# HgCuPS<sub>4</sub>: An Exceptional Infrared Nonlinear Optical Material with Defect Diamond-like Structure

Meng-Yue Li,<sup>†,‡,#</sup> Zuju Ma,<sup>I,#</sup> Bingxuan Li,<sup>§</sup> Xin-Tao Wu,<sup>†</sup> Hua Lin,<sup>\*, †</sup>and Qi-Long Zhu<sup>\*,†</sup>

<sup>†</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

<sup>‡</sup>College of Chemistry, Fuzhou University, Fuzhou 350002, China

<sup>§</sup>Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute

of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

<sup>*II*</sup> School of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, China

\*M. Y. Li and Z. Ma contributed equally to this work.\*E-mail: linhua@fjirsm.ac.cn and glzhu@fjirsm.ac.cn.

#### **CONTENTS**

#### **1. Property Characterization**

- 1.1 Second Harmonic Generation (SHG) Measurements
- 1.2 Laser Induced Damage Threshold (LIDT) Measurements

#### 2. Computational Details

#### 3. Figures and Tables

Figure S1. The EDX results of HgCuPS<sub>4</sub>.

**Figure S2.** The thermogravimetric analysis (TGA) for HgCuPS<sub>4</sub> was performed on a NETZSCH STA 449C simultaneous analyzer under a constant flow of  $N_2$  atmosphere at a heating rate of 10 K/min.

**Figure S3.** The first Brillouin zone with high symmetry points (red). The labeled *k*-points are G (0 0 0), Z (0 0 0.5), T (-0.5 0 0.5), Y (-0.5 0 0), S (-0.5 0.5 0), X (0 0.5 0), U (0 0.5 0.5) and R (-0.5 0.5 0.5).

Figure S4. Energy dependences of the real part  $\varepsilon_1$  (a) and imaginary part  $\varepsilon_2$  (b) of HgCuPS<sub>4</sub>.

Figure S5. The calculated refractive index (n) of HgCuPS<sub>4</sub>.

Figure S6. The calculated absorption coefficient ( $\alpha$ ) of HgCuPS<sub>4</sub>.

Figure S7. The calculated reflectivity (*R*) of HgCuPS<sub>4</sub>.

Figure S8. The dipole moments of the  $[HgS_4]$ ,  $[CuS_4]$  and  $[PS_4]$  units in  $HgCuPS_4$  shown by different arrowheads.

 Table S1. Atomic coordinates and equivalent isotropic displacement parameters of

 HgCuPS<sub>4</sub>.

Table S2. Selected bond lengths (Å) and angles (°) of HgCuPS<sub>4</sub>.

Table S3. Property comparison between the AGS,  $Zn_3P_2S_8$  and  $M^I$ - $M^{II}$ -P- $S_4$  system.

Table S4. Calculative local dipole moment ( $\mu$ ) of different units for HgCuPS<sub>4</sub> in Debye.

4. References

#### **1. Property Characterization**

#### 1.1 Second Harmonic Generation (SHG) Measurements

The powder SHG measurements were carried out with the Kurtz-Perry method using a 2050 nm Q-switch laser.<sup>1</sup> AgGaS<sub>2</sub> (AGS) was used as a benchmark material, which is offered from Anhui Institute of Optics and Fine Mechanics Chinese Academy of Sciences. HgCuPS<sub>4</sub> and AGS were ground and sieved into distinct particle size ranges  $(30-46, 46-74, 74-106, 106-150, 150-210 \mu m)$ . The SHG signals of the frequency-doubled output emitted from the sieved samples were detected using a photomultiplier tube and recorded on the oscilloscope.

#### 1.2 Laser Induced Damage Threshold (LIDT) Measurements

The LIDT of HgCuPS<sub>4</sub> in the range of 150–210  $\mu$ m was measured through single pulse measurement method<sup>2</sup> and crushed AGS single crystal as the reference. Both samples were packed into identical plastic holders (thickness: 1 mm and diameter: 8 mm). After exposed to the high-power 1064 nm laser radiation with pulse width  $\tau_p$  of 10 ns, the apparent change of sample was monitored by an optical microscope. The power of laser beam and the damage spot radius were respectively measured by a Nova II sensor with a PE50-DIF-C energy sensor and a Vernier caliper.

#### **2.** Computational Details

The imaginary part of the dielectric function due to direct inter-band transitions is given by the expression:

$$\varepsilon_{2}(\mathsf{h}\omega) = \frac{2e^{2}\pi}{\Omega\varepsilon_{0}} \sum_{k,v,c} \left| \left\langle \psi_{k}^{c} \left| u \cdot r \right| \psi_{k}^{v} \right\rangle \right|^{2} \delta(E_{k}^{c} - E_{k}^{v} - E)$$

where  $\Omega$ ,  $\omega$ , u, v and c are the unit-cell volume, photon frequencies, the vector

defining the polarization of the incident electric field, valence and conduction bands, respectively. The real part of the dielectric function is obtained from  $\varepsilon_2$  by a Kramers-Kronig transformation:

$$\varepsilon_{1}(\omega) = 1 + (\frac{2}{\pi}) \int_{0}^{+\infty} d\omega' \frac{{\omega'}^{2} \varepsilon_{2}(\omega)}{{\omega'}^{2} - {\omega}^{2}}$$

The refractive index  $n(\omega)$  can be obtained based on  $\varepsilon_1$  and  $\varepsilon_2$ .

The so-called length-gauge formalism is adopted to calculate the static  $\chi^{(2)}$  coefficients  $(d_{ij})^{3, 4}$  and a scissor operator has been added to correct the conduction band energy. In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as:

$$\chi^{abc}(-2\omega,\omega,\omega) = \frac{e^3}{h^2\Omega} \sum_{nml,k} \frac{r_{nm}^a \{r_{ml}^b r_{ln}^c\}}{\omega_{nm} \omega_{ml} \omega_{ln}} [\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}] + \frac{i}{4} \frac{e^3}{h^2\Omega} \sum_{nm,k} \frac{f_{nm}}{\omega_{mn}^2} [r_{nm}^a (r_{mn;c}^b + r_{mn;b}^c) + r_{nm}^b (r_{mn;c}^a + r_{mn;a}^c) + r_{nm}^c (r_{mn;b}^a + r_{mn;a}^b)]$$

where *r* is the position operator,  $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$  is the energy difference for the bands *m* and *n*,  $f_{mn} = f_m - f_n$  is the difference of the Fermi distribution functions, subscripts *a*, *b*, and *c* are Cartesian indices, and  $r^{b}_{mn}$ ; a is the so-called generalized derivative of the coordinate operator in *k* space,

$$r_{nm;a}^{b} = \frac{r_{nm}^{a}\Delta_{mn}^{b} + r_{nm}^{b}\Delta_{mn}^{a}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \times \sum_{l} (\omega_{lm}r_{nl}^{a}r_{lm}^{b} - \omega_{nl}r_{nl}^{b}r_{lm}^{a})$$

where  $\Delta^{a}_{nm} = (p^{a}_{nn} - p^{a}_{mm}) / m$  is the difference between the electronic velocities at the bands n and m.

# 3. Figures and Tables

			Atomic %	Hg	Cu	Р	s	]
	1		EDX (ave.)	1.0(4)	1.0(2)	0.9(3)	4.1(5)	
G			_					
J				<b>6</b> •	•	•		
0	2	4	6 8	10	12	14	16	1

Figure S1. The EDX results of HgCuPS<sub>4</sub>.



Figure S2. The thermogravimetric analysis (TGA) for HgCuPS<sub>4</sub> was performed on a NETZSCH STA 449C simultaneous analyzer under a constant flow of  $N_2$  atmosphere at a heating rate of 10 K/min.



**Figure S3.** The first Brillouin zone with high symmetry points (red). The labeled *k*-points are G (0 0 0), Z (0 0 0.5), T (-0.5 0 0.5), Y (-0.5 0 0), S (-0.5 0.5 0), X (0 0.5 0), U (0 0.5 0.5) and R (-0.5 0.5 0.5).



Figure S4. Energy dependences of the real part  $\epsilon_1$  (a) and imaginary part  $\epsilon_2$  (b) of HgCuPS<sub>4</sub>.



Figure S5. The calculated refractive index (n) of HgCuPS<sub>4</sub>.



Figure S6. The calculated absorption coefficient ( $\alpha$ ) of HgCuPS<sub>4</sub>.



Figure S7. The calculated reflectivity (R) of HgCuPS<sub>4</sub>.



Figure S8. The dipole moments of the  $[HgS_4]$ ,  $[CuS_4]$  and  $[PS_4]$  units in  $HgCuPS_4$  shown by different arrowheads.

HgCuP	<b>S</b> <sub>4</sub> .						
Atom	Wyckoff	x	у	Ζ	$U_{(eq)}^{*}$	Осси.	
Hg1	4 <i>a</i>	0.07253(3)	0.23035(6)	0.5257(2)	0.0224(2)	0.935(2)	
Hg2	4 <i>a</i>	0.1603(5)	0.0023(2)	0.022(4)	0.031(2)	0.065(2)	
Cu	4 <i>a</i>	0.1609(9)	0.4964(2)	0.0280(6)	0.0190(3)	1.0	
Р	4 <i>a</i>	0.4086(2)	0.2417(3)	0.0352(7)	0.0076(4)	1.0	
<b>S</b> 1	4 <i>a</i>	0.0655(2)	0.2375(4)	0.1167(5)	0.0131(5)	1.0	
S2	4 <i>a</i>	0.3282(2)	0.0180(4)	0.1509(4)	0.0122(5)	1.0	
S3	4 <i>a</i>	0.3309 (2)	0.4579(4)	0.1768(5)	0.0144(5)	1.0	
S4	4 <i>a</i>	0.1086(2)	0.7593(3)	0.2000(4)	0.0145(5)	1.0	
$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.							

 Table S1. Atomic coordinates and equivalent isotropic displacement parameters of

 HgCuPS<sub>4</sub>.

Hg1-S1	2.497(3)	∠S1–Hg1–S3	113.49(9)
Hg1-S3	2.524(3)	∠S1–Hg1–S4	112.78(8)
Hg1-S4	2.530(4)	∠S3–Hg1–S4	108.07(9)
Hg1-S2	2.578(3)	∠S1–Hg1–S2	107.21(9)
Hg2-S3	2.140(2)	∠S3–Hg1–S2	107.91(9)
Hg2-S1	2.183(9)	∠S4–Hg1–S2	107.07(9)
Hg2-S4	2.191(2)	∠S3–Hg2–S1	114.2(8)
Hg2-S2	2.270(2)	∠S3–Hg2–S4	112.2(5)
Cu-S4	2.299(3)	∠S1–Hg2–S4	110.6(7)
Cu-S2	2.310(5)	∠S3–Hg2–S2	107.4(6)
Cu-S1	2.319(3)	∠S1–Hg2–S2	112.6(6)
Cu-S3	2.354(3)	∠S4–Hg2–S2	98.7(7)
P-S1	2.056(3)	∠S4–Cu–S2	114.4(2)
P-S4	2.060(5)	∠S4–Cu–S1	115.8(2)
P-S3	2.061(3)	∠S2–Cu–S1	108.7(2)
P-S2	2.061(3)	∠S4–Cu–S3	100.9(2)
		∠S2–Cu–S3	109.7(2)
		∠S1–Cu–S3	106.7(2)
		∠S1–P–S4	109.7(2)
		∠S1–P–S3	107.7(2)
		∠S4–P–S3	108.46(17)
		∠S1–P–S2	117.09(19)
		∠S4–P–S2	109.74(17)
		∠S3–P–S2	103.68(17)

**Table S2.** Selected bond lengths (Å) and angles (°) of HgCuPS<sub>4</sub>.

Compounds	AgGaS <sub>2</sub>	$7n_2P_2S_2$	LiZnPS <sub>4</sub>	CuZnPS <sub>4</sub>	AgZnPS <sub>4</sub>	CuHgPS <sub>4</sub>
Compounds	(AGS)	ZII3F 2 <b>3</b> 8				(this work)
Unit cell	Tetragonal	Tetragonal	Tetragonal	Orthorhombic	Tetragonal	Orthorhombic
G	I <del>4</del> 2m	$P\overline{4}n2$	I <del>4</del>	$Pna2_1$	I <del>4</del> 2m	Pna2 <sub>1</sub>
Space group	(No.121)	(No.118)	(No.82)	(No.33)	(No.121)	(No.33)
DL type	Normal	Defect	Defect	Defect	Defect	Defect
VEC*	4	4.92	4.752	4.752	4.752	4.752
$E_{g}(eV)$	2.56	3.07	3.38	3.0	2.76	2.03
$d_{ij}$ (× AGS)	1	2.6	0.8	3.0	1.8	6.5
LIDT (× AGS)	1	N/A	N/A	6.0	N/A	4.2
PM/NPM**	PM	PM	PM	РМ	PM	PM
$\Delta n$ (calculated)	0.039	0.04	0.073	0.07	0.051	0.11

Table S3. Property comparison between the AGS,  $Zn_3P_2S_8$  and  $M^{I}$ - $M^{II}$ -P-S<sub>4</sub> system.

\*VEC = valence electron concentration, defined as  $(ME_A+NE_B+...)/(M+N+...)$ , where  $E_A$  and  $E_B$  are the valence electron numbers of compositional elements A and B in [AB<sub>4</sub>] tetrahedral units, respectively; while M and N represent the atomic numbers of A and B.

\*\*PM = phase-matching; NPM = non-phase-matching.

**Table S4.** Calculative local dipole moment  $(\mu)$  of different units for HgCuPS<sub>4</sub> in Debye.

unit	$\mu_{\mathrm{x}}$	$\mu_{y}$	$\mu_z$	$\mu_{total}$
[HgS <sub>4</sub> ]	0	0	-3.0708	3.0708
[CuS <sub>4</sub> ]	0	0	-4.0436	4.0436
[PS <sub>4</sub> ]	0	0	-0.5492	0.5492

#### 4. References

1. Kurtz, S. K.; Perry, T. T. A Powder Technique for the Evaluation of Nonlinear Optical Materials. *J. Appl. Phys.* **1968**, *39*, 3798–3813.

2. Zhang, M. J.; Jiang, X. M.; Zhou, L. J.; Guo, G. C. Two phases of Ga<sub>2</sub>S<sub>3</sub>: promising infrared second–order nonlinear optical materials with very high laser induced damage thresholds. *J. Mater. Chem. C* **2013**, *1*, 4754–4760.

3. Aversa, C.; Sipe, J. E. Nonlinear optical susceptibilities of semiconductors: Results with a length–gauge analysis. *Phys. Rev. B*, **1995**, *52*, 14636–14645.

4. Rashkeev, S. N.; Lambrecht, W. R. L.; Segall, B. Efficient ab initio method for the calculation of frequency-dependent second-order optical response in semiconductors. *Phys. Rev. B* 1998, *57*, 3905.