M_6PS_5X (M = Ag, Cu; X = Cl, Br) chalcohalides exhibiting strong nonlinear optical responses and high laser damage resistances

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CONTENTS

1. Synthesis of Title Compounds

Used reagents with high purity (≥ 99.9%) including MX (AgCl, AgBr, CuCl, CuBr), M_2S, P and S were purchased from the Beijing Hawk Science & Technology Co., Ltd without further purification. Title compounds were synthesized by the stoichiometric ratio of raw materials (MX : M_2S : P : S = 1 : 2.5 : 1 : 2.5). In order to remove the corrosive effect between halides and silica tubes, we have put the graphite crucible into the silica tubes. The mixture was placed in the vacuum-sealed silica tubes and then put them into the muffle furnace. Temperature curves were set to be the following procedure: firstly, heating temperature to the 700 ^{o}C with the ratio of 10 ^{o}C/h and sintering at 700 ^{o}C for 5 days; secondly, slowly cooled to room temperature with the rate at 3 ^{o}C/h. Red crystals with high yield (>95 %) in silica tubes were obtained and they are stable in the air. Synthesized microcrystals by the spontaneous crystallization are used for the following property measurement.

2. Structural Refinement and Crystal Data

Selected high-quality crystals were used for data collections on a Bruker D8 VENTURE diffractometer using Mo Kα radiation (λ = 0.71073 Å) at room temperature. The crystal structures were solved by direct method and refined using the SHELXTL program package. Multi-scan method was used for absorption correction. Rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. Detail refinement parameters and data were shown in Table S1.

3. Property Characterization

3.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) patterns of title compounds were collected on a Bruker D2 X-ray diffractometer 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

Diffuse-reflectance spectra were measured by a Shimadzu SolidSpec-3700DUV

spectrophotometer in the wavelength range of 200−1100 nm at room temperature.

3.3 Raman spectra

Hand-picked crystals were first 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 and $AgGaS_2$ as the reference were investigated by a Q-switch laser (2.09 μm, 3 Hz, 50 ns) at six particle sizes: 38−55, 55-88, 88-110, 110-150, 150-200 and 200-250 μm, respectively.

3.5 LDT Measurement

The LDTs of title compounds were evaluated on powder sample (38−55 μm) with a pulsed YAG laser. Similar size of $AgGaS_2$ is chosen as the reference. To adjust different laser beams, an optical concave lens is added into the laser path. The damage spot is measured by the scale of optical microscope.

3.6 Computational Description

Utilized the plane-wave pseudopotential method implemented in the CASTEP, the electronic structures of title compounds were performed on DFT. All of them were optimized by The Perdew-Burke-Ernzerhof (PBE) exchange-correlation of Generalized Gradient Approximation (GGA). A Kleinman-Bylander representation of the ultrasoft pseudopotential is automatically introduced and the valance electrons of the related atoms were: Ag: $4p^6\ 4d^{10}\ 5s^1$, Cu: $3p^6\ 3d^{10}\ 4\ s^1$, P: $3s^2\ 3p^3$, S: $3s^2\ 3p^4$, Cl: $3s^2\ 3p^5$, Br: $4s^2\ 4p^5$, respectively. Also, kinetic energy cut-offs were set to be 720.0 eV with a density of fewer than 0.05 $Å^{-1}$ in the Brillouin zone (BZ) was adopted. As important parameter for NLO crystals, SHG coefficient was calculated with suitable scissors operators.

4. Figures and Tables

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

Empirical formula	Ag_6PS_5Cl	Ag_6PS_5Br	Cu_6PS_5Cl	Cu_6PS_5Br
formula weight	873.94	918.40	607.96	652.42
crystal system	Cubic			
space group	*F*-43*m*			
cell parameter *a* (Å)	10.3514(3)	10.3765(10)	9.6962(4)	9.7321(13)
Z, *V* (Å^3)	4, 1109.17(10)	4, 1117.26(3)	4, 911.60(11)	4, 921.8(4)
D_c (g/cm^3)	5.234	5.460	4.430	4.701
μ (mm^{-1})	11.651	14.904	15.282	19.159
goodness-of-fit on F^2	1.234	1.331	1.160	1.192
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0401,0.1109	0.0636,0.1779	0.0407,0.1044	0.0343,0.0859
R_1, wR_2 (all data) [a]	0.0401,0.1109	0.0636,0.1779	0.0426,0.1059	0.0347,0.0859
absolute structure parameter	0.04(3)	0.08(19)	0.01(4)	0.04(3)
largest diff. peak and hole (e·Å^{-3})	0.895,–0.644	1.303,–0.706	1.587,–0.649	1.011,–0.364

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

Table S2. Comparison on LDTs between title compounds and $AgGaS_2$.

compounds	damage energy (mJ)	spot diameter (mm)	LDT (MW/cm^2)	LDT (× AGS)*
$AgGaS_2$	0.58	0.5	29.6	1
Ag_6PS_5Cl	0.98	0.5	50.3	1.7
Ag_6PS_5Br	0.98	0.5	50.3	1.7
Cu_6PS_5Cl	1.33	0.5	68.1	2.3
Cu_6PS_5Br	1.33	0.5	68.1	2.3

*AGS = $AgGaS_2$

Table S3. Property comparison among NLO materials in the M-P-S-X system.

compound	Space group	$E_{g(exp./cal.)}$ (eV)	SHG (×AGS)	d_{ij} (pm/V)	LDT (×AGS)
Ag_3PS_4	*Pmn*2$_1$	2.43/1.14	1.3	15.77	1.0
Cu_3PS_4	*Pmn*2$_1$	2.25/1.46	0.8	−10.1	-
$Ag_{1.5}Cu_{1.5}PS_4$	*Pmn*2$_1$	2.37/1.28	0.5	13.42	-
$Ag_5PS_4Cl_2$	*Amm*2	2.71/1.20	2.5	-22.7	3.8
Ag_6PS_5Cl	*F*-43*m*	2.01/1.35	2.7	-26.7	1.7
Cu_6PS_5Cl	*F*-43*m*	2.22/1.55	2.0	18.7	2.3
Ag_6PS_5Br	*F*-43*m*	1.95/1.32	2.7	-31.2	1.7
Cu_6PS_5Br	*F*-43*m*	2.20/1.51	2.0	20.9	2.3

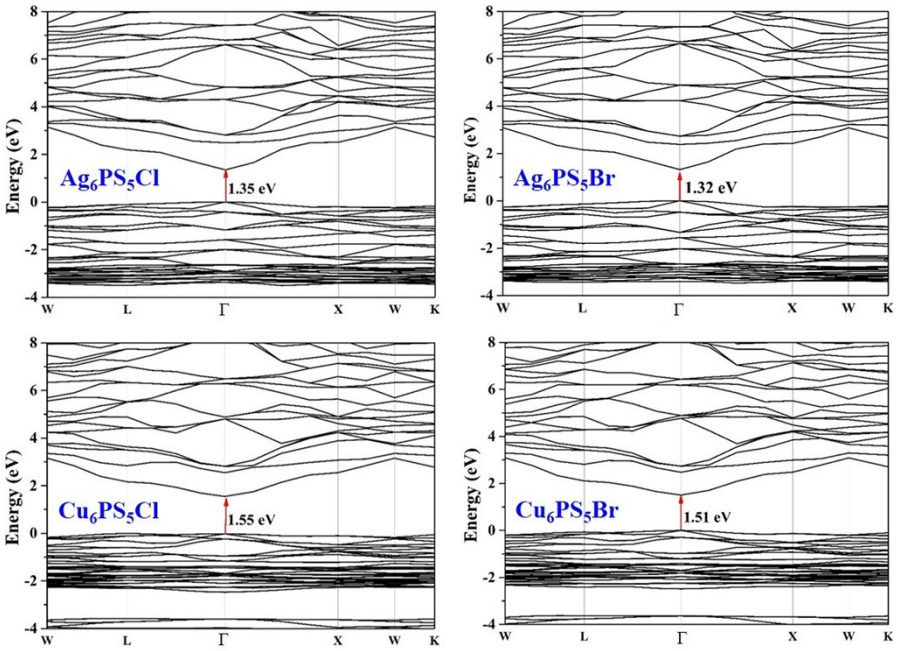

Figure S1. Calculated electronic structures of title compounds.

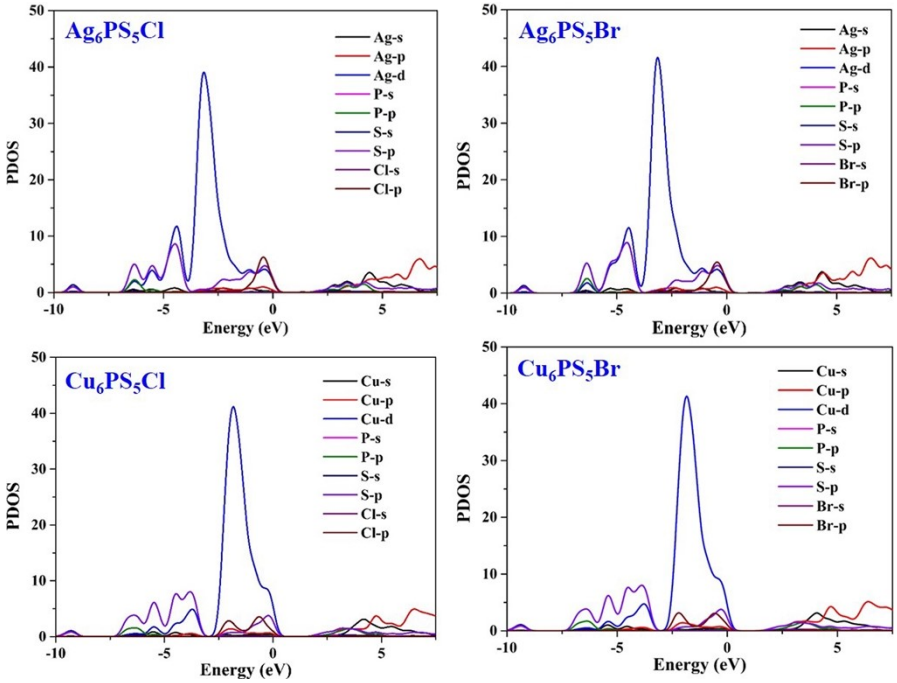

Figure S2. Calculated PDOS diagrams of title compounds.

Figure S3. SHG intensity *versus* particle size among title compounds and $AgGaS_2$.