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**PUBLISHED NONLINEAR OPTICAL USES OF ZINC
GERMANIUM DIPHOSPHIDE**

NILS C FERNELIUS

APRIL 1996

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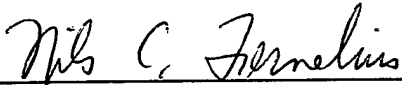
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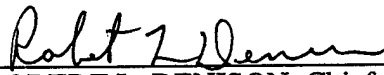
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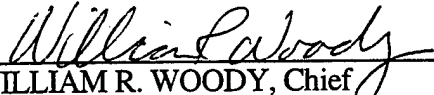
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13. ABSTRACT (Maximum 200 words) This report gives capsule summaries of all published work using the nonlinear optical properties of zinc germanium diphosphide (ZnGeP ₂). It is organized in several groupings—early American work, Russian, and recent Western work. A general bibliography is given as an appendix.				
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PUBLISHED NONLINEAR OPTICAL USES OF ZINC GERMANIUM DIPHOSPHIDE

by Nils C. Fernelius

INTRODUCTION

Currently the crystal of choice for optical parametric oscillators (OPO) operating in the 3-5 μm atmospheric window range is zinc germanium diphosphide (ZGP). The OPO is usually pumped by a holmium laser operating around 2 μm . Several factors delayed the common usage of ZGP in nonlinear optical (NLO) devices. First there was the problem of obtaining crack free crystals. The other serious problem, still not completely resolved, is a native defect optical absorption shoulder on the short wavelength side of the transparency window which extends beyond 2 μm . This degrades high power operation when using a 2 μm pump.

The first NLO uses of ZGP were demonstrated at Bell Labs in 1971 as a result of the interaction of the NLO group with the ternary semiconductor group. Most of the work entailed sum and difference frequency generation (SFG) & (DFG) plus one second harmonic generation (SHG) paper. There were five papers by G.D. Boyd et al. in 1971-1972. The work was summarized in an Avionics Lab tech report by Nichols, Corbin and Donlan in 1974. Due to reorganizations, both civilian and military, work in the area ceased. For almost the next 20 years, all research on this material was done in the Soviet Union. In the last few years, NLO ZGP work in the West has been revived.

This work will try to summarize the literature in three categories: early American, Russian, and recent Western work. Each category consists of a list of papers, the affiliation of the authors and a capsule summary of the work. The following were grouped in the Russian section: the paper by Churnside et al. since it was performed on a crystal brought from Russia when Gribenyukov was on sabbatical, some later work of Gopal Bhar even though it was performed in India, and the work of Vodopyanov after he started working at Imperial College, London.

Gopal Bhar did some significant work which does not fit in the above categories. Initially he published a number of papers obtaining Sellmeier equations by reanalyzing Boyd's data. From this he published a number of SHG and OPO tuning curves including temperature dependences. These papers will be listed in the general bibliography combining all categories.

EARLY AMERICAN WORK

A1 - G.D. Boyd, E. Buehler & F.G. Storz, Bell Telephone Laboratories, Murray Hill, New Jersey

Linear and nonlinear optical properties of ZnGeP₂ and CdSe
Appl. Phys. Lett. **18** 301-304 (1971)

measures n_o , n_e , dn_o/dT , dn_e/dT

shows three-frequency phase matching plots for $\theta_m = 90^\circ, 74^\circ, 66^\circ, 60^\circ$

A2 - G.D. Boyd, W.B. Gandrud & E. Buehler, BTL
Phase-matched up conversion of 10.6- μ radiation in ZnGeP₂
Appl. Phys. Lett. **18** 446-448 (1971)

Sum frequency generation (SFG): 10.6 & 1.06 μ m

Experimental: $\theta_m = 84^\circ$, $d\theta_m/dT = -0.007$ deg/ $^\circ$ C

crystal length = 1 cm

A3 - G.D. Boyd, T.J. Bridges, C.K.N. Patel & E. Buehler, BTL
Phase-matched submillimeter wave generation by difference-frequency mixing in ZnGeP₂

Appl. Phys. Lett. **21** 553-555 (1972)

Difference frequency generation (DFG) using two step-tunable CO₂ lasers

Phase-matched outputs between 70 cm⁻¹ (143 μ m) and 110 cm⁻¹ (91 μ m)

A4 - Elgene R. Nichols, John C. Corbin, Jr. and Vincent L. Donlan
Avionics & Materials Laboratories, Wright-Patterson AFB, Ohio
A Review of Parametric Oscillators and Mixers and an Evaluation of Materials for 2-6 μ m Applications

Air Force Avionics Laboratory Tech Report

AFAL-TR-74-161, July, 1974

gain/watt 1cm long crystal vs output wavelength plots for pump wavelengths 1.06, 1.3, 1.83, and 2.1 μ m. pp.22-24

Optical parametric oscillator (OPO) performance for $\lambda_{\text{pump}} = 1.06, 1.3$ and 2.10 μ m.
pp. 30-34

A5 - J.L. Shay & J.H. Wernick **Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications**, Pergamon Press, Oxford, 1975

Chapter 6 - Nonlinear Optical Applications pp. 153-174

RUSSIAN USE OF ZnGeP₂ IN NLO

R1 - N.P. Andreeva, S.A. Andreev, I.N. Matveev, S.M. Pshenichnikov & N.D. Ustinov
Parametric conversion of infrared radiation in zinc germanium diphosphide
Sov.J. Quantum Electron. **9** 208-210 (1979)
Russian reference: Kvantovaya Elektron. (Moscow) **6** 357-359 (1979)

Use as PARAMETRIC CONVERTER output @ 960 nm
PUMP CHARACTERISTICS:

Nd:YAG (1.06 μ) $\tau = 30$ ns power density = 3 MW/cm² rep rate = 12.5 Hz
Laser @ 3 MW/cm² no damage seen over 30 min

@ 20 MW/cm² damage after 5-10 pulses

CO₂ Laser (10.6 μ) CW power ~ 1 W

@ 10 W/cm² no damage over 3-4 cycles of 30 min

CRYSTAL: single crystal ZnZGeP₂ working faces polished

thickness 3 mm

$\Theta_{pm} = 82.5^\circ$

$\alpha(960\text{nm}) = 10 \text{ cm}^{-1}$

$\alpha(1.06 \mu) = 8 \text{ cm}^{-1}$

$\alpha(10.6 \mu) = 2 \text{ cm}^{-1}$

R2 - Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, O.Ya. Zyryanov, I.I. Ippolitov,
A.N. Morozov, A.V. Sosnin & G.S. Khmel'nitskii

Institute of Atmospheric Optics, Tomsk

Efficient generation of the second harmonic of tunable CO₂ laser radiation in ZnGeP₂
Sov. J. Quantum Electron. **14** 1021-1022 (1984)

Russian reference: Kvantovaya Elektron. (Moscow) **11**,1511-1512 (August 1984)

SHG of CO₂

PUMP CHARACTERISTICS: CW and pulsed rep rate 1.5 kHz $\tau = 0.1$ -10 ms
average power in TEM₀₀ was 0.5 - 5 W depending on transition

damage threshold 60-65 MW/cm² @ $\lambda = 10.6 \mu$

no damage observed for CW of 1 kW/cm²

best pulsed power conversion efficiency, 5%, was @ 0.6 kW pump

CRYSTAL: Bridgman mechanical & chemodynamic polishing

no AR coatings

$\alpha(2.5$ -12 $\mu)$ less than 0.1 cm⁻¹

in 8.5-9.45 μ and $\lambda > 10.6 \mu$ have phonon absorption

cross section area ~ 3 cm² $\Theta = 76^\circ$

R3 - Yu.M. Andreev, T.V. Vedernikova, A.A. Betin, V.G. Voevodin, A.I. Gribenyukov,
O.Ya. Zyryanov, I.I. Ippolitov, V.I. Masychev, O.V. Mitropol'skii, V.P. Novikov, M.A.

Novikov & A.V. Sosin Inst. Atmosph. Optics, Tomsk

Conversion of CO₂ and CO laser radiations in a ZnGeP₂ crystal to the 2.3-3.1 μ
spectral range Sov.J. Quantum Electron. **15** 1014-1015 (1985)

Russian ref.: Kvantovaya Elektron. **12** 1535-1537 (July 1985)

4th harmonic of CO₂ efficiency ~ 0.1 % should get to 20%
2nd harmonic of CO " (0.0025-0.010)%

PUMP CHARACTERISTICS:

TEA CO₂ $\tau \sim 170$ ns energy 200 mJ/pulse
first 2nd harmonic type I ee \rightarrow o ZnGeP₂ in oven efficiency ~ 2%
energy 4 - 10 mJ

second 2nd harmonic crystal 5 mm $\Theta = 48^\circ 54'$ $\varphi = 0^\circ 25'$
4th harmonic at least 0.2 mJ efficiency ~ 0.1%

$\alpha(2-12\mu) \sim 2$ cm⁻¹

CO SHG output power 8.5 W strongest line 0.8W SH 2 μ W

$\alpha(2.8\mu) \sim 2.8$ cm⁻¹

$\alpha(5\mu) \sim 3.8$ cm⁻¹

CW CO @ 10 kW/cm² for 6 hours showed no sign of damage

R4 - K.L. Vodop'yanov, V.G. Voevodin, A.I. Gribenyukov, & L.A. Kulevskii
Institute of General Physics, Moscow

Picosecond parametric superluminescence in the ZnGeP₂ crystal
Bulletin of the Academy of Sciences of the USSR, Physical Series **49** 146-149 (1985)

Russian reference:

Izvestiya Akademii Nauk SSSR, Seriya Fizicheskaya **49** 569-572 (1985)

use as OPO

PUMP CHARACTERISTICS:

Erbium laser (2.94 μ m) train of 25 pulses, $t = 80$ ps, rep rate 1 Hz,
total energy in train of 10-15 mJ

ZnGeP₂ CRYSTAL:

single crystal by Bridgmen

α did not exceed 0.2 cm⁻¹ for $\lambda = 2.5-8.5$ μ m

in three-phonon absorption band (8.3-9.5 μ m) $\alpha = 0.3$ cm⁻¹ ($l = 8.8$ μ)

calculate o-ee and o-eo tuning curves

experiment o-eo : $\Theta = 84.5^\circ-79.3^\circ$ covering $\lambda = 5.51-5.38$ & $6.29-6.46$ μ m

Crystal 42 mm long cut at an angle of 64°

max pump intensity 4×10^9 W cm⁻¹

R5 - L.I. Andreeva, K.L. Vodop'yanov, S.A. Kaidalov, Yu.M.Kalinin, M.E. Karasev, L.A. Kulevskii & A.V. Lukashev
Institute of General Physics, Moscow

Picosecond erbium-doped YAG laser ($\lambda = 2.94$ μ) with active mode locking

Sov.J. Quantum Electron. **16** 326-333 (1986)

Russian Ref.: Kvantovaya Elektron. **13** 499-509 (March 1986)

use as OPO with ZnGeP₂

PUMP CHARACTERISTICS: $Y_3Al_5O_{12}:Er^{3+}$ $\lambda = 2.94 \mu m$ rep rate 1-1.5 Hz
 generated train with energy 12 mJ of 25 pulses with energy 0.5 mJ (+/-
 3%) per spike and 40+/-10 ps duration at 4th harmonic
 pulse separation 6.7 ns FWHM envelope 160 ns

CRYSTAL optic axis to \perp at end surface was 84°
 the polar angle was $\phi = 45^\circ$ o-eo interaction
 signal $\lambda = 6.3 \mu m$ idler $\lambda = 5.5 \mu m$

R6 - V.E. Zuev, Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, V.A. Kapitanov, A.V. Sosnin, G.A. Stuchebrov, & G.S. Khelnitskii

Institute of Atmospheric Optics, Tomsk

Multifrequency dial sensing of the atmospheric gaseous constituents using the first and second harmonics of a tunable CO_2 laser radiation
 Proceedings 13th International Laser Radar Conference, Toronto, Canada 1986,
 NASA Conference Publication 2413 108-110 (1986)

SHG of CO_2

PUMP CHARACTERISTICS: 16 CO_2 wavelengths from R14 to R32
 60 MW/cm² for 200 ns pulses
 200 kW/cm² for CW

CRYSTAL: 10 x 20 mm cross section
 3-10 mm thickness with polished ends

R7 - Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, & V.P. Novikov

Institute for Applied Physics, Gorki

Mixing of frequencies of CO_2 and CO lasers in $ZnGeP_2$ crystals
 Sov.J. Quantum Electron. 17 748-749 (1987)
 Russian ref: Kvantovaya Elektronika 14 1177-1178 (June,1987)

Summed CO and CO_2

PUMPS: CO_2 5.7 W CO 4.7 W

CRYSTALS:

Length mm	Θ_{pm} normal incidence $^\circ$	Azimuthal angle $^\circ$	Absorption coefficient @ CO_2 in cm ⁻¹			Damage threshold kW/cm ²	
			CO_2	CO	CO_2+CO	CO_2	CO
3.1	48	0	0.83	0.32	0.41	200	250
8.0	90	45	0.46	0.1	0.2		

damage threshold for pulsed CO_2 60 MW/cm² for 200 ns pulses

R8 - Yu.M. Andreev, A.D. Belykh, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.A.

Gurashvili & S.V. Izyumov Inst. Atmospheric Optics, Tomsk

Doubling of the emission of CO lasers with an efficiency of 3%.
 Sov.J. Quantum Electron. 17 490-491 (1987)
 Russian ref.: Kvantovaya Elektron. 14 782-783 (April 1987)

SHG of CO

PUMP: CO Q-switched energy per pulse 2 mJ @ 10 Hz; 0.6 mJ @ 100 Hz
 0.1 mJ @ 200 Hz

CRYSTAL 7 mm long $\Theta = 47^{\circ}30'$ $\phi = 0$ chemodynamic polish, no AR
maximum external efficiency of whole SHG system 3.2%

R9 - Yu.M. Andreev, A.I. Gribenyukov, V.V. Zuev, N.V. Karlov, V.D. Karyshev, A.V. Kisetsov, I.O. Kovalev, A.V. Korablev, G.P. Kuz'min, L.A. Kulevskii & A.A. Nesterenko
Institute of General Physics, Moscow
Second-harmonic generation in ZnGeP₂ pumped by a continuously tunable CO₂ laser
Sov. Tech. Phys. Lett. **13** 595-596 (1987).
Russian ref.: Pis'ma v Zhurnal Tekhnicheskoi Fiziki **13** 1423-1426
(12 Dec 1987)

SHG of CO₂

PUMP CHARACTERISTICS:

could tune CO₂ over 9.19-9.7 μm & 10.15-10.8 μm
linearly polarized 15-70 mJ, pulse length FWHM \sim 50 ns
achieved doubled tuning over 5.15-5.11, 4.80-4.73, 4.65-4.61 μm

CRYSTAL:

4.4 mm thick $\theta = 76^{\circ}$ $\phi = 0^{\circ}$ $\alpha = 2.1 \text{ cm}^{-1}$
spot 1.5 mm diameter, surface damage above 65 mJ or \sim 4 J/cm²

R10 - K.L. Vodop'yanov, V.G. Voevodin, A.I. Gribenyukov & L.A. Kulevskii
High-efficiency picosecond parametric superradiance emitted by a ZnGeP₂ crystal in
the 5-6.3 μm range Inst. of General Physics, Moscow
Sov.J. Quantum Electron. **17** 1159-1161 (1987)
Russian ref: Kvantovaia Elektronika **14** 1815-1819 (Sept. 1987)

OPO

PUMP CHARACTERISTICS:

Er³⁺:Cr³⁺:YSGG yttrium scandium gallium garnet $\lambda = 2.79 \mu\text{m}$
 $\tau = 150 \text{ ps} \pm 25$ rep rate 1 Hz up to 2 mJ/spike
laser spot \sim 0.1 mm diameter (area = 0.00017 cm²)

CRYSTAL:

Bridgman α in range 2.8-8.3 μ did not exceed 0.1 cm⁻¹
no AR coatings Type II o \rightarrow eo $\theta = 84^{\circ}$ $\lambda_1 = 5.96 \mu\text{m}$, $\lambda_2 = 5.25 \mu\text{m}$
for $I_p > 7.8 \text{ GW/cm}^2$ efficiency of conversion 16%
for $I_p = 16 \text{ GW/cm}^2$, efficiency 17.6%
surface damage threshold 30 GW/cm²
vary θ 76-90 $^{\circ}$, output 5-5.3, 5.9-6.3 μm with quantum efficiency 17%,
output power \sim 1 MW

R11 - Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.V. Zuev, A.S. Solodukhin, S.A. Trushin, V.V. Churakov & S.F. Shubin
Inst. Atmospheric Optics, Tomsk
Transformation of the frequencies of nontraditional (4.3 and 10.4 μm) CO₂ laser
radiation bands in ZnGeP₂ Sov.J. Quantum Electron. **17** 1362-3 (1987)
Russian Russian ref: Kvantovaia Elektronika **14** 2137-2138 (Nov. 1987)

SHG 4.3 μm + SFG with 10.4 μm

PUMP CHARACTERISTICS:

average power of 4.3 μm band did not exceed 10 mW

CRYSTAL: ZnGeP₂ Type I interactions 7-13 mm thick

cut at angles $\theta = 53$ & 48.5° $\varphi = 0$

best results from crystal 7mm length with $\theta = 47^\circ 30'$ and $\varphi = 0$

AR coating gave transmission up to 87.5% @ $\lambda = 4.3\mu$; 73% @ 10.4μ

measured SH phase-matching angle $55^\circ 50'$

R12 - Yu.M. Andreev, V.Yu. Baranov, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, S.V. Izyumov, S.M. Kozochin, V.D. Pis'mennyi, Yu.A. Satov & A.P. Strel'tsov
I.V.Kurchatov Institute of Atomic Energy, Moscow

Efficient generation of the second harmonic of a nanosecond CO₂ laser radiation pulse
Sov.J.Quantum Electron. **17** 1435-1436 (1987)

Russian Ref.: Kvantovaya Elektronika **14** 2252- 2254 (Nov. 1987)

SHG of CO₂

PUMP CHARACTERISTICS: CO₂ 2 ns pulse 9.52 μm

CRYSTAL: type I conversion

second harmonic generator: $\Theta = 76^\circ$, $\varphi = 0$ length 3 mm

fourth harmonic generator: $\Theta = 47^\circ$, $\varphi = 0$ length 10 mm both

crystals chemodynamic polished, no AR coating

α did not exceed 0.1 cm^{-1} from 2.5-8 μm

calculation showed that that length of 3mm optimal for 1 GW/cm^2

damage threshold for fresh surface 2.5 J/cm^2

R13 - Yu.M. Andreev, P.P. Geiko, V.V. Zuev, V.E. Zuev, O.A. Romanovskii, & S.F. Shubin
Inst. Atmospheric Optics, Tomsk

Advances in Gas-Analyzers Based on IR Molecular Lasers

Laser & Optical Remote Sensing: Instrumentation & Techniques, 28 Sept.- 1 Oct. 1987, North Falmouth, MA pp 152-155

SHG & sum frequency addition of CO₂ lines can cover much of the 2-5 and 8-12 μm part of the spectrum

R14 - Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.V. Zuev, V.E. Zuev
institute of Atmospheric Optics, Tomsk, USSR

Effective source of coherent radiation based on CO₂ lasers and ZnGeP₂ frequency converters
Laser & Optical Remote Sensing: Instrumentation & Techniques, 28 Sept.- 1 Oct. 1987 North Falmouth, MA, Optical Society of America 1987 Technical Digest Series, Vol. 18, pp. 300-303

R17 - Yu.M. Andreev, P.P. Geiko, V.V. Zuev, O.A. Romanovskii & S.F. Shubin
 Inst. Atmospheric Optics, Tomsk
 Control of gas pollution of air medium with the aid of CO₂ and CO lasers equipped with
 frequency converters
 XIII International Conference on Coherent & Nonlinear Optics, Minsk, 6-9 Sept 1988,
 Part II, Sections IX-XVI, pp. 221-222

SHG & SFG of CO₂
 LASER: rep rate 100Hz
 pulse length 100 ms
 Peak power 150 W
 peak power of second harmonic 10 mW

R18 - Yu.M. Andreev, P.P. Geiko & V.V. Zuev
 High-efficiency frequency conversion of IR lasers with ZnGeP₂ and CdGeAs₂
 IAO, Tomsk

Advances in Laser Science III. Third International Laser Science Conference
 Atlantic City, NJ 1-4 Nov. 1987 AIP Conference Proceedings **172** 190-2 (1988), eds.
 Andrew C. Tam, James L. Gole & William C. Stwalley
 Results on ZnGeP₂

FC type	Laser	λ in μm	τ in s
SHG	CO ₂	9.28	2 10 ⁻⁹
	SH CO ₂	4.64	1.5 10 ⁻⁹
	CO ₂	9.2-10.8	2 10 ⁻⁷
	CO	5.3-6.1	4 10 ⁻⁵
	CO	4.3	3.3 10 ⁻⁷
FHG	CO ₂	9.28	2 10 ⁻⁹
SFG	CO ₂	4.3	3 10 ⁻⁷
		10.4	6 10 ⁻⁷
	CO & CO ₂	5.3-6.1 10.6	CW CW

CRYSTAL: boules 20-25 mm diameter, up to 150 mm length

R19 - Yu.M. Andreev, P.P. Geiko, V.V. Zuev, O.A. Romanovskii IAO, Tomsk
 Gas Analysis Using CO₂ Laser Frequency Converters
Advances in Laser Science III. Third International Laser Science Conference
 Atlantic City, NJ 1-4 Nov. 1987 AIP Conference Proceedings **172** 193-5 (1988), eds.
 Andrew C. Tam, James L. Gole & William C. Stwalley

SHG & SFG of CO₂ & CO lasers using ZGP & TAS
 frequency doubled 10.3 μm by heating ZGP above 100°C

R20 - V.E. Zuev, M.V. Kabanov, Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I.
 Gribenyukov, V.V. Zuev Atmospheric Optics Inst., Tomsk
 Applications of efficient parametric IR-laser frequency converters
 Bull. Academy Sci., USSR, Physical Sciences **52** 87-92 (1988)
 Russian ref.: Izvestiya Akademii Nauk SSSR, Seriya Fizicheskaya **52**(6) 1142-1148
 (1988)

plot of efficiency vs. crystal length
 CRYSTALS: 20-25 mm diameter X up to 150 mm long
 Results for ZnGeP₂ crystal

Form	Laser	λ in μm	τ in sec
SHG	CO ₂	9.28	$2 \cdot 10^{-9}$
	CO ₂	10.2-10.3	
	SH CO ₂	4.64	$1.5 \cdot 10^{-9}$
	CO ₂	9.2-10.8	$2 \cdot 10^{-7}$
	CO	5.3-6.1	$4 \cdot 10^{-5}$
	CO ₂	4.3	$3.3 \cdot 10^{-7}$
FHG	CO ₂	9.28	$2 \cdot 10^{-9}$
SFG	CO ₂	4.3	$3 \cdot 10^{-9}$
		10.4	$6 \cdot 10^{-7}$
	CO &	4.3	$3 \cdot 10^{-7}$
	CO ₂	10.4	$6 \cdot 10^{-7}$

R21 - G.C. Bhar, S. Das, U. Chatterjee, & K.L. Vodopyanov
 Burdwan U., India & Gen.Phys. Inst., Moscow
 Temperature-tunable second-harmonic generation in zinc germanium diphosphide
 Appl.Phys.Lett. **54** 313-314 (1989)

SHG of CO₂
 CRYSTAL:

$\alpha(3-8\mu\text{m})$ less than 0.2 cm^{-1} size 2.5 cm diameter, 15 cm length
 type I phase match with 48° cut 9.18-9.6 μm doubled varying phase
 match angle and temperature

R22 - Yu.M. Andreev, A.N. Bykanov, A.I. Gribenyukov, V.V. Zuev, V.D. Karyshev, A.V. Kismetsov, I.O. Kovalev, V.I. Konov, G.P. Kuz'min, A.A. Nesterenko, A.E. Osorgin, Yu.M. Starodumov & N.I. Chapliev Inst.General Physics, Moscow
 Conversion of pulsed laser radiation from the 9.3-9.6 mm range to the second harmonic in ZnGeP₂ crystals
 Sov. J. Quantum Electron. **20** 410-414 (1990)
 Russian Ref.: Kvantovaya Elektron. **17** 476-480 (April 1990)

SHG of CO₂
 PUMP CHARACTERISTICS: pulsed TEA CO₂ tunable 9.2-9.8 μm
 110-120 ns spike with 1-1.1 μs low intensity tail

CRYSTAL:

length mm	λ μm	Θ_{pm}	α cm^{-1}	1.4x1.4 cm cross section
4.6	9.3	64.4	0.8-3.0	
4.0	9.3	62.7	0.6-1.2	
	9.6	64.9		

best Russian crystals had $\alpha(9\mu) = 0.5-0.4 \text{ cm}^{-1}$; $\alpha(4.5\mu) = 0.1-0.2 \text{ cm}^{-1}$
 paper includes plots of efficiency vs. a, energy, energy density
 also plot of phase matching angle vs. temperature

R23 - K.L. Vodopyanov, L.A. Kulevskii, V.G. Voevodin, A.I. Gribenyukov, K.R. Allakhverdiev, & T.A. Kerimov General Physics Inst., Moscow
 High efficiency middle IR parametric superradiance in ZnGeP₂ and GaSe crystals pumped by an erbium laser
 Optics Communications **83** 322-326 (1991)

OPO

PUMP CHARACTERISTICS:

Er³⁺:YAG, $\lambda = 2.94 \mu$ $\tau = 110 \text{ ps} \pm 10$, 0.5-2 mJ, rep rate 1.2 Hz

Er³⁺:YSGG, $\lambda = 2.79 \mu$

CRYSTALS:	Type I (o-ee)	Type II (o-eo)
Crystal orientation	$\Theta = 47^\circ, \varphi = 0$	$\Theta = 84^\circ, \varphi = 31^\circ$ (45°optimal)
Range of Θ variation	47-49.55°	76-90°
Tuning range achieved	4-10 μ	5.2-5.6, 6.2-6.7 μ
Crystal length	11 mm	42 mm
Damage threshold	6.5 GW/cm ²	30 GW/cm ²

R24 - Yu.M. Andreev, P.P. Geiko & G.M. Krekov Tomsk Medicine Institute, Tomsk
 O.A. Romanovskii Inst. Atmospheric Optics, Tomsk
 Detection of trace concentration of some simple pollutants in Tomsk
 SPIE Vol. **1811** High-Resolution Molecular Spectroscopy pp. 367-370 (1991)

SHG, SFG of CO₂ also THG using TAS

R25 - K.L. Vodopyanov, L.A. Kulevskii, A.I. Gribenyukov, and K.R. Allakhverdiev
 General Physics Inst., Moscow
 High efficiency middle IR parametric superradiance in ZnGeP₂ and GaSe crystals pumped by an erbium laser
 Journal de Physique IV: Colloque 7, supplement au Journal de Physique III, Vol. 1, Decembre 1991 pp. C7-391 - C7-394
 same as R23?

R26 - A.A. Betin, V.G. Voevodin, K.V. Ergakov, A.V. Kirsanov & V.P. Novikov
 Inst. Applied Physics, Siberian Polytechnical Inst., Tomsk
 Generator of infrared radiation at the second-harmonic frequency of a TEA CO₂ laser
 Sov.J. Quantum Electron. **21** 735-738 (1991)
 Russian Ref.: Kvantovaya Elektron. **18** 812-816 (July 1991)

SHG of CO₂

PUMP CHARACTERISTICS: TEA CO₂ short peak 170-200 ns + μ s tail
 maximum energy per pulse 3J

CRYSTAL: $\alpha(\text{CO}_2) = 0.3\text{-}2 \text{ cm}^{-1}$

max breakdown threshold after mechanical polish + surface treatment 60-80
 MW/cm²(10-15 J/cm²);
 after chemodynamic polish 40-60 MW/cm²
 absorption band in 9.0-9.1 μm range :
 max. absorption in best crystals 0.3 cm⁻¹; worst, 1.5 cm⁻¹
 best large crystals, ~ 1 cm, a(3-8μm) not more than 0.1 cm⁻¹
 $\alpha(\text{TEA CO}_2 \text{ fundamental}) = 0.35\text{-}0.70 \text{ cm}^{-1}$
 room temperature phase matching ends at 10.2 μm
 max. in SHG energy observed for $\lambda = 10.55 \mu\text{m}$ at T=160-190°C with
 $\Theta_{\text{pm}} = 76^\circ$; crystals degrade above 400° C
 talk about greater than 5 cm crystals;
 9.3mm & 9.8mm long with 2 cm² aperture
 damage threshold 45 MW/cm²
 noted considerable absorption inhomogeneity over face, up to a factor of 3 or 4
 obtained an external efficiency of 6-8% (surfaces not AR coated)
 maximum energy of SH pulse was 0.16 J

R27 - J.H. Churnside, J.J. Wilson, A.I. Gribenyukov, S.F. Shubin, S.I. Dolgii, Y.M.
 Andreev, V.V. Zuev Wave Propagation Lab., Boulder & Institute
 for Atmospheric Optics, Tomsk
 Frequency conversion of a CO₂ Laser with ZnGeP₂
 NOAA Technical Memorandum ERL WPL-224 July, 1992

SHG & FHG of CO₂
 SHG conversion efficiency 26%
 FHG (2 SHG) conversion efficiency 0.04%

R28 - Yu.M. Andreev, S.D. Velikanov, A.S. Yerutin, A.F. Zapol'skii, D.V. Konkin, S.N.
 Mishkin, S.V. Smirnov, Yu.N. Frolov, and V.V. Shchurov
 All-Russian Scientific-Research Institute of Experimental Physics, Arzamas-16, Nizhnii
 Novgorod Oblast
 Second Harmonic generation from DF laser radiation in ZnGeP₂
 Sov. J. Quantum Electronics **22**(11) 1035 (November 1992)
 Russian ref.: Kvantovaya Elektron.(Moscow) **19** 1110 (November 1992)

SHG of DF
 pulse length sharp rise with trailing edge: 150 ns(half.max),500 ns (at 0.1)
 crystal length 10.1 mm, external efficiency 4%;internal eff. 7.6%
 " " 13.6 " " 6.2%; " " 11.8%

R29 - K.L. Vodopyanov General Physics Inst., Moscow
 Parametric generation of tunable infrared radiation in ZnGeP₂ and GaSe pumped at 3
 μm J.Opt.Soc.Am.B **10**(9) 1723-1729 (September 1993)

OPO pumped by Er³⁺:YAG (2.94 μm) or Er³⁺:Cr³⁺:YSGG(2.79 μm)

Property	Type I (o-ee)	Type II (o-eo)
Crystal orientation	$\theta = 47^\circ, \varphi = 0^\circ$	$\theta = 84^\circ, \varphi = 31^\circ$
Range of q variation	47-49.55 deg	76-90 deg
Tuning range on μm	4-10	5.2-5.6, 6.2-6.7
Crystal length in mm	12	42
Walk-off in mm	0.14($\theta=48^\circ$)	0.11($\theta=84^\circ$)
Effective length	12	19
OPG threshold GW/cm ²	0.5	0.35
I _{max} used "	6.5	30
Max. OPG quantum eff.	3%	17.6%
I _{damage} GW/cm ²	6.5	30

R30- A.A. Barykin, S.V. Davydov, V.D. Dorokhov, V.P. Zakharov, & V.V. Butuzov
 Samarskoe Science-Industrial Union for Automated Systems
 Generation of the second harmonic of CO₂ laser pulses in a ZnGeP₂ crystal
 Quantum Electronics **23**(8) 688-693 (August 1993)
 Russian ref.: Kvantovaya Elektron. **20** 794-800 (August 1993)

SHG of CO₂
 CRYSTAL: 12.5 X 10.62 x 7.2 mm length
 9.3-9.6 μm to 4.6-4.8 μm

R31 - K.L. Vodop'yanov General Physics Inst., Moscow
 Yu.A. Andreev Siberian State Medical University, Tomsk
 G.C. Bhar Burdwan Univ., Burdwan, India
 Parametric superluminescence in a ZnGeP₂ crystal with temperature tuning and
 pumping by an erbium laser Quantum Electronics
23(9) 763-766 (Sept. 1993)
 Russian ref.: Kvantovaya Elektron. **20** 879-882 (September 1993)

OPO
 PUMP: Q-switched Er:YSGG laser, $\lambda = 2.79 \mu\text{m}$, repetition rate 1.2 Hz
 working energy reached 20 J
 single pulse from resonator, 100 ps, energy 0.5-1 mJ
 CRYSTAL: length 42 mm in direction of Type II phase matching
 $\theta = 84^\circ$ and $\varphi = 31^\circ$
 by temperature tuning could reach 5.3 - 5.9 μm
 threshold energy density for superluminescence 0.35 GW/cm²
 working pump energy density 5-10 GW/cm² at superluminescence
 efficiency of 10% and damage threshold of 35 GW/cm²

R32 - K.L. Vodopyanov

General Physics Inst., Moscow
Imperial College, London

2.8 μm Er-laser pumped nonlinear devices

pp.10-13 in **Technical Digest: EQEC'93-EQUAP'93**, Vol.1, Frieenze, Italy,
10-13 September 1993, edited by P. de Natale, R. Meucci, S. Pelli

OPO

PUMP: flashlamp pumped $\text{Er}^{3+}:\text{Cr}^{3+}:\text{YSGG}$ @ $\lambda = 2.8\mu\text{m}$
Q-switched, single pulses 100 ± 10 ps TEM_{00} mode, 0.5 mJ
after amplification, 2-4 mJ

repetition rate 1-3 sec

when a passive InAs shutter was added, got 30-50 ps pulses

CRYSTAL: length 12 mm for angle tuning

for Type II interaction, length = 42 mm

OPO Type I tuning range 4-10 μm

Type II tuning range 5-6.3 μm , quantum efficiency 18%

Travelling wave OPO threshold 0.35 GW/cm^2 , which is 100 times smaller than
the optical damage threshold

R33 - K.L. Vodopyanov

General Physics Inst., Moscow
Imperial College, London

2.8 μm Er-laser-pumped non-linear devices

Leituvos fizikos zurnalas **33** (5-6) 301-304 (1993)

OPO

PUMP: mode-locked $\text{Sr}:\text{Cr}:\text{YSGG}$ laser @ $\lambda = 2.8\mu\text{m}$
single pulses 100 ± 10 ps, TEM_{00} mode, about 0.5 mJ

CRYSTALS: $L = 11$ mm, $\theta = 47^\circ$ for Type I phase matching and

$L = 42$ mm, $\theta = 84^\circ$ for Type II phase matching

OPO Type II tuning covered 5-5.3 μm (signal) and 5.9-6.3 μm (idler)

with typical linewidth of $10\text{-}20\text{ cm}^{-1}$

OPG threshold was as low as $0.35\text{ GW}/\text{cm}^2$

surface damage threshold for 100 ps 2.8 μm pulses was
 $30\text{ GW}/\text{cm}^2$

Type I had broad OPG lines especially near degeneracy, 1300 cm^{-1}

at $\lambda = 10\text{ }\mu\text{m}$ got linewidth of 50 cm^{-1}

4-10 μm tuning was achieved with 1-2% efficiency

OPG threshold as low as $0.25\text{ GW}/\text{cm}^2$ for 2.8 μm pump

R34 - Konstantin L. Vodopyanov

General Physics Inst., Moscow
Imperial College, London

Wide tuning range OPG's pumped by short Er-laser pulses at $\lambda = 2.8\text{ }\mu\text{m}$

Advanced Solid State Lasers, OSA Proceedings, Vol. **24**, Memphis, TN 30
Jan-2 Feb 1995, 194-197, [1995 Technical Digest, Vol. 8, pp.340-342, WG3-1-3]

PUMP: Er³⁺:Cr³⁺:YSGG laser, $\lambda = 2.8 \mu\text{m}$, rep rate 3 Hz
 with active mode locking, $\tau = 90 \text{ ps}$, with 0.7 mJ
 with passive mode locking, 30-50 ps pulses,
 after amplification 3-4 mJ energy per pulse
 Travelling-wave Optical Parametric Generator(TOPG):
 ZGP tuning range, 3.9-10 μm , for both type I & II
 OPG pump threshold, 0.25 GW/cm² for 11 mm long crystal
 Type II had conversion efficiency up to 18% for MW peak power
 with linewidth 30-40 cm⁻¹
 Type I broader linewidth especially near degeneracy point

R35 - K.L. Vodopyanov Imperial College, London
 V.G. Voevodin Siberian Physical-Technical Inst., Tomsk
 Type I and II ZnGeP₂ travelling-wave optical parametric generator tunable between
 3.9 and 10 μm
 Optics Communications **117** 277-282 (1995)

PUMP: mode locked Er³⁺:Cr³⁺:YSGG laser @ $\lambda = 2.8 \mu\text{m}$
 pulse duration $100 \pm 10 \text{ ps}$, energy 2-3 mJ, rep rate 3 Hz
 CRYSTAL: Type I (o \rightarrow ee): L = 11 mm, $\theta = 47^\circ$ -cut, $\varphi = 0^\circ$ (walk-off 0.13 mm)
 Type II(o \rightarrow eo): L = 30 & 17 mm, $\theta = 63.5^\circ$, $\varphi = 31^\circ$
 (walk-off 0.3 & 0.17 mm)
 OPG: Type I tuning range_ 3.9 - 10 μm
 Type II tuning ranges_ signal 6 - 10 μm , idler 3.9 - 5.1 μm
 OPG linewidths exp. & theor. given at various wavelengths
 OPG thresholds for 2.8 μm pump for various lengths given

R36 - Yu.M. Andreev, V.V. Butuzov, G.A. Verozub, A.I. Gribenyukov,
 S.V. Davydov, and V.P. Zakharov Samara State Research & Production
 Association of Automatic Systems, Samara, Russia
 Generation of the second harmonic of pulsed CO₂-laser radiation in AgGaSe₂ and
 ZnGeP₂ single crystals
 Laser Physics **5(5)** 1014-1019 (1995)

SHG
 PUMP CHARACTERISTICS:
 pulsed electric discharge CO₂ laser
 output radiation energy 150 mJ
 output aperture 6.8 mm
 FWHM of leading spike $\tau_1 \equiv \tau_{0.5} \sim 45 - 50 \text{ ns}$
 with total pulse duration about 100 ns
 maximum gain lines at $\lambda = 9.3, 9.59, 10.26, 10.61 \mu\text{m}$

PUMP: Er³⁺:Cr³⁺:YSGG laser, $\lambda = 2.8 \mu\text{m}$, rep rate 3 Hz
 with active mode locking, $\tau = 90 \text{ ps}$, with 0.7 mJ
 with passive mode locking, 30-50 ps pulses,
 after amplification 3-4 mJ energy per pulse
 Travelling-wave Optical Parametric Generator(TOPG):
 ZGP tuning range, 3.9-10 μm , for both type I & II
 OPG pump threshold, 0.25 GW/cm² for 11 mm long crystal
 Type II had conversion efficiency up to 18% for MW peak power
 with linewidth 30-40 cm⁻¹
 Type I broader linewidth especially near degeneracy point

R35 - K.L. Vodopyanov Imperial College, London
 V.G. Voevodin Siberian Physical-Technical Inst., Tomsk
 Type I and II ZnGeP₂ travelling-wave optical parametric generator tunable between
 3.9 and 10 μm
 Optics Communications **117** 277-282 (1995)

PUMP: mode locked Er³⁺:Cr³⁺:YSGG laser @ $\lambda = 2.8 \mu\text{m}$
 pulse duration $100 \pm 10 \text{ ps}$, energy 2-3 mJ, rep rate 3 Hz
 CRYSTAL: Type I (o \rightarrow ee): L = 11 mm, $\theta = 47^\circ$ -cut, $\phi = 0^\circ$ (walk-off 0.13 mm)
 Type II(o \rightarrow eo): L = 30 & 17 mm, $\theta = 63.5^\circ$, $\phi = 31^\circ$
 (walk-off 0.3 & 0.17 mm)
 OPG: Type I tuning range_ 3.9 - 10 μm
 Type II tuning ranges_ signal 6 - 10 μm , idler 3.9 - 5.1 μm
 OPG linewidths exp. & theor. given at various wavelengths
 OPG thresholds for 2.8 μm pump for various lengths given

R36 - Yu.M. Andreev, V.V. Butuzov, G.A. Verozub, A.I. Gribenyukov,
 S.V. Davydov, and V.P. Zakharov Samara State Research & Production
 Association of Automatic Systems, Samara, Russia
 Generation of the second harmonic of pulsed CO₂-laser radiation in AgGaSe₂ and
 ZnGeP₂ single crystals
 Laser Physics **5(5)** 1014-1019 (1995)

SHG
 PUMP CHARACTERISTICS:
 pulsed electric discharge CO₂ laser
 output radiation energy 150 mJ
 output aperture 6.8 mm
 FWHM of leading spike $\tau_1 \int \tau_{0.5} \sim 45 - 50 \text{ ns}$
 with total pulse duration about 100 ns
 maximum gain lines at $\lambda = 9.3, 9.59, 10.26, 10.61 \mu\text{m}$

CRYSTALS:

No.	Thickness	Area of face	Angle of shear	Absorption Coefficient	
	in mm	in mm ²	plane of Xtal	at λ_1	λ_2 in cm ⁻¹
1	12	10 x 15	75 deg	0.7	0.01
2	7.2	12.5 x 10.62	76	0.8	0.4
3	10.4	7.3 x 15	72	0.7	0.01

R37 - Konstantin L. Vodopyanov and Chris C. Phillips
Imperial College, London

Travelling wave mid-IR ZnGeP₂ and GaSe optical parametric generators and their spectroscopic applications, pp.170-174 in **Solid State Lasers and Nonlinear Crystals**, 5-7 February 1995, San Jose, CA, edited by Gregory J. Quarles, Leon Esterowitz and L.K. Cheng, SPIE Proceedings Vol. 2379
OPO

PUMP CHARACTERISTICS: Er³⁺:Cr³⁺: YSGG laser @ $\lambda = 2.79 \mu\text{m}$
pulse length $\tau = 100 \pm 10$ ps, TEM₀₀, rep rate 3 Hz
energy about 0.5 mJ, after passing through amplifier 2-4 mJ

CRYSTAL: absorption at pump wavelength, $\alpha < 0.1 \text{ cm}^{-1}$
lengths: Type I, 11 mm; Type II, 42 and 30 m
tuning range 4-10 μm for both I & II
typical quantum efficiency 1-2 %; for type II, near degeneracy, achieved 18%
QPG threshold intensity was 0.24-0.35 GW/cm², a value 100 times smaller than the optical damage threshold

SUMMARY OF RUSSIAN ZnGeP₂ NLO WORK

SUM FREQUENCY GENERATOR (SFG)

Nd:YAG + CO ₂	1
CO + CO ₂	7,14,16,18, 20
4.3 + 10.4 μm	11,14
CO ₂ + CO ₂	13,17, 18, 19, 20, 21, 24

SECOND HARMONIC GENERATOR (SHG)

CO ₂	2,6,9,12,13,14,16,17,18,19,20,21, 22,24,26,27,30,36
CO	3,8,17
4.3 μm	11
DF	28

FOURTH HARMONIC GENERATOR (FHG)

CO ₂	3,14,15,18,20,27
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OPTICAL PARAMETRIC OSCILLATOR (OPO)

Er:YALO	4,5
Er:Cr:YSGG	11,23,25,29,31,32,33,34,35, 37
Er:YAG	23,25,29

RECENT WESTERN WORK IN ZnGeP₂

C1 - P.A. Budni, K. Ezzo, P.G. Schunemann, S. Minnigh, J.C. McCarthy & T.M. Pollak, "2.8 micron pumped optical parametric oscillation in ZnGeP₂", pp.334-338 in **Advanced Solid State Lasers**, Hilton Head, South Carolina, 18-20 March 1991, editors George Dube and Lloyd Chase, Optical Society of America Proceedings, Vol. 10

PUMP: methane Raman shifted Nd:YAG 1.06 μ m \Rightarrow 2.8 μ m
max SRS output 2.1 mj

CRYSTAL: 6x6x18 mm, faces cut normal to <102> direction
 $\alpha(2.8\mu\text{m}) = 0.06 \text{ cm}^{-1}$, $\alpha(5.6\mu\text{m}) < 0.02 \text{ cm}^{-1}$

OPO RESULTS: Type I phase matching. For input, 2.1 mj, spot size 1.2 mm, 8-12 ns pulsewidth get peak power density up to 45 MW/cm², 150 μ j per pulse, for an optical efficiency of 7%
Threshold for OPO output, 18-20 MW/cm²

C2 - Norman P. Barnes, "Tunable mid-infrared sources using second-order nonlinearities", International Journal of Nonlinear Optical Physics, 1, 639-672 (1991)

internal phase-matching angles vs wavelength for 1.73 & 2.10 μ m pumps, range of incident angles 63 $^{\circ}$ for 1.73 μ m; 13 $^{\circ}$ for 2.10 μ m

C3 - P.A. Budni, P.G. Schunemann, M.G. Knights, T.M. Pollak & E.P. Chicklis, "Efficient, high average power optical parametric oscillator using ZnGeP₂", pp. 380-383 in **Advanced Solid State Lasers**, Sante Fe, New Mexico, 17-19 February 1992, editors Lloyd L. Chase & Albert A. Pinto, OSA Proceedings, Vol. 13

PUMP: 2 μ m from diode pumped, repetitively Q-switched Tm,Ho:YLF oscillator amplified by tungsten-lamp pumped Er,Tm,Ho:YLF amplifier. At 77K, 40 W average power output, pulse repetition frequency (PRF) 1-90 kHz, FWHM pulsewidth 15-525 ns. A 2-pass pre-amplifier output is 10 W: with 2 single pass stages added, the total power output > 40 W

CRYSTAL: 6x6x12 mm, boule grown along [112], $\alpha(2.05\mu\text{m})=0.26 \text{ cm}^{-1}$
Type I phase matching, $\theta = 55^{\circ}$.

OPO RESULTS: Using 10 W input: rep rate 2.5 kHz, 23 ns pulsewidth, 28.5% slope efficiency ; 4 kHz, 27 ns, 27.3%, highest overall efficiency, 18%; using 13 W input: 10 kHz, 28 ns, highest total power, 1.6 W
Continuous tunability from 3.45 - 5.05 μ m.

C4 - M. Knights & P. Budni, Tunable Mid-IR Laser Program, Final Technical Report, WL-TR-92-5031, August 1992, Wright Laboratory, Solid State Electronics Directorate, WL/ELOS, Contract F33615-89-C-1059

OPO

PUMP: 2 μm holmium YLF laser and amplifier, TEM₀₀ output average power of 44 Watts with pulsewidths of 25 ns @ 10 kHz
Pump repetition rates of 2.5, 4, 10, 20 and 30 kHz had pump pulsewidths of 23, 27, 28, 60 and 97 nsecs respectively

CRYSTAL: type I phase matching, $\theta = 55^\circ$, 6 x 6 x 12 mm
experimentally verified 2 μm pumped phase matching curve over 3.45-5.05 μm range energy slope conversion efficiency of 28.5% and overall conversion to 18% achieved @ 2.5 kHz; conversion efficiency of 27.3 % @ 4 kHz demonstrated high PRF operation: 2-30 kHz demonstrated 1.6 W average power @ 10 kHz for 13 W input: 1.4 W @ 20 kHz; 0.8 W @ 30 kHz

C5 - M. Knights & P. Budni, Characterization of AgGaSe₂ and ZnGeP₂ OPO's Pumped with High Power 2 Micron Lasers, Final Technical Report, WL-TR-93-5016, November 1992, Wright Laboratory, Solid State Electronics Directorate, WL/ELOS, Contract F33615-89-C-1059, modification P0007

OPO

PUMP: Cryogenically cooled, diode pumped Ho:YLF @ 2 μm
3W CW or Q-switched @ 1.5 kHz with 18-nsec FWHM
high power thermal effects used 20 W CW multimode tungsten pumped LN₂ oscillator

OPO RESULTS: absorption coefficient α_o is temperature dependent.

$$\alpha_o(300^\circ\text{K}) = 2 \times \alpha_o(77^\circ\text{K})$$

α_e shows no change with temperature
beam diameter 0.57 mm 1/e² points

For high loss ZGP crystals ($\alpha_o = 0.36\text{cm}^{-1}$), length 14.5 mm long
slope efficiency is 6% @ 300^oK and 27% @ 77^oK
with $\alpha_o = 0.26\text{ cm}^{-1}$ crystal, slope efficiency is 37.5%

C6 - P.G. Schunemann, P.A. Budni, M.G. Knights, T.M. Pollak, E.P. Chicklis, & C.L. Marquardt, "Recent advances in ZnGeP₂ mid-IR optical parametric oscillators", 131-133, Advanced Solid-State Lasers / Compact Blue-Green Lasers, New Orleans, Louisiana, 1-4 February 1993, Optical Society of America 1993 Technical Digest Series Vol.2; pp. 166-168 in **OSA Proceedings on Advanced Solid-State Lasers, Vol 15**, A.A. Pinto and T.Y. Fan, ed., (Optical Society of America, Washington, DC 1993)

OPO

PUMP LASER: diode pumped A/O Q-switched Tm:Ho:YLF @ 77 K
 $\lambda = 2.05\ \mu\text{m}$, TEM₀₀ mode, linearly polarized,
pulse width 18 ± 1 nsec (FWHM)
rep rate 1500 Hz, 1/e² diameter = 0.57 mm at center of Xtal

CRYSTALS: 6x6x11 mm³ & 4.5x4.5x14.6 mm³

Orientation $\Theta = 55^\circ$ for Type I phasematch @ 2.05 μm pump

Absorption coefficients @ 2.05 μm : ($\alpha_o=0.26$; $\alpha_e=0.58$) cm^{-1} &

($\alpha_o=0.38$; $\alpha_e=0.77$) cm^{-1} respectively @ RT

In situ: high loss crystal @ 2.05 μm measured

$\alpha_o=0.36\pm0.01$ cm^{-1} ; $\alpha_e = 0.78\pm0.01$ cm^{-1} @ RT;

$\alpha_o=0.17\pm0.01$ cm^{-1} ; $\alpha_e = 0.77\pm0.01$ cm^{-1} @ LNT

AR Coatings: each 2.05 μm & 3.5-5.0 μm

Laser damage threshold: > 1.2 J/cm²

OPO RESULTS: Collinearly pumped & doubly resonant

Low loss Xtal @ RT: total power conversion efficiency = 26%

with 679 mW threshold, 37% slope

maximum sustained power output: 585 mW @ pump

fluence ≈ 1.2 J/cm²

High loss Xtal : @ RT, threshold was 520 mW and slope $\approx 6\%$

@LNT, threshold ≈ 400 mW and slope efficiency $\approx 25\%$ after

realignment at LNT, threshold was 295 mW and slope efficiency

was 27%. Pumping with 2.3 W obtained OPO output of 552 mW,

an absolute power conversion efficiency of 24%

C7 - M.G. Knights, P.A. Budni, P.G. Schunemann, T.M. Pollak, & E.P. Chicklis, "Multi-watt mid-IR optical parametric oscillator using ZnGeP₂", 259-261, OSA Topical Meeting on **Advanced Solid State Lasers**, Salt Lake City, UT, 7-10 Feb 1994, OSA 1994 Technical Digest Vol.20

OPO

PUMP LASER: Q-switched Tm,Ho:YLF @2.06 μm + single-pass rod amplifier capable of 9 W, 6.5 W incident on OPO corresponding to 1.6 mJ/pulse @ 4 KHz. Focussed to beam waist of 600 μm , this yielded 1.15 J/cm² or 144 MW/cm² in 8 nsec.

CRYSTAL: 6x6x11 mm, $\Theta = 55^\circ$, $\alpha_o(2.05\mu\text{m}) = 0.26$ cm^{-1}

OPO RESULTS: Doubly resonant oscillator with double degeneracy point at 4.1 μm .

Highest average power achieved was 2.66 W with conversion efficiency of 40%. [3.3 W output shown at meeting].

Highest conversion efficiency was 46% @ 4.65 W drive level.

First 4 data points yield a slope efficiency of $\approx 65\%$ which extrapolates to a threshold of 1.32 W pump input.

C8 - C.L. Marquardt, W.T. Whitney, B.J. Feldman, G.C. Catella, D.S. Burlage, M.G. Knights, P.A. Budni, & P.G. Schunemann, "Thermal effects in zinc germanium phosphide optical parametric oscillators", 201, **CLEO'94, Summaries of papers presented at the Conference on Lasers and Electro-Optics**, Anaheim, CA, 8-13 May 1994, Optical Society of America 1994 Technical Digest Series Vol. 8

C9 - P.D. Mason, D.J. Jackson & E.K. Gorton
CO₂ laser frequency doubling in ZnGeP₂
Optics Comm. **110** 163-166 (1994)
Erratum Optics Comm. **114** 529 (1995)

SHG

PUMP: TEA CO₂ laser. single axial mode, 9P(20) transition, $\lambda = 9.55 \mu\text{m}$.

Typical peak power 14 kW, pulse duration 240 ns (FWHM)

CRYSTAL: 7.7x7.5 mm aperture, 1 cm long, cut 70° to c-axis

$\alpha(9.6 \mu\text{m}) = 0.56 \text{ cm}^{-1}$, $\alpha(4.8 \mu\text{m}) = 0.155 \text{ cm}^{-1}$

RESULTS: For 9.55 μm , phase match angle 67.7°

Maximum peak conversion efficiency was 8.1% for a pump internal intensity of 30 MW/cm² and energy density 18 J/cm²

C10 - Norman P. Barnes, Keith E. Murray, Mehendra G. Jani, & Thomas M. Pollak, WG5-1-3, 346-349, "ZnGeP₂ parametric amplifier", **Technical Digest- Advanced Solid State Lasers**, Memphis TN, 30 Jan- 2 Feb 1995, Optical Society of America
OPA

PUMP: Ho:Tm:Er:YLF @ 2.06 μm , pulse length ≈ 50 ns, 30 mJ

CRYSTAL: 9 mm long

SIGNAL: 3.39 μm from HeNe was absorbed in ZGP yielding gain of ≈ 0.7 single pass, small signal gain was 10 for 2.064 μm

C11 - J.M. Auerhammer, A.F.G. van der Meer, & P. W. van Amersfoort, "Efficient frequency doubling of picosecond pulses of a free-electron laser in ZnGeP₂", Paper CTul20, CLEO/QELS 95, Baltimore, MD, 23 May 1995, CLEO'95, Vol. 15, 1995 Technical Digest Series OSA, P.99, (p.87 Advance Program)

SHG

PUMP: free-electron laser, FELIX, $\lambda = 5.5$ -9.0 μm , high-power, short-pulse external efficiencies 49% - 15%

At $\lambda = 7.8 \mu\text{m}$, generated 14 mW of SHG average power, 0.8 MW peak power, pulse energy 0.8 μJ .

CRYSTAL: 7 mm long, Type I phase matching

C12 - J.M. Auerhammer, A.F.G. van-der-Meer, P.W. van-Amersfoort, Q.H.F. Vreken & E.R. Eliel, "Efficient frequency doubling of ps-pulses from a free-electron laser in ZnGeP₂", Optics Communications, **118** 85-89 (1995)

PUMP: FELIX (free electron laser for infrared experiments), p-polarized, 5-110 μm , 1 ps pulses at 1 GHz rep rate contained inside 'macropulse' typically 5 μs repeated every 200 ms. Average power of laser 10-100 mW. Experiments done at $\lambda = 5.5, 6.3, 7.8, 8.3$ & 9.0 μm . Measured external conversion efficiencies η_{ext} are respectively: 0.48, 0.46, 0.36, 0.29 & 0.12, for 1 MW incident power.

CRYSTAL: 7 mm long, Type I phase matching

APPENDIX

The following pages are a bibliography of nonlinear optics use of ZnGeP₂, listed alphabetically by first author.

ZnGeP2

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