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Mixed-Metal Thiophosphate CuCd<sub>3</sub>PS<sub>6</sub>: an Infrared Nonlinear Optical Material Activated by Three-in-One Tetrahedra-Stacking

A novel mixed-metal thiophosphate CuCd<sub>3</sub>PS<sub>6</sub> has been first discovered and fully characterized. Careful experimental and theoretical investigations demonstrate that CuCd<sub>3</sub>PS<sub>6</sub> is a benign infrared nonlinear optical material with moderate second harmonic generation response of  $0.9 \times AgGaS_2$  at 41-74  $\mu$ m, large laser damage threshold of 4.1 × AgGaS<sub>2</sub>, wide band gap of 2.24 eV and low melting point of 603 °C. Moreover, first principles calculations indicate CuCd<sub>3</sub>PS<sub>6</sub>'s intriguing nonlinear optical performance is activated by its three-in-one tetrahedra-stacking architecture.

Architecture

The limited commercially available lasing sources in mid and far infrared (IR) region has made it a hotspot to design and synthesize new IR nonlinear optical (NLO) materials with excellent overall performance which possess indispensable function to convert existing lasers' frequencies to target ones.<sup>1-9</sup> Over the past decades, researchers have made tremendous efforts in this field and summarized many useful strategies, including (1) introducing strongly electropositive alkali and alkaline-earth metal cations to reduce the band dispersion, and hence increase materials' band gap, which is beneficial for improving laser induced damage threshold (LDT); (2) increasing the packing density of NLO-functional groups and optimizing their spatial arrangement by cation tuning (conductive to the generation of large nonlinearity); (3) selecting heavier chalcogen as the electronegative element to lower the lattice vibrational phonon energy and broaden the mid-far IR transmission range; (4) hybridizing different type of

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NLO-active units and utilizing the synergistic effect to increase the NLO response; (5) taking advantage of first principles calculation based molecular design from parent models to lessen the trial and error process in exploratory synthesis, etc. Surely, the core idea of these strategies is to optimize the type, packing density and spatial arrangement of the NLO active units by adjusting the synthesis route and reaction system, making the product satisfied with key criteria of IR NLO materials, i.e. wide IR optical transparency, strong NLO response, good phase matchability, high LDT, etc.

In chalcogenides, the typical NLO active units encompass MX<sub>4</sub> tetrahedra (M = Cu, Ag, Zn, Cd, Hg, Ga, In, Ge, Sn, P, etc.; X = chalcogen), second-order Jahn-Teller (SOJT) cation (e.g., Ti<sup>4+</sup>, Nb<sup>5+</sup>) centered polyhedra, stereo-chemically active lone pair (SCALP) cation (e.g., Pb<sup>2+</sup>, As<sup>3+</sup>) centered polar units,  $\pi$  conjugated trigonal planar units (e.g., HgSe<sub>3</sub>, AgSe<sub>3</sub>), etc.<sup>10–16</sup> Among these units, MX<sub>4</sub> tetrahedra have been studied most widely owing to its intrinsic asymmetry, species diversity, substitution flexibility and multifarious linkage modes.<sup>17</sup> Commendably, these explorations in tetrahedra-based chalcogenides have led to the discovery of many excellent IR NLO crystals, including commercial  $AgGaQ_2$  (Q = S, Se) themselves,<sup>18,19</sup>  $BaGa_4Q_7$  (Q = S, Se),<sup>15,20</sup>  $BaGa_2MSe_6$  (M = Si, Ge),<sup>21</sup> I<sub>2</sub>AE  $M^{IV}Q_4$  (I = Li, Na, K, Cu, Ag; AE = Ba, Sr;  $M^{IV}$  = Si, Ge, Sn; Q = S, Se) family,<sup>22–26</sup> AM<sup>II</sup>M<sup>IV</sup>Q<sub>4</sub> (A = Eu, Sr, Ba; M<sup>II</sup> = Mn, Zn, Cd, Hg;  $M^{IV}$  = Si, Ge, Sn; Q = S, Se) family,<sup>27–33</sup>  $AX^{II}_{4}X^{III}_{5}Q_{12}$  (A = K, Rb, Cs;  $X^{II}$  =Mn, Zn, Cd, Hg;  $X^{III}$  = Ga, In; Q = S, Se, Te) family,<sup>34–40</sup> etc. However, most of these newly-developed crystals are constructed by only one or two types of covalent MX<sub>4</sub> tetrahedra. Heterogeneous hybridization of three or more types of MX<sub>4</sub> tetrahedra in one compound, which may trigger novel covalent framework and strengthen synergistic effect, is relatively few.

IB and IIB group metals with d<sup>10</sup> electronic configurations can form distorted MX<sub>4</sub> tetrahedra with large polarizations and show benign connectivity with p-block metal centered tetrahedra.<sup>17</sup> In addition, the introduction of PS<sub>4</sub> tetrahedra tends to lower the melting temperature (beneficial for

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Fig. 1 (a) Tetrahedra arrangement of layer I; (b) Unit cell of CuCd<sub>3</sub>PS<sub>6</sub>; (c) Tetrahedra arrangement of layer II.

reducing sulfur vapor pressure during crystal growth) and strengthen the covalent architecture (make for improving LDT).<sup>41–43</sup> Thus, we conduct elaborative exploration in IB–IIB–P–S reaction system, which gives rise to the discovery of a new IR NLO crystal CuCd<sub>3</sub>PS<sub>6</sub> featuring three-in-one tetrahedra-stacking architecture.

Red block-shaped crystals of CuCd<sub>3</sub>PS<sub>6</sub> were grown via the spontaneous crystallization in a vacuumed fused-silica tube with Cu<sub>2</sub>S, CdS and  $P_2S_5$  as staring materials.<sup>44–48</sup> Crystal structure of CuCd<sub>3</sub>PS<sub>6</sub> was solved based on single-crystal X-ray diffraction data, which indicates it belongs to monoclinic space group Cc with the cell dimensions of a = 12.0326(11) Å, b = 6.9383(3) Å, c = 13.8825(13) Å,  $\beta$  = 125.005(14) and Z = 4. Besides, Energy Dispersive X-ray analysis and field emission scanning electron microscope analysis were performed on some selected CuCd<sub>3</sub>PS<sub>6</sub> crystals. The results imply that Cu, Cd, P and S are evenly distributed on the crystal. And molar ratio of these elements is about 1: 3: 1: 6 which is consistent with the solved molecular formula CuCd<sub>3</sub>PS<sub>6</sub> (Figure S1). The bond lengths of Cu-S, Cd-S and P-S fall in the range of 2.309(6) to 2.406(6) Å, 2.456(6) to 2.894(6) Å and 2.022(7) to 2.063(7) Å, which are in accordance with those of related compounds.<sup>17,42,43</sup> Note that Cd–S bonds exhibit a wide length range, indicating large distortion in CdS<sub>4</sub> tetrahedra. In addition, the bond valence sums (BVS) of compositional elements are calculated to be Cu: 1.17, Cd: 1.964-2.10, P: 5.20, S: 1.89-2.27, demonstrating that these atoms are all in reasonable oxidation states. There are one, three, one and six crystallographically independent Cu, Cd, P and S atoms in an asymmetric unit of the title compound. Interestingly, all the cations are four-coordinated with S, forming three different types of distorted tetrahedra. As demonstrated in Figure 1b, the crystal structure of CuCd<sub>3</sub>PS<sub>6</sub> can be regarded as the heterogeneous hybridization of CuS<sub>4</sub>, CdS<sub>4</sub> and PS<sub>4</sub>, and features alternating stack of two kinds of tetrahedral layer. Layer I is depicted in Figure 1a. Cd(1)S<sub>4</sub> and PS<sub>4</sub> connect with each other hand in hand alternatively and extend infinitely to form [CdPS<sub>6</sub>]<sub> $\infty$ </sub> chains which are further interlinked by isolated CuS<sub>4</sub> tetrahedra to construct layer I. In contrast, layer II is composed of pure CdS<sub>4</sub> tetrahedra (Figure 1c). Cd(2)S<sub>4</sub> and Cd(3)S<sub>4</sub> joint together via sharing corner S to form Cd<sub>2</sub>S<sub>7</sub> units which further interconnect to constitute [CdS<sub>3</sub>]<sub> $\infty$ </sub> wavy chains. And, these wavy chains pile up to form layer II. Finally, layer I and layer II are connected with each other alternatively by sharing corner S atoms to build the covalent framework.



Fig. 2 The relative SHG response (Green) and LDT (Red) of  $CuCd_3PS_6$  and  $AgGaS_2$  in particle range of 41-74  $\mu m.$ 

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Polycrystalline powder sample of CuCd<sub>3</sub>PS<sub>6</sub> was synthesized via high temperature solid state reaction of stoichiometric binary starting materials. And its purity was verified by PXRD (Figure S2). To assess the NLO performance of CuCd<sub>3</sub>PS<sub>6</sub>, second harmonic generation (SHG) responses of  $CuCd_3PS_6$  and benchmark  $AgGaS_2$  (as reference) were measured according to Kurtz-Perry technique using a 2.09 µm laser (Q-switched Ho:Tm:Cr:YAG) as the pumping source.<sup>49</sup> As shown in Figure 2 and S3, CuCd<sub>3</sub>PS<sub>6</sub> demonstrates a moderate SHG intensity of about 0.9 times that of AgGaS<sub>2</sub> at  $41-74 \mu m$ , which is comparable to previously reported IR NLO crystals Li<sub>2</sub>ZnSiS<sub>4</sub> (1.1×AgGaS<sub>2</sub>),<sup>50</sup> Na<sub>2</sub>ZnGeS<sub>6</sub> (0.9×AgGaS<sub>2</sub>)<sup>51</sup> and  $LiCd_3PS_6$  (0.8 × AgGaS<sub>2</sub>).<sup>42</sup> And, SHG response vs. particle size curve is depicted in Figure S4. It indicates CuCd<sub>3</sub>PS<sub>6</sub> is nonphase-matchable. In addition, a so called single-pulse method was employed to preliminarily evaluate LDT of CuCd<sub>3</sub>PS<sub>6</sub> and AgGaS<sub>2</sub> powder samples at 41–74  $\mu m,$  using a 1064 nm, 8ns, Q-switch laser.<sup>52,53</sup> Incidence laser energy gradually increased from 0.01 mJ and stopped until the dark damaged spot was observed under the optical microscope. Test results show that 0.062 mJ and 0.015 mJ are the cut off energy of CuCd<sub>3</sub>PS<sub>6</sub> and AgGaS<sub>2</sub>, indicating CuCd<sub>3</sub>PS<sub>6</sub> has a high LDT of about 4.1 times that of AgGaS<sub>2</sub> (Figure 2). And, such high LDT is favourable for high power laser output.



Fig. 3 (a) UV-vis/NIR diffuse reflectance spectrum of  $CuCd_3PS_6$ ; (b) Differential scanning calorimetric curve of  $CuCd_3PS_6$ .

The optical diffuse reflectance spectra of CuCd<sub>3</sub>PS<sub>6</sub> are depicted in Figure 3a, from which band gap of CuCd<sub>3</sub>PS<sub>6</sub> can be deduced to be 2.24 eV based on Kubelka-Munk equation. The band gap agrees well with its red color. Moreover, differential scanning calorimetric (DSC) measurements were conducted to investigate thermal behavior of CuCd<sub>3</sub>PS<sub>6</sub>. As illustrated in Figure 3b, there are one endothermic peak at 603 °C (melting point) and one exothermic peak at 595 °C (recrystallization point) during one heating/cooling cycle, indicating that CuCd<sub>3</sub>PS<sub>6</sub> melts congruently. Thus, it is possible to grow large size CuCd<sub>3</sub>PS<sub>6</sub> single crystal by Bridgeman–Stockbarger method. Interestingly, melting point of CuCd<sub>3</sub>PS<sub>6</sub> is much lower than commercial chalcopyrite AgGaS<sub>2</sub> (998 °C), AgGaSe<sub>2</sub> (860 °C), and ZnGeP<sub>2</sub> (1025 °C), which is beneficial for crystal growth via Bridgeman-Stockbarger method owing to the lower vapor pressure and less corrosion of the quartz tubes.<sup>54</sup> Moreover, such low melting point is one of the characteristics of thiophosphate, which is also observed in Zn<sub>3</sub>P<sub>2</sub>S<sub>8</sub> (594°C), AgZnPS<sub>4</sub> (534 °C), etc.<sup>55</sup> IR and Raman spectra of CuCd<sub>3</sub>PS<sub>6</sub> powder sample are shown in Figure S5 and S6. Peaks located at 524, 542, 573 cm<sup>-1</sup> in IR spectra and 584 cm<sup>-1</sup> in Raman spectra can be designated to the vibrations of P-S bonds while peak at 291 cm<sup>-1</sup> belongs to Cu-S or Cd-S bonds.<sup>42</sup>

![](_page_3_Figure_8.jpeg)

Fig. 4 (a) Total and partial density of states of  $CuCd_3PS_{6}$ ; (b) Electron band structure of  $CuCd_3PS_6$ ; (c) Dispersion curves of the refractive indexes and birefringence of  $CuCd_3PS_6$ 

deep and thorough understanding of For а structure-performance relationship in CuCd<sub>3</sub>PS<sub>6</sub>, first principles calculations on the basis of density functional theory (DFT) were performed.<sup>56–60</sup> The electronic band structures indicate that CuCd<sub>3</sub>PS<sub>6</sub> is a direct transition semiconductor with bandgap of 1.53 eV (Figure 4b). The valence band maximum (VBM) and conduction band minimum (CBM) simultaneous locate at the G point. Noting that the calculated bandgap value is smaller than the experimental one (2.24 eV), which can be attributable to the discontinuity of the exchange-correlation energy for GGA calculation. Thus, a scissor operator is adopted to correct the conduction band to right position. Moreover, the total and partial density of states (DOS) of CuCd<sub>3</sub>PS<sub>6</sub> are depicted in Figure 4a. There is an obvious overlap between Cu, Cd, P orbitals and S orbitals in both valence bands (VB) and conduction bands (CB). It indicates CuCd<sub>3</sub>PS<sub>6</sub> adopts a strong covalent architecture built by CuS<sub>4</sub>, CdS<sub>4</sub>, PS<sub>4</sub> tetrahedra. Besides, upper part of VB (-10-0 eV) and the bottom part of CB (0-5 eV) are occupied by the orbitals of all Cu, Cd, P and S atoms, from which we can infer CuS<sub>4</sub>, CdS<sub>4</sub>, PS<sub>4</sub> tetrahedra show good synergy and are the main contributors of the nonlinear optical properties of CuCd<sub>3</sub>PS<sub>6</sub> because optical performance of a crystal is determined by the electronic transitions between the quantum states of the VBs and the CBs nearby the Fermi level. Thus, CuCd<sub>3</sub>PS<sub>6</sub>, as an IR NLO material, is activated by its threein-one tetrahedra-stacking architecture. Generally, ionically bonded alkali and alkali earth metals have little influence on the overall NLO response as well as birefringence. They only serve as electron donors to stabilize the framework and tune crystal structure since they have little covalent anisotropy, such as Sr in  $Sr_5ZnGa_6S_{15}$ ,<sup>45</sup> K in  $KHg_4Ge_5Se_{12}$ ,<sup>39</sup> and Na in Na<sub>2</sub>ZnGeS<sub>4</sub>.<sup>51</sup> In contrast, compounds made up of pure covalent architectures tend to trigger high density of NLO-active units and synergistic effect among them, for example, Zn<sub>3</sub>P<sub>2</sub>S<sub>8</sub>,<sup>55</sup> Hg<sub>2</sub>GeSe<sub>4</sub><sup>61</sup> and Cd<sub>4</sub>GeS<sub>6</sub>.<sup>17</sup> The title compound CuCd<sub>3</sub>PS<sub>6</sub> adopts a pure covalent architecture stacked by CuS<sub>4</sub>, CdS<sub>4</sub>, PS<sub>4</sub> tetrahedra and crystalize in

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noncentrosymmetric space group *Cc.* Thus, we calculate its non-vanishing independent SHG coefficients, which shows  $d_{11}$ = -1.439 pm/V,  $d_{15}$  = -2.752 pm/V,  $d_{12}$  = -6.359 pm/V,  $d_{13}$  = 1.866 pm/V,  $d_{24}$  = 0.935 pm/V,  $d_{33}$  = 8.503 pm/V. The largest value  $d_{33}$  = 8.503 pm/V for CuCd<sub>3</sub>PS<sub>6</sub> is smaller than that of AgGaS<sub>2</sub> (13 pm/V). This can be attributed to the mutually tilted spatial arrangement of CuS<sub>4</sub>, CdS<sub>4</sub>, PS<sub>4</sub> units which makes the respective NLO effect cancel each other out to some degree. In addition, dispersion curves of the refractive indexes and birefringence of CuCd<sub>3</sub>PS<sub>6</sub> are calculated and displayed in Figure 4c. CuCd<sub>3</sub>PS<sub>6</sub> exhibits a moderate birefringence of 0.018@1064nm.

In summary, mixed-metal thiophosphate  $CuCd_3PS_6$  has been discovered as a novel IR NLO material for the first time. It features three-dimensional covalent framework stacked by three different kinds of tetrahedral units ( $CuS_4$ ,  $CdS_4$ ,  $PS_4$ ). Experimental investigations on powder sample of  $CuCd_3PS_6$ indicate that it exhibits a moderate SHG response of 0.9 × AgGaS<sub>2</sub> and a high LDT of 4.1 × AgGaS<sub>2</sub> at 41-74 µm, striking a good balance. Besides,  $CuCd_3PS_6$  shows a wide band gap of 2.24 eV and a low melting point of 603 °C. Moreover, detailed theoretical calculations are performed, which illustrates that the synergism of NLO-active  $CuS_4$ ,  $CdS_4$  and  $PS_4$  tetrahedra is the main contributor of  $CuCd_3PS_6$ 's NLO effects.

### **Conflicts of interest**

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There are no conflicts to declare.

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![](_page_6_Figure_4.jpeg)

A new infrared nonlinear optical material  $CuCd_3PS_6$  is activated by three-in-one tetrahedra-stacking architecture.