Femtosecond parametric generation in ZnGeP$_2$

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We report traveling-wave optical parametric generation in short (2-mm) ZnGeP$_2$ samples with reduced anomalous absorption, using femtosecond pump pulses near 2 $\mu$m. The signal and the idler waves generated could be tuned from 2.5 to 10 $\mu$m, and they extend the tunability of the $\beta$-barium borate optical parametric generator used as a pump source to the mid-infrared. At a single-pass internal conversion efficiency of 2.5% we estimate pulse durations of 75 fs (signal near 3 $\mu$m) and 200 fs (idler near 6 $\mu$m).

Received November 13, 1998

OCIS codes: 190.4970, 190.7110, 320.7110, 190.2620, 190.4400.

ZnGeP$_2$ is transparent from 0.7 to 12 $\mu$m and possesses the highest nonlinearity ($d_{14} = 75$ pm/V) of all commercially available birefringent nonlinear optical materials. These properties are very attractive for traveling-wave optical parametric generation by use of short pump pulses to produce tunable signal and idler pulses in the mid infrared (MIR). Earlier work on optical parametric generators (OPG’s) with ZnGeP$_2$ was based on mode-locked Er:Cr:YSGG (2.8-$\mu$m) or Er:YAG (2.94-$\mu$m) lasers delivering 100-ps-long pump pulses.$^{1,2}$ A lower limit of $\approx 2.5$ $\mu$m on the pump wavelength in these experiments with 4-cm long ZnGeP$_2$ samples was imposed by the anomalous near-band-edge absorption in the near infrared (NIR).$^3$ Most recently, 1-ps MIR pulses were generated with a ZnGeP$_2$ OPG employed in a cascaded scheme with pumping by the idler (2.9–3.5 $\mu$m) from a seeded MgO:LiNbO$_3$ OPG.$^4$ In this case a 1-cm-long ZnGeP$_2$ crystal was used, and it is clear that when even-shorter pump pulses are used the group walk-off effects become the restricting factor for the crystal length and the residual NIR absorption becomes a less-stringent limitation.

Here we present what are believed to be the first experiments with femtosecond pumping of ZnGeP$_2$ in the NIR. Although we succeeded in extending the operation regime of our MgO:LiNbO$_3$ OPG to the femtosecond time scale,$^7$ pumping at shorter wavelengths in the NIR is highly desirable because conventional and more-powerful $\beta$-barium borate–based OPG’s can be used. We demonstrate here that 2-mm-long samples of ZnGeP$_2$ provide 2.5% internal parametric conversion efficiency in a single pass when one uses pump wavelengths from 1.9 to 2.1 $\mu$m and can cover spectrally (signal and idler) the 2.5–10-$\mu$m MIR range at femtosecond durations.

As a pump source we used a commercial NIR OPG (IR-OPA; Clark) that in turn was pumped at a 1-kHz repetition rate by 400-$\mu$J 100-fs pulses from a Ti:sapphire regenerative amplifier (TRA-1000; Clark) that were tunable near 800 nm. Since type II interaction in $\beta$-barium borate takes place in the NIR OPG the signal and the idler are perpendicularly polarized, allowing continuous tuning from 1.15 to 2.5 $\mu$m at 120–140-fs pulse durations and single-pulse energies ranging from 10 to 40 $\mu$J. The idler (or signal) beam was focused by a 200-mm best-shape lens, and the ZnGeP$_2$ samples were positioned before the focal point. Spatial walk-off effects were negligible in the geometry used. Care was also taken to extract only the idler or the signal beam and to suppress any visible radiation coming out of the NIR parametric generator by use of color glass long-wave-pass filters and polarizers. For the energy measurement of both the NIR pump pulses and the MIR signal and idler pulses from the ZnGeP$_2$ OPG we used a pyroelectric detector with an amplifier providing a sensitivity of $\approx 1$ nJ. For separation of the MIR signal and idler pulses, reflective long-wave-pass filters (Northumbria Optical Coatings, Ltd.) were applied. The spectral properties of the MIR radiation that was collected by a 10-cm lens were characterized with a 0.5-m monochromator (150-line/mm grating blazed at 4 $\mu$m) in combination with a nitrogen-cooled HgCdTe photodetector or a PbS photodiode.

The three samples of ZnGeP$_2$ had an aperture of 6 mm $\times$ 6 mm and thickness $L = 2$ mm. The samples were uncoated and cut at $\theta = 52.5^\circ, 55^\circ$, and 67$^\circ$. The azimuthal angle $\varphi$ is 0$^\circ$ for type I (ee $\rightarrow$ o) phase matching, which resulted in an effective nonlinearity $d_{\text{eff}} = d_{14} \sin 2\varphi$. The samples were cut from a boule grown at Sanders by the horizontal gradient freeze technique$^6$ that exhibited exceptionally low residual NIR absorption (Fig. 1), $<0.05$ cm$^{-1}$ at 2.05 $\mu$m.$^3$ Thus the absorption losses for a pump wavelength $\lambda_P = 2.05$ $\mu$m do not exceed 1% in our case. Previously the use of crystals of such high quality resulted in substantial improvement of the performance (threshold and output power) of Ho:YLF laser ($\lambda_P = 2.05$ $\mu$m) pumped nanosecond OPO’s.$^3$ The low absorption losses at the pump wavelength are therefore an additional argument for trying pumping of ZnGeP$_2$ in the NIR with $\lambda_P > 1.5$ $\mu$m, where two-photon absorption is expected to be unimportant. In principle, both type I and type II phase matching could be used with ZnGeP$_2$. Type II phase matching is in any case preferable in the $>1$-ps regime, since it provides much narrower and nearly wavelength-independent...
bandwidths. These bandwidth characteristics are a consequence of the fact that in both type I and type II interactions the spectral acceptance determined by the crystal length cannot be restricted to the Fourier limit by use of longer crystals, because the crystal sizes available at present are limited to lengths of \( \sim 4 \) cm. Under these conditions type II interaction provides, at the same crystal length, narrower spectral acceptance. This is, however, not the case when one is dealing with femtosecond pulses, for which the optimum crystal thickness is determined by the inverse group-velocity mismatch (GVM) and not by the availability of large sizes. When one moves to shorter (NIR) pump wavelengths, the GVM increases, and type I phase matching also has the potential to provide narrow bandwidths corresponding to the Fourier limit. The advantages of using type I interaction are, in any case, the broader tuning range that is achievable with angle tuning and the lower pump threshold, defined as \( I_m L^2 \) (\( I_m \) is the peak on-axis pump intensity),\(^1,2\) which is important in femtosecond OPG’s, in which relatively high pump intensities are applied. Figure 2 shows the potential tuning range (signal and idler) for type I phase matching by use of several NIR pump wavelengths \( \lambda_P \). For this calculation we used the Sellmeier expansion from Ref. 7. In Fig. 3 the GVM parameter \( 1/v_S - 1/v_I \), which is inversely proportional to the spectral acceptance in the small-signal limit, assuming a monochromatic pump, is plotted. As can be seen, there are broad nearly level regions when we are pumping with \( \lambda_P = 2.05, 1.9, \) or \( 1.65 \) \( \mu \)m if the degeneracy and the retracing limits are avoided. This result means that type I phase matching has the potential to provide not only sufficiently narrow but also nearly constant bandwidths. The latter is a prerequisite for the generation of nearly bandwidth-limited femtosecond pulses at the signal and the idler wavelengths in broad spectral regions.

Since our purpose in this initial study was to estimate the spectral bandwidths with type I interaction and pumping in the NIR, we examined the three samples only at normal incidence and in a single pass. Note that in unseeded femtosecond OPG’s of the traveling-wave type the main problems related to deviation from the bandwidth-limited case originate from spectral broadening owing to off-axial interaction; however, the temporal features of the pulses can be reliably predicted on the basis of the GVM data.

At \( \lambda_P = 2.07 \) \( \mu \)m the 52.5° sample had a pump threshold for parametric generation of \( I_m = 25 \) GW/cm\(^2\) at a pump-pulse duration of 140 fs, which results in \( I_m L^2 = 1 \) GW, which is comparable with the estimations in Ref. 1 but somewhat higher than what was measured with 2.7-ps pump pulses in the MIR.\(^4\) We attribute this higher threshold to the shorter temporal walk-off lengths in the femtosecond regime. At \( I_m = 60 \) GW/cm\(^2\) the ZnGeP\(_2\) OPG produced 215 nJ of output energy (signal and idler) at an incident pump energy as low as 16 \( \mu \)J. The recorded spectra in this case (Fig. 4) reveal well-defined spectral shapes. Assuming a Fourier product of 0.5, equal to that measured for the pump pulses, the spectral widths lead to pulse durations of 75 fs (signal) and 200 fs (idler). Such estimations are in reasonable agreement with the GVM behavior: At this pump wavelength both the idler and the signal pulses travel faster than the pump: \( 1/v_I - 1/v_P = -125 \) fs/mm and \( 1/v_S - 1/v_P = -65 \) fs/mm. The peak powers estimated amount to \( \approx 2 \) MW (near 3 \( \mu \)m) and \( \approx 0.4 \) MW (near 6 \( \mu \)m).

At \( \lambda_P = 1.89 \) \( \mu \)m we tested both the 52.5° and the 55°-cut ZnGeP\(_2\) samples. The threshold was 28 GW/cm\(^2\) in the first case and 55 GW/cm\(^2\) in the second. In both cases the increased threshold can be attributed to the stronger group-walk-off effects. At shorter pump wavelengths we tried the 67°-cut sample, but the threshold for parametric fluorescence could not be reached. We increased the pump intensity to \( >100 \) GW/cm\(^2\) (\( \lambda_P = 1.66 \) \( \mu \)m) and \( >150 \) GW/cm\(^2\) (\( \lambda_P = 1.3 \) \( \mu \)m), and at such intensities unwanted
nonlinear effects could be observed: self-phase modulation-induced spectral broadening of the pump pulses, self-focusing of the pump pulses, and non-phase-matched second-harmonic generation. The above values are to our knowledge the first estimations of a lower limit for the (surface) damage threshold with femtosecond pulses, but in terms of pump fluence they still lie approximately 2 orders of magnitude below the surface-damage thresholds reported for this material with 70-ns pulses at 2.08 \mu m.\textsuperscript{8} All the accompanying effects could be ruled out when we were characterizing the nonlinear transmission of the samples for the pump pulses, where a definite tendency of increasing nonlinear losses with shortening the pump wavelength could be observed. Thus at \( I_m = 50 \text{ GW/cm}^2 \) the transmission was 51.5\% for \( \lambda_P = 2.13 \text{ \mu m} \), i.e., only slightly below the small-signal value of 54\%, whereas for \( \lambda_P = 1.3 \text{ \mu m} \) it was already \( \sim 33\% \) — much less than the linear value of 46.5\%. The observed losses were independent of the phase-matching condition, and their intensity dependence could not be fitted in general with a two- or three-photon absorption process only. Although the wavelength dependence of the losses is an argument for attributing them to the species responsible for the anomalous NIR absorption, we proved in a separate pump-and-probe experiment at \( \lambda_P = 1.3 \text{ \mu m} \) that these losses are instantaneous and therefore have a completely different origin than the pump-induced losses described in Ref. 9. The losses exhibit a threshold character, and the loss coefficient tends to increase linearly with the intensity only at higher powers. The threshold decreases with \( \lambda_P \), and at \( \lambda_P = 1.3 \text{ \mu m} \) is practically zero. A rough estimation of the nonlinear loss coefficient, assuming a two-photon absorption process at this wavelength and Gaussian temporal and spatial intensity distribution, gave \( \beta = 0.25 \text{ cm/GW} \). The unidentified loss mechanism seems to impose a lower limit on \( \lambda_P \), but in fact at \( \lambda_P < 1.9 \text{ \mu m} \) the GVM increases rapidly, suppressing operation in the femtosecond regime, and tuning-angle variation (Fig. 2) is impractical. At \( \lambda_P > 2.1 \text{ \mu m} \), on the other hand, no constant bandwidths can be expected (Fig. 3). Summarizing, the NIR spectral region 1.9–2.1 \mu m seems to be optimum for femtosecond pumping of a type I ZnGeP\(_2\) OPG to cover its entire MIR transparency range by the generated signal and idler pulses.

In conclusion, we have studied the feasibility of ZnGeP\(_2\) as a femtosecond OPG pumped in the NIR near 2 \mu m. Substantial improvement of the present results in terms of energy and conversion efficiency should be possible with antireflection crystal coatings and addition of a second amplifying stage.

P. G. Schunemann thanks the U.S. Air Force Research Laboratory Materials Directorate for supporting the ZnGeP\(_2\) crystal development under contract F33615-94-C-5413. V. Petrov’s e-mail address is petrov@mbi-berlin.de.

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