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Supporting Information for

Mixed-Metal Thiophosphate CuCd₃PS₆: an Infrared Nonlinear Optical Material Activated by Three-in-One Tetrahedra-Stacking Architecture

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Experimental details

1. Synthesis

Cu (99.99%), Cd (99.99%), P (99.9%), S (99.999%) and P₂S₅ (99.9%) were directly purchased from Sinopharm Chemical Reagent Co., Ltd. All manipulations were performed in an Ar–filled glovebox with H₂O and O₂ contents less than 0.1 ppm. The binary starting materials Cu₂S and CdS were prepared by the stoichiometric reaction of the elements at high temperatures in sealed silica tubes evacuated to 10^{-3} Pa. Polycrystalline sample of CuCd₃PS₆ was obtained by traditional solid state reaction in a stoichiometric mixture of Cu₂S, CdS and P₂S₅ (in a molar ratio of 1: 6: 1). The raw materials were loaded into fused–silica tubes and then, the ampoules were flame–sealed under a vacuum of 10^{-3} Pa. The tubes were then placed in a computer–controlled furnace and heated to 773 K within 24 h, left for 120 h. Finally, the furnace was turned off. Single crystals of CuCd₃PS₆ were prepared through spontaneous crystallization. The reaction mixture of Cu₂S, CdS and P₂S₅ in a molar ratio of 1: 3: 1 was mixed and loaded into a fused–silica tube. Then the tube was flame–sealed and gradually heated to 1223 K in a computer–controlled horizontal furnace, kept for 96 h, and then slowly cooled at a rate of 3 K/h and finally cooled to room temperature by switching off the furnace. The product consists of hundreds of red crystals.

2. Structure determination

Single crystal X–ray diffraction data were recorded on a Xcalibur Ecos diffractometer equipped with a graphite–monochromated Mo– K_{α} ($\lambda = 0.71073$ Å) radiation at 293 K. The structures were solved with direct method by SHELXS–97 and refined by the full matrix least squares on F² by SHELXL–97, respectively. The detailed crystallographic data were summarized in Table S1. The atomic coordinates, occupancy and equivalent displacement parameters are given in Table S2. The important bond lengths and angles are listed in Table S3.

3. Property Characterization

Powder X-ray Diffraction

The powder X-ray diffraction pattern of the as-obtained polycrystalline powders were performed at room temperature on a Bruker D8 Focus diffractometer with Cu K_a ($\lambda = 1.5418$ Å) radiation. The scanning step width of 0.02° and a fixed counting time 0.1 s/step were applied to record the patterns in the 2θ range of $10 - 70^{\circ}$.

Element Analysis

Elemental analysis of compositions of the single crystals were performed on an energy–dispersive X–ray (EDX)–equipped Hitachi S–4800 scanning electron microscopy (SEM) instrument.

Diffuse reflectance spectroscopy

A Cary 5000 UV–vis–NIR spectrophotometer with a diffuse reflectance accessory was used to measure the spectrum of $CuCd_3PS_6$ and $BaSO_4$ (as a reference) in the range 200 nm (6.2 eV) to 2500 nm (0.496 eV).

Raman Spectra

The Raman spectra were recorded on a Lab RAM Aramis spectrometer equipped with a 532 nm laser at room temperature on polycrystalline powder with the spectral resolution of 1 cm⁻¹.

Infrared spectrum

Infrared (IR) spectroscopy was collected on a Varian Excalibur 3100 spectrometer. The CuCd₃PS₆ and KBr samples with mass ratio about 1:100 were mixed thoroughly.

Thermal Analysis

By applying the LabsysTM TG-DTA16 (SETARAM) thermal analyzer equipped with the nitrogen flow at a rate of about 30 ml/min, the thermal stability of $CuCd_3PS_6$ was investigated in detail. Appropriate amounts of the polycrystalline powder were thoroughly ground, then were placed in a silica tube (5 mm o.d. × 3 mm i.d.) and subsequently sealed under a high vacuum. The tube was heated from room temperature to 1173 K and then cooled to room temperature with the heating/cooling rate both at 15 K min⁻¹.

Powder SHG Measurement

The optical SHG response of $CuCd_3PS_6$ was measured by means of the Kurtz–Perry method. The fundamental light was the 2090 nm light generated with a Q-switched Ho: Tm: Cr: YAG laser. The polycrystalline powder of $CuCd_3PS_6$ was thoroughly ground and sieved into a series of

particle size ranges: 20 - 41, 41 - 74, 74 - 105, 105 - 150 and $150 - 200 \mu m$. These samples were then clamped by two glass microscope slides and secured with tape in a 1 mm thick aluminum holder. Microcrystalline AgGaS₂ was ground and sieved into the same particle size range of $41 - 74 \mu m$ as a reference.

Powder LDT Measurement

The single-pulse measurement method was used to estimate the powder LDT of CuCd₃PS₆ and the reference AgGaS₂. Powder sample of CuCd₃PS₆ and AgGaS₂ in the same size range (41–74 μ m) were selected and pressed into glass microscope cover slides. The samples were subjected to high-power 1064 nm laser radiation with a pulse width τ_p of 8 ns. The measurements were taken under an optical microscope once single-pulse radiation was passed, and the laser power increased until the damaged spot was observed. Then, the laser power was marked, and the area of the damaged spot was measured as the damage threshold parameters of the sample.

4. Computational methods

The first-principles calculations for $CuCd_3PS_6$ were performed by CASTEP, a plane-wave pseudopotential total energy package based density functional theory (DFT). The functional developed by Perdew-Burke-Emzerhoff (PBE) functional within the generalized gradient approximation (GGA) form were adopted to describe the exchange-correlation energy. The optimized norm-conserving pseudopotentials in the Kleinman-Bylander form for all the elements are used to model the effective interaction between atom cores and valence electrons. And Cu 3p63d104s1, Cd 4p64d105s2, P 3s23p3, S 3s23p4 electrons were treated as valence electrons, allowing the adoption of a relatively small basis set without compromising the computational accuracy. The high kinetic energy cutoff 800 eV and dense $3 \times 3 \times 1$ Monkhorst-Pack k-point meshes in the Brillouin zones were chosen for CuCd₃PS₆. Our tests showed that the above computational set ups are sufficiently accurate for present purposes. The scissor operators were adopted to shift all the conduction bands to match the calculated band gaps with the measured values. Based on the electronic band structure, the imaginary part of the dielectric function is calculated and the real part of the dielectric function is determined using the Kramers-Kronig transform, from which the refractive indices n (and the birefringence Δn) are obtained. Furthermore, the second order susceptibility $\chi^{(2)}$ and the second-harmonic generation (SHG) coefficients d_{ij} are calculated using

an expression originally proposed by Rashkeev et al. and developed by Lin et al. The second-order susceptibility χ_{ijk} is represented as:

$$\chi_{ijk} = \chi_{ijk} (VE) + \chi_{ijk} (VH) + \chi_{ijk} (twobands)$$

where χ_{ijk} (VE) and χ_{ijk} (VH) denote the contributions from virtual-electron processes and virtual-hole processes, respectively, and χ_{ijk} (two bands) gives the contribution from two band processes to $\chi^{(2)}$. The formulas for calculating χ_{ijk} (VE), χ_{ijk} (VH) and χ_{ijk} (two bands) are as following:

$$\chi_{ijk} (VE) = \frac{e^3}{2h^2m^3} \sum_{vc'} \int \frac{d^3k}{4\pi^3} P(ijk) \operatorname{Im}[p_{vc}^i p_{cc'}^j p_{c'v}^k] \left(\frac{1}{\omega_{cv}^3 \omega_{vc'}^2} + \frac{2}{\omega_{vc}^4 \omega_{c'v}} \right)$$

$$\chi_{ijk} (VH) = \frac{e^3}{2h^2m^3} \sum_{vv'c} \int \frac{d^3k}{4\pi^3} P(ijk) \operatorname{Im}[p_{vv}^i p_{v'c}^j p_{cv}^k] \left(\frac{1}{\omega_{cv}^3 \omega_{v'c}^2} + \frac{2}{\omega_{vc}^4 \omega_{cv'}} \right)$$

$$\chi_{ijk} (twobands) = \frac{e^3}{h^2m^3} \sum_{vc} \int \frac{d^3k}{4\pi^3} P(ijk) \frac{\operatorname{Im}[p_{vc}^i p_{cv}^j (p_{vc}^k - p_{cc}^k)]}{\omega_{vc}^5}$$

Here, *i*, *j* and *k* are Cartesian components, *v* and *v*' denote VB, and *c* and *c*' denote CB. P(ijk) denotes full permutation. It should be emphasized that the refractive indices and SHG coefficients can be accurately obtained by DFT in principle because these optical properties are determined by the virtual electronic excited processes which are described by the first- and second-order perturbations, respectively, on the ground state wavefunctions.



5. Figure S1

(a) Scanning electron microscopy (SEM) image of $CuCd_3PS_6$ grown by spontaneous crystallization. (b) Elemental analysis of $CuCd_3PS_6$ by EDX spectroscopy. (c) Elemental distribution of the as-grown crystal (from left to right: Cu, Cd, P, S).

6. Figure S2



Experimental and simulated powder XRD patterns of CuCd₃PS₆.

7. Figure S3



Oscilloscope traces of the SHG signals for CuCd_3PS_6 and AgGaS_2 (reference) in the particle size of 41–74 $\mu m.$

8. Figure S4



SHG response vs. particle size curve of CuCd₃PS₆

9. Figure S5



IR spectrum of CuCd₃PS₆.

10. Figure S6



Raman spectrum of CuCd₃PS₆.

11. Table S1 Crystallographic data and structure refinement for CuCd₃PS₆.

Empirical formula	CuCd ₃ PS ₆	
Formula weight	624.07	
Space group	Сс	
a/Å	12.0326(11)	
b/Å	6.9383(3)	
c/Å	13.8825(13)	
α/°	90.00	
β/°	125.005(14)	
$\gamma/^{\circ}$	90.00	

$V/Å^3$	949.33(19)		
Ζ	4		
$ ho_{calc} \mathrm{g/cm^3}$	4.366		
μ/mm^{-1}	10.248		
<i>F</i> (000)	1136.0		
Radiation	MoKa ($\lambda = 0.71073$ Å)		
2θ range for data collection/°	6.886 to 52.744		
Index ranges	$-14 \leq h \leq 14$, $-8 \leq k \leq 8$,		
index ranges	-17≤1≤17		
Reflections collected	5770		
Independent reflections	1830 [Rint = 0.0391, Rsigma =		
	0.0346]		
Data/restraints/parameters	1830/2/100		
Absolute structure parameter	0.06(3)		
GOF on F^2	1.253		
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0427, wR_2 = 0.1185$		
Final <i>R</i> indexes [all data]	$R_1 = 0.0430, wR_2 = 0.1186$		

12. Table S2 Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for CuCd₃PS₆. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{ij} tensor.

Atom	X	y	Z	U(eq)
Cd1	7596.5(18)	4308(3)	4268.2(16)	27.3(5)
Cd2	8996.1(16)	3791(3)	7560.7(14)	20.4(4)
Cd3	6853.3(18)	8415(2)	5600.8(15)	19.5(4)
Cu1	5257(3)	3104(5)	5652(3)	22.0(7)
S1	6982(6)	4869(7)	5658(5)	11.2(10)
S2	3356(5)	5077(7)	4972(4)	9.6(10)
S3	3521(6)	4992(7)	2667(5)	11.4(10)
S4	1058(6)	2404(8)	2632(4)	12.4(10)
S5	993(5)	7196(7)	2434(4)	10.1(10)
S6	4732(6)	323(8)	4558(5)	14(1)
P1	2221(5)	4802(7)	3170(4)	6.2(10)

13. Table S3 Selected bond lengths (Å) and angles (°) for $CuCd_3PS_6$

Cd1–S1	2.461(5)	S6 ¹ -Cd1-S5 ²	116.15(18)
Cd1–S4 ¹	2.895(6)	S1-Cd2-S3 ³	104.13(19)
Cd1-S5 ²	2.592(5)	S1-Cd2-S54	112.73(18)

Cd1-S6 ¹	2.465(6)	S54-Cd2-S33	88.88(16)
Cd2-S1	2.462(6)	S6 ³ -Cd2-S1	129.09(19)
Cd2-S3 ³	2.709(6)	S6 ³ -Cd2-S3 ³	97.57(19)
Cd2-S54	2.599(5)	S6 ³ -Cd2-S5 ⁴	113.18(18)
Cd2-S6 ³	2.456(6)	S1-Cd3-S2 ¹	113.48(18)
Cd3-S1	2.464(5)	S1-Cd3-S3 ⁵	113.01(19)
Cd3-S2 ¹	2.679(6)	S1-Cd3-S6 ⁶	125.3(2)
Cd3-S3 ⁵	2.622(6)	S3 ⁵ -Cd3-S2 ¹	86.52(16)
Cd3-S6 ⁶	2.474(6)	S6 ⁶ -Cd3-S2 ¹	103.99(18)
Cu1-S1	2.406(6)	S6 ⁶ -Cd3-S3 ⁵	107.47(19)
Cu1-S ²	2.349(6)	S2-Cu1-S1	110.1(2)
Cu1–S4 ³	2.360(5)	S2-Cu1-S4 ³	102.0(2)
Cu1-S6	2.309(6)	S4 ³ -Cu1-S1	107.3(2)
S2-P1	2.059(7)	S6-Cu1-S1	109.7(2)
S3-P1	2.050(7)	S6-Cu1-S2	112.8(2)
S4-P1	2.022(7)	S6-Cu1-S4 ³	114.6(2)
S5-P1	2.063(7)	S2-P1-S5	108.3(3)
S1-Cd1-S41	98.82(17)	S3-P1-S2	107.7(3)
S1-Cd1-S5 ²	118.06(18)	S3-P1-S5	104.4(3)
S1-Cd1-S6 ¹	125.5(2)	S4-P1-S2	111.2(3)
S5 ² -Cd1-S4 ¹	82.41(17)	S4-P1-S3	115.4(3)
S61-Cd1-S41	93.07(18)	S4-P1-S5	109.4(3)