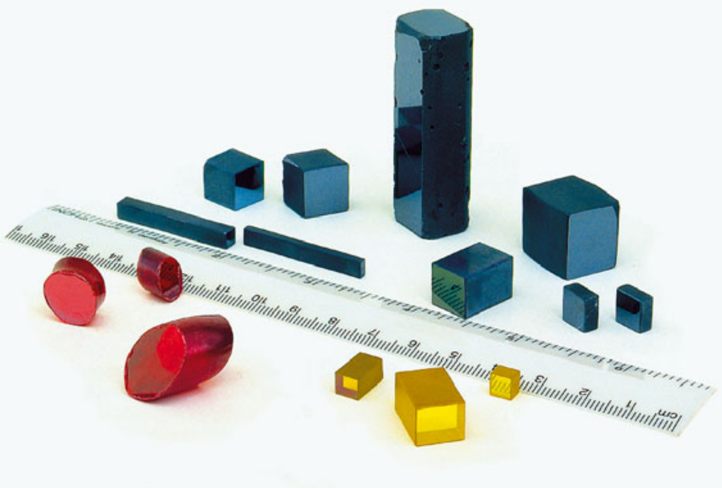
EKSPLA
An EKSMA Group Company

EKSPLA, Photonics Division
Mokslininku 11, 08412 Vilnius, LITHUANIA
Ph.: +370 5 2729900, fax: +370 5 2729299
photonics@ekspla.com
www.ekspla.com

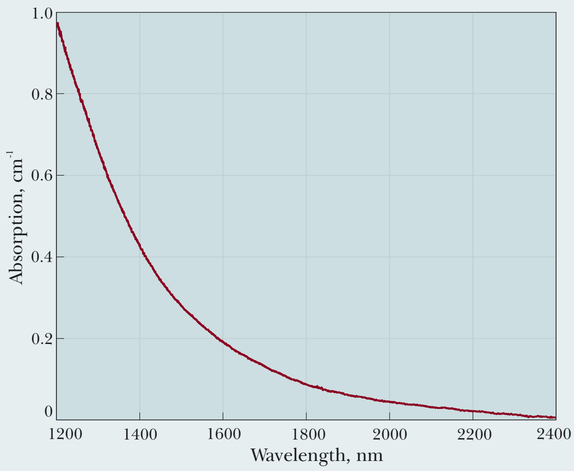
Infrared Nonlinear Crystals



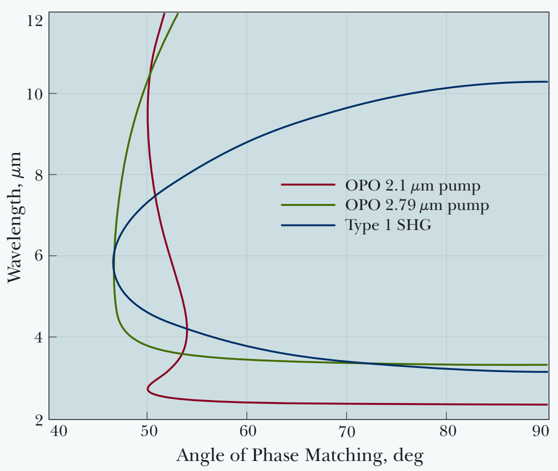
Optical nonlinear crystals like $ZnGeP_2$, $AgGaSe_2$, $AgGaS_2$, GaSe have gained tremendous interest for the middle and deep infrared applications due to their unique features. The crystals have large effective optical nonlinearity, wide spectral and angular acceptances, broad transparency range, non-critical requirements for temperature stabilization and vibration control, are well mechanically processed (except of GaSe).

$ZnGeP_2$ has band edges at 0.74 and 12 μm with useful transmission range from 1.9 to 10.6 μm. $ZnGeP_2$ has the largest nonlinear optical coefficient and relatively high laser damage threshold. It was successfully used in the following applications: up-conversion of CO_2 laser light to near IR range(1) via mixing with 10.6 μm; sum frequency generation of CO and CO_2 laser radiation(2); efficient SHG of pulsed CO(3), CO_2(4) and chemical DF-laser(5), OPO light generation in mid infrared when pumped by erbium(6,7) and holmium(8) lasers.

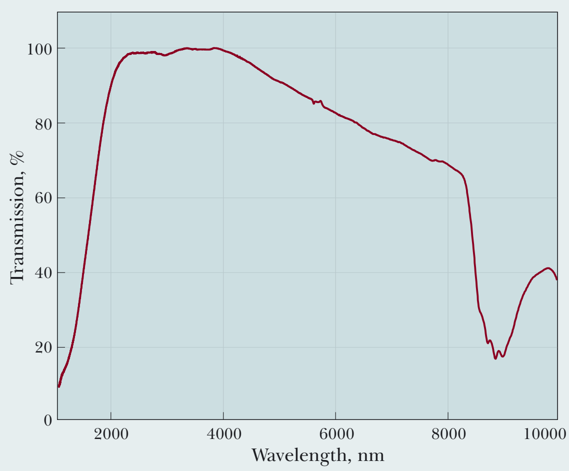
Crystals with lowest absorption < 0.04 cm^{-1} @ 2.1 μm are available from our company for better suitability for OPO or OPA application, then pumping 2.05–2.1 μm, with antireflection coatings.



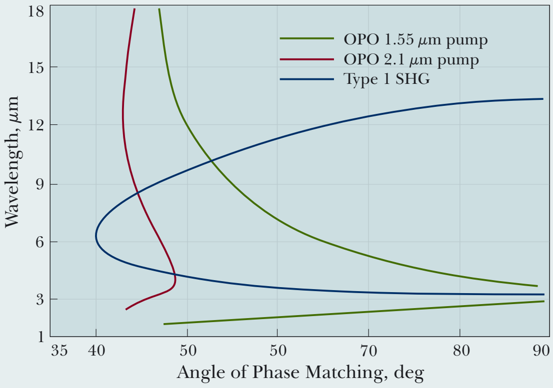
Absorption spectra of $ZnGeP_2$ crystal near 2 μm



Type 1 OPO and SHG tuning curves in $ZnGeP_2$

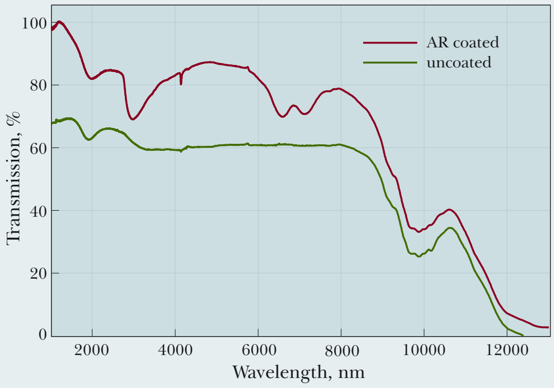


Transmission spectra of 15 mm long AR coated $ZnGeP_2$ crystal for OPO @ 2.1 μm

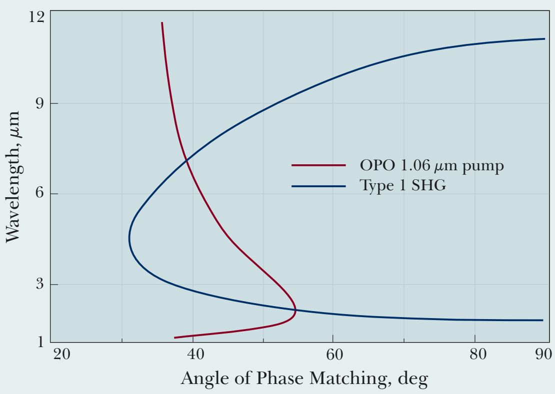


Type 1 OPO and SHG tuning curves in $AgGaSe_2$

Transmission spectra of 25 mm long AR coated $AgGaSe_2$ crystal



Transmission spectra of 14 mm long AR coated and uncoated $AgGaS_2$ crystal used for OPO pumped by Nd:YAG laser

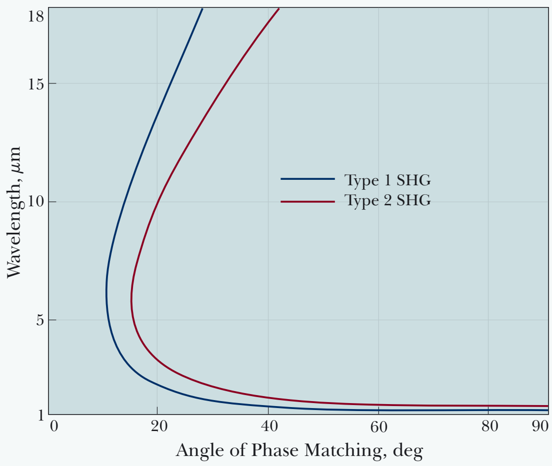


Type 1 OPO and SHG tuning curves in $AgGaS_2$

$AgGaSe_2$[9] has band edges at 0.73 and 18 μm. Its useful transmission range lying within 0.9–16 μm and wide phase match ability provide excellent potential for OPO applications when pumped by variety of currently available lasers. Tuning within 2.5–12 μm was obtained when pumped by Ho:YLF laser at 2.05 μm[10]; NCPM operation within 1.9–5.5 μm was achieved[11] pumping at 1.4–1.55 μm. Efficient SHG of pulsed CO_2 laser is demonstrated[12].

$AgGaS_2$ is transparent from 0.53 to 12 μm. Although nonlinear optical coefficient is the lowest among the above mentioned infrared crystals, its high short wavelength transparency edging at 550 nm is used in OPOs[13,14] pumped by Nd:YAG laser; in numerous difference frequency mixing experiments[15,16,17,18] using diode, Ti:Sapphire, Nd:YAG and IR dye lasers covering 3–12 μm range; direct infrared countermeasure systems, and SHG of CO_2 laser[19].

GaSe has band edges at 0.65 and 18 μm. GaSe has been successfully used for efficient SHG of CO_2 laser[21], for SHG of pulsed CO, CO_2 and chemical DF-laser (λ = 2.36 μm) radiation[27]; up conversion of CO and CO_2 laser radiation into the visible range[20]; infrared pulses generation via difference frequency mixing of Neodymium and infrared dye laser[22,15] or (F-)-centre laser pulses[25]; OPG light generation within 3.5–18 μm[24]; efficient TeraHertz generation in 100–1600 μm range[39]. It is impossible to cut crystals for certain phase matching angles because of material structure (cleave along (001) plane) limiting areas of applications.



Type 1 and Type 2 SHG tuning curves in GaSe

Properties of $ZnGeP_2$, $AgGaSe_2$, $AgGaS_2$, GaSe

		$ZnGeP_2$	$AgGaSe_2$	$AgGaS_2$	GaSe
CRYSTAL DATA					
Crystal Symmetry		Tetragonal	Tetragonal	Tetragonal	Hexagonal
Point Group		42m	42m	42m	62m
Lattice Constants, Å	a	5.465	5.9901	5.757	3.742
	c	10.771	10.8823	10.305	15.918
Density, g/cm^3		4.175	5.71	4.56	5.03
OPTICAL PROPERTIES					
Optical transmission, μm		0.74÷12[23]	0.73÷18[9]	0.53÷12[32]	0.65÷18[27]
Indices of Refraction at					
1.06 μm	n_o	3.2324	2.7005	2.4508	2.9082
	n_e	3.2786	2.6759	2.3966	2.5676
5.3 μm	n_o	3.1141	2.6140	2.3954	2.8340
	n_e	3.1524	2.5823	2.3421	2.4599
10.6 μm	n_o	3.0725	2.5915	2.3466	2.8158
	n_e	3.1119	2.5585	2.2924	2.4392
Absorption Coefficient, cm^{-1} at					
1.06 μm		3.0[28]	<0.02[9]	<0.09	0.25[6]
2.5 μm		0.03[28]	<0.01	0.01	0.05[6]
5.0 μm		0.02[28]	<0.01	0.01	0.05[6]
7.5 μm		0.02[28]	-	0.02	0.05[6]
10.0 μm		0.4[28]	-	<0.6	0.05[6]
11.0 μm		0.8[28]	-	0.6	0.05[6]
NONLINEAR OPTICAL PROPERTIES					
Laser damage threshold, MW/cm^2		60[29]	25[38]	10[13]	28[21]
at pulse duration, ns		100	50	20	150
at wavelength, μm		10.6	2.05	1.06	9.3
Nonlinearity, pm/V		111[21]	43[11]	31[34]	63[21]
Phase matching angle for Type 1 SHG at 10.6 μm, deg		76	55	67	14
Walk-off angle at 5.3 μm, deg		0.57[21]	0.67[11]	0.85[19]	3.4[21]
THERMAL PROPERTIES					
Melting point, °C		1298[30]	851[12]	998[26]	1233
Thermal Expansion Coefficient, 10^{-6}/°K					
	⊥	17.5[31,a]	23.4[33,c]	12.5[35]	9.0
	⊥	9.1[31,b]	18.0[33,d]		
	||	1.59[31,a]	-6.4[33,c]	-13.2[35]	8.25
	||	8.08[31,b]	-16.0[33,d]		

a) at 293-573 K, b) at 573-873 K, c) at 298-423 K, d) at 423-873 K

Nonlinear and Laser Crystals

SELLMEIER EQUATIONS FOR CALCULATION OF INDICES OF REFRACTION

Crystal		A	B	C	D	E	F	Ref.	Expression
$ZnGeP_2$	n_o	8.0409	1.68625	0.40824	1.2880	611.05	–	37	$n^2 = A + B\lambda^2/(\lambda^2 - C) + D\lambda^2/(\lambda^2 - E)$
	n_e	8.0929	1.8649	0.41468	0.84052	452.05	–		
$AgGaSe_2$	n_o	6.8507	0.4297	0.15840	0.00125	–	–	36	$n^2 = A + B/(\lambda^2 - C) - D\lambda^2$
	n_e	6.6792	0.4598	0.21220	0.00126	–	–		
$AgGaS_2$	n_o	3.3970	2.3982	0.09311	2.1640	950.0	–	13	$n^2 = A + B/(1 - C/\lambda^2) + D/(1 - E/\lambda^2)$
	n_e	3.5873	1.9533	0.11066	2.3391	1030.7	–		
GaSe	n_o	7.443	0.405	0.0186	0.0061	3.1485	2194	4	$n^2 = A + B/\lambda^2 + C/\lambda^4 + D/\lambda^6 + E/(1 - F/\lambda^2)$
	n_e	5.76	0.3879	-0.2288	0.1223	1.855	1780		

REFERENCES

1. G. D. Boyd, W.B.Bandrud, E.Buehler, Appl. Phys. Lett., v.18, 446 (1971)
2. Yu.M.Andreev, V.G.Voevodin, A.I.Gribenyukov, A.P.Novikov, Sov. J. Quant. Electr., v.17, 748 (1987)
3. Yu.M.Andreev et al., Sov. J. Quant. Electr., v.17, 490 (1987)
4. K.L.Vodopyanov, L.A. Kulevskyi, Opt. Commun., in print
5. Yu. M.Andreev et al., Kvantovaya Elektronika, v.19, 1110 (1992), in Russian
6. K.L.Vodopyanov, JOSA B, v.10, 1723 (1993)
7. P.A.Budni, K.Ezzo, P.G.Shuneman, S.Minnigh, J.C.McCarthy, T.M.Pollack, OSA Proceedings, v.10, 335 (1991)
8. P.A.Budni, P.G.Shuneman, M.G.Knights, T.M.Pollack, E.P.Chicklis, OSA Proceedings, v.13, 380 (1992)
9. V.V.Badikov et al., Kvantovaya Electronika, v.19, 782 (1992) in Russian
10. G.J.Quarles, C.L.Marquardt, L.Esterowitz, LEOS'90 Proceedings, Boston, MA, 128 (1990)
11. H.Komine, J.M.Fukumoto, W.H.Long, E.A.Stappaerts, CLEO'94 Technical Digest, paper CPD 14-1/31
12. R.C Eckardt, Y.X.Fan, R.L.Byer, R.K.Route, R.S.Feigelson, J.van der Laan, Appl. Phys. Lett., v.47, 786 (1985)
13. Y.X.Fan, R.C.Eckardt, R.L.Byer, Appl. Phys. Lett., v.45, 313 (1984)
14. T.Elsaesser, A.Seilmeier, W.Kaiser, P.Koidl, G.Brandt, Appl. Phys. Lett., v.44, 383 (1984)
15. T.Dahinten et al., IEEE J. Quant. Electr., v.29, 2245 (1993)
16. K.Kato, IEEE J. Quant. Electr., v.20, 698 (1984)
17. P.Canarelli, Z.Benko, R.Curl, F.K.Tittel, JOSA B, v.9, 197 (1992)
18. G.C.Bhar, S.Das, D.K.Ghosh, L.K.Samanta, IEEE J. Quant. Electr., v.24, 1492 (1988)
19. P.J.Kupecek, C.A.Schwartz, D.S.Chemla, IEEE J. Quant. Electr., v.10, 540 (1974)
20. G.B Abdullaev et al., Sov. J. Quant. Electr., v.5, 665 (1975)
21. G.B Abdullaev et al., Sov. J. Quant. Electr., v.17, 494 (1989)
22. J.L.Oudar, P.J.Kupecek, D.S.Chemla, Opt. Commun., v.29, 119 (1979)
23. G. D. Boyd, E.Buehler, F.Storz, Appl. Phys. Lett., v.18, 301 (1971)
24. K.L.Vodopyanov et al., Opt. Commun., v.83, 322 (1991)
25. Yu.A.Gusev et al., Sov.Tech. Phys. Lett., v.6, 541 (1980)
26. D.S.Chemla, P.J.Kupecek, D.S.Robertson, R.C.Smith Opt. Comm., v.3, p.29 (1971)
27. G.B Abdullaev et al., Sov. J. Exp. Tech. Phys Lett., v.16, 90 (1972)
28. K.LVodopyanov, L.A.Kulevsky, V.G.Voevodin, A.I.Gribenyukov, Bul. Acad. Sci. USSR, Phys. Ser., v.49, 146 (1985)
29. Yu.M.Andreev et al., Sov. J. Quant. Electr., v.14, 1021 (1984)
30. K.Masumoto, S.Isomura, W.Goto, J. Phys. Chem. Solids, v.27, 1939 (1969)
31. I. I. Kogina, Vestnik LGU, Ser. fis. chim., v.22, 87 (1971) in Russian
32. G.C.Bhar, R.C.Smith, IEEE J. Quant. Electr., v.10, 546 (1974)
33. D.Eimerl , J.Marion, E.K.Graham, H.A.McKinstry, S.Haussuhl, IEEE J. Quant. Electr., v.27, 142 (1991)
34. P.Canarelli et al., IEEE J. Quant. Electr., v.28, 52 (1992)
35. P.Kovaczak, C.B.Staff, J. Cryst. Growth, v.24/25, 386 (1974)
36. K.Kato at IEEE J. Selected Topics Quant. Electr., v.1, 44 (1995)
37. D.E.Zelmon, E.A.Hanning, P.G.Schunemann, J. Opt. Soc. Am. B, Vol.18, No. 9, 1307 (2001)
38. R.C.Eckardt, Y.X.Fan, R.L.Byer, C.L.Marquardt, M.E.Storm, L.Esterowitz, Appl. Phys. Lett., v.49, 608 (1986)
39. N.Fernelius, K.Vodopyanov, W.Shi, Y.J.Ding, Opt. Lett., v. 27, No. 16, 1454 (2002)