$CdSiP_2$: a new nonlinear optical crystal for 1- and 1.5-micron-pumped mid-IR generation

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Abstract: $CdSiP_2$ is an exciting NLO crystal for mid-IR OPOs. Here we report reduced absorption losses, refined sellmeier coefficients, and a measured nonlinear coefficient – 84.5pm/V – far higher than other crystals pumped at 1μm.

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In the search for new nonlinear optical (NLO) materials, it is rare to find a crystal that exhibits substantially superior properties to the best existing materials and can be grown and fabricated with high optical quality. Cadmium silicon phosphide, $CdSiP_2$ or CSP, is one of these rare exceptions. [1] Its properties are listed in Table 1, and high optical quality samples used for fundamental property measurements are shown in Fig. 1.

Table 1. Properties of the new NLO crystal

Material Property	$CdSiP_2$
Transparency Range (μm)	0.5-9
Band Gap, E_g (eV)	2.45
Refractive Index, n	3.0
Birefringence (n_e-n_o)	-0.05
Nonlinear Coefficient, d_{36} (pm/V)	84.5
Thermal Conductivity (W/mK)	13.6
Knoop Hardness (kg/mm^2)	930
Melting Point (°C)	1133

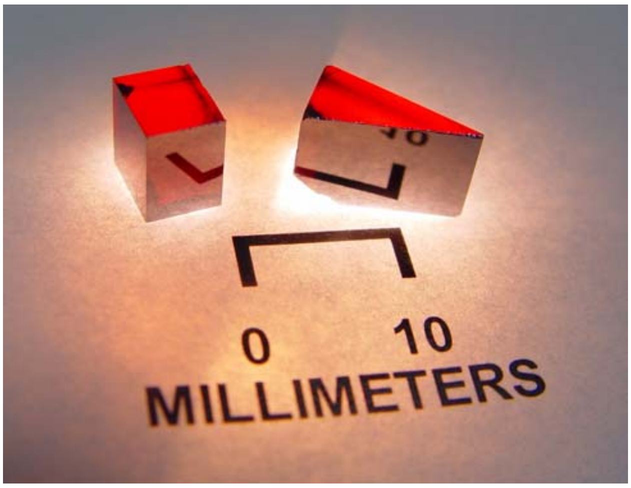
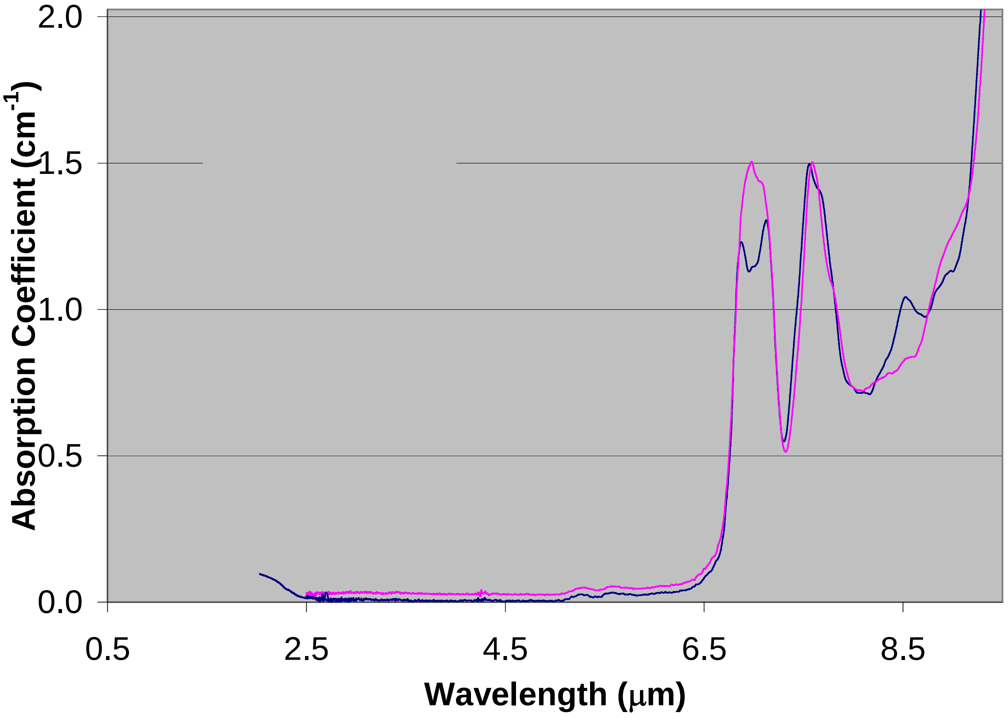


Fig. 1. High optical quality single crystal

$CdSiP_2$ is a negative uniaxial II-IV-V_2 chalcopyrite compound semiconductor (space group 42m) with a reported band gap of 2.45eV (506nm) [2] that allows 1064nm pumping without two-photon absorption, and is transparent out to 9μm. The refractive index is very close to 3.0 throughout most of its transparency range, and its birefringence of -0.05 is large enough for phase matching 1μm, 1.5μm, and

2µm lasers into the mid-infrared. [1]. Its high thermal conductivity (13.6 W/mK) is higher than that of YAG, and 10-15 times higher than existing NLO crystals $AgGaS_2$ (1.4 W/mK) and $AgGaSe_2$ (1.0 W/mK) used for shifting 1,06-µm and 1.55-µm lasers into the mid-IR. This property, along with a relatively high hardness (930 kg/mm^3) and melting point (1133°C) make it attractive for high average power applications and facilitates cutting and polishing of optical components. The very high nonlinear coefficient of 84.5 pm/V is reported here for the first time, along with reduced absorption losses and refined sellmeier coefficients.

$CdSiP_2$ crystal growth was investigated in the 1970's: tiny 2 x 2 x 0.2 mm^3 crystals were grown from a molten tin flux by Itoh *et al.* [2], and slightly larger 5 x 2 x 1 mm^3 were grown by halogen-assisted vapor transport by Buehler and Wernick [3] but even the largest of these was of insufficient size and quality to fabricate NLO devices or to measure the linear and nonlinear optical properties. Previous attempts at melt growth of $CdSiP_2$ failed due to reaction with – or explosion of - the fused silica ampoules used to encapsulate the melt.[3] We, however, have successfully grown large, high optical quality $CdSiP_2$ single crystals from stoichiometric melts using the horizontal gradient freeze (HGF) technique. The compound was successfully synthesized from high purity (> 99.9999%) Cd, Si, and red P starting materials which were sealed into heavy-walled fused silica ampoules and reacted using the two-temperature method. The pre-synthesized charge was re-encapsulated in a PBN boat, and single crystals measuring 19mm in diameter by several centimeters in length were grown by directional solidification in a modified, high-temperature transparent furnace.[4] From these we were able to fabricate oriented single crystal samples of sufficient size and clarity (Fig. 1) for fabricating and evaluating nonlinear optical device performance. Furthermore, we have reduced the impurity-related absorption losses in the near infrared compared to our earliest crystals [1], as shown by the polarized absorption spectra in Fig. 2, and expect additional improvements as we refine our process. Note that intrinsic multi-phonon peaks at 7.1µm and 7.65µm limit the transparency beyond 6.5µm, but the losses in the important 3-5 µm atmospheric window remain very low.



We recently measured the nonlinear coefficient of $CdSiP_2$ using SHG near 4.6 µm and femtosecond pulses generated from a seeded $KNbO_3$ optical parametric amplifier. The SHG efficiency was compared for uncoated samples of $CdSiP_2$ and $ZnGeP_2$, both 0.5 mm thick, in the low conversion limit (<10% internal conversion efficiency) which justifies the use of the plane wave approximation. Since for both crystals absorption losses could be neglected, the spectral and angular acceptances are extremely large and the birefringence walk-off very low, the result had to be corrected only for the slightly different Fresnel losses and index of refraction. Taking into account the experimentally determined phase-matching angles for type-I SHG (oo-e type in $CdSiP_2$ and ee-o type in $ZnGeP_2$), which were in good agreement with the existing Sellmeier approximations, we arrived at $d_{36}(CdSiP_2) = 1.07 * d_{36}(ZnGeP_2) = 84.5$pm/V, which is surprising given the larger band-gap of $CdSiP_2$. The reliability of the measurement was tested at the same wavelength by comparing $ZnGeP_2$ with $HgGa_2S_4$ which led to the result $d_{36}(ZnGeP_2)$˜$3d_{36}(HgGa_2S_4)$, in very good agreement with previous estimations.

The ordinary and extraordinary refractive indices of $CdSiP_2$ were measured at AFRL as a function of wavelength from 660-5000nm using the minimum deviation technique described in [5] using the 30° prism shown in Fig. 1: refinements in the data led to the improved sellmeier equations (1) and (2):

$$n_o^2 = 3.0811 + \frac{6.2791 * \lambda^2}{\lambda^2 - 0.10452} - 0.0034888 * \lambda^2 \tag{1}$$

and

$$n_e^2 = 3.4343 + \frac{5.6137 * \lambda^2}{\lambda^2 - 0.11609} - 0.0034264 * \lambda^2 \tag{2}$$

These sellmeier equations indicate that $CdSiP_2$ can indeed be pumped with both 1.064µm and 1.55µm solid state lasers to generate output beyond 4µm in a single OPO step: 1.55µm pumping yields continuous tunability from 1.7 to 9.5 microns whereas 1.064µm pumping produces noncritically-phase-matched output at 6.18µm, which is an important wavelength range for laser surgery.

References

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