Materials and Devices for Direct Nonlinear Frequency Conversion to the mid-IR above 4 μm with near 1 μm Pumping

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ABSTRACT

Non-oxide nonlinear crystals that can be pumped by pulsed lasers near 1 μm, without deleterious two-photon absorption, are compared, with emphasis on $GaS_{0.4}Se_{0.6}$ and $CdSiP_2$. Nanosecond optical parametric oscillation with idler tunability extending up to 8.8 μm is achieved with $LiInSe_2$ and non-critical operation near 6.2 μm - with $CdSiP_2$.

1. INTRODUCTION

Since solid state lasers obviously cannot directly cover the spectral range above 3 μm 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 μm spectral range and ensure tunability. Oxide-based crystals, for example phosphates and arsenates belonging to the $KTiOPO_4$ (KTP) family of isomorphs, or iodates, niobates and tantalates like $LiIO_3$, $LiNbO_3$, $KNbO_3$, $LiTaO_3$, as well as all their periodically poled counterparts, perform well at the short of this spectral range, but their performance above 4μm 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_2 chalcopyrite crystals, only $AgGaS_2$ but not $AgGaSe_2$, 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_2 chalcopyrites offer superior properties in comparison to the I-III-VI_2 chalcopyrite crystals in terms of nonlinearity, low scattering losses, hardness, and thermo-optical and thermo-mechanical parameters, but even the most developed compound, $ZnGeP_2$, requires pump wavelengths near 2 μm (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 μm.

2. MATERIAL SURVEY

Imposing the condition that the band-gap should correspond to a wavelength near or below 532 nm (2.33 eV), say ≥2 eV, all existing crystals for which 1064 nm pumping is eventually possible, are summarized in Table 1 (see [1] for the sources used). A specific nonlinear process, the generation of an idler wavelength of 6.45 μm is selected for comparison. More exotic crystals with extreme transparency, for which d_{eff}<1 pm/V, are not included in the table.

$AgGaS_2$ is the only commercially available crystal from Table 1. Besides its modest nonlinearity, it exhibits low thermal conductivity and strongly anisotropic thermal expansion. $HgGa_2S_4$ shows improved nonlinearity but the growth of this crystal in large sizes with sufficient homogeneity is still problematic and several phases exist [2]. $Cd_xHg_{1-x}Ga_2S_4$, with x=0.55 adjusted to have non-critical phase-matching for the selected process, is a solid solution in the system $HgGa_2S_4$ – $CdGa_2S_4$ and can be grown in larger sizes but its composition cannot be maintained constant [2].

The Li-compounds with wurtzite type structure [3] 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 to the thermal load.

$InSP_4$ was grown 25-35 years ago only by the chemical vapour transport method. The monoclinic $Sn_2P_2S_6$ 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.

$GaS_{0.4}Se_{0.6}$ 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 $GaS_{0.4}Se_{0.6}$ 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.

Table 1. Summary of important properties of all existing nonlinear crystals that can be pumped at 1064 nm to generate 6.45 µm light: The effective nonlinear coefficients d_{eff} are calculated at the corresponding phase-matching angle θ or φ, the nonlinear tensor components, d_{il}, used for this calculation were derived from the literature applying Miller's rule. The wavelength λ_F (fundamental) at which the nonlinear coefficients have been estimated by SHG is also included. For $Sn_2P_2S_6$, d_{eff} is taken directly from the literature.

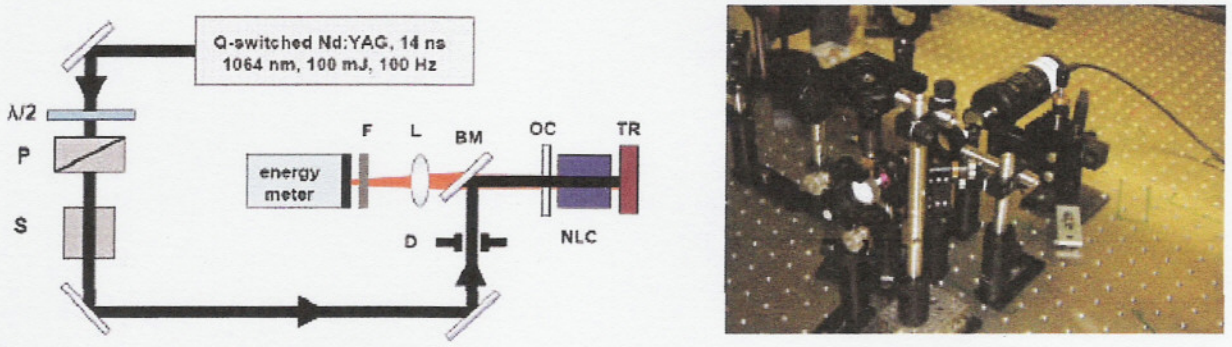
Crystal Symmetry – Plane	**θ / φ [°] (Interaction)**	**d_{eff} [pm/V]**	**Thermal conductivity [W/mK]**	**Band-gap E_g [eV]**	**d_{il} or Miller's δ [pm/V] @ λ_F for SHG**	**d_{il} + Miller's correction [pm/V]**
$AgGaS_2$ $\bar{4}2m$	40.50 (oo-e) 45.53 (eo-e)	8.86 13.65	1.4 //*c* 1.5 ⊥*c*	2.70	δ_{36}=0.12	d_{36}=13.65
$HgGa_2S_4$ $\bar{4}$	45.87 (oo-e) 51.21 (eo-e)	15.57 21.18	2.49-2.85 //*c* 2.36-2.31 ⊥*c*	2.79	d_{36}=27.2 1064 nm	d_{36}=24.56
$Cd_xHg_{1-x}Ga_2S_4$ (θ=90°, x=0.55) $\bar{4}$	90.00 (oo-e)	24.94	1.8-1.92 //*c* 1.62-1.81 ⊥*c* (x=0.27-0.3)	3.22 (x=0.55)	d_{36}=27.2 @ 1064 nm	d_{36}=24.94
$LiGaS_2$ xz *mm*2 xy	47.77 (oo-e) 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
$LiInS_2$ xz *mm*2 xy	40.01 (oo-e) 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
$LiGaSe_2$ xz *mm*2 xy	51.45 (oo-e) 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
$LiInSe_2$ xz *mm*2 xy	36.97 (oo-e) 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
$InPS_4$ $\bar{4}$	38.80 (ee-o) 42.67 (oe-o)	34.40 23.87 @ optimum φ	NA	3.2	δ_{31}=0.39 δ_{36}=0.30	d_{31}=27.87 d_{36}=21.53
$Sn_2P_2S_6$ *m*	(ss-f) (fs-f)	~4 ~2	0.4-0.55	2.35	…	…
$GaS_{0.4}Se_{0.6}$ $\bar{6}2m$	22.31 (oo-e) 24.67 (eo-e)	51.70 43.16	1.3 //*c* 10 ⊥*c*	2.4	d_{22}=48.2 @ 4.65 µm	d_{22}=55.88 d_{22}=52.26
$CdSiP_2$ $\bar{4}2m$	80.46 (oo-e)	90.99	13.6	2.2-2.45	d_{36}=84.5 @ 4.56 µm	d_{36}=92.27
$AgGaGeS_4$ xz *mm*2 xy	53.99 (oo-e) 35.74 (oo-e)	3.32 5.43	0.399	3.0	d_{32}=6.2 d_{31}=10.2 @ 1064 nm	d_{32}=5.65 d_{31}=9.30
Ag_3AsS_3 3*m*	22.04 (oo-e) 24.01 (eo-e) 65.63 (oe-e)	22.89 16.44 3.35	0.113 //*c*, 0.092 ⊥*c*	2.2	d_{31}=10.4 d_{22}=16.6 @ 10.6 µm	d_{31}=12.34 d_{22}=19.70
Ag_3SbS_3 3*m*	47.14 (oo-e) 52.84 (eo-e)	14.34 3.80	~0.1 //*c*, ~0.09 ⊥*c*	2.2	d_{31}=7.8 d_{22}=8.2 @ 10.6 µm	d_{31}=9.90 d_{22}=10.41

$AgGaGeS_4$ is in fact a solid solution in the $AgGaS_2$ – GeS_2 system [2], 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 $AgGa(Se_xS_{1-x})_2$ and $AgIn_xGa_{1-x}S_2$ 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_3AsS_3 (proustite) and the related Ag_3SbS_3 (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 $AgGaS_2$, because of their poor thermo-mechanical properties and low laser damage threshold.

Table 1 shows that $CdSiP_2$, whose growth technology was developed only very recently [4], outperforms all other crystals not only in terms of the parameters used for comparison but also in terms of hardness, damage threshold or anisotropy of the thermal expansion, and the possibility of non-critical phase-matching with maximized effective nonlinearity without being a solid solution. A practical upper limit of 6.5 μm is set by its intrinsic multi-phonon absorption while the main problem yet to be solved is the residual absorption close to the band-gap which is not intrinsic.

3. NANOSECOND OPTICAL PARAMETRIC OSCILLATORS

Operation in the nanosecond regime is free of restrictions related to the spectral acceptance or higher order nonlinear effects and has the best potential for achieving high average power and single pulse energy. Nanosecond optical parametric oscillators (OPOs), pumped in the 1 μm range, have been demonstrated, however, only with 5 of the 14 compounds included in Table 1: Ag_3AsS_3, $AgGaS_2$, $HgGa_2S_4$, $LiInSe_2$, and $Cd_xHg_{1-x}Ga_2S_4$. In most cases, the pump threshold lies above the surface damage limit. Apart from the archive Ag_3AsS_3 [5], oscillation at idler wavelengths exceeding 4.4 μm has been demonstrated only with $AgGaS_2$ [6], achieving impressive tunability from 3.9 to 11.3 μm.



(a) (b)

Fig. 1. Experimental set-up (a) and photograph (b) of the compact OPO. λ/2: half-wave plate, P: polarizer, S: mechanical shutter, F: cut-on filter, L: BaF_2 lens, D: diaphragm, BM: bending mirror, OC: output coupler, TR: total reflector, NLC: nonlinear crystal.

For the first time, OPO operation above 4 μm will be reported now using $LiInSe_2$ and the novel $CdSiP_2$. The set-up of the singly resonant OPO and the pump source used are shown in Fig. 1. The wavelength tunability for the idler extends up to 8.8 μm while non-critical OPO operation with ~1 μm pumping is achieved for the first time.

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