Continuous-wave difference frequency generation in the mid-infrared with orientation-patterned gallium phosphide (OP-GaP) crystals


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ABSTRACT

Orientation-patterned gallium phosphide (OP-GaP) crystals are used here for the first time for the generation of continuous-wave coherent mid-infrared radiation around 5.85 µm by difference frequency generation (DFG) of a Nd:YAG laser at 1064 nm and a diode-laser at 1301 nm. We provide the first characterization of the linear, thermo-optic and nonlinear properties of OP-GaP in a DFG configuration, and we derive an effective nonlinear coefficient $d_{eff} = 17$ pm/V (3) for first-order quasi-phase-matched OP-GaP. This novel nonlinear material can be used to referenced the mid-IR light to a frequency standard by locking the pump and signal laser to a near-IR optical frequency comb.

Keywords: Frequency metrology, nonlinear materials, difference frequency generation, orientation patterned gallium phosphide, narrow line width mid-infrared sources, laser stabilization

1. INTRODUCTION

Tunable and spectrally pure coherent sources in the mid-infrared (mid-IR) are required both for high-sensitivity and high-precision molecular spectroscopy. The mid-IR region of the electromagnetic spectrum is well covered by quantum cascade lasers (QCLs). This compact devices are characterized by typical emitted powers of the order of tens of mW and tuning ranges of the order of hundreds of GHz. Their free running line width typically ranges from hundreds of kHz to several MHz, mainly due to the noise contributions from the QCL current driver and from temperature fluctuations. The frequency stabilization and reduction of their line width is therefore a mandatory step for applications in high resolution spectroscopy and new challenging experiments.

Several techniques have been used to date to reduce the QCLs line width. One approach relies on locking the laser frequency to the narrow resonance of ultra-stable cavities with a very high quality factors. Ultra-low expansion materials can be used to build ultra-stable cavities in the near infrared and mirrors with residual absorptions at the ppm level can provide finesse larger than $10^6$. Unfortunately, as the laser wavelength increases towards the mid and far infrared, the efforts for realizing stable and high finesse cavities increase tremendously, mainly due to the difficulties in the development of mirror coatings and to the limitations due to substrate residual absorption. However, progress in the processing of high-purity materials, such as calcium fluoride, makes possible the realization of crystalline micro-resonators for mid infrared radiation with high finesse.\(^1\)\(^2\)

The main advantage of this apparatuses, as compared to those using standard Fabry-Perot cavities, is that the micro-resonator works over the whole transparency range of the material used to realize the device.
Table 1. Properties of OP-GaP \cite{10, 15, 16}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency Range</td>
<td>0.57–12 µm</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>110 W/mK</td>
</tr>
<tr>
<td>Thermal Linear Expansion</td>
<td>$4.65 \times 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>Effective nonlinear coefficient @ 6 µm</td>
<td>17 pm/V</td>
</tr>
</tbody>
</table>

Different approaches involve frequency stabilization on sub-Doppler molecular transitions \cite{3} or phase-locking to infrared frequency combs \cite{4}. These techniques have demonstrated the capability to achieve sub-kHz line widths. A drawback of these approaches, though, is that a suitable molecular transition or an optical frequency comb has to be available at the frequency of interest.

Furthermore, to measure absolute frequencies the laser source must be ultimately referenced to the primary frequency standard, which is based on the hyperfine ground-state splitting of cesium. The comparison between frequencies in the optical domain or near-IR domain (hundreds of THz) to the microwave cesium frequency standard (around 9 GHz) can be done using optical frequency combs.

A robust approach to lock a mid-IR laser source to the primary frequency standard relies on phase-locking the laser to a difference frequency generated radiation. In this case the two near-IR sources (pump and probe) used in the DFG process can be locked to a near-IR optical frequency comb. The main problem is thus the availability of a nonlinear material to be employed on the DFG process.

Unfortunately the majority of commercial crystals are not transparent in the region above 5 µm. Oxide birefringent crystals, like LiNbO$_3$, LiTaO$_3$ or KTiOPO$_4$, have been extensively used for cw multi-mW DFG or OPO \cite{5, 6}, but they are transparent only at wavelengths lower than about 5 µm. CdSiP$_2$, AgGaSe$_2$, AgGaS$_2$ and LiInSe$_2$ are moderately transparent, but their absorption is still large, thus cw generation is sometimes difficult to achieve. Moreover, their low nonlinear coefficients strongly limit the generated power. As an example, AgGaS$_2$ has been used to produce cw radiation over the 5–12.5 µm range \cite{7, 8}, but the idler power was limited to the 10–1000 nW-range.

Recently, the development of orientation pattern (OP) techniques \cite{9} has opened up the possibility to use different materials with higher nonlinear coefficients like GaAs and GaP adding also the advantages of quasi-phase matching (QPM). OP-GaAs has been used for quasi-cw parametric oscillation around 4.7 µm with a Ho:YAG pump laser source at 2.1 µm \cite{10}, for SFG of a cw QCL at 5.4 µm \cite{11} and very few papers reports on cw DFG with OP-GaAs above 6 µm \cite{12}. One of the limiting factors of GaAs is its strong absorption at 1.064 µm, which makes difficult its use with the highly-stable and powerful laser sources available in this region. To date only few papers have been published on OP-GaP \cite{13, 14}. The main difference between OP-GaAs and OP-GaP is the much broader transparency region of OP-GaP. In addition, compared with GaAs, it has a lower refractive index, larger nonlinear coefficient and thermal conductivity, and a lower thermal expansion coefficient. The properties of OP-GaP are listed in Tab.1.

Here we report on the first continuous-wave DFG source around 5.85 µm wavelength using OP-GaP crystals \cite{16}. A Nd:YAG laser at 1064 nm and a diode-laser at 1301 nm are used as pump and signal, respectively. Up to 65 µW of single-frequency idler radiation was generated from about 10 W of pump and 40 mW of signal, limited by thermal dephasing effects arising from the non-negligible absorption at the pump and signal wavelengths. Following the cw Gaussian beam DFG theory \cite{17}, the nonlinear properties of OP-GaP have been characterized.

## 2. EXPERIMENTAL SETUP

The basic experimental setup used to produce DFG at 5.8 µm is shown in Fig. 2. A single frequency Nd:YAG laser (InnoLight GmbH, Mephisto MOPA 55W, $\Delta \nu \sim 1$ kHz over 100 msec) is used to provide up to 10 W of cw, linearly polarized radiation at $\lambda_p \simeq 1064$ nm. An extended cavity tunable fiber coupled diode laser (Toptica Photonics AG, DL PRO, $\Delta \nu \sim 100$ kHz) is used to provide up to 50 mW of linearly polarized, cw radiation at
Figure 1. Experimental scheme to obtain DFG in the OP-GaP crystals. Two lasers emitting at 1064 nm and 1301 nm are combined in a dichroic mirror and focused on the crystal by means of lens L1. A germanium window is used to separate the pump and signal beams from the idler, which is collected by lens L2 and focalized into a 200 $\mu$m active area HgCdTe detector by lens L3.

$\lambda_s \simeq 1301$ nm. The pump laser passes through an optical isolator and then it is split into two arms by means of a polarizing beam splitter: a small part of the light is sent to a wave meter (Bristol Instruments, Inc., Wavelength Meters 671 Series NIR) while the remaining light is sent to the crystal. Similarly the diode laser is split into two collimated arms: one is sent to the wave meter and the other one is sent to the crystal. The pump and signal beams, nearly TEM$_{00}$, are superimposed by a dichroic mirror and coaxially focalized with a plano-convex lens (L1) on the crystal. Four different values for the L1 focal length (Tab. 2) have been used: $f=50, 75, 100$ and 150 mm. After the crystal, a germanium window is used to separate the idler from the two near-IR beams. As the mid-IR radiation exiting from the crystal is strongly divergent, a calcium fluoride lens (L2) is used to collect and collimate the idler beam. The radiation is then focused (L3) on a thermoelectrically cooled HgCdTe detector with 200 $\mu$m active area (Vigo System S. A., PVI-4TE-5/MIP-DC-10M). All beams are linearly polarized: the pump and signal wave are polarized vertically (along the [001] crystallographic axis) and horizontally (along [110]), respectively, yielding to horizontally polarized idler radiation. This configuration ensures a full coupling of the nonlinear coefficient $d_{14}$. The absolute responsivity of the HgCdTe detector is calibrated at 5.85 $\mu$m using a calibrated radiometer. For the calibration, a quantum cascade laser, emitting at the same frequency as the idler beam, is carefully aligned on the Vigo detector and on the radiometer. The QCL output is scanned from 2 $\mu$W to 60 $\mu$W, as measured with the radiometer. The absorption and reflection of the different optics used in the two beam paths are taken into account and the power is corrected accordingly. The OP-GaP crystal is housed inside a massive copper block whose temperature is stabilized by a digital PI servo controller and it can be tuned from room temperature to 200° C. The crystal-oven system is mounted on a XYZ-$\theta\phi$ manipulator to optimize the alignment with the optical beams.
3. DATA ANALYSIS AND RESULTS

For the analysis of the generation efficiency, we have used two OP-GaP crystals, with $L = 11.5$ and $24.6$ mm lengths. The effective nonlinear coefficient $d = (2/\pi)d_{14}$ can be derived from the DFG process efficiency $\eta_{\text{DFG}}$ following equation

$$\eta_{\text{DFG}} = \frac{8\omega_0^2 d_{14}^2 L}{\pi c_0^3 n_i n_p n_s n_i} \exp(-\alpha_i L)(k_s^{-1} - k_p^{-1})^{-1} h(a, L/z_{\text{RI}}, f_c, z_{\text{RI}}, \Delta k z_{\text{RI}})$$

(1)

For all the involved parameters, the subscripts $i$, $p$ or $s$ indicate to which beam (idler, pump or signal) the parameters is referred to. Therefore $\omega$ indicates the angular frequency, $n$ the index of refraction, $k$ the wave vector, $\alpha$ the absorption coefficient and $w_0$ the beam waist. The function $h(a, L/z_{\text{RI}}, f_c, z_{\text{RI}}, \Delta k z_{\text{RI}})$, called aperture function, depends on all the following parameters:

$$w_{\text{RI}} = \frac{w_{0i} w_{0s}}{\sqrt{w_{0p}^2 + w_{0s}^2}}$$

$$z_{\text{RI}} = \frac{1}{2} k_{0i} w_{0i}^2$$

$$a = \frac{\alpha_p + \alpha_s - \alpha_i}{2} z_{\text{RI}}$$

$$\Delta k = k_p - k_s - k_i - \frac{2\pi}{\Lambda}$$

(2)

The parameter $z_{\text{RI}}$ is the Rayleigh range for the generated beam and can be expressed as a function of $w_{\text{RI}}$, which represents the beam waist of the idler beam; the quantity $\Delta k$ is called phase mismatch and it is a function of the orientation patterned period $\Lambda$ that is $24 \mu m$ in our case; the other two remaining parameters $a$ and $f_c$ are respectively the normalized absorption and the common position of the pump and signal foci inside the crystal in unit of $z_{\text{RI}}$.

To evaluate Eq. (1), the shape and waists of the pump and signal beam have to be determined. The beam shapes are close to TEM$_{00}$ thanks to the type of laser that were used. The beam waists have been measured by using the calibrated pinhole technique, in which the power transmitted through a set of diameter-calibrated pinholes is measured. We can calculate the transmission factor $T$ of a circular aperture of diameter $\phi$ coaxial to a Gaussian beam of waist $w_0$ as

$$T(\phi, w_0) = \frac{2}{\pi w_0^2} \int_0^{\phi/2} 2\pi r \exp\left(-\frac{2r^2}{w_0^2}\right) dr$$

(3)

If the transmission factor $T$ is experimentally measured for a value of $\phi$ and the pinhole is not too small compared to the beam area, we can derive the waist from the relation

$$w_0 = \left[-\frac{\phi^2}{2 \ln(1-T)}\right]^{1/2}$$

(4)

For each beam, the waist was measured by using several pinholes with different diameters. The measurements are consistent with each other within a $10\%$ error. The averaged values are reported in Tab. 2, together with the calculated idler waist and Rayleigh range using Eq. (2). The measurements satisfy the relation $w = (4/\pi)\lambda f / D$, where $D$ is the beam diameter and $f$ the focal length of the lens L1, with a ratio $w_s/w_p \approx \lambda_s/\lambda_p$. Although such a waist ratio does not correspond to the equal confocal parameter focusing condition, which theoretically yields optimal efficiency, it is sufficiently close to it.

Moreover, the absorption coefficients of the three waves involved have to be considered. For this reason we measured the absorption for the pump and signal waves, obtaining absorption coefficients of $\alpha_p \approx 0.17 \text{ cm}^{-1}$ and $\alpha_s \approx 0.12 \text{ cm}^{-1}$ inside the $400 \mu m$ thick OP region. In the substrate, much higher coefficients are found:
Table 2. Experimental values of waist for pump \((w_{0p})\) and signal \((w_{0s})\) laser at different focusing condition (L1). The
waists are measured using the calibrated pinhole techniques from which we obtain an uncertainty of 10 \%. \(w_{0i} = w_{0p}w_{0s}/(w_{0p}^2 + w_{0s}^2)^{1/2}\) is the calculated idler waist and \(z_{Ri} = k_{i}w_{0i}^2/2\) is the calculated Rayleigh range, where \(k_{i} = 2\pi n_{i}/\lambda_{i}\) is the wave vector. For the GaP crystal we assumed a refractive index at 5.85 \(\mu\)m of \(n_{i} = 3.18\).

<table>
<thead>
<tr>
<th>(f [\text{mm}])</th>
<th>(w_{0p} [\mu\text{m}])</th>
<th>(w_{0s} [\mu\text{m}])</th>
<th>(w_{0i} [\mu\text{m}])</th>
<th>(z_{Ri} [\text{mm}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>67</td>
<td>82</td>
<td>52</td>
<td>4.7</td>
</tr>
<tr>
<td>100</td>
<td>45</td>
<td>55</td>
<td>35</td>
<td>2.1</td>
</tr>
<tr>
<td>75</td>
<td>27</td>
<td>33</td>
<td>21</td>
<td>0.8</td>
</tr>
<tr>
<td>50</td>
<td>19</td>
<td>23</td>
<td>15</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(\alpha_{p} \approx 0.58 \text{ cm}^{-1}\) and \(\alpha_{s} \approx 0.53 \text{ cm}^{-1}\). The idler absorption coefficient is assumed to be \(\alpha_{i} \approx 0.007 \text{ cm}^{-1}\), value measured using a Perkin Elmer Spectrum GX FTIR.\(^{13}\)

In order to derive the efficiency of the nonlinear process, the absolute idler power is measured as a function of the pump power for a fixed signal power of 40 mW with the longer crystal. The results of these measurements are shown on the left side of Fig. 2. Each curve corresponds to one of the focusing conditions summarized in Tab. 2. The error bars represent a relative uncertainty of 5 \%.

The maximum generated idler power is around 65 \(\mu\)W with slightly less than 10 W of 1064 nm and 40 mW of signal power. The highest efficiency is achieved for the strongest focusing case, corresponding to a \(f = 50 \text{ mm}\) L1 lens. The non negligible absorption of the GaP at the two input waves results in an heating of the material and consequently in a modification of local index of refraction, affecting the quasi-phase matching condition. Heating is mainly due to absorption of the pump beam, because of its high power and higher absorption coefficient. Absorptions at 1064 nm and at 1301 nm are around 35\% and 25\%, respectively. In all measurements this effect is partially corrected by adjusting the crystal temperature to maximize the generated power. As expected, the optimal generation efficiency is found at a lower crystal temperature as the pump power increases. A second

\(\text{The reason of this difference is that the substrate is grown by means of a Czochralski process in which there is a contamination due to unintentional impurities which are not present in the high-purity vapor-grow (HVPE) OP layer.}\)

\(\text{Figure 2. Idler power generated as function of the pump power with the long crystal and with the short one. The signal power is kept constant over the measurements at around 40 mW and 45 mW respectively. For each point the crystal temperature is optimized to achieve the best phase matching. The data show a linear slope at low pump powers, where they can be fitted with a line. An example of such a fit is shown for the loosest focusing data set for the long crystal data. The slope of this line is used to calculate the conversion efficiency } \eta_{DFG} = P_i/(P_p P_s) \text{ plotted in Fig. 3.}\)
effect arise from the finite thermal conductivity of the material that yields a transverse temperature gradient $\Delta T(r)$, with $r$ the radial coordinate transverse to the propagation axis of the incident beams. Such gradient spatially changes the quasi-phase matching condition. When the pump power is low, the QPM condition is satisfied throughout the whole beam volume, i.e. for any radial coordinate $r$. At higher pump powers, though, the QPM condition cannot be satisfied for all $r$. The temperature of any ring with radius $r$ is different from the temperature of a ring with radius $r'$ and, since the phase-matching condition is temperature dependent, this effect leads to a position-dependent dephasing. Unfortunately, there is no way to recover the phase matching condition and the resulting effect is that the DFG power saturates or even decreases. In Fig. 2 the saturation due to thermal effect is clearly visible for increasing pump power, whereas a linear behavior would be expected for not absorbing crystals over the entire graph.

In order to derive the nonlinear coefficient $d_{14}$, only the linear portions of the plots shown in Fig. 2 are taken into account. In this way the thermal effects do not affect the analysis. The results of the numerical simulations, obtained solving Eq. (1), are shown in Fig. 3 together with the experimental data. Each point reported in

![Figure 3. Conversion efficiency $\eta_{\text{DFG}} = P_i/(P_p P_s)$ as function of the focusing parameter $l = L/z_{\text{Rd}}$ that expresses the crystal length in units of the Rayleigh length of the idler. The points represent the experimental data while the solid line shows the optimized theoretical efficiency calculated with the waist ratio $w_s/w_p = \lambda_s/\lambda_p$. In red and in black are shown the data and simulation relative to the short and long crystals respectively.](/ proc of spie vol 10088 100880w-6)
In order to derive the non linear coefficient, only data with loose focusing with $f = 100$ and $f = 150$ mm have been used, for which the modes of all three waves are confined within the active QPM layer volume. Using both experimental data form short and long crystal, the $d_{14}$ value is derived from Eq. (1) resulting in an effective nonlinear coefficient equal to

$$d_{\text{eff}} = \frac{2}{\pi} d_{14} = (17 \pm 3) \text{ pm/V}$$

Levine\textsuperscript{20} reported the values of $d_{14} = (37 \pm 2) \text{ pm/V}$ at $10.6 \mu\text{m}$, $d_{14} = (49 \pm 9) \text{ pm/V}$ at $1.32 \mu\text{m}$ and $d_{14} = (47 \pm 10) \text{ pm/V}$ at $2.12 \mu\text{m}$ using different non-phase-matched techniques. Shoij et al.\textsuperscript{21} measured the second-order nonlinear optical coefficient $d_{14}$ of GaP by means of non-phase matched SHG using the wedge technique. In this work, a couple of wedged GaP crystal are pumped at $1313 \text{nm}$ and the generated radiation is collected in a photomultiplier tube: they reported the most accurate value to date for the nonlinear $d_{14}$ coefficient $d_{14} = (36.8 \pm 4) \text{ pm/V}$.

Since the $d$-coefficients are wavelength dependent, the value reported by Shoij has to be rescaled to our idler wavelength. R. C. Miller empirically noted that while the $d$-value depends on frequencies, if divided with the opportune function of refractive index, it yields a constant value which is called Miller’s Delta.\textsuperscript{22} The Miller’s rule can be used to calculate the rescaling factor

$$M_{14} = \prod_{i=1}^{3} \frac{n^2(\lambda_i) - 1}{n^2(\lambda_i)} - 1$$

where the $\lambda_i$ are the wavelengths used by Shoij’s and $\lambda$ the wavelengths used in our DFG process. In order to evaluate the rescaling factor, the precise index of refraction value of GaP at all the involved wavelengths has to be considered. Recently, a new temperature-dependent Sellmeier equation\textsuperscript{13} has been derived based on recent refractive index data measured in\textsuperscript{23} on a bulk GaP prism. The Sellmeier equation results in the following expression

$$n^2 = A + \frac{(B + CF)\lambda^2}{\lambda^2 - (D + EF)^2} + (H + GF)\lambda^2$$

$$F = (T - T_0)(T + T_0 + 546.30)$$

where the temperature is expressed in degree Celsius and the coefficients are listed in Tab. 3. Using the Eq. (6) in conjunction with Eq. (7) we obtain a rescaling factor of $M_{14} = 0.82$ that can be used to convert the Shoij’s $d_{14}$ coefficient measured at $1.31 \mu\text{m}$ at our wavelength of $5.85 \mu\text{m}$. The result of the rescaling is $d_{14}^{\text{Shoij}}(5.85 \mu\text{m}) = 30.2 \text{ pm/V}$. This value yields to a $d_{\text{eff}} = (19 \pm 2) \text{ pm/V}$, in good agreement with our experimental value.

4. SUMMARY

In summary, we have demonstrated cw difference frequency generation in a novel orientation patterned gallium phosphide crystal at about $5.85 \mu\text{m}$ producing up to $\sim 65 \mu\text{W}$ of idler radiation, mainly limited by thermal effect arising from absorption at $1064 \text{nm}$. The radiation can be tuned by means of pump or signal laser frequencies and it can be used for mid-IR molecular spectroscopy. Moreover, a near-IR optical frequency comb referenced to the primary standard can be used to phase-locked the two near-IR lasers involved in the nonlinear process thus producing a metrological-grade mid-IR radiation.
Table 3. Coefficients for the Sellmeier equation relative to gallium phosphide.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>2.78649</td>
</tr>
<tr>
<td>$B$</td>
<td>6.32098</td>
</tr>
<tr>
<td>$C$</td>
<td>$1.02 \times 10^{-6} , ^\circ\text{C}^{-1}$</td>
</tr>
<tr>
<td>$D$</td>
<td>0.29903 [$\mu$m]</td>
</tr>
<tr>
<td>$E$</td>
<td>$5.92 \times 10^{-8} , \mu\text{m} , ^\circ\text{C}^{-1}$</td>
</tr>
<tr>
<td>$G$</td>
<td>$9.18 \times 10^{-9} , \mu\text{m}^{-2} , ^\circ\text{C}^{-1}$</td>
</tr>
<tr>
<td>$H$</td>
<td>$-0.00307 , \mu\text{m}$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>22.9 $^\circ\text{C}$</td>
</tr>
</tbody>
</table>

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REFERENCES


