [SrS_6], [BaS_6], and [$MgCl_6$] groups.

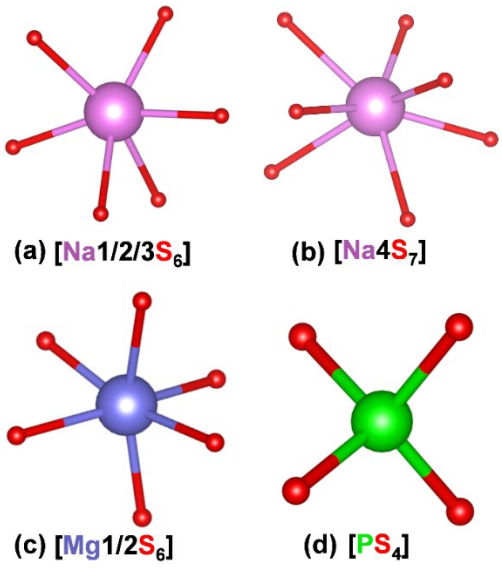

Fig. S2. Coordination environment of Na1/2/3 (a), Na4 (b), Mg1/2 (c) and P (d).

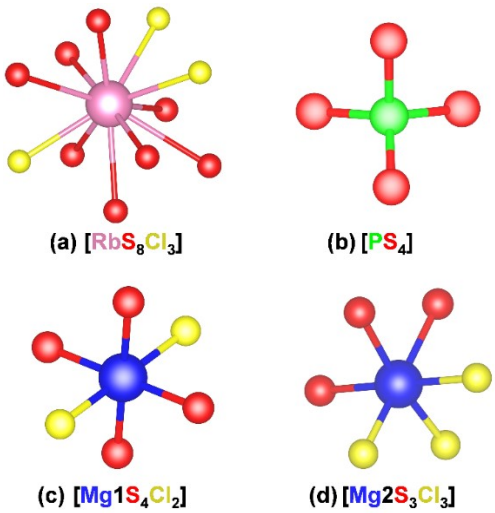

Fig. S3. Coordination environment of Rb (a), P (b), Mg1 (c) and Mg2 (d).

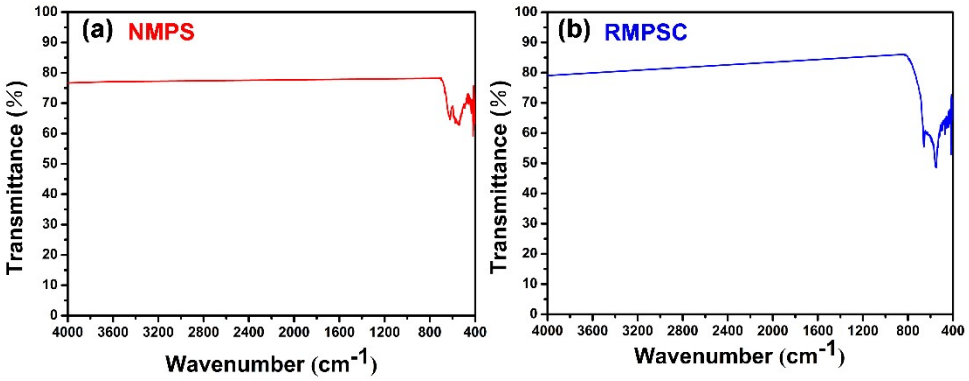

Fig. S4. IR curves of NMPS and RMPSC.

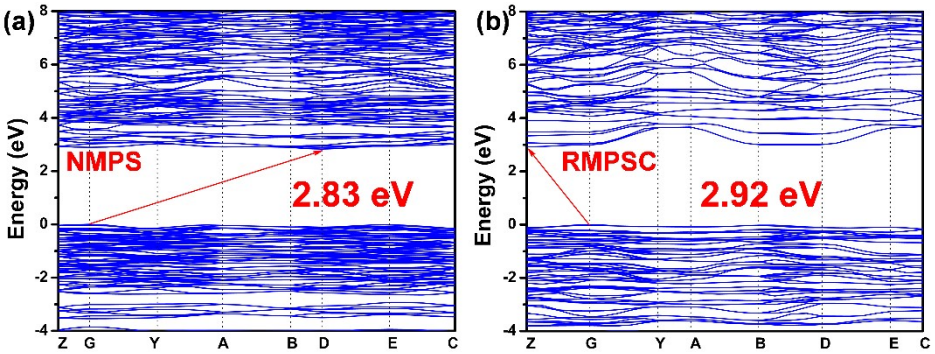

Fig. S5. (a) The calculated band structure of NMPS based on GGA function. (b) The calculated band structure of RMPSC based on GGA function.

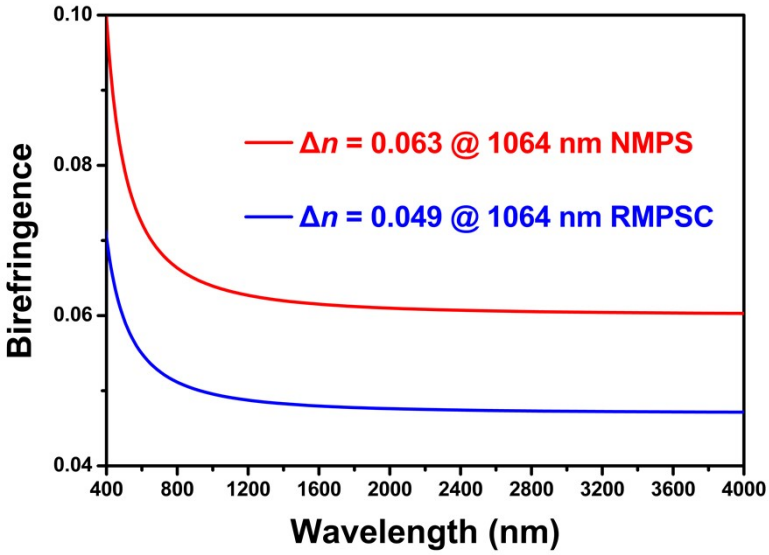

Fig. S6. (a) The birefringence values of NMPS and RMPSC

6. References

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