## Supporting Information

# $\mathrm{HgCuPS}_{4}$ : An Exceptional Infrared Nonlinear Optical Material with Defect Diamond-like Structure 

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## 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 $\mathrm{HgCuPS}_{4}$.

## Supporting Information

Figure S2. The thermogravimetric analysis (TGA) for $\mathrm{HgCuPS}_{4}$ was performed on a
NETZSCH STA 449C simultaneous analyzer under a constant flow of $\mathrm{N}_{2}$ atmosphere at a heating rate of $10 \mathrm{~K} / \mathrm{min}$.

Figure S3. The first Brillouin zone with high symmetry points (red). The labeled $k$-points are $\mathrm{G}(000), \mathrm{Z}(000.5), \mathrm{T}(-0.500 .5), \mathrm{Y}(-0.500), \mathrm{S}(-0.50 .50), \mathrm{X}(00.5$ $0), \mathrm{U}(00.50 .5)$ and $R(-0.50 .50 .5)$.

Figure S4. Energy dependences of the real part $\varepsilon_{1}$ (a) and imaginary part $\varepsilon_{2}$ (b) of $\mathrm{HgCuPS}_{4}$.

Figure S5. The calculated refractive index ( $n$ ) of $\mathrm{HgCuPS}_{4}$.
Figure S6. The calculated absorption coefficient $(\alpha)$ of $\mathrm{HgCuPS}_{4}$.

Figure S7. The calculated reflectivity $(R)$ of $\mathrm{HgCuPS}_{4}$.
Figure S8. The dipole moments of the $\left[\mathrm{HgS}_{4}\right],\left[\mathrm{CuS}_{4}\right]$ and $\left[\mathrm{PS}_{4}\right]$ units in HgCuPS 4 shown by different arrowheads.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of $\mathrm{HgCuPS}_{4}$.

Table S2. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ of $\mathrm{HgCuPS}_{4}$.
Table S3. Property comparison between the AGS, $\mathrm{Zn}_{3} \mathrm{P}_{2} \mathrm{~S}_{8}$ and $\mathrm{M}^{\mathrm{I}}-\mathrm{M}^{\mathrm{II}}-\mathrm{P}-\mathrm{S}_{4}$ system.
Table S4. Calculative local dipole moment ( $\mu$ ) of different units for $\mathrm{HgCuPS}_{4}$ in Debye.

## 4. References

## Supporting Information

## 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. ${ }^{1} \mathrm{AgGaS}_{2}$ (AGS) was used as a benchmark material, which is offered from Anhui Institute of Optics and Fine Mechanics Chinese Academy of Sciences. $\mathrm{HgCuPS}_{4}$ and AGS were ground and sieved into distinct particle size ranges (30-46, 46-74, 74-106, 106-150, 150-210 $\mu \mathrm{m}$ ). 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 $\mathrm{HgCuPS}_{4}$ in the range of $150-210 \mu \mathrm{~m}$ was measured through single pulse measurement method ${ }^{2}$ and crushed AGS single crystal as the reference. Both samples were packed into identical plastic holders (thickness: 1 mm and diameter: 8 $\mathrm{mm})$. After exposed to the high-power 1064 nm laser radiation with pulse width $\tau_{\mathrm{p}}$ 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:

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

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

## Supporting Information

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:

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

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 $\left(d_{\mathrm{ij}}\right)^{3,4}$ 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:

$$
\begin{gathered}
\chi^{a b c}(-2 \omega, \omega, \omega)=\frac{e^{3}}{\mathrm{~h}^{2} \Omega} \sum_{n m l, k} \frac{r_{n m}^{a}\left\{r_{m l}^{b} r_{\ln }^{c}\right\}}{\omega_{n m} \omega_{m l} \omega_{\mathrm{ln}}}\left[\omega_{n} f_{m l}+\omega_{m} f_{\mathrm{ln}}+\omega_{l} f_{n m}\right]+ \\
\frac{i}{4} \frac{e^{3}}{\mathrm{~h}^{2} \Omega} \sum_{n m, k} \frac{f_{n m}}{\omega_{m n}^{2}}\left[r_{n m}^{a}\left(r_{m n ; c}^{b}+r_{m n ; b}^{c}\right)+r_{n m}^{b}\left(r_{m n ; c}^{a}+r_{m n ; a}^{c}\right)+r_{n m}^{c}\left(r_{m n ; b}^{a}+r_{m n ; a}^{b}\right)\right]
\end{gathered}
$$

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

$$
r_{n m ; a}^{b}=\frac{r_{n m}^{a} \Delta_{m n}^{b}+r_{n m}^{b} \Delta_{m n}^{a}}{\omega_{n m}}+\frac{i}{\omega_{n m}} \times \sum_{l}\left(\omega_{l m} r_{n l}^{a} r_{l m}^{b}-\omega_{n l} r_{n l}^{b} r_{l m}^{a}\right)
$$

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

## Supporting Information

## 3. Figures and Tables



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## Supporting Information



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Supporting Information


Figure S7. The calculated reflectivity $(R)$ of $\mathrm{HgCuPS}_{4}$.


Figure S8. The dipole moments of the $\left[\mathrm{HgS}_{4}\right],\left[\mathrm{CuS}_{4}\right]$ and $\left[\mathrm{PS}_{4}\right]$ units in HgCuPS 4 shown by different arrowheads.

## Supporting Information

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of $\mathrm{HgCuPS}_{4}$.

| Atom | Wyckoff | $x$ | $y$ | $z$ | $U_{(\mathrm{eq})}{ }^{*}$ | Occu. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Hg 1 | $4 a$ | $0.07253(3)$ | $0.23035(6)$ | $0.5257(2)$ | $0.0224(2)$ | $0.935(2)$ |
| Hg 2 | $4 a$ | $0.1603(5)$ | $0.0023(2)$ | $0.022(4)$ | $0.031(2)$ | $0.065(2)$ |
| Cu | $4 a$ | $0.1609(9)$ | $0.4964(2)$ | $0.0280(6)$ | $0.0190(3)$ | 1.0 |
| P | $4 a$ | $0.4086(2)$ | $0.2417(3)$ | $0.0352(7)$ | $0.0076(4)$ | 1.0 |
| S 1 | $4 a$ | $0.0655(2)$ | $0.2375(4)$ | $0.1167(5)$ | $0.0131(5)$ | 1.0 |
| S 2 | $4 a$ | $0.3282(2)$ | $0.0180(4)$ | $0.1509(4)$ | $0.0122(5)$ | 1.0 |
| S 3 | $4 a$ | $0.3309(2)$ | $0.4579(4)$ | $0.1768(5)$ | $0.0144(5)$ | 1.0 |
| S 4 | $4 a$ | $0.1086(2)$ | $0.7593(3)$ | $0.2000(4)$ | $0.0145(5)$ | 1.0 |
|  | $* U_{\text {(eq) }}$ is defined as one-third of the trace of the orthogonalized $U_{\mathrm{ij}}$ tensor. |  |  |  |  |  |

## Supporting Information

Table S2. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ of $\mathrm{HgCuPS}_{4}$.

| $\mathrm{Hg} 1-\mathrm{S} 1$ | $2.497(3)$ | $\angle \mathrm{S} 1-\mathrm{Hg} 1-\mathrm{S} 3$ | $113.49(9)$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{Hg} 1-\mathrm{S} 3$ | $2.524(3)$ | $\angle \mathrm{S} 1-\mathrm{Hg} 1-\mathrm{S} 4$ | $112.78(8)$ |
| $\mathrm{Hg} 1-\mathrm{S} 4$ | $2.530(4)$ | $\angle \mathrm{S} 3-\mathrm{Hg} 1-\mathrm{S} 4$ | $108.07(9)$ |
| $\mathrm{Hg} 1-\mathrm{S} 2$ | $2.578(3)$ | $\angle \mathrm{S} 1-\mathrm{Hg} 1-\mathrm{S} 2$ | $107.21(9)$ |
| $\mathrm{Hg} 2-\mathrm{S} 3$ | $2.140(2)$ | $\angle \mathrm{S} 3-\mathrm{Hg} 1-\mathrm{S} 2$ | $107.91(9)$ |
| $\mathrm{Hg} 2-\mathrm{S} 1$ | $2.183(9)$ | $\angle \mathrm{S} 4-\mathrm{Hg} 1-\mathrm{S} 2$ | $107.07(9)$ |
| $\mathrm{Hg} 2-\mathrm{S} 4$ | $2.191(2)$ | $\angle \mathrm{S} 3-\mathrm{Hg} 2-\mathrm{S} 1$ | $114.2(8)$ |
| $\mathrm{Hg} 2-\mathrm{S} 2$ | $2.270(2)$ | $\angle \mathrm{S} 3-\mathrm{Hg} 2-\mathrm{S} 4$ | $112.2(5)$ |
| $\mathrm{Cu}-\mathrm{S} 4$ | $2.299(3)$ | $\angle \mathrm{S} 1-\mathrm{Hg} 2-\mathrm{S} 4$ | $110.6(7)$ |
| $\mathrm{Cu}-\mathrm{S} 2$ | $2.310(5)$ | $\angle \mathrm{S} 3-\mathrm{Hg} 2-\mathrm{S} 2$ | $107.4(6)$ |
| $\mathrm{Cu}-\mathrm{S} 1$ | $2.319(3)$ | $\angle \mathrm{S} 1-\mathrm{Hg} 2-\mathrm{S} 2$ | $112.6(6)$ |
| $\mathrm{Cu}-\mathrm{S} 3$ | $2.354(3)$ | $\angle \mathrm{S} 4-\mathrm{Hg} 2-\mathrm{S} 2$ | $98.7(7)$ |
| $\mathrm{P}-\mathrm{S} 1$ | $2.056(3)$ | $\angle \mathrm{S} 4-\mathrm{Cu}-\mathrm{S} 2$ | $114.4(2)$ |
| $\mathrm{P}-\mathrm{S} 4$ | $2.060(5)$ | $\angle \mathrm{S} 4-\mathrm{Cu}-\mathrm{S} 1$ | $115.8(2)$ |
| $\mathrm{P}-\mathrm{S} 3$ | $2.061(3)$ | $\angle \mathrm{S} 2-\mathrm{Cu}-\mathrm{S} 1$ | $108.7(2)$ |
| $\mathrm{P}-\mathrm{S} 2$ | $2.061(3)$ | $\angle \mathrm{S} 4-\mathrm{Cu}-\mathrm{S} 3$ | $100.9(2)$ |
|  |  | $\angle \mathrm{S} 2-\mathrm{Cu}-\mathrm{S} 3$ | $109.7(2)$ |
|  |  | $\angle \mathrm{S} 1-\mathrm{Cu}-\mathrm{S} 3$ | $106.7(2)$ |
|  |  | $\angle \mathrm{S} 1-\mathrm{P}-\mathrm{S} 4$ | $109.7(2)$ |
|  | $\angle \mathrm{S} 1-\mathrm{P}-\mathrm{S} 3$ | $107.7(2)$ |  |
|  |  | $\angle \mathrm{S} 4-\mathrm{P}-\mathrm{S} 3$ | $108.46(17)$ |
|  |  | $\angle \mathrm{P} 3-\mathrm{S} 2-\mathrm{P} 2-\mathrm{S} 2$ | $117.09(19)$ |
|  |  | $109.74(17)$ |  |
|  |  | $103.68(17)$ |  |

## Supporting Information

Table S3. Property comparison between the $\mathrm{AGS}, \mathrm{Zn}_{3} \mathrm{P}_{2} \mathrm{~S}_{8}$ and $\mathrm{M}^{\mathrm{I}}-\mathrm{M}^{\mathrm{II}}-\mathrm{P}-\mathrm{S}_{4}$ system.

| Compounds | $\mathrm{AgGaS}_{2}$ <br> (AGS) | $\mathrm{Zn}_{3} \mathrm{P}_{2} \mathrm{~S}_{8}$ | $\mathrm{LiZnPS}_{4}$ | $\mathrm{CuZnPS}_{4}$ | $\mathrm{AgZnPS}_{4}$ | $\mathbf{C u H g P S}_{4}$ <br> (this work) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Unit cell | Tetragonal | Tetragonal | Tetragonal | Orthorhombic | Tetragonal | Orthorhombic |
| Space group | $I \overline{4} 2 m$ | $P \overline{4} n 2$ | $I \overline{4}$ | Pna2 ${ }_{1}$ | $1 \overline{4} 2 m$ | Pnal ${ }_{1}$ |
|  | (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 |
| $\mathrm{Eg}_{\mathrm{g}}(\mathrm{eV})$ | 2.56 | 3.07 | 3.38 | 3.0 | 2.76 | 2.03 |
| $d_{\mathrm{ij}}(\times \mathrm{AGS})$ | 1 | 2.6 | 0.8 | 3.0 | 1.8 | 6.5 |
| LIDT ( $\times$ AGS $)$ | 1 | N/A | N/A | 6.0 | N/A | 4.2 |
| PM/NPM** | PM | PM | PM | PM | PM | $\mathbf{P M}$ |
| $\Delta \mathrm{n}$ (calculated) | 0.039 | 0.04 | 0.073 | 0.07 | 0.051 | 0.11 |

${ }^{*}$ VEC $=$ valence electron concentration, defined as $\left(\mathrm{ME}_{\mathrm{A}}+\mathrm{NE}_{\mathrm{B}}+\ldots\right) /(\mathrm{M}+\mathrm{N}+\ldots)$, where $E_{A}$ and $E_{B}$ are the valence electron numbers of compositional elements $A$ and $B$ in $\left[\mathrm{AB}_{4}\right]$ tetrahedral units, respectively; while M and N represent the atomic numbers of A and B .
${ }^{* *} \mathrm{PM}=$ phase-matching; $\mathrm{NPM}=$ non-phase-matching.

## Supporting Information

Table S4. Calculative local dipole moment ( $\mu$ ) of different units for $\mathrm{HgCuPS}_{4}$ in Debye.

| unit | $\mu_{\mathrm{x}}$ | $\mu_{\mathrm{y}}$ | $\mu_{\mathrm{z}}$ | $\mu_{\text {total }}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{HgS}_{4}\right]$ | 0 | 0 | -3.0708 | 3.0708 |
| $\left[\mathrm{CuS}_{4}\right]$ | 0 | 0 | -4.0436 | 4.0436 |
| $\left[\mathrm{PS}_{4}\right]$ | 0 | 0 | -0.5492 | 0.5492 |

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