



MIRSURG

Mid-Infrared Solid-State Laser Systems for Minimally Invasive Surgery

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Dissemination Level

PU	Public	PU
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
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The purpose of this deliverable is to provide a review of the relevant properties of all existing nonlinear optical crystals (NLC's) that can be pumped near 1 μm without the onset of two-photon absorption (TPA) at the pump wavelength, capable of generating mid-IR light (idler) near 6450 nm in an optical parametric oscillator (OPO) device. TPA is a higher order nonlinear effect, which sets the limit for the pump wavelength to half the band-gap value. This complete survey includes all commercially available materials and such that can be obtained only from laboratories, archived crystals and also recently discovered crystals for which the essential properties are now at least partially known and indicate promising performance or at least allow one to speculate on their potential use.

There are oxide crystals that are partially transparent in the mid-IR but not more than 4-5 μm . Indeed, the performance of oxide based NLC's is affected by multi-phonon absorption starting in the best case from about 4 μm . Thus oxide crystals are obviously not suited for generation of longer wavelengths and in particular 6450 nm.

The non-oxide mid-IR NLC's include unary, binary, ternary and quaternary arsenides, phosphides, sulphides, selenides or tellurides. Some of these inorganic crystals transmit up to 20-30 μm before multi-phonon absorption occurs as an intrinsic limit. In contrast with the oxides, which can be grown by well mastered and harmless hydrothermal, flux or Czochralski methods, the more complex Bridgman-Stockbarger growth technique in sealed (high atmosphere) ampoules, with volatile and chemically reactive starting components, is the only method used to produce large size single domain non-oxide crystals, and this certainly hampered their development all the more that special post-growth treatments are needed to restore stoichiometry and improve their optical quality. As a matter of fact such materials exhibit more defects and the residual losses (absorption and scatter) are more than one order of magnitude larger than in the best oxide crystals.

Note that the longer the long-wave transmission limit the smaller the band-gap of such non-oxide NLC's which means that down-conversion will require laser pump sources operating at longer wavelengths, or if such do not exist, cascaded schemes based on oxides in the first stage. This restriction is even more pronounced when using short (nanosecond) and ultrashort (picosecond or femtosecond) pulses for pumping non-oxide materials because of the detrimental role of TPA. However, other limitations related to the residual loss, nonlinearity, phase-matching, thermo-mechanical properties, or simply growth and availability, also exist.

There are exceptions of widely transmitting mid-IR NLC's such as the ternary halides whose short-wave limit extends down to the ultraviolet (UV) [1] but estimations of the nonlinear coefficients d_{ij} of these materials (until now only by the powder SHG method) show that the values do not exceed 1 pm/V. Hence, such materials will not be considered here. On the contrary, typical mid-IR NLC's exhibit nonlinear coefficients on the order of 10 pm/V or above, in the best cases few tens of pm/V, with the record value of ~ 600 pm/V for Te.

There are fundamental relations between the nonlinearity and the index of refraction and although d_{ij} may vary a lot, the quantity $\delta = d_{ij}/(n^2-1)^3 = d_{ij}/(\chi^{(1)}-1)^3$ (Miller's delta) remains almost constant (e.g. within one order of magnitude, Miller's empirical rule) [2]. Mid-IR NLCs have $n > 2$ and empirical formulae indicate that the index of refraction depends on the material band-gap as $\sim E_g^{-1/4}$ [2], hence, at $n \gg 1$, $d \sim E_g^{-3/2}$ (here d is some average nonlinearity). The index of refraction also enters the expression for the coupling constant in three-photon interaction equations and it is not the d -tensor that should be compared for different materials but rather some figure of merit, such as $FM \sim d^2/n^3$, which determines the conversion efficiency. Thus, at $n \gg 1$, $FM \sim n^9 \sim E_g^{-9/4}$ [2]. When comparing operation at different wavelengths one should have in mind that besides the weak dependence (dispersion) of the d_{ij} elements, which can be estimated from Miller's rule on the basis of the refractive index dispersion, there is much stronger dependence through the coupling constant and the figure of merit can be redefined as $FM^* \sim d^2/(n^3 \lambda_1 \lambda_2 \lambda_3)$. Thus, operation at longer (idler) wavelengths in general means lower conversion efficiency.

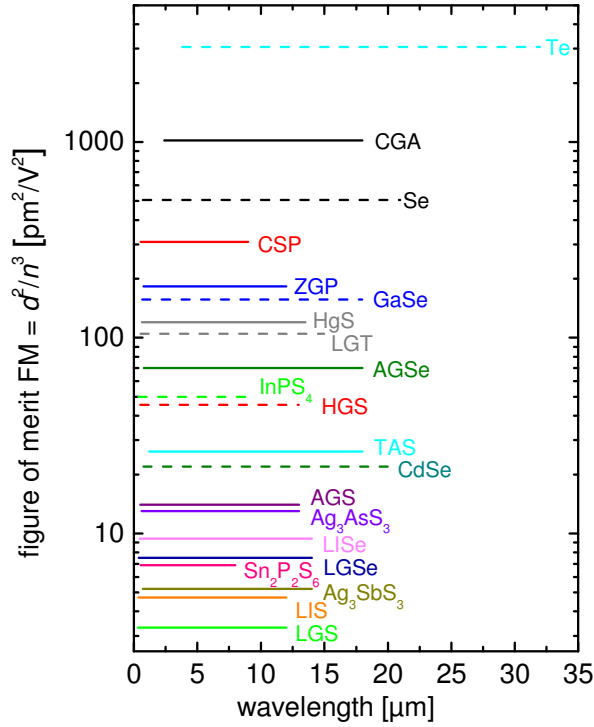


Fig. 1: Nonlinear figure of merit of non-oxide birefringent NLC's versus transparency range. The data on HgS, TAS, and Se is very old and the FM error in this diagram is $\pm 50\%$. Note that oxide NLC's typically have much lower FM, in the best cases (e.g. KNbO_3) reaching $\sim 10 \text{ pm}^2/\text{V}^2$.

The list of NLC's combining a transparency extending into the mid-IR range above $\sim 5 \mu\text{m}$ (the upper limit of oxide materials) and large-enough birefringence to permit phase-matching over their transparency ranges is not very long. Their FM's are shown in Fig. 1 versus transparency range. As already mentioned, non-oxide NLC's show higher nonlinearity but lower band-gap in comparison to oxides and their refractive index is also higher. Unfortunately there are no ferroelectrics among them to be used for quasi-phase-matching (QPM). The binary and ternary birefringent non-centrosymmetric crystals now in use in this spectral region include the chalcopyrite semiconductors AgGaS_2 (AGS), AgGaSe_2 (AGSe), ZnGeP_2 (ZGP) and CdGeAs_2 (CGA), the defect chalcopyrite HgGa_2S_4 (HGS), GaSe, CdSe, and Ti_3AsSe_3 (TAS) [3]. Some other crystals like proustite (Ag_3AsS_3) and pyrargyrite (Ag_3SbS_3) have already lost their importance because they were completely replaced by the more technological AGS while the growth technology of HgS (mineral) and InPS_4 (chemical vapour transport) was never developed [4,5]. The list of the non-oxide birefringent inorganic crystals used in the past will be full if the elemental (unary) Se and Te are added: Their linear losses are, however, so high that at present they could be interesting, in particular Te, only for diagnostic purposes of ultrashort pulses at longer wavelengths [4]. All these mid-IR NLC's are uniaxial. All of them have their specific advantages but also some drawbacks: AGS and AGSe have low residual absorption but poor thermal conductivity and anisotropic thermal expansion with different sign, ZGP has excellent nonlinearity and thermal conductivity but multi-phonon and residual absorption limit its transparency from both sides so that pump wavelengths should lie above $2 \mu\text{m}$ which corresponds to less than $1/3$ of its bandgap, CGA possesses extremely high nonlinearity but exhibits also absorption features and low temperatures are required to avoid residual losses, HGS has a high FM but its growth technology is very difficult (several phases exist) and only small sizes are available, GaSe has large nonlinearity and birefringence but it is a soft, cleaving compound, with very low damage threshold, i.e. difficult for polishing and coating, CdSe is transparent up to $18 \mu\text{m}$ but its birefringence and nonlinearity are quite modest, TAS exhibits rather low losses in its transparency range but its thermal conductivity, as that of Ag_3AsS_3 and Ag_3SbS_3 , is extremely low, and finally Te is a unique nonlinear material having in mind its

extended wavelength range and superior nonlinear susceptibility but as already mentioned, its applicability is limited by the high linear losses. At present only AGS, AGSe, ZGP, GaSe, CdSe and Te can be considered as commercially available (HGS, LIS, LISe, LGS and LGSe – available from some institutions in limited sizes/quantity). The monoclinic (biaxial) $\text{Sn}_2\text{P}_2\text{S}_6$ is included in Fig. 1 for completeness: it is a relatively well characterized compound possessing ferroelectric properties but a phase transition at 338 K to a centrosymmetric phase makes it impractical [6].

The above mentioned NLC's are known for quite a long time, for some of them (e.g. AGS, AGSe, ZGP, CGA) improvement of grown technology, reduction of residual losses etc. still continue after few decades of development, others were never developed (HgS , InPS_4) or abandoned (Ag_3AsS_3 and Ag_3SbS_3) in favor of more promising ones. Improved NLC's are, however, critical for advancing mid-IR coherent source development and especially to increase the conversion efficiency and the output power. Important challenges include also compatibility with powerful 1 μm pump sources (Nd and Yb laser systems) or, in the femtosecond domain, even 0.8 μm (Ti:sapphire laser systems), which means relatively wide band-gap. As already mentioned, this unfortunately contradicts the basic requirement for high nonlinear coefficients. Other desirable properties include low residual losses, high damage threshold, high thermal conductivity and the possibility for non-critical phase-matching (NCPM). Problems that occur include the already mentioned TPA (except for the cw regime), the achievable sizes (especially for OPO), the homogeneity of the grown crystals, the surface (chemical) stability, and the damage resistivity of the anti-reflection (AR) coatings necessary when cavities are employed.

Few trends can be observed in the development of new mid-IR crystals in the last decade that are, to a greater part, related to the development of laser pump sources. The first one is in fact a rather old idea of doping or mixing binary or ternary compounds to obtain new, more complex ternary compounds like $\text{GaS}_x\text{Se}_{1-x}$ [7] or quaternary compounds like $\text{AgIn}_x\text{Ga}_{1-x}\text{S}(\text{e})_2$, $\text{Cd}_x\text{Hg}_{1-x}\text{Ga}_2\text{S}_4$ or $\text{Ag}_x\text{Ga}_x\text{Ge}_{1-x}\text{S}(\text{e})_2$ [8,9]. Adding S to GaSe not only improves the thermo-mechanical properties (the same does In) but increases the band-gap thus helping to avoid TPA at 1064 nm (see Table 1). Mixing AGS(e) or HGS compounds with the isostructural but low-birefringence $\text{AgInS}(\text{e})_2$ or CdGa_2S_4 compounds, respectively, allows NCPM configurations with maximized effective nonlinearity to be achieved. In decreases the band-gap and slightly improves the nonlinearity of AGS(e) crystals while Cd has the opposite effect on HGS. Indeed, the latter enabled pumping of $\text{Cd}_x\text{Hg}_{1-x}\text{Ga}_2\text{S}_4$ at 1064 nm (Table 1). Mixing AGS(e) compounds with $\text{GeS}(\text{e})_2$ produces new orthorhombic (biaxial) structure, different from the chalcopyrite structure of AGS(e), and the resulting quaternary compounds (see Fig. 2) exhibit increased band-gap and improved damage resistivity. $\text{CdGe}(\text{As}_{1-x}\text{P}_x)_2$ and $\text{AgGa}(\text{Se}_{1-x}\text{S}_x)_2$ have also been studied, they are quaternary compounds which are isostructural to their parent ternary compounds and the mixing permits to engineer the band-gap, the nonlinearity and the birefringence (phase-matching properties).

The main problem with such mixed crystals is the varying composition along the grown boule and also in radial direction. It seems that it is easier to achieve constant composition when the new mixed compound exhibits different crystallographic structure, e.g. $\text{Ag}_x\text{Ga}_x\text{Ge}_{1-x}\text{S}(\text{e})_2$ and $\text{GaS}_x\text{Se}_{1-x}$ (Figs. 2 and 3). Nevertheless, the problem seems to have no real solution and the interest in such crystals seems to decline. An elegant way to utilize the variation of the composition for tuning of an OPO, has been demonstrated with $\text{Cd}_x\text{Hg}_{1-x}\text{Ga}_2\text{S}_4$ [8] and such an active element is shown in the upper part of Fig. 2.

A second trend in the development of new mid-IR NLC's is to trade a property which is available in abundance, such as the high nonlinearity, for properties which favour low loss and damage threshold. The best example here is the development of the chalcopyrite CdSiP_2 (CSP) by P. Schunemann at BAE Systems [10]. In this case moving to a wider band-gap among the chalcopyrite compounds of the II-IV-V₂ class is associated with higher hardness and thermal conductivity but also with higher melting point and vapour pressures, and more difficult crystal growth. Nevertheless, in this case the result was impressive: CSP turned out to have nonlinearity exceeding that of ZGP but in contrast to ZGP it is phase-matchable for 1064 nm (and also 1.5 μm) pumping without TPA and the only crystal that can offer NCPM for a 1064 nm

pumped OPO with idler output in the 6 μm range. In fact, the nonlinear coefficient of CSP is not only the highest among all NLC's that can be pumped at 1064 nm (Table 1), it is the highest of a new inorganic crystal in almost 40 years. As can be seen from Fig. 1, CSP has a very high FM but multiphonon absorption limits its practical wavelength range to $\sim 6.5 \mu\text{m}$.

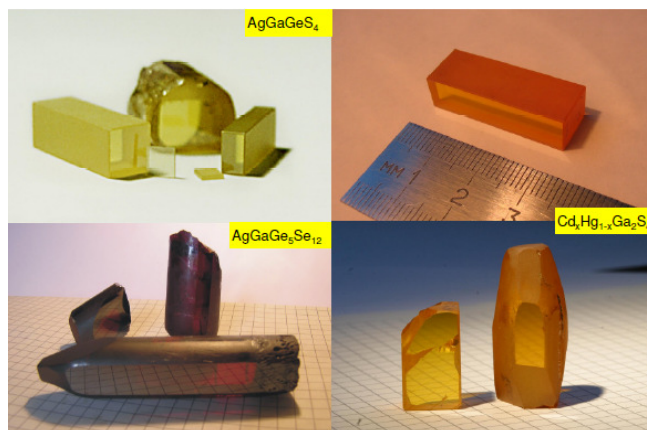


Fig. 2. Crystals of quaternary AgGaGeS_4 and $\text{AgGaGe}_5\text{Se}_{12}$ (left), and $\text{Cd}_x\text{Hg}_{1-x}\text{Ga}_2\text{S}_4$ (right) grown by the Bridgman-Stockbarger method [courtesy of V. Badikov, Kuban State University].

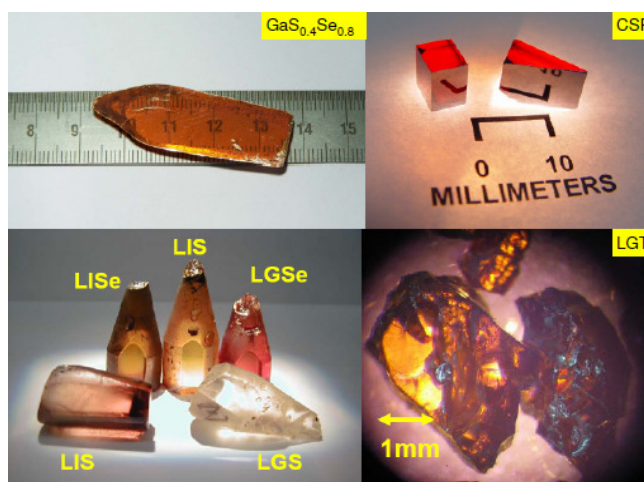


Fig. 3. Layered crystal of $\text{GaS}_{0.4}\text{Se}_{0.6}$: the maximum S-content preserving the non-centrosymmetric structure of the mixed compound (the transmission in the visible is obviously improved in comparison with GaSe), cube and prism made of CSP to measure thermo-mechanical and dispersive properties, ingots of orthorhombic Li-compounds after annealing, and first grown samples of LGT [courtesy of V. Panyutin (Kuban State University), top-left, P. Schunemann (BAE Systems), top-right, and L. Isaenko and A. Yelissejev (Institute of Geology and Mineralogy), bottom pictures].

In the last decade, considerable progress has been made also with four orthorhombic (biaxial) wide band-gap ternary chalcogenides, LiInS_2 (LIS), LiInSe_2 (LISe), LiGaS_2 (LGS), and LiGaSe_2 (LGSe), whose growth technology had been improved to such an extent that it was possible to perform extensive characterization and even realize some applications [11-14]. Moreover, their attractive features already stimulated the study of further crystals belonging to the same class, like LiGaTe_2 (LGT) which is now under development [15]. Li-compounds exhibit wider band-gap than their Ag-analogues (AGS, AGSe, etc.). Their wurtzite type structure (except for LGT) leads to better thermo-mechanical and damage properties. However, the nonlinearity of the Li-compounds is lower compared to their Ag-analogues and the FM's are among the lowest (Fig. 1), comparable to some oxide NLC's. Nevertheless, LGS, LIS, and

LGSe are the only known non-oxide materials that can be pumped by femtosecond Ti:sapphire laser systems operating near 800 nm without TPA. Two related compounds, BaGa₄S₇ (BGS) and BaGa₄Se₇ (BGSe) could be recently added to this group (Table 1) but the nonlinear coefficients of BGSe are still not precisely known [16,17]. LGT in turn shows extremely wide band-gap for a telluride compound and its FM is quite high (Fig. 1). In contrast to AgGaTe₂, LGT is sufficiently birefringent and can be even pumped at 1064 nm (Table 1). However, the surface of this material is chemically unstable.

The third trend is the manufacturing of QPM orientation patterned structures with highly nonlinear but isotropic semiconductors, e.g. GaAs which has a mature technology [18], as an alternative to patterned electric field poling which is applicable only to ferroelectric oxide crystals. This has few essential advantages: (i) large nonlinear coefficient for QPM ($d_{\text{eff}} \sim 60$ pm/V), (ii) NCPM with long interaction lengths (especially important for cw operation) reaching e.g. 70 mm, (iii) low absorption losses (≤ 0.02 cm⁻¹), (iii) wide transparency range (1-18 μm), (iv) high thermal conductivity (46 W/mK). The chief obstacle to achieving QPM in GaAs and similar cubic crystals (GaP, InAs, InP, InSb, ZnSe etc.) is the process of creating a modulated structure from a non-ferroelectric material. While previous attempts relied on diffusion bonding of stacks, the current approach is based on orientation patterned crystal growth (orientation-patterned GaAs, or OPGaAs). Diffusion bonding provides large apertures but the period is set by polishing, the fabrication process is serial, the sample lengths are limited and short periods scale poorly. The orientation-patterned crystal growth requires a template for the growth of the structure. Its advantages include the possibility to set the period by photolithography, the parallel fabrication process, the long sample lengths that can be achieved and the short periods that are equally possible. The basic limitation is the small aperture (thickness) that can be obtained with sufficient quality of the structure. It is expected, however, that gratings of few millimeter thickness will be available soon on the basis of OPGaAs. The high growth rates (>150 $\mu\text{m}/\text{h}$) are promising for bulk devices. We will not go here into further details because OPGaAs is only compatible with 2 μm pumping (again because of TPA) and because the progress in its development is considered by another project partner (TRT) within Deliverables D1.1-D1.6.

Table 1 summarizes the properties of all non-oxide NLC's that can be phase-matched by birefringence at a pump wavelength of 1064 nm (Nd:YAG laser) without TPA. TPA is a major limitation effect which affects not only OPO's but also any other short or ultrashort pulse down-conversion optical parametric device such as synchronously pumped OPO (SPOPO), optical parametric generator (OPG), seeded optical parametric amplifier (OPA), and difference-frequency generation (DFG). Pump lasers and amplifiers near 1 μm are essentially based on Nd-doped materials but Yb-based systems are also under development and they show larger variation of the exact oscillation wavelength in dependence on the host crystal. That is why, in order to compare different nonlinear crystals, in Table 1 we select for pumping the wavelength of 1064 nm corresponding to Nd:YAG, the most popular solid-state system, but the limit for the band-gap to avoid TPA is not strictly fixed at $\lambda_g = 532$ nm but instead some $\pm 5\%$ deviation is considered as acceptable (note that the band-gap E_g in eV and this wavelength in μm are related as $\lambda_g = 1.24/E_g$). To consider one and the same process when comparing the different NLC's and in particular the corresponding effective nonlinearity d_{eff} , the idler wavelength is fixed at 6450 nm, the target wavelength for the MIRSURG application while all kinds of interactions are taken into account with respect to the polarization of the three interacting waves. Thus, sufficient birefringence for phase-matching of at least one interaction type is a further requirement when considering potential NLC candidates.

CSP, GaS_{0.4}Se_{0.6}, BGS, BGSe and the solid solution LGSe (not included in Table 1 because its properties are similar to the parent compounds LGSe and LSe), as well as the new compound Pbln₆Te₁₀ (also not included in Table 1 because the TPA limitation requires pump wavelengths of at least 2 μm) were characterized for the first time within the MIRSURG project. With the exception of CSP all these NLC's were synthesized for the first time and provided especially for this EU project. A BGS OPO element has been already prepared and such an experiment is at present under consideration.

Table 1. Summary of important properties of birefringent NLC's that can be pumped at 1064 nm to generate 6450 nm light: The effective nonlinearity d_{eff} (column 3) is calculated at the corresponding phase-matching angle θ or φ (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 λ_F (fundamental) at which the nonlinear coefficients have been estimated by SHG is also shown in column 6. For $\text{Sn}_2\text{P}_2\text{S}_6$, d_{eff} is taken directly from the literature [6]. Damage threshold values are not included in the table because comparable data (under same experimental conditions) is not available.

Crystal Point group Plane	θ/φ [°] (Interaction)	d_{eff} [pm/V]	Thermal conductivity [W/mK]	Band- gap E_g [eV]	Miller's δ [pm/V] or d_{ij} [pm/V] @ λ_F for SHG	+ 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 \perp c	2.70	$\delta_{36}=0.12$	$d_{36}=13.65$
$\text{HgGa}_2\text{S}_4^*$ $\bar{4}$	45.87 (oo-e) 51.21 (eo-e)	15.57 21.18	2.49-2.85 //c 2.36-2.31 \perp c	2.79	$d_{36}=27.2$ 1064 nm	$d_{36}=24.56$
$\text{Cd}_x\text{Hg}_{1-x}\text{Ga}_2\text{S}_4^*$ ($\theta=90^\circ$, $x=0.55$) $\bar{4}$	90.00 (oo-e)	24.94	1.8-1.92 //c 1.62-1.81 \perp c ($x=0.27-0.3$)	3.22 ($x=0.55$)	$d_{36}=27.2$ @ 1064 nm	$d_{36}=24.94$
LiGaS_2^{**} $mm2$	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	$d_{31}=5.71$ $d_{24}=5.21$
LiInS_2 $mm2$	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	$d_{31}=7.23$ $d_{24}=5.93$
LiGaSe_2 $mm2$	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	$d_{31}=10$ $d_{24}=8.16$
LiInSe_2^* $mm2$	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	$d_{31}=12.08$ $d_{24}=8.65$
LiGaTe_2 $\bar{4}2m$	36.38 (ee-o) 40.05 (oe-o)	46.20 31.12	NA	2.41	$d_{36}=43$ 4600 nm	$d_{36}=48.37$
BaGa_4S_7 $mm2$	xz 4.64 (oo-e)	5.4	NA	3.54	$d_{31}=5.1$ 4620 nm	$d_{31}=5.4$
BaGa_4Se_7 m	yz 30.30 (oe-o) xz 50.68 (ee-o) xz 54.38 (oe-o)	NA	NA	2.64	NA	NA
InPS_4 $\bar{4}$	38.80 (ee-o) 42.67 (oe-o)	34.40 23.87 @ optimum φ	NA	3.2	$\delta_{31}=0.39$ $\delta_{36}=0.30$	$d_{31}=27.87$ $d_{36}=21.53$
$\text{Sn}_2\text{P}_2\text{S}_6$ m	(ss-f) (fs-f)	≈ 4 ≈ 2	0.4-0.55	2.35
$\text{GaS}_{0.4}\text{Se}_{0.6}$ $\bar{6}2m$	22.31 (oo-e) 24.67 (eo-e)	45.80 40.88	1.3 //c 10 \perp c	2.4	$d_{22}=44.1$ @ 4.65 μm	$d_{22}=49.51$
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 $mm2$	xz 53.99 (oo-e) xy 35.74 (oo-e)	3.32 5.43	0.399	3.0	$d_{32}=6.2$ $d_{31}=10.2$ @ 1064 nm	$d_{32}=5.65$ $d_{31}=9.30$
$\text{Ag}_3\text{AsS}_3^*$ $3m$	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 μm	$d_{31}=12.34$ $d_{22}=19.70$
Ag_3SbS_3 $3m$	47.14 (oo-e) 52.84 (eo-e)	14.34 3.80	~ 0.1 //c, ~ 0.09 \perp c	2.2	$d_{31}=7.8$ $d_{22}=8.2$ @ 10.6 μm	$d_{31}=9.90$ $d_{22}=10.41$

*crystals for which OPO with ~ 1 μm pump wavelength has been already demonstrated,

**OPO realized for the first time by MBI within the MIRSURG project

CSP is definitely the crystal of choice for direct 1064 to 6450 nm frequency conversion for all the reasons mentioned before. MIRSURG has contributed essentially to its development.

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