

# The Nonlinear Coefficient $d_{36}$ of CdSiP<sub>2</sub>

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## ABSTRACT

The new nonlinear crystal for the mid-IR CdSiP<sub>2</sub> was discovered only very recently but the interest in this chalcopyrite is enormous because it possesses most of the attractive properties of the related ZnGeP<sub>2</sub> but allows in addition pumping at 1064 nm without two-photon absorption and uncritical phase-matching for 6  $\mu\text{m}$  generation with maximized effective nonlinearity. The last feature is due to the fact that this crystal is negative uniaxial in contrast to ZnGeP<sub>2</sub> which shows positive birefringence. We now measured its nonlinear coefficient using SHG of femtosecond pulses generated near 4.6  $\mu\text{m}$  from a seeded KNbO<sub>3</sub> optical parametric amplifier. The SHG efficiency was compared for uncoated samples of CdSiP<sub>2</sub> and ZnGeP<sub>2</sub>, both  $\approx 0.5$  mm thick, in the low conversion limit ( $< 10\%$  internal conversion efficiency) which justifies the use of the plane wave approximation. Taking into account the experimentally determined phase-matching angles for type-I SHG (oo-e type in CdSiP<sub>2</sub> and ee-o type in ZnGeP<sub>2</sub>), which were in good agreement with the existing Sellmeier approximations, we arrived at  $d_{36}(\text{CdSiP}_2) \sim d_{36}(\text{ZnGeP}_2)$  which is rather unexpected having in mind the larger band-gap of CdSiP<sub>2</sub>. The reliability of the measurement was tested at the same wavelength by comparing ZnGeP<sub>2</sub> with HgGa<sub>2</sub>S<sub>4</sub> which led to the result  $d_{36}(\text{ZnGeP}_2) \sim 3d_{36}(\text{HgGa}_2\text{S}_4)$ , in very good agreement with previous estimations.

Key words: nonlinear crystals; second order nonlinearity; mid-infrared; chalcopyrites; second harmonic generation

## 1. INTRODUCTION

Since solid state lasers obviously cannot directly cover the spectral range above 3  $\mu\text{m}$  in the mid-IR, there is a need for improved nonlinear optical crystals that can shift the output of widely-used high-power diode-pumped laser systems, such as Nd:YAG, to wavelengths in the 3-12  $\mu\text{m}$  spectral range and ensure tunability. Oxide-based crystals, for example phosphates and arsenates belonging to the KTiOPO<sub>4</sub> (KTP) family of isomorphs, or iodates, niobates and tantalates like LiIO<sub>3</sub>, LiNbO<sub>3</sub>, KNbO<sub>3</sub>, LiTaO<sub>3</sub>, as well as all their periodically poled counterparts, perform well at the short of this spectral range, but their performance above 4  $\mu\text{m}$  is dramatically affected by the onset of multi-phonon mid-IR absorption. On the other hand, since efficient frequency conversion is only possible using pulsed laser sources (femtosecond to nanosecond) most of the typical mid-IR crystals will suffer two-photon absorption (TPA) at the pump wavelength of 1064 nm because of their low band-gap. Although TPA is the major limitation in many cases residual absorption at the pump wavelength or insufficient birefringence for phase-matching represent additional constraints. Thus, from the I-III-VI<sub>2</sub> chalcopyrite crystals, only AgGaS<sub>2</sub> but not AgGaSe<sub>2</sub>, can be phase-matched and pumped without TPA at 1064 nm, however, sulfides exhibit in general substantially lower second order nonlinearity than selenides. II-IV-V<sub>2</sub> chalcopyrites offer superior properties in comparison to the I-III-VI<sub>2</sub> chalcopyrite crystals in terms of nonlinearity, low scattering losses, hardness, and thermo-optical and thermo-mechanical parameters,<sup>1</sup> but even the most developed compound, ZnGeP<sub>2</sub>, requires pump wavelengths near 2  $\mu\text{m}$  (less common sources like Tm- or Ho-lasers) in order to avoid two-photon and residual absorption as well as to enable phase-matching. The TPA problem precludes also the pumping of the newly developed orientation patterned GaAs at wavelengths near 1  $\mu\text{m}$ .

Imposing the condition that the band-gap should correspond to a wavelength near or below 532 nm (2.33 eV), say  $\geq 2$  eV, we summarized in Table 1 all existing crystals for which 1064 nm pumping has been demonstrated or is eventually possible. A specific nonlinear process, the generation of an idler wavelength of 6.45  $\mu\text{m}$  is selected for comparison.

Table 1. Summary of important properties of all existing nonlinear crystals that can be pumped at 1064 nm to generate 6.45  $\mu\text{m}$  light: The citations in column 2 refer to the Sellmeier equations used. The effective nonlinear coefficients  $d_{\text{eff}}$  (column 3) are calculated at the corresponding phase-matching angle  $\theta$  or  $\varphi$  (column 2), the nonlinear tensor components,  $d_{ij}$ , used for this calculation were derived from the literature (column 6) applying Miller's rule (column 7). The wavelength  $\lambda_F$  (fundamental) at which the nonlinear coefficients have been estimated by SHG is also included in column 6. For  $\text{Sn}_2\text{P}_2\text{S}_6$ ,  $d_{\text{eff}}$  is taken directly from the literature. Citations in the first column refer to the whole row. More rare crystals with extreme transparency, for which  $d_{\text{eff}} < 1$  pm/V, are not included in the table.

Crystal Point group [Reference] Plane	$\theta / \varphi$ [°] (Interaction)	$d_{\text{eff}}$ [pm/V]	Thermal conductivity [W/mK]	Band-gap $E_g$ [eV]	Miller's $\delta$ [pm/V] or $d_{ij}$ [pm/V] @ $\lambda_F$ for SHG	+ Miller's correction [pm/V]
$\text{AgGaS}_2^*$ $\bar{4}2m$	40.50 (oo-e) 45.53 (eo-e) [2]	8.86 13.65	1.4 //c 1.5 $\perp$ c [3]	2.70 [4]	$\delta_{36}=0.12$ [5]	$d_{36}=13.65$
$\text{HgGa}_2\text{S}_4^*$ $\bar{4}$	45.87 (oo-e) 51.21 (eo-e) [6]	15.57 21.18	2.49-2.85 //c 2.36-2.31 $\perp$ c [7]	2.79 [7]	$d_{36}=27.2$ 1064 nm [7]	$d_{36}=24.56$
$\text{Cd}_x\text{Hg}_{1-x}\text{Ga}_2\text{S}_4^*$ ( $\theta=90^\circ$ , $x=0.55$ ) $\bar{4}$	90.00 (oo-e) [7]	24.94	1.8-1.92 //c 1.62-1.81 $\perp$ c ( $x=0.27-0.3$ ) [7]	3.22 ( $x=0.55$ ) [7]	$d_{36}=27.2$ @ 1064 nm [7]	$d_{36}=24.94$
$\text{LiGaS}_2$ $mm2$ [8]	xz 47.77 (oo-e) xy 40.36 (eo-e)	4.23 5.50	NA	3.76	$d_{31}=5.8$ $d_{24}=5.1$ @ 2300 nm	$d_{31}=5.71$ $d_{24}=5.21$
$\text{LiInS}_2$ $mm2$ [9]	xz 40.01 (oo-e) xy 36.37 (eo-e)	4.65 6.77	6.2 //x 6.0 //y 7.6 //z	3.57	$d_{31}=7.25$ $d_{24}=5.66$ @ 2300 nm	$d_{31}=7.23$ $d_{24}=5.93$
$\text{LiGaSe}_2$ $mm2$ [8]	xz 51.45 (oo-e) xy 37.61 (eo-e)	7.82 9.31	NA	3.65	$d_{31}=9.9$ $d_{24}=7.7$ @ 2300 nm	$d_{31}=10$ $d_{24}=8.16$
$\text{LiInSe}_2^*$ $mm2$ [9]	xz 36.97 (oo-e) xy 41.62 (eo-e)	7.26 10.57	4.7-4.5 //x 4.7-4.8 //y 5.5-5.8 //z	2.86	$d_{31}=11.78$ $d_{24}=8.17$ @ 2300 nm	$d_{31}=12.08$ $d_{24}=8.65$
$\text{InPS}_4$ $\bar{4}$	38.80 (ee-o) 42.67 (oe-o) [10]	34.40 23.87 @ optimum $\varphi$	NA	3.2 [11]	$\delta_{31}=0.39$ $\delta_{36}=0.30$ [12]	$d_{31}=27.87$ $d_{36}=21.53$
$\text{Sn}_2\text{P}_2\text{S}_6$ $m$	(ss-f) (fs-f)	$\approx 4$ $\approx 2$ [13]	0.4-0.55 [14]	2.35 [15]	...	...
$\text{GaS}_{0.4}\text{Se}_{0.6}$ $\bar{6}2m$	22.31 (oo-e) 24.67 (eo-e) [16]	51.70 43.16	1.3 //c 10 $\perp$ c [17]	2.4 [18,19]	$d_{22}=48.2$ @ 4.65 $\mu\text{m}$ [19]	$d_{22}=55.88$ $d_{22}=52.26$
$\text{CdSiP}_2$ $\bar{4}2m$	<b>80.46 (oo-e)</b> <b>[20]</b>	<b>90.99</b>	<b>13.6</b> <b>[1]</b>	<b>2.2-2.45</b> <b>[21]</b>	<b><math>d_{36}=84.5</math></b> <b>@ 4.56 <math>\mu\text{m}</math></b> <b>this work</b>	<b><math>d_{36}=92.27</math></b>
$\text{AgGaGeS}_4$ $mm2$	xz 53.99 (oo-e) xy 35.74 (oo-e) [22]	3.32 5.43	0.399 [7]	3.0 [7]	$d_{32}=6.2$ $d_{31}=10.2$ @ 1064 nm [7]	$d_{32}=5.65$ $d_{31}=9.30$
$\text{Ag}_3\text{AsS}_3^*$ $3m$ [23]	22.04 (oo-e) 24.01 (eo-e) 65.63 (oe-e)	22.89 16.44 3.35	0.113 //c, 0.092 $\perp$ c	2.2	$d_{31}=10.4$ $d_{22}=16.6$ @ 10.6 $\mu\text{m}$	$d_{31}=12.34$ $d_{22}=19.70$
$\text{Ag}_3\text{SbS}_3$ $3m$	47.14 (oo-e) 52.84 (eo-e) [24]	14.34 3.80	$\sim 0.1$ //c, $\sim 0.09$ $\perp$ c [25]	2.2 [26]	$d_{31}=7.8$ $d_{22}=8.2$ @ 10.6 $\mu\text{m}$ [24]	$d_{31}=9.90$ $d_{22}=10.41$

\*crystals for which optical parametric oscillation (OPO) with  $\sim 1$   $\mu\text{m}$  pump wavelength has been already demonstrated.

AgGaS<sub>2</sub> is the only commercially available crystal from Table 1. Besides its modest nonlinearity, it exhibits low thermal conductivity and strongly anisotropic thermal expansion. HgGa<sub>2</sub>S<sub>4</sub> shows improved nonlinearity but the growth of this crystal in large sizes with sufficient homogeneity is still problematic and several phases exist. Cd<sub>x</sub>Hg<sub>1-x</sub>Ga<sub>2</sub>S<sub>4</sub>, with x=0.55 adjusted to have non-critical phase-matching for the selected process, is a solid solution in the system HgGa<sub>2</sub>S<sub>4</sub> – CdGa<sub>2</sub>S<sub>4</sub> and can be grown in larger sizes but its composition cannot be maintained constant. The Li-compounds with wurtzite type structure exhibit the largest band-gaps of all mid-IR crystals but their nonlinear coefficients are too low. The improved thermal conductivity in these materials still cannot be utilized in OPO experiments because residual absorption contributes the thermal load. InSP<sub>4</sub> was grown 25-35 years ago only by the chemical vapour transport method and we are not aware of any further progress. The monoclinic Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> is a ferroelectric material but has a phase transition at 338 K to a centrosymmetric phase; in addition, although the nonlinear coefficients are quite high, for such phase-matched processes the effective nonlinearity is very low. GaS<sub>0.4</sub>Se<sub>0.6</sub> is also a solid solution but in a system of non-isostructural parent compounds, GaS – GaSe. Whereas such doping of the well-known nonlinear crystal GaSe with S increases substantially the band-gap, the layered structure is preserved and plates can be only cleaved at present, for propagation along the optical axis. Although rather high nonlinear coefficient has been measured recently, the exact structure of GaS<sub>0.4</sub>Se<sub>0.6</sub> is still under investigation (the same symmetry as for GaSe is assumed in Table 1). The main problem, related to the low hardness (roughly two times better than that of GaSe) and the possibility to cut, polish and coat such crystals, remains. AgGaGeS<sub>4</sub> is in fact a solid solution in the AgGaS<sub>2</sub> – GeS<sub>2</sub> system, whose symmetry differs from that of both parent compounds. The effective nonlinearity in this material is very low. Estimates indicate that other solid solutions such as AgGa(Se<sub>x</sub>S<sub>1-x</sub>)<sub>2</sub> and AgIn<sub>x</sub>Ga<sub>1-x</sub>S<sub>2</sub> require high dopant concentrations to achieve non-critical phase-matching which lead to band-gaps that are too low for ~1 μm pumping without TPA (note that both Se and In reduce the band-gap). Ag<sub>3</sub>AsS<sub>3</sub> (proustite) and the related Ag<sub>3</sub>SbS<sub>3</sub> (pyrargyrite), are archive crystals, included in Table 1 only for completeness. Being one of the first mid-IR crystals studied, their development has been cancelled in favor of the chalcopyrites such as AgGaS<sub>2</sub>, because of their poor thermo-mechanical properties and low laser damage threshold.

Table 1 is the best evidence for the unique capabilities of CdSiP<sub>2</sub> for down conversion to the mid-IR at pump wavelengths near 1 μm because this material, whose growth technology was developed only very recently,<sup>1</sup> outperforms all other crystals included in the table in all aspects, not only those used for comparison in the table, but also in terms of hardness, damage threshold or anisotropy of the thermal expansion, as well as the possibility of non-critical phase-matching with maximized effective nonlinearity without being a solid solution. A practical upper limit of 6.5 μm can be assumed due to the onset of intrinsic multi-phonon absorption: This defines a range of 4 to 6.5 μm for very important applications of CdSiP<sub>2</sub> in the field of chemical sensing, minimally invasive laser surgery and directed countermeasures.<sup>1</sup>

## 2. PROPERTIES OF CdSiP<sub>2</sub>

CdSiP<sub>2</sub> belongs to the tetragonal point group  $\bar{4}2m$ , with lattice constants  $a=5.68 \text{ \AA}$ ,  $c=10.431 \text{ \AA}$ , and  $Z=4$  for the unit cell parameters.<sup>27</sup> It was grown in the past in small sizes that did not allow to measure essential physical properties.<sup>28-33</sup> The microhardness of CdSiP<sub>2</sub> amounts to 9.3 GPa.<sup>34</sup> CdSiP<sub>2</sub> is optically negative uniaxial chalcopyrite which means that, in contrast to the positive ZnGeP<sub>2</sub>, the only commercially available II-IV-V<sub>2</sub> type chalcopyrite, non-critical type-I (oo-e) phase-matching is feasible. The birefringence of CdSiP<sub>2</sub>, ( $n_e-n_o$ ), was found to be -0.06 approaching 6 μm,<sup>28</sup> -0.051 near 2 μm,<sup>33</sup> -0.05 at 1 μm,<sup>31</sup> and -0.045 at 840 nm,<sup>29</sup> in earlier work. An isotropic point was also observed close to the band-edge.<sup>31-33</sup> At room temperature this point occurs at 2.41 eV (514.5 nm)<sup>32-33</sup> and near this point, optical activity can be observed in CdSiP<sub>2</sub>.<sup>32</sup> Sellmeier equations were created before, on the basis of first principle calculations, adjusting the coefficients to the very limited experimental data.<sup>35</sup>

Recently, however, high optical quality crystals with sizes reaching 19 mm in diameter and 30 mm in length were grown successfully from the melt using high purity starting materials via the horizontal gradient freeze technique.<sup>1</sup> Important physical properties have already been measured using large single crystals (Fig. 1) and the data that already appeared elsewhere,<sup>1,20,36</sup> is summarized in Table 2. Two versions of Sellmeier equations appeared already, based on index measurement by the minimum deviation method with 30° prisms.<sup>1,20</sup> The latter one predicts an isotropic point at 508.8 nm.<sup>20</sup> Note that, based on older data of the temperature dependence of the birefringence,<sup>33</sup> thermo-optic coefficients have also been fitted for CdSiP<sub>2</sub>.<sup>37</sup>

The thermal expansion value perpendicular to the  $c$ -axis, Table 2, coincides with an older estimation,<sup>38</sup> whereas parallel to the  $c$ -axis, it is not vanishing but slightly negative, in accordance with theoretical predictions.<sup>39</sup> Nevertheless, in  $\text{AgGaS}_2$  this coefficient is also negative and more than an order of magnitude larger which means much stronger anisotropy.

Table 2. Summary of important properties of  $\text{CdSiP}_2$ .

Material Property	$\text{CdSiP}_2$
Melting Point [ $^{\circ}\text{C}$ ]	1133
Specific Heat [ $\text{J/kgK}$ ]	446
Thermal Diffusivity [ $\text{mm}^2/\text{s}$ ]	7.69
Thermal Conductivity [ $\text{W/mK}$ ]	13.6
Thermal Expansion [ $\text{K}^{-1}$ ]	// $c$ $-1 \times 10^{-6}$ $\perp c$ $11 \times 10^{-6}$
Transparency Range [ $\mu\text{m}$ ]	0.52-9.5
Birefringence ( $n_e - n_o$ ) @ 4 $\mu\text{m}$	-0.051

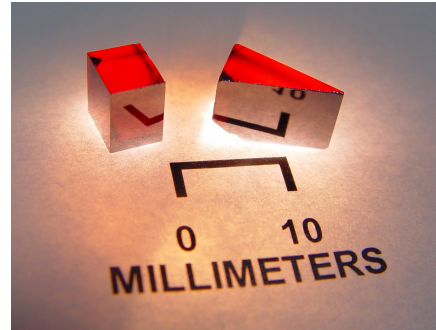


Fig. 1. High optical quality single crystal samples of  $\text{CdSiP}_2$ .

### 3. EXPERIMENTAL SETUP AND RESULTS

The value of the  $d_{36}$  nonlinear optical coefficient of  $\text{CdSiP}_2$  was estimated relative to  $\text{ZnGeP}_2$  by SHG near 4.6  $\mu\text{m}$ , Fig. 2. The source was a femtosecond  $\text{KNbO}_3$ -based optical parametric amplifier (OPA) at a repetition rate of 1 kHz. Direct generation of this wavelength is impossible starting from an  $\sim 800$  nm, 45-fs Ti:sapphire regenerative amplifier system. Instead, a BBO type-II OPA was pumped near 800 nm and its idler output was frequency doubled in a BBO type-I crystal to provide a seed at the signal wavelength near 1  $\mu\text{m}$  for the  $\text{KNbO}_3$  crystal (6-mm, type-I,  $\theta=41.9^{\circ}$ ), which was also pumped near 800 nm by the same regenerative amplifier. The idler pulses of the  $\text{KNbO}_3$  OPA were temporally broadened but simultaneously spectrally narrowed (typical FWHM of 90 nm). The uncoated  $\text{CdSiP}_2$  sample was 0.53 mm thick with an aperture of  $7 \times 7$   $\text{mm}^2$ . It was cut at  $\theta=43^{\circ}$ ,  $\varphi=45^{\circ}$  for type-I SHG. The transmission of this sample when approaching the band-edge is shown in Fig. 3. Even close to the band-edge the dependence on the polarization is weak. An uncoated sample of  $\text{ZnGeP}_2$ , cut at  $\theta=50.5^{\circ}$ ,  $\varphi=0^{\circ}$ , with identical size and thickness, was used as a reference.

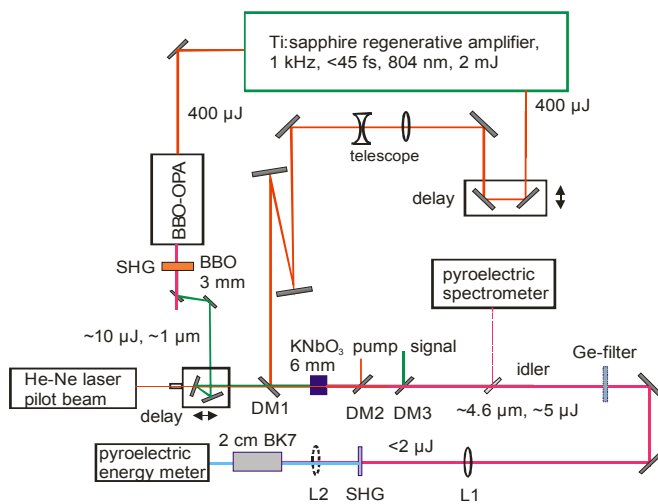


Fig. 2. Experimental setup: DM, dichroic mirrors, L, lenses.

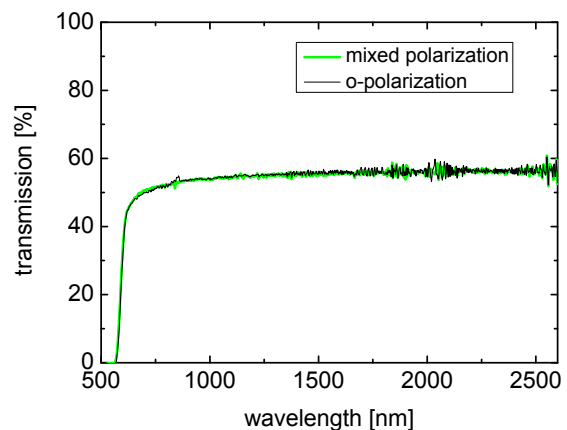


Fig. 3. Polarized transmission of the 0.53 mm thick  $\text{CdSiP}_2$  sample.

For the chosen wavelength and crystal thickness, the spectral acceptance was much larger than the spectral extent of the pump pulses (~12 times for CdSiP<sub>2</sub> and ~7 times for ZnGeP<sub>2</sub>). Taking into account the beam size and the focusing properties of the 25-cm BaF<sub>2</sub> lens L1 (Fig. 2), there was also an excess of angular acceptance (>11 times for CdSiP<sub>2</sub> and >16 times for ZnGeP<sub>2</sub>). Finally, having in mind the beam diameter at the position of the crystals, also the birefringence walk-off ( $\tan\rho=0.009$  for CdSiP<sub>2</sub> and  $\tan\rho=0.005$  for ZnGeP<sub>2</sub>) could be neglected. The incident pulse energy near 4.6  $\mu\text{m}$  was limited to less than 2  $\mu\text{J}$  and the internal conversion efficiency was below 10%. This justifies the plane wave approximation and the effective nonlinear coefficient was estimated by correcting the relative SHG efficiency only for the different Fresnel losses and index of refraction although both corrections did not exceed 5%. An average of 20 measurements for each crystal was taken, in which the results in terms of SHG output did not deviate by more than  $\pm 5\%$ . The experimentally measured internal phase-matching angles (for both crystals they deviated by less than  $0.5^\circ$  from the calculated ones) were used then to derive the ratio for the  $d_{36}$  coefficients:  $d_{36}(\text{CdSiP}_2)=1.07d_{36}(\text{ZnGeP}_2)$  with a relative error estimate of  $\pm 5\%$ . Assuming a value of 75 pm/V for  $d_{36}(\text{ZnGeP}_2)$  at a fundamental wavelength of 9.6  $\mu\text{m}$ ,<sup>23,24</sup> which corrected to  $\lambda_F=4.56$   $\mu\text{m}$  gives 79 pm/V, one arrives at  $d_{36}(\text{CdSiP}_2)=84.5$  pm/V at  $\lambda_F=4.56$   $\mu\text{m}$  (Table 1). As a test for the reliability of the measurement, we also measured  $d_{36}(\text{HgGa}_2\text{S}_4)$  relative to  $d_{36}(\text{ZnGeP}_2)$  using a sample of 0.48 mm thickness cut at  $\theta=38.6^\circ$ ,  $\varphi=45^\circ$  for type-I SHG. The result,  $d_{36}(\text{HgGa}_2\text{S}_4)=0.328d_{36}(\text{ZnGeP}_2)$  at  $\lambda_F=4.58$   $\mu\text{m}$ , leading to  $d_{36}(\text{HgGa}_2\text{S}_4)=25.9$  pm/V near 4.6  $\mu\text{m}$  is in very good agreement with previous estimates using the Maker fringe technique at 1064 nm or SHG at 3.5  $\mu\text{m}$ , which give  $d_{36}(\text{HgGa}_2\text{S}_4)\approx 1.8d_{36}(\text{AgGaS}_2)$ , see Table 1.<sup>7,23,24</sup>

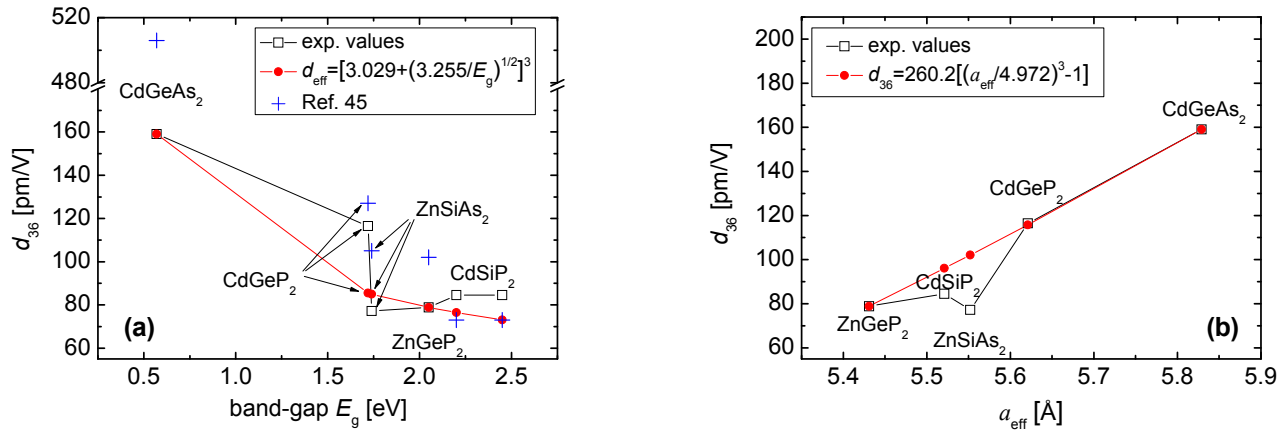


Fig. 4. Nonlinear coefficient  $d_{36}$  of II-IV-V<sub>2</sub> chalcopyrites, rescaled by Miller's rule to SHG at  $\lambda_F=4.6$   $\mu\text{m}$ , versus band-gap (a) and versus effective primitive cell size (b).

The obtained nonlinear coefficient for CdSiP<sub>2</sub> obviously does not follow the trend one expects for the II-IV-V<sub>2</sub> chalcopyrites as a function of band-gap.<sup>40</sup> From Miller's relationship and the well-known  $(E_g)^{-1/4}$  dependence of the refractive index,<sup>40</sup> one can fit the data available for such compounds by an  $[A+(E/E_g)^{1/2}]^3$  law. Such dependence is shown by full circles in Fig. 4a for all the compounds for which data on the nonlinear coefficient  $d_{36}$  exists. The band-gap values were taken from Ref. 41 whereas for CdSiP<sub>2</sub>, two values appear as in Table 1.<sup>21</sup> The experimental  $d_{36}$  values, shown by open squares in Fig. 4a, are taken from: For CdGeP<sub>2</sub> and ZnSiP<sub>2</sub> at  $\lambda_F=10.6$   $\mu\text{m}$  from Ref. 42, assuming  $d_{36}(\text{GaAs})=90$  pm/V as a reference, a value leading to consistency in the measurements of  $d_{36}(\text{ZnGeP}_2)$ <sup>43</sup>; for ZnGeP<sub>2</sub>,  $d_{36}=75$  pm/V at  $\lambda_F=9.6$   $\mu\text{m}$ ;<sup>23,24,43</sup> and for CdGeAs<sub>2</sub>, from  $d_{36}(\text{CdGeAs}_2)=4.7d_{36}(\text{AgGaSe}_2)$  at  $\lambda_F=10.6$   $\mu\text{m}$ ,<sup>23</sup> with  $d_{36}(\text{AgGaSe}_2)=29.5$  pm/V for SHG at  $\lambda_F=10.2$   $\mu\text{m}$ .<sup>44</sup> The two constants  $A$  and  $E$  were fitted from the data on the two most studied crystals, ZnGeP<sub>2</sub> and CdGeAs<sub>2</sub>. It can be seen that CdSiP<sub>2</sub> deviates from the expected trend. The blue crosses in Fig. 4a show first principles theoretical calculations which were presented in Ref. 45 versus the same band-gap values. These calculated  $d_{36}$  values also deviate substantially from the experiment, in particular for CdGeAs<sub>2</sub>.

In Fig. 4b, we have plotted the same experimental values versus the effective primitive cell size defined by  $(a_{\text{eff}})^3=a^2c/2$ . The unit cell parameters for all crystals were taken from Ref. 46. The fit shown by the full squares corresponds to an

$d_{36}=B[(a_{\text{eff}}/a)^3-1]$  law where the two constants were determined again from the  $d_{36}$  values of ZnGeP<sub>2</sub> and CdGeAs<sub>2</sub>. The assumed dependence corresponds to inverse proportionality to the average valence electron density, which equals  $32/(a_{\text{eff}})^3$  for the chalcopyrite structure. It can be seen that this simple assumption provides a qualitative agreement with the result obtained in the present work for CdSiP<sub>2</sub>. It should be noted that the measurements of  $d_{36}$  for CdGeP<sub>2</sub> and ZnSiAs<sub>2</sub> are very old and based on the wedge method (phase-matching is also absent in CdGeP<sub>2</sub>).

#### 4. CONCLUSION

In summary, we measured the nonlinear coefficient  $d_{36}$  of CdSiP<sub>2</sub> using SHG near 4.6 μm and femtosecond pulses generated from a seeded KNbO<sub>3</sub> optical parametric amplifier by comparing the SHG efficiency with that obtained with ZnGeP<sub>2</sub>. At very low average powers of the order of 1 mW, we obtained  $d_{36}(\text{CdSiP}_2) \sim d_{36}(\text{ZnGeP}_2)$  which does not reflect the trend of having lower nonlinearity with increasing band-gap. Reliable estimation of the nonlinear coefficient of the newly developed CdSiP<sub>2</sub> is essential for its future potential applications in the 4 to 6.5 μm spectral range.

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