

# Parametric generation of tunable infrared radiation in ZnGeP<sub>2</sub> and GaSe pumped at 3 μm

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Traveling-wave parametric generators with angular tuning with the use of ZnGeP<sub>2</sub> and GaSe crystals pumped by 100-ps pulses from an actively mode-locked Er laser ( $\lambda \approx 3 \mu\text{m}$ ) are reported. The continuous-tuning range achieved was 4–10 μm (ZnGeP<sub>2</sub>; length, 12 mm) and 3.5–18 μm (GaSe; length, 12 mm) in a type-I interaction, with a quantum conversion efficiency of a few percent. In the case of ZnGeP<sub>2</sub> (length, 42 mm) and type-II phase matching, the pump threshold was 0.35 GW/cm<sup>2</sup> and the quantum efficiency achieved was 17.6%, corresponding to an output peak power of 3 MW near 5–6 μm.

## INTRODUCTION

By the beginning of the 1970's both ZnGeP<sub>2</sub><sup>1</sup> and GaSe<sup>2</sup> crystals were proposed to be the most promising nonlinear materials for parametric devices in the middle IR region of the spectrum because of their wide transparency range and large second-order nonlinearities. However, the first demonstration of parametric generation in these crystals was reported only recently.<sup>3,4</sup> This is connected with considerable improvement in nonlinear-crystal-growth technology,<sup>5,6</sup> so that ZnGeP<sub>2</sub> and GaSe crystals of a few centimeters in length and <0.1 cm<sup>-1</sup> absorption at both pump and parametric wavelengths can now be grown. In addition, progress in the field of growing new crystalline laser media has led to the creation of efficient room-temperature flash-lamp-pumped Er lasers that emit light near the wavelength of 3 μm. These lasers have shown themselves to be extremely suitable for pumping parametric devices based on ZnGeP<sub>2</sub> and GaSe because their use entails small linear losses at the pump wavelength and an absence of two-photon absorption and because they fit the phase-matching conditions. In this paper I show that pumping of ZnGeP<sub>2</sub> and GaSe crystals with 100-ps pulses from an Er laser in a traveling-wave configuration (without a cavity) makes it possible to produce tunable radiation over almost the entire transparency range of these crystals, with the pump threshold for parametric generation being 100 times smaller than the crystal's damage threshold.

Optical parametric generators (OPG's), which use nonlinear processes of the lowest order, are now widely used to generate megawatt-power radiation over the whole optical range, especially in the mid IR, where tunable lasers are lacking. In this paper I also distinguish between traveling-wave parametric generators and parametric devices, which contain a resonator cavity [optical parametric oscillators (OPO's)]. The main advantages of OPG's are simplicity and small dimensions. To date, mid-IR tunable radiation has been obtained by use of parametric generators with various crystals: Elsaesser reported<sup>7</sup> a traveling-wave OPG in the range 1.2–8 μm with a proustite crystal Ag<sub>3</sub>AsS<sub>3</sub> and Nd:YAG laser ra-

diation as a pump source ( $\lambda = 1.06 \mu\text{m}$ , pulse duration  $t_p = 21 \text{ ps}$ , threshold pump intensity  $I_{\text{thr}} = 6 \text{ GW/cm}^2$ ). The energy conversion efficiency amounted to  $10^{-2}$ – $10^{-4}$ , and the OPG-pulse spectral bandwidth was  $10$ – $40 \text{ cm}^{-1}$ , with OPG-pulse duration being  $\sim 8 \text{ ps}$ . The IR traveling-wave parametric-generator conversion efficiency was significantly improved when an AgGaS<sub>2</sub> crystal was used. Two crystals (length  $L = 1.5$  and  $3 \text{ cm}$ ) were pumped by picosecond Nd:YAG laser radiation, and a conversion efficiency  $\eta = 10^{-1}$ – $10^{-3}$  was achieved<sup>8</sup> with output radiation in the range of 1.2–10 μm and a pumping threshold  $I_{\text{thr}} = 3 \text{ GW/cm}^2$ . A high-efficiency OPO was obtained by use of a CdSe crystal<sup>9</sup>; the efficiency of power conversion to parametric radiation with  $\lambda_{\text{signal}} = 2.26$ – $2.23 \mu\text{m}$  and  $\lambda_{\text{idler}} = 9.8$ – $10.4 \mu\text{m}$  reached 40%. As a pump source, Nd:YAG laser radiation was used with  $\lambda = 1.833 \mu\text{m}$ ,  $\tau = 30 \text{ ns}$ , and pump intensity  $I_0 = 2 \times 10^7 \text{ W/cm}^2$ . With pumping by Dy:CaF<sub>2</sub> laser radiation ( $\lambda = 2.36 \mu\text{m}$ ,  $\tau = 40 \text{ ns}$ ) an even larger tuning range<sup>10</sup> was obtained: 7.9–13.7 μm. The conversion efficiency was 15% at  $I_0 = 10^7 \text{ W/cm}^2$ , and crystal length was 30 mm. CdSe crystals, however, can only be operated over limited tuning ranges: broadband continuous tuning is not possible in this material because of phase-matching limitations. Effective generation of parametric radiation in the OPO based on an AgGaSe<sub>2</sub> crystal<sup>11</sup> has been reported for the wavelength range of 2.65–9.02 μm. In this study Q-switched Ho:YLF laser radiation ( $\lambda = 2.05 \mu\text{m}$ ) was used as a pump source. The crystal length was 18–21 mm; the conversion efficiency amounted to 18% at an output power  $P = 100 \text{ kW}$  and  $\tau = 30 \text{ ns}$ . Recently the full continuous-tuning range between 2.5 and 12.5 μm of a 2.05-μm-pumped AgGaSe<sub>2</sub> OPO was achieved with a single angle-tuned crystal,<sup>12</sup> with output OPO energies varying between 30 μJ and a few millijoules.

## SOME FEATURES OF ZnGeP<sub>2</sub> AND GaSe CRYSTALS

The distinctive features of ZnGeP<sub>2</sub> and GaSe crystals, proposed as materials for nonlinear optics,<sup>1,2</sup> are a wide trans-

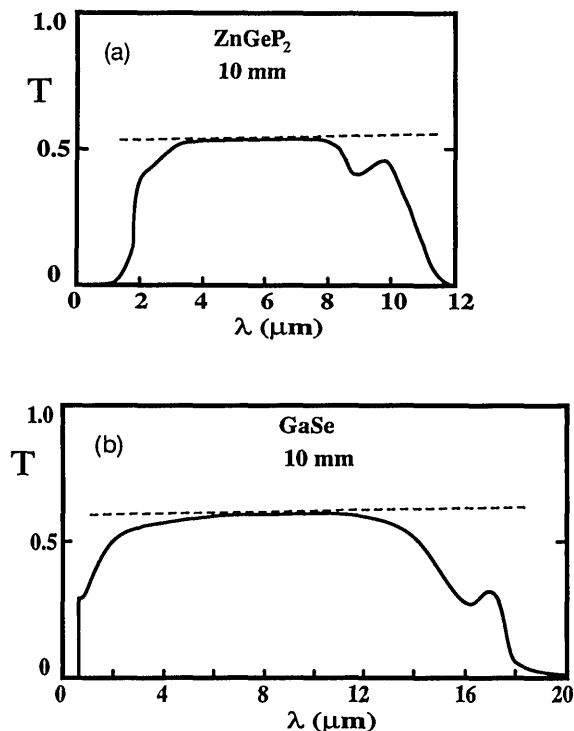


Fig. 1. Transmission spectra taken at room temperature. (a)  $\text{ZnGeP}_2$  ( $L = 10$  mm). (b)  $\text{GaSe}$  ( $L = 10$  mm). Dashed curves, Fresnel losses.

mission range (Fig. 1) spreading beyond  $10 \mu\text{m}$  in the IR and extremely high second-order nonlinearities. Semiconductor uniaxial crystals  $\text{ZnGeP}_2$  (point group  $\bar{4}2m$ ) and  $\text{GaSe}$  (point group  $\bar{6}2m$ ) both have band gaps in the visible and are grown by use of the Bridgman–Stockbarger method. Table 1 summarizes some properties of  $\text{ZnGeP}_2$  and  $\text{GaSe}$  crystals compared with other crystals that are suitable for OPG's in the mid IR. One can see that the nonlinear figure of merit  $d^2/n^3$  for  $\text{ZnGeP}_2$ , for instance, is 80 times higher than the corresponding value for  $\text{LiNbO}_3$  and 19 times higher than that for  $\text{AgGaS}_2$ .

Thus far  $\text{ZnGeP}_2$  crystals have been especially used in the following nonlinear optical-frequency conversion processes in the mid IR: upconversion of  $\text{CO}_2$  laser light into the near-IR range<sup>15</sup> through phase-matched mixing of 10.6- and 1.06- $\mu\text{m}$  radiation, sum-frequency generation of CO and  $\text{CO}_2$  laser radiation,<sup>16</sup> and efficient second-harmonic generation (SHG) of CO (Ref. 17) and  $\text{CO}_2$  (Ref. 18) laser radiation (in the latter case an efficiency of 49% was achieved). Parametric generation in a traveling-wave geometry in the 5–6.3- $\mu\text{m}$  region was performed with 17.6%

quantum efficiency by use of type-II phase matching and Er lasers ( $\lambda \approx 3 \mu\text{m}$ ) as a pump source.<sup>3,14</sup> A type-I OPO was obtained<sup>19</sup> in  $\text{ZnGeP}_2$  ( $l = 13$  mm) by use of nanosecond pumping with  $\lambda = 2.8 \mu\text{m}$ . The 2.8- $\mu\text{m}$  light (2.1-mJ pulse energy, 8–12-ns duration) was generated by Raman shifting Q-switched Nd:YAG laser radiation to the second Stokes in pressurized methane gas. The continuous-tuning range achieved was 4.7–6.9  $\mu\text{m}$ , with a 7% overall efficiency. A type-I traveling-wave OPG in  $\text{ZnGeP}_2$  was demonstrated<sup>4</sup> with 100-ps pulses from the Er:YAG laser ( $\lambda = 2.94 \mu\text{m}$ ) as a pumping source, which had an efficiency of a few percent and the wide tuning range of 4–10  $\mu\text{m}$ . Optical parametric oscillation that was highly efficient (18%), of high average power (1.6 W), and tunable in the range of 3.45–5.05  $\mu\text{m}$  was demonstrated quite recently<sup>20</sup> in a 12-mm-long  $\text{ZnGeP}_2$  crystal pumped with a high-pulse-repetition-frequency (2.5–10-kHz) Ho:YLF laser with  $\lambda = 2.05 \mu\text{m}$ .

$\text{GaSe}$  crystals have been successfully used for the SHG of  $\text{CO}_2$ , CO, and Dy: $\text{CaF}_2$  (2.36- $\mu\text{m}$ ) laser radiation,<sup>2</sup> for the upconversion of  $\text{CO}_2$  and CO laser radiation into the visible range,<sup>21</sup> for difference-frequency generation in the region of 9–19  $\mu\text{m}$  by use of Nd:YAG and IR dye-laser radiation,<sup>22</sup> and for 7–16- $\mu\text{m}$  radiation from Nd:YAG and F<sup>-</sup>-center lasers.<sup>23</sup> The signal and idler waves from a Nd:YAG-laser-pumped  $\text{LiNbO}_3$  parametric oscillator were mixed in  $\text{GaSe}$ , and a difference frequency that was tunable in the 4–8- $\mu\text{m}$  range was produced.<sup>24</sup> SHG of  $\text{CO}_2$  laser radiation was achieved with a 9% efficiency, and it was shown that both  $\text{GaSe}$  and  $\text{ZnGeP}_2$  crystals could be effectively used for purposes of  $\text{CO}_2$  laser frequency doubling.<sup>25</sup> The first OPG that used  $\text{GaSe}$ <sup>4</sup> was demonstrated in a traveling-wave geometry by means of 100-ps pulses from an Er:YAG laser (2.94  $\mu\text{m}$ ) with the tuning range covering 3.5–18  $\mu\text{m}$ . Lately, pulses of 1-ps duration that were tunable between 6 and 18  $\mu\text{m}$  were generated<sup>26</sup> by difference-frequency mixing Nd:glass laser pulses and IR dye-laser pulses in a  $\text{GaSe}$  crystal. The energy of mid-IR pulses was of the order of microjoules, and the photon conversion efficiency was  $\sim 2\%$ .

### 3- $\mu\text{m}$ Er LASERS AS PUMPING SOURCES

In the past decade there have been extensive studies related to the development of 3- $\mu\text{m}$  solid-state lasers based on Er<sup>3+</sup>-doped crystals, such as YAG, YSGG, YLF,  $\text{YAlO}_3$ , and  $\text{CaF}_2$ . These lasers are well suited as pumping sources for parametric devices based on  $\text{ZnGeP}_2$  and  $\text{GaSe}$  crystals because of the good transparency of these nonlinear crystals (absorption coefficient  $< 0.1 \text{ cm}^{-1}$ ) and the

Table 1. Some Properties of Mid-IR Nonlinear Crystals

Property	Crystal <sup>a</sup>						
	$\text{LiNbO}_3$	$\text{Ag}_3\text{AsS}_3$	$\text{AgGaS}_2$	$\text{AgGaSe}_2$	$\text{CdSe}$	$\text{ZnGeP}_2$	$\text{GaSe}$
Transparency range ( $\mu\text{m}$ )	0.33–5.5	0.6–13	0.5–13	0.71–18	0.75–20	0.74–12	0.65–18
$n_0$ (near $\lambda = 3 \mu\text{m}$ )	2.16	2.75	2.42	2.65	2.44	3.13	2.85
$n_e$	2.09	2.54	2.36	2.62	2.46	3.17	2.46
Nonlinearity $d_{\text{eff}}$ ( $10^{-12}$ m/V)	5.44	18	13.4	33	18	88	54.4
Nonlinear figure of merit, $d^2/n^3$ ( $10^{-24}$ m <sup>2</sup> /V <sup>2</sup> )	3.1	17.6	13.2	59.5	22	247.8	127.8

<sup>a</sup>See Refs. 13 and 14 for  $\text{ZnGeP}_2$  and Ref. 13 for all other crystals.

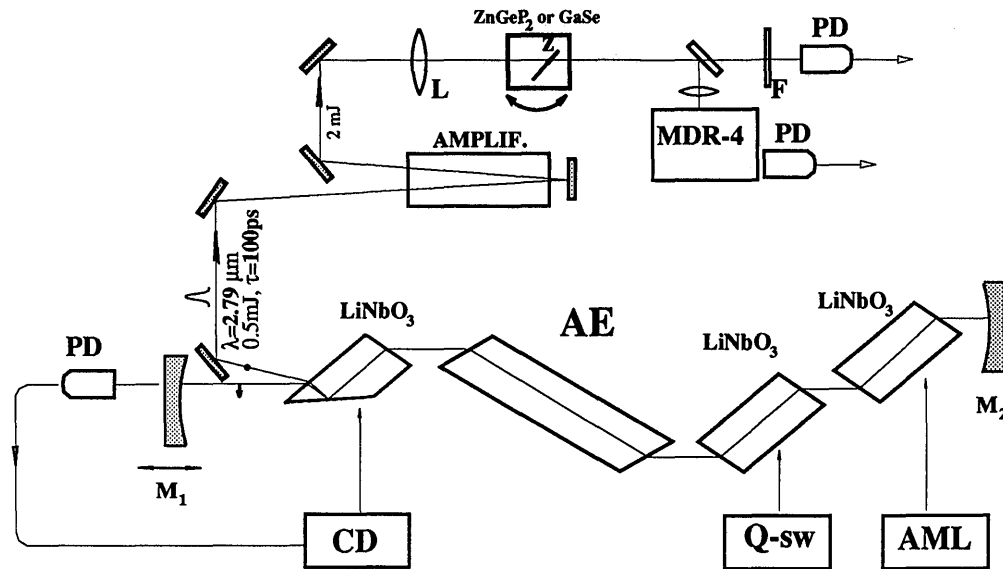


Fig. 2. Experimental setup:  $M_1$ , dielectric 99% mirror;  $M_2$ , Cu mirror; AE, laser active element; AMPLIF., laser amplifier; AML, active mode-locking circuit; Q-sw, Q-switching circuit; CD, cavity-dumping circuit; PD, photodetectors; L, one or two  $\text{CaF}_2$  lenses; F, InAs filter; MDR-4, monochromator.

small amount of Stokes losses (compared with  $1.06\text{-}\mu\text{m}$ -pump radiation) resulting from the smaller difference between pump and idler photon energies (and leading to a larger absolute conversion efficiency at a given quantum efficiency), the absence of two-photon absorption, and the existence of the phase-matching conditions for three-wave interactions in the whole transparency region.

The laser used in this study was based on flash-lamp-pumped  $\text{Er}^{3+}:\text{YAG}$  ( $\lambda = 2.94\ \mu\text{m}$ )<sup>27</sup> or  $\text{Er}^{3+}:\text{Cr}^{3+}:\text{YSGG}$  crystal ( $\lambda = 2.79\ \mu\text{m}$ )<sup>28</sup> with typical dimensions of  $\text{Ø}4 \times (80\text{--}110)$  mm. A schematic of an actively mode-locked Er laser is shown in Fig. 2. The laser resonator was formed by use of two 99% 2.5-m concave mirrors. To eliminate Fresnel losses and mode-selection effects, all the optical elements within the laser cavity (the active element and the three  $\text{LiNbO}_3$  electro-optical elements) were put at the Brewster angle. Brewster faces also functioned as partial polarizers.  $\text{LiNbO}_3$  crystals, in which light traveled along the  $z$  axis, were controlled by three separate high-voltage electronic drivers to perform Q switching, mode locking, and cavity dumping. In the case of mode locking, a 60-MHz, 3-kV amplitude signal was applied along the  $x$  axis of the  $3\ \text{mm} \times 6\ \text{mm} \times 35\ \text{mm}$  crystal, and the laser cavity length was adjusted with the use of a micrometer screw within the  $\pm 30\text{-}\mu\text{m}$  accuracy to fit the resonance. In the cavity-dumping element CD there is one internal reflection, in which the angle depends on polarization. For resonant polarization both input and output faces are approximately at the Brewster angle. After applying a step-like high-voltage (5-kV) pulse, with  $\sim 1\text{-ns}$  front edge, along the  $x$  axis of the  $3\ \text{mm} \times 6\ \text{mm} \times 30\ \text{mm}$  specially shaped  $\text{LiNbO}_3$  crystal, the polarization of the light changes by 90 deg, and the beam emerges from the crystal and cavity at an angle differing by 6 deg from its initial direction. Single pulses extracted from the resonator had a duration of  $100 \pm 10\ \text{ps}$  (close to the Fourier-transform spectral width), a spatial mode of  $\text{TEM}_{00}$ , and an energy of  $\sim 0.5\ \text{mJ}$ . After passing through a two- or three-pass amplifier (which was used only in the case of  $\text{Er}^{3+}:\text{Cr}^{3+}:\text{YSGG}$  active media with  $\lambda = 2.79\ \mu\text{m}$ ), the pulse energy

amounted to 2–4 mJ. The laser repetition rate was 1–2 Hz, and typical flash-lamp pump energy was 10–20 J for the oscillator and 100 J for the amplifier, in the case of the  $\text{Er}^{3+}:\text{Cr}^{3+}:\text{YSGG}$  crystal, and 50–100 J for the  $\text{Er}^{3+}:\text{YAG}$  oscillator.

## EXPERIMENTAL SETUP

A traveling-wave (mirrorless) OPG with an angle tuning was used in these experiments. The main advantage of this scheme is that it requires no cavity. It is hardly possible to make dichroic mirrors for an OPO that are suited for the whole tuning range, and therefore changing the mirrors is inevitable in the process of wavelength tuning. A traveling-wave scheme became possible here because of very high ( $>1\ \text{GW}/\text{cm}^2$ ) beam intensities of the pump light at moderate energies, with an energy fluence, however, that was much lower than the crystal-damage threshold. Ultrashort pulses from the Er laser described above were focused onto the nonlinear crystal by use of one or two  $\text{CaF}_2$  lenses. In the case of  $\text{ZnGeP}_2$ , I used  $f = 25\ \text{cm}$  for the focusing lens L (for type-I phase matching) or a  $4\times$  telescope formed by two lenses of 10- and 2.5-cm focal lengths (for type-II phase matching). For  $\text{GaSe}$  I used the combination of a 30-cm spherical lens and a 4-cm cylindrical lens to focus laser radiation mostly perpendicular to the  $(\mathbf{k}, \mathbf{z})$  plane because of the significant walk-off, reaching 0.56 mm in the 12-mm crystal. The OPG output signal (Fig. 2) was monitored with a Ge: Au (77 K) detector or a calibrated pyroelectric detector; an InAs filter was used to cut down the pump-laser light (cutoff wavelength,  $3.7\ \mu\text{m}$ ). The OPG spectrum was analyzed with the use of an MDR-4-grating 0.25-m monochromator.

## EXPERIMENTAL RESULTS WITH $\text{ZnGeP}_2$ AND $\text{GaSe}$

I studied two  $\text{ZnGeP}_2$  crystals of exceptional optical quality with respect to state-of-the-art crystal growth, with orientations of  $\theta = 47\ \text{deg}$  and  $\theta = 84\ \text{deg}$ , that were suited

for type-I and type-II phase matching, respectively. The type-I interaction is effective for obtaining frequency tuning in the entire transmission range of the ZnGeP<sub>2</sub> crystal, but it is characterized by larger OPG linewidths (see Fig. 3 below) than occur in the case of type-II phase matching, especially near degeneracy. The effective nonlinearity is given by the formulas<sup>13</sup>

$$\begin{aligned} \text{Type I (o-ee)} \quad d_{\text{eff}} &= d_{36} \sin(2\theta)\cos(2\varphi), \\ \text{Type II (o-eo)} \quad d_{\text{eff}} &= d_{36} \sin(\theta)\sin(2\varphi). \end{aligned} \quad (1)$$

For the second crystal the azimuthal angle  $\varphi = 31$  deg (see Table 2 below) was not optimal; it should be 45 deg to give the maximum  $d_{\text{eff}}$ .

For GaSe, optically perfect surfaces were obtained by cleavage along (001) planes ( $z$ -cut crystal). At present it is not possible to polish GaSe at arbitrary angles (only  $z$  cut is available) because of the crystal's flaky nature, but because of the crystal's large birefringence (Table 1), the internal phase-matching angles are small, and most of the interactions can be achieved by use of the  $z$  cut. The effective nonlinear coefficients depend on the polar ( $\theta$ ) and azimuthal ( $\varphi$ ) angles in the following way<sup>13</sup>:

$$\begin{aligned} \text{Type I (e-oo)} \quad d_{\text{eff}} &= d_{22} \cos(\theta)\sin(3\varphi), \\ \text{Type II (e-oe)} \quad d_{\text{eff}} &= d_{22} \cos^2(\theta)\cos(3\varphi). \end{aligned} \quad (2)$$

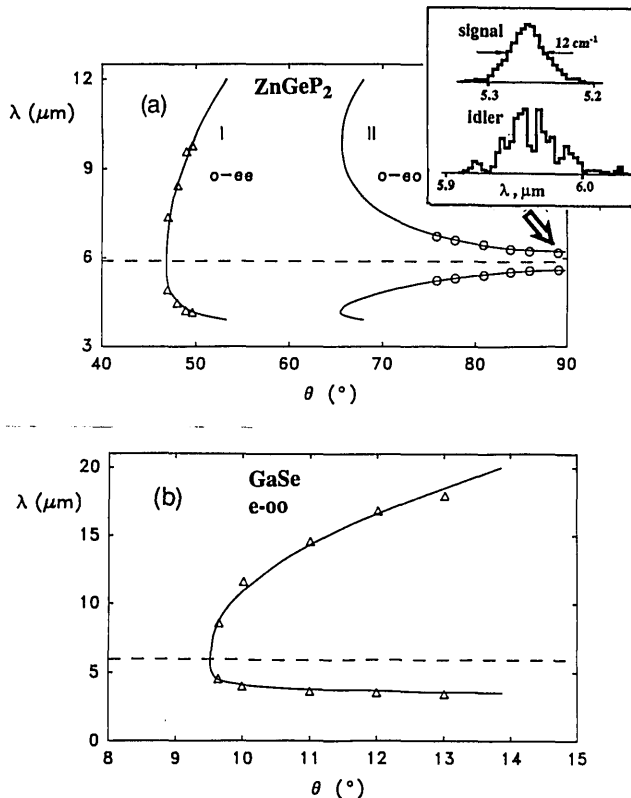


Fig. 3. Angular-tuning curves for a pump with  $\lambda = 2.94 \mu\text{m}$ . (a) ZnGeP<sub>2</sub> (types I and II); solid curves, calculated from data in Ref. 29. (b) GaSe (type I); solid curve, calculated from data in Ref. 2. Inset: spectral characteristics of the OPG at the signal and idler frequencies for the type-II phase-matched ( $\theta = 84$  deg) ZnGeP<sub>2</sub> crystal pumped by a 2.79-mm laser. At the idler frequency the results were affected by atmospheric absorption ( $L \approx 1.5$  m).

The type-I interaction for GaSe was chosen for this experiment because in this case smaller angles  $\theta$  are necessary to obtain phase matching over the entire tuning range. To obtain the highest effective nonlinearity, the proper azimuthal angle  $\varphi$  selection is important. According to the crystal symmetry, there are six  $\varphi$ -angle orientations maximizing  $d_{\text{eff}}$  for a  $z$ -cut crystal. For the type-I interaction,  $\varphi = \pm 90$  deg can be used, corresponding to  $|\sin(3\varphi)| = 1$ . This means that the crystalline  $y$  axis should lie in the  $(\mathbf{k}, z)$  plane, where  $\mathbf{k}$  is a beam wave vector. On the lateral surface of the crystal, one can see crystal-growth defects in the form of an equilateral triangle by use of an optical microscope. The direction perpendicular to any side of these triangles may be taken as a  $y$  axis of the GaSe crystal.

Figure 3 shows experimental and theoretical tuning curves for both crystals, corresponding to the pump wavelength of  $2.94 \mu\text{m}$ . There is fairly good agreement between experimental and calculated angular-tuning curves at both pump wavelengths  $\lambda = 2.94$  and  $2.79 \mu\text{m}$ . Most of the experimental results are given in Table 2.

The experimentally measured OPG spectral width  $\Delta\nu$  is presented in Table 2 (see also Fig. 3 inset for ZnGeP<sub>2</sub>). It is in reasonably good agreement (within a factor of 2) with calculated spectral width, corresponding to the condition  $\Delta\kappa(L) = \pm\pi$ , where  $\Delta\kappa(L)$  is a phase mismatch. For type-I phase matching the OPG linewidth is larger than in type II, especially near degeneracy.

The walk-off length is given by  $\rho L$ , where  $\rho$  is a Poynting-vector walk-off angle<sup>13</sup>  $\rho \approx (\Delta n/n)\sin(2\theta)$ ;  $\Delta n$  is a birefringence value and  $n$  is the mean refractive index. The effective crystal length is calculated here, taking into account the walk-off effect and linear absorption.

The OPG threshold intensity (i.e., the intensities incident upon the crystal) was as small as 0.5 and 0.35  $\text{GW}/\text{cm}^2$  in ZnGeP<sub>2</sub> and an order of magnitude higher in GaSe, mostly because of the smaller effective length in the latter. A threshold here is broadly regarded as a start of the stimulated process. A properly designed geometry of the focusing optics would reduce the threshold to  $<1 \text{ GW}/\text{cm}^2$  for a 12-mm-long GaSe crystal, since the nonlinear figures of merit differ only by a factor of 1.9 for these two crystals.

A single-pass power gain in the case of superfluorescence (single-pass) parametric emission for zero-phase mismatch is  $1/4 \exp(2\Gamma L)$ , where  $\Gamma$ , the gain increment, is given by<sup>30</sup>

$$\Gamma^2 = \frac{2\omega_1\omega_2 d_{\text{eff}}^2 I_{\text{pump}}}{n_1 n_2 n_3 \epsilon_0 c^3}. \quad (3)$$

Here  $\omega_1$  and  $\omega_2$  are idler and signal frequencies;  $n_1$ ,  $n_2$ , and  $n_3$  refer to idler, signal, and pump waves, respectively. To achieve the threshold for a traveling-wave OPG, a certain value of  $\Gamma l$  must be achieved, with the quantum-noise seeding value playing a minor role. This is why I compared the values of  $(d_{\text{eff}}^2/n^3)L_{\text{eff}}^2 I_{\text{thr}}$  (Table 2), which should be approximately the same for all the crystals. The close values (within a factor of 2) of this term for ZnGeP<sub>2</sub> and GaSe show that the experimental results are in good agreement with the values of nonlinear coefficients taken from the literature and that the OPG thresholds are close to those predicted.

The dependence of the OPG energy for the ZnGeP<sub>2</sub> crystal ( $L = 42$  mm) and  $\theta = 84$  deg (type-II phase matching)

**Table 2. Experimental Results with the ZnGeP<sub>2</sub> and GaSe OPG's**

Property	Crystal		
	ZnGeP <sub>2</sub> ( $n_o < n_e$ )		GaSe ( $n_o > n_e$ )
Interaction	Type I (o-ee) <sup>a</sup>	Type II (o-eo)	Type I (e-oo)
Crystal orientation	$\theta = 47$ deg, $\varphi = 0$ deg	$\theta = 84$ deg, $\varphi = 31$ deg	$\theta = 0$ deg, $\varphi = 90$ deg
Effective nonlinearity, $d_{\text{eff}}$ ( $10^{-12}$ m/V)	88	77.5	52.8
Range of $\theta$ variation	47–49.55 deg	76–90 deg	9.5–13 deg
Tuning range achieved ( $\mu\text{m}$ )	4–10	5.2–5.6 6.2–6.7	3.5–18
OPG linewidth ( $\text{cm}^{-1}$ )	540 ( $\lambda_i = 5.9 \mu\text{m}$ ) 80 ( $\lambda_i = 8 \mu\text{m}$ ) 30 ( $\lambda_i = 10 \mu\text{m}$ )	12 ( $\lambda_i = 6.7 \mu\text{m}$ )	850 ( $\lambda_i = 5.9 \mu\text{m}$ ) 63 ( $\lambda_i = 10 \mu\text{m}$ ) 10 ( $\lambda_i = 15 \mu\text{m}$ ) 6 ( $\lambda_i = 18 \mu\text{m}$ )
Pump beamwaist parameter $w_0$ (mm)	0.28	0.1	Ellipse $0.13 \times 0.28$
Crystal length $L$ (mm)	12	42	12
Walk-off (mm)	0.14 ( $\theta = 48$ deg)	0.11 ( $\theta = 84$ deg)	0.56 ( $\theta = 10$ deg)
Effective length $L_{\text{eff}}$ (mm)	12	19	5
OPG threshold intensity $I_{\text{thr}}$ ( $\text{GW}/\text{cm}^2$ )	0.5	0.35	6
$(d^2/n^3) L_{\text{eff}}^2 I_{\text{thr}}$ (a. u. <sup>b</sup> )	17.9	24.1	18.1
$I_{\text{max}}$ used ( $\text{GW}/\text{cm}^2$ )	6.5	30	12
Max. OPG quantum efficiency	3%	17.6%	1%
OPG divergence outside the crystal (rad)	0.1	0.11	0.1
$I_{\text{dam}}$ ( $\text{GW}/\text{cm}^2$ )	6.5	30	30

<sup>a</sup>o, ordinary; e, extraordinary.

<sup>b</sup>Arbitrary units.

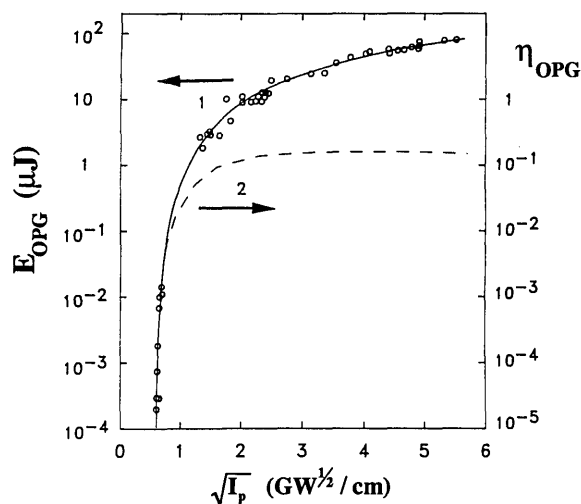


Fig. 4. Dependences of OPG output energy  $E_{\text{OPG}}$  (curve 1) and quantum efficiency  $\eta$  (curve 2) on the 2.79- $\mu\text{m}$ -laser pump intensity for ZnGeP<sub>2</sub> (42 mm, type II). Curve 2 was derived from curve 1.

at  $\lambda_{\text{pump}} = 2.79 \mu\text{m}$  ( $\lambda_{\text{signal}} = 5.25 \mu\text{m}$ ,  $\lambda_{\text{idler}} = 5.96 \mu\text{m}$ ) and of quantum efficiency  $\eta_{\text{OPG}}$  on the pump intensity  $I_p$  are plotted in Fig. 4. The OPG energy (signal + idler) was measured by use of a calibrated pyroelectric detector that had weak wavelength selectivity. In the case of small OPG energies, only the signal (high-frequency) OPG wave was measured by use of Ge:Au photoresistance (laser radiation was cut off by an InAs filter). For  $I_p > 7.8 \text{ GW}/\text{cm}^2$  the laser conversion efficiency into both parametric branches exceeded 16%, whereas for  $I_p = 16 \text{ GW}/\text{cm}^2$  it reached its maximum of 17.6%. When  $I_p$  was varied by

2 orders of magnitude the OPG signal changed by almost 6 orders. The OPG quantum efficiency could be further improved by antireflection coating the surfaces, to the extent that in the present scheme the surfaces were not coated and the Fresnel losses were of the order of 45%. The spatial extent of the pump-laser pulse, corresponding to  $\tau = 100$  ps, was only  $c\tau/n \approx 1$  cm within the crystal, which is less than the crystal's length, so that Fresnel reflection cannot function as a partial resonator feedback. Another reason is that the ZnGeP<sub>2</sub> crystal's faces were not parallel ( $\sim 1$ -deg angle).

The surface-damage threshold of the ZnGeP<sub>2</sub> crystal was  $30 \text{ GW}/\text{cm}^2$  (energy fluence,  $3 \text{ J}/\text{cm}^2$ ), which was 100 times higher than the laser intensity at the OPG threshold. The bulk-damage threshold was  $>30 \text{ GW}/\text{cm}^2$ . The laser-damage thresholds  $I_{\text{dam}}$  for 100-ps, 3- $\mu\text{m}$  pulses were approximately the same for the ZnGeP<sub>2</sub> and GaSe crystals, except that, in the former, crystal surface damage occurred first and, in the latter, volume damage was observable. For the 12-mm-long ZnGeP<sub>2</sub> crystal the lower surface-damage threshold was due to imperfect polishing. I used a single-crystal geometry in the OPG experiments; in a double-crystal traveling-wave scheme, in which two parametric crystals are separated by a distance of 30–50 cm, the OPG divergence might be sufficiently diminished, thus reducing spectral width.

## CONCLUSION

Pumping of ZnGeP<sub>2</sub> and GaSe crystals with 100-ps Er laser pulses ( $\lambda \approx 3 \mu\text{m}$ ) has generated intense continuously tunable radiation in the ranges of 4–10  $\mu\text{m}$  (ZnGeP<sub>2</sub>) and 3.5–18  $\mu\text{m}$  (GaSe) with a frequency tuning practically as

high as the long-wave transmission limit of these crystals. The quantum efficiency achieved (17.6% for ZnGeP<sub>2</sub>) reaches the highest reported value for mid-IR traveling-wave OPG's. The output peak power in the region of 5–6 μm reached 3 MW. The main feature of the traveling-wave scheme used in this study is its simplicity: the whole tuning range can be covered with a single crystal without the use of a resonator cavity. At the same time, the OPG threshold for ZnGeP<sub>2</sub> of 0.35 GW/cm<sup>2</sup>, which is the lowest reported threshold for traveling-wave OPG's, is 100 times lower than the crystal's optical-damage threshold. This is possible because of the improved optical quality of the crystals, their large nonlinear figure of merit, and the use of short 3-μm pumping pulses. These new sources of intense continuously tunable mid-IR pulses can be successfully applied in the fields of molecular spectroscopy, atmospheric monitoring, and solid-state physics and with different types of resonance interaction of radiation with matter.

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