Series of M$_3$PS$_4$ (M = Ag, Cu and Ag/Cu) thiophosphates with diamond-like structures exhibiting large second harmonic generation responses and moderate ion conductivities

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1. Synthesis of Title Compounds

All of the raw materials including S powder (99.99%), P powder (99.9%), Cu_2S powder (99.9%), Cu powder (99.9%) and Ag block (99.9%) were purchased from the Beijing Hawk Science & Technology Co., Ltd. The crystals of Ag_3PS_4 and Cu_3PS_4 were synthesised by stoichiometric ratio (Ag:P:S=3:1:4 for Ag_3PS_4, Cu_2S:P:S=1.5:1:2.5 for Cu_3PS_4), but the $Ag_{1.5}Cu_{1.5}PS_4$ crystal was synthesised by non-stoichiometric ratio (Ag:Cu:P:S=1:2:1:4). Raw mixtures including were firstly loaded into the graphite crucibles and then put them into silica tubes. Using the flame gun and air extractor, silica tubes were carefully vacuum-sealed with the internal vacuum degree (~ 10^{-3} Pa) in ampoules. Muffle furnace was used to complete the crystallization reaction and the setting temperature process was shown as following: firstly heated them from room temperature to 400 ℃ with 40 ℃/h and kept this temperature for 10 h; then raised to 750 ℃ in 10 h and kept this high temperature for 5 days; finally, downed to the 400 ℃ with 5 ℃/h and naturally cooled the room temperature before turning off the muffle furnace. The yellow crystals of Ag_3PS_4, Cu_3PS_4 and $Ag_{1.5}Cu_{1.5}PS_4$ were found in the tubes after washed with N, N-dimethylformamide (DMF) solvent and they are stable in the air within several months.

2. Structure Refinement and Crystal data

Selected high-quality crystals were used for data collections on a Bruker SMART APEX II 4K CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 296 K. The crystal structures were solved by direct method and refined using the SHELXTL program package.[1] Multi-scan method was used for absorption correction.[2] Rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. PLATON was also used to check the final structures and no other symmetries were found. Detail refinement parameters and data were shown in Table S1.

3. Property Characterization

3.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) of title compounds were ground and collected on a Dandong Haoyuan DX-27mini with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10-70° with a step size of 0.02° and a fixed counting time of 1s/step.

3.2 UV-Vis-Near-IR (NIR) Diffuse-Reflectance Spectra

Optical Diffuse-reflectance spectra were measured by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 200−1100 nm at room temperature, and using the $BaSO_4$ for baseline correction.

3.3 Raman Spectra

Hand-picked crystals were firstly put on an object slide, and then a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm laser was used to record the Raman spectra. The integration time was set to be 5 s.

3.4 Second-Harmonic Generation Measurement

Powder SHG responses of title compounds were investigated by a Q-switch 2.09 μm laser (3 Hz, 50 ns) at 38-55, 55-88, 88-105, 105-150, 150-200 and 200-250μm particle size. The $AgGaS_2$ (as the reference) crystal was ground and sieved into the same size range to a distinct measure.

3.5 Conductivity Measurements

The electrochemical impedance spectra (EIS) of title compounds have measured by an electrochemical workstation (Biologic, VSP) and the frequency ranged from 1MHz to 1Hz. Powder sample of three compounds were pelleted with a thickness of approximate 1mm and a diameter of 13mm under 20 ton of pressure. Then taking these pellets into air oven about 3-5 h after covering silver paste. The temperature-dependent AC impedance spectra for title compounds were studied at different temperature from 10 to 80℃ with an increment of 5 or 10 ℃. The ionic conductivity was obtained through the equation $\sigma=L/S \cdot R$, where L is pelleted thickness, S is the area, and the total resistance R is equal to real impedance when imaginary impedance approaches zero ($Z''\approx0$).

3.6 Computational Description

In order to further investigate the structure–property relationships, the electronic structures of title compounds were studied by density functional theory (DFT) based on ab initio calculations.[3] The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.[4] The following orbital electrons were treated as valence electrons, Cu: $3p^6 3d^{10} 4s^1$, Ag: $4p^6 4d^{10} 5s^1$, P: $3s^2 3p^3$, S: $3S^2 3P^4$. To achieve energy convergence, a plane-wave basis set energy cutoff was 750 eV within normal-conserving pseudo-potential (NCP),[5] and the Monkhorst–Pack scheme was $3 \times 3 \times 2$ in the Brillouin Zone (BZ) of the primitive cell are chosen. The dipole moments of the AgS_4, CuS_4,

PS$_4$, and (Ag/Cu)S$_4$ units were calculated with a simple bond-valence method. Distribution of the electron on the each atom was estimated by the bond-valence theory $v_{ij} = \exp[(r' - r_{ij})/B$; where r' is the empirical constant, r_{ij} is the actual bond length, and B is commonly taken to be a universal constant equal to 0.37 Å. The geometrical position was taken from the unit cell of the experimental X-ray crystal structure. The Debye equation $\mu = neR$, where μ is the net dipole moment in Debye, n is the total number of electrons, e is the charge on an electron, and R is the difference in *cm* between the "centroids" of positive and negative charges, was used to calculate the dipole moment.

4. Tables and Figures

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Figure S2. Band structures for title compounds.

Figure S3. Partial Density of State (PDOS) and calculated birefringences for title compounds.

Figure S4. Raman spectra for title compounds.

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Table S1. Crystal data and structure refinement for title comounds.

	Ag_3PS_4	Cu_3PS_4	$Ag_{1.5}Cu_{1.5}PS_4$
Formula weight	482.82	349.83	416.33
Space group	$Pmn2_1$		
a (Å)	7.6383(13)	7.2889(16)	7.718(7)
b (Å)	6.8528(11)	6.3341(14)	6.542(6)
c (Å)	6.4976(11)	6.0828(14)	6.318(6)
V (Å^3)	340.11(10)	280.45(11)	320.0(5)
Z	2	2	2
D_c (g/cm^{-3}) (calculated density)	4.715	4.143	4.321
μ(mm^{-1}) (absorption coefficient)	9.890	12.892	10.906
goodness-of-fit on F^2	1.099	0.954	1.100
R_1, wR_2 (I$>2\sigma$(I))[a]	0.0260, 0.0430	0.0144, 0.0347	0.0375, 0.0729
R_1, wR_2(all data)	0.0298, 0.0441	0.0147, 0.0349	0.0411, 0.0744
absolute structure parameter	0.11(10)	0.036(19)	0.06(10)
largest diff. peak and hole (e·Å^{-3})	0.938, -1.034	0.342, -0.289	1.009, -1.043

[a]$R_1=F_O-F_C/F_O$ and $wR_2=[w(F_O^2-F_C^2)]^2/wF_o^4]^{1/2}$

Table S2. Bond Valence sum (*vu*) of title compounds.

Compounds	M^{1+}	P^{5+}	S^{2-}
Ag_3PS_4	1.163-1.259	5.174	2.174-2.243
Cu_3PS_4	1.102-1.196	4.893	2.059-2.139
$Ag_{1.5}Cu_{1.5}PS_4$	0.829-1.267	4.882	1.976-2.162

Table S3. Calculated Dipole Moment (debye) of anionic groups (MS_4 and PS_4) for title compounds.

Group	x	y	z	dipole moment (Debye)
Ag_3PS_4				
AgS_4	0	0.47	-2.07	2.12
PS_4	0	1.71	-1.49	2.13
Total	0	2.186	-3.56	4.18
Cu_3PS_4				
CuS_4	-0.04	-2.36	3.87	4.53
PS_4	0	-0.77	0.40	0.87
Total	-0.04	-3.13	4.27	5.29
$Ag_{1.5}Cu_{1.5}PS_4$				
$(Ag/Cu)S_4$	0	0.34	-2.11	2.14
PS_4	0	5.14	-2.69	5.80
Total	0	5.49	-4.80	7.29

Table S4. Comparison of important performance of the title compounds and $AgGaS_2$ (AGS) as a reference.

Compounds	Ag_3PS_4	Cu_3PS_4	$Ag_{1.5}Cu_{1.5}PS_4$	$AgGaS_2$
Space group	*Pmn2₁*			*I-42d*
Band gap (exp./cal.) (eV)	2.43/1.14	2.25/1.46	2.37/1.28	2.64
SHG response (×AGS)	1.3	0.5	0.8	1.0
Calculated NLO coefficient d_{ij}(pm V^{-1})	15.77	-10.1	13.42	13.9
Birefringence (Δn)	0.065	0.07	0.064	0.039

Table S5. The ion conductivities for title compounds at diverse temperatures.

σ_T(S/cm) Compounds	Ag_3PS_4	Cu_3PS_4	$Ag_{1.5}Cu_{1.5}PS_4$
10℃	1.647×10^{-7}	1.882×10^{-6}	2.766×10^{-7}
20/25℃	2.946×10^{-7}（20℃）	2.809×10^{-6}（25℃）	6.591×10^{-7}（25℃）
30℃	4.701×10^{-7}	3.681×10^{-6}	7.388×10^{-7}
40℃	9.017×10^{-7}	5.670×10^{-6}	1.278×10^{-6}
50℃	1.065×10^{-6}	8.276×10^{-6}	1.875×10^{-6}
60℃	1.667×10^{-6}	1.157×10^{-5}	2.801×10^{-6}
70℃	2.407×10^{-6}	1.542×10^{-5}	3.939×10^{-6}
80℃	3.416×10^{-6}	2.051×10^{-5}	5.474×10^{-6}
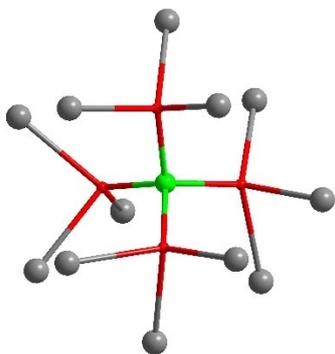
Figure S1. One PS$_4$ unit is surrounded by 12 (Ag/Cu)S$_4$ units in Ag$_{1.5}$Cu$_{1.5}$PS$_4$.
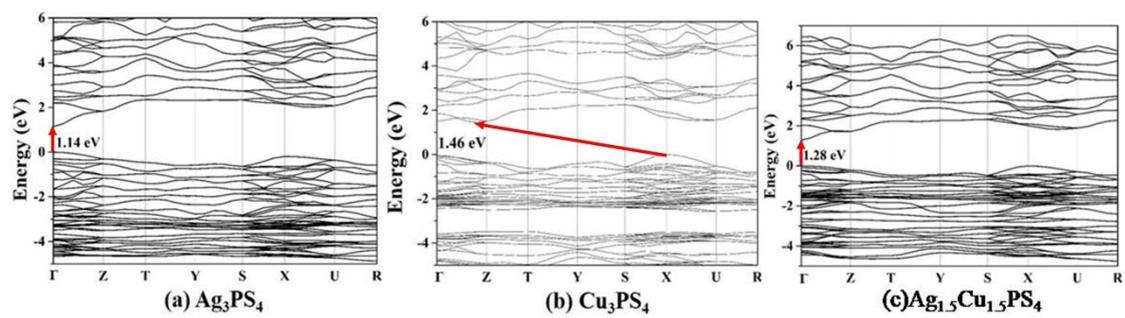
Figure S2. Band structures for title compounds.
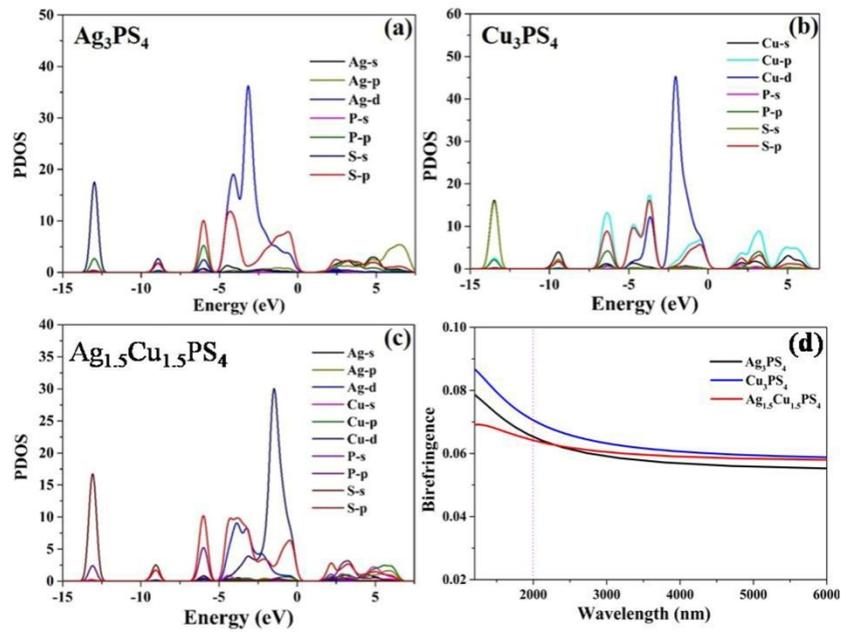
Figure S3. (a, b and c) Partial Density of State (PDOS) and (d) calculated birefringences for title crystals.
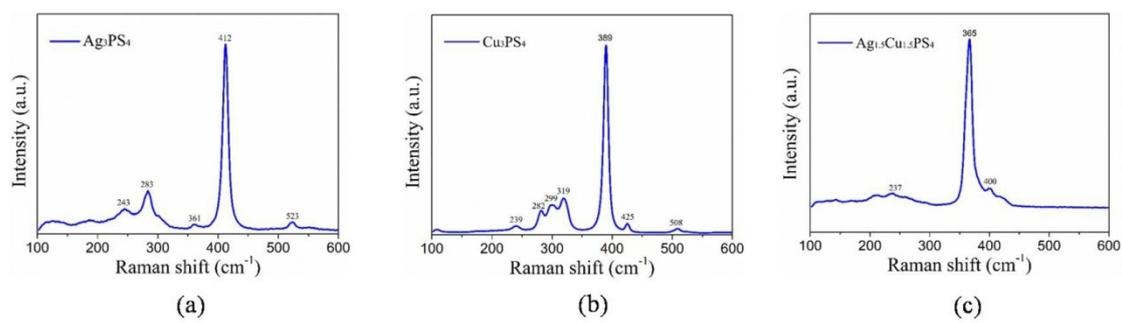
Figure S4. Raman spectra for title compounds.
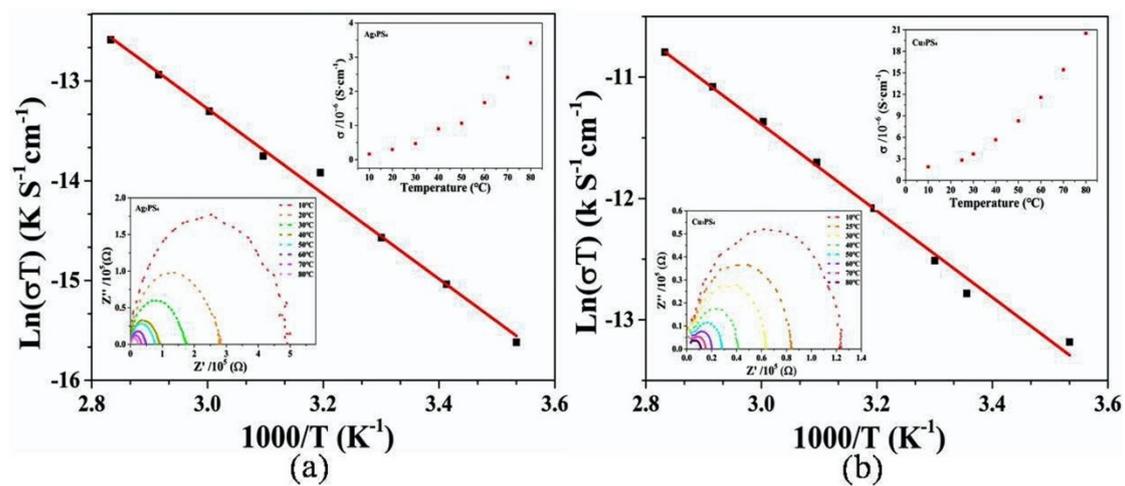
Figure S5. The Arrhenius plots with a linear fit all are $R^2 = 0.993$ for (a) Ag_3PS_4 and (b) Cu_3PS_4, the complex impedance plots (insets) are in the bottom left and ion conductivity plots (insets) are in the upper right from low to high temperatures.

5. References

[1] SAINT, version 7.60A; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2008.

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