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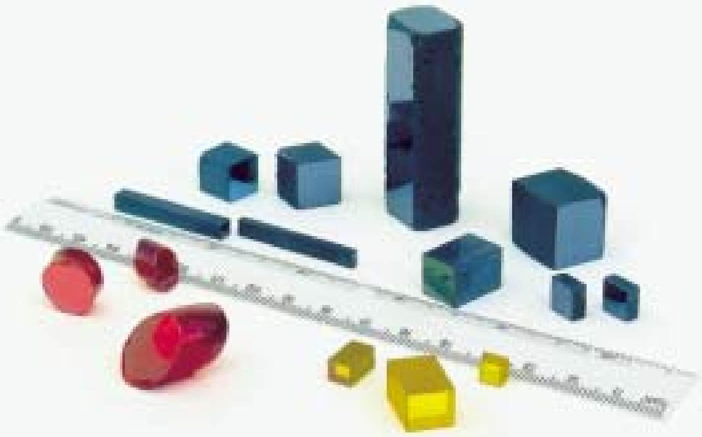
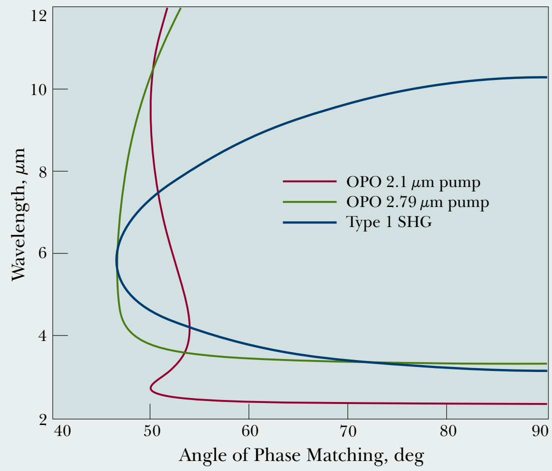
Infrared Nonlinear Crystals



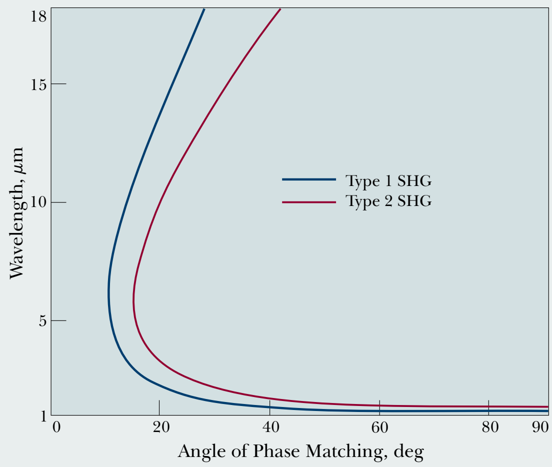
Optical nonlinear crystals like $ZnGeP_2$, $AgGaSe_2$, $AgGaS_2$, GaSe, Tl_3AsSe_3 have gained tremendous interest for the middle and deep infrared applications due to their unique features. The crystals have large effective optical nonlinearity, wide spectral and angular acceptance, broad transparency range, noncritical requirements for temperature stabilisation and vibration control, are well mechanically processed (except of GaSe and Tl_3AsSe_3).

$ZnGeP_2$ has band edges at 0.74 and 12 μm. Its useful transmission range ($a < 0.3$ cm^{-1}) lies from 2.1 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 1.06 mm; sum frequency generation of CO and CO_2 laser radiation[2]; efficient SHG of pulsed CO[3], CO_2[4] (49% efficiency at 1 GW/cm^2 intensity of 2 ns pulses, 9.52 mm wavelength) and chemical DF-laser[5], OPO light generation in mid infrared when pumped by erbium[6,7] and holmium[8] lasers.

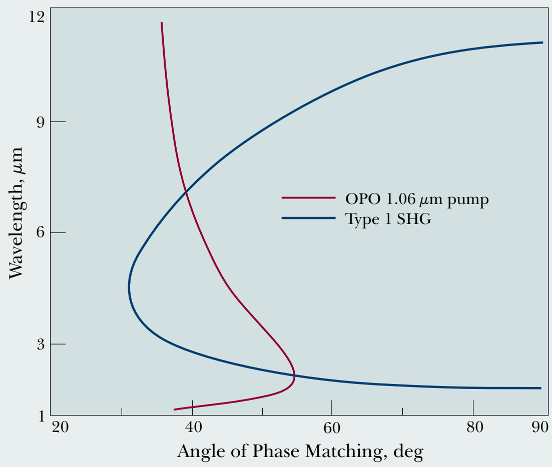
$AgGaSe_2$[9] has band edges at 0.73 and 18 μm. Its useful transmission range lying within 0.9–16 μm and wide phase matchability provide excellent potential for OPO applications when pumped by variety of currently available lasers. Tuning within 2.5–12 μm was obtained when pumped by Ho:YLF laser at 2.05 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].



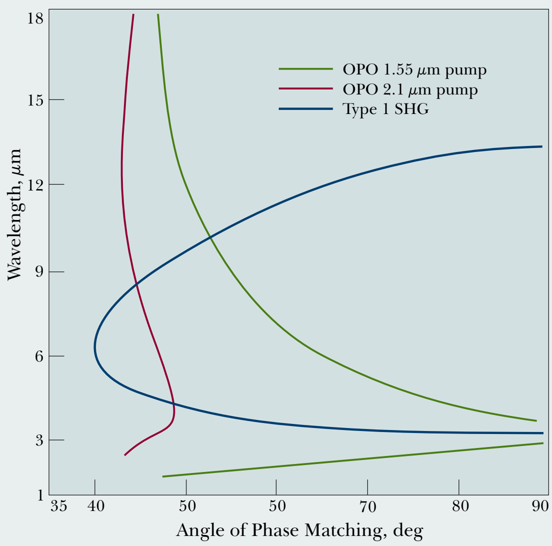
Type 1 OPO and SHG tuning curves in $ZnGeP_2$



Type 1 and Type 2 SHG tuning curves in GaSe



Type 1 OPO and SHG tuning curves in $AgGaS_2$



Type 1 OPO and SHG tuning curves in $AgGaSe_2$

$AgGaS_2$ 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] (up to 9% conversion); for SHG of pulsed CO, CO_2 and chemical DF-laser ($\lambda = 2.36$ μm) radiation[27]; upconversion 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]. It is impossibile to cut crystals for certain phase matching angles because of material structure (cleave along (001) plane) limiting areas of applications.

SELLMEIER EQUATIONS FOR CALCULATION OF INDICES OF REFRACTION

Crystal		A	B	C	D	E	F	Ref.	Expression
$ZnGeP_2$	n_o	4.4733	5.26576	0.13381	1.49085	662.55	–	37	$n^2 = A + B / (1 - C / \lambda^2) + D / (1 - E / \lambda^2)$
	n_e	4.63318	5.34215	0.14255	1.45785	662.55	–		
$AgGaSe_2$	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	
Tl_3AsSe_3	n_o	1	10.21	0.444	0.522	25	–		$n^2 = A + B / (1 - C / \lambda^2) + D / (1 - E / \lambda^2)$
	n_e	1	8.993	0.444	0.308	25	–		

Please contact EKSMA for further information or nonstandard specifications.

Properties of $ZnGeP_2$, $AgGaSe_2$, $AgGaS_2$, GaSe, Tl_3AsSe_3

		$ZnGeP_2$	$AgGaSe_2$	$AgGaS_2$	GaSe	Tl_3AsSe_3
CRYSTAL DATA						
Crystal Symmetry		Tetragonal	Tetragonal	Tetragonal	Hexagonal	Trigonal
Point Group		42m	42m	42m	62m	R3m
Lattice Constants, Å	a	5.465	5.9901	5.757	3.742	9.80
	c	10.771	10.8823	10.305	15.918	7.08
Density, g/cm^3		4.175	5.71	4.56	5.03	7.83
OPTICAL PROPERTIES						
Optical transmission, μm		0.74÷12[23]	0.73÷18[9]	0.53÷12[32]	0.65÷18[27]	1.23÷18[39]
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	3.357
	n_e	3.1524	2.5823	2.3421	2.4599	3.171
10.6 μm	n_o	3.0725	2.5915	2.3466	2.8158	3.331
	n_e	3.1119	2.5585	2.2924	2.4392	3.152
Absorption Coefficient, cm^{-1} at						
1.06 μm		3.0[28]	<0.02[9]	<0.09	0.25[6]	
2.5 μm		0.2[28]	<0.01	0.01	0.05[6]	<0.2
5.0 μm		0.1[28]	<0.01	0.01	0.05[6]	<0.2
7.5 μm		0.1[28]	–	0.02	0.05[6]	<0.1
10.0 μm		0.3[28]	–	<0.6	0.05[6]	<0.1
11.0 μm		0.8[28]	–	0.6	0.05[6]	<0.1
NONLINEAR OPTICAL PROPERTIES						
Laser damage threshold, MW/cm^2		60[29]	25[38]	10[13]	28[21]	10[40]
at pulse duration, ns		100	50	20	150	70
at wavelength, μm		10.6	2.05	1.06	9.3	9.6
Nonlinearity, pm/V		111[21]	43[11]	31[34]	63[21]	46[41]
Phase matching angle for Type 1 SHG at 10.6 μm, deg		76	55	67	14	12
Walk-off angle at 5.3 μm, deg		0.57[21]	0.67[11]	0.85[19]	3.4[21]	1.7
THERMAL PROPERTIES						
Melting point, °C		1298[30]	851[12]	998[26]	1233	584[77]
Thermal Expansion Coefficient, 10^{-6}/°K						
	⊥	17.5[31,a]	23.4[33,e]	12.5[35]	9.0	
	⊥	9.1[31,b]	18.0[33,d]			
	||	1.59[31,a]	-6.4[33,e]	-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

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