Design considerations of an infrared spectrometer based on difference–frequency generation in AgGaSe$_2$

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The availability of new nonlinear optical materials such as AgGaS$_2$ and AgGaSe$_2$ and improvements in compact, tunable, pulsed and continuous-wave (cw) solid-state pump lasers now make it possible to generate tunable, infrared narrow-band coherent radiation over a wide wavelength range (4–18 μm) by means of difference–frequency generation (DFG). This article describes the wavelength and output-power characteristics of a tunable infrared source based on AgGaSe$_2$ and certain proven cw near-infrared pump sources for application to high-resolution spectroscopy.

Key words: Nonlinear optics, design of specific laser systems, infrared spectra.

Introduction

There is a need for continuing improvement of convenient laser-based sources applicable to high-resolution spectroscopy. As virtually all fundamental vibrational modes of molecules and molecular ions lie in the 2–20-μm-wavelength fingerprint region, tunable monochromatic probe lasers in this wavelength range are particularly useful for high-sensitivity, high-resolution (<100 MHz) and time-resolved molecular spectroscopy. Optimum spectral control and frequency stability are achieved with cw laser sources. Suitable cw tunable infrared-laser sources are presently limited to color-center lasers, lead salt diode lasers, sources based on sideband generation by CO and CO$_2$ lasers, and difference–frequency mixing sources. The color-center lasers require liquid nitrogen operation and are limited to a relatively small spectral region between 1.4 and 3.5 μm.$^1$ Lead salt diode lasers cover the 3–30-μm-wavelength range, but also require cryogenic operating temperatures (<100 K).$^2$ As the wavelength-tuning range per individual diode is limited to ~100 cm$^{-1}$ (~400 cm$^{-1}$ for MBE structures) and has many undesirable discontinuities, a large collection of diodes is required to cover the fingerprint-wavelength range. With continuous-tuning ranges limited to only 0.5 cm$^{-1}$, CO and CO$_2$ sideband lasers provide tunable infrared radiation between 5 and 6 μm and 9 and 11 μm, respectively.$^3$

A source that is based on DFG, which was originally developed by Pine,$^4$ and in which an Ar$^+$ laser was mixed with a cw dye laser in LiNbO$_3$, has proved very useful for high-resolution infrared spectroscopy, but it is limited to wavelengths shorter than 4 μm by the infrared transmission characteristics of LiNbO$_3$. Using LiIO$_3$ as the nonlinear medium, Oka and coworkers$^5$ extended the long-wavelength limit for cw DFG sources to nearly 5 μm. Recently, we demonstrated the operation of a continuously tunable cw DFG spectrometer in the 4–9-μm-wavelength range based on 90° type I phase matching in AgGaS$_2$.$^6$ A 45-mm-long nonlinear optical crystal was pumped by two single-frequency (dye and Ti:sapphire) lasers. Using this spectroscopic source, absorption spectra of several stable molecular systems have been detected, e.g., H$_2$O, N$_2$O, NH$_3$, and CO. Additionally, we have observed transient spectra of vibrationally excited CO ($v = 1, 2$), generated by 193-nm ArF excimer laser-flash photolysis of acetone.

This paper describes the design considerations of a novel, midinfrared DFG-based laser source that is continuously tunable from 4–18 μm by mixing two cw single-frequency lasers in AgGaSe$_2$. It is based on design parameters resulting from the recent commercial availability of improved nonlinear optical crystals and new solid-state pump-laser sources.
Characteristics of AgGaSe$_2$

A nonlinear optical material must meet several criteria to be useful in a three-wave parametric-mixing process. The material must be transparent for all three beams—pump, signal, and idler—participating in the process. Other conditions important to achieving a high nonlinear conversion efficiency are a large effective nonlinear coefficient $d_{33}$, a long crystal length, a high optical damage threshold, and phase matchability for available pump sources. The ternary chalcopyrite AgGaSe$_2$ shows a wide transparency range from 0.71 to 18 $\mu$m. These crystals have recently become available commercially in large linear dimensions (>40 mm) and with high optical quality. The absorption coefficient of this material in its transmission range is comparable with that of AgGaS$_2$. AgGaSe$_2$ is a birefringent uniaxial negative crystal ($n_e - n_o = -0.032$ at 5 $\mu$m) with a large nonlinear coefficient $d_{33}$. A value of 33 pm/V ± 10% has been determined for $d_{33}$ from second-harmonic-generation (SHG) experiments in AgGaSe$_2$ with a Q-switched CO$_2$ laser at 10.6 $\mu$m as a pump source. The optical-surface-damage threshold for AgGaSe$_2$ has been determined to be as high as 20–30 MW/cm$^2$ for 10-ns pulses at 2 $\mu$m. The optical properties of several nonlinear optical materials useful for infrared DFG are summarized in Table 1. ZnGeP$_2$ has the highest figure of merit ($d_{eff}^2$/$n^3$) among these materials, owing to its extremely large nonlinear optical coefficient. As this material suffers from strong absorption in the 0.74–2-$\mu$m-wavelength region, the DFG process requires infrared pump sources emitting at wavelengths longer than 2 $\mu$m. However, noncritical phase matching in ZnGeP$_2$ cannot be realized for pump sources beyond 2 $\mu$m, as shown by our calculations based on the Sellmeier equations from Ref. 13, thus restricting the usefulness of ZnGeP$_2$. The figure of merit for AgGaSe$_2$, which scales linearly with the infrared DFG power, is nearly two times smaller than that for ZnGeP$_2$, but nearly six times larger than that for AgGaS$_2$. Optimized parametric-frequency conversion requires phase matching of the three interacting waves. For a birefringent, nonlinear optical crystal this can be accomplished by means of crystal orientation, temperature, and pump-laser wavelength tunability.

In the case of AgGaSe$_2$, the ability to tune the wavelength by varying the temperature is small. Hence, we propose to use either two tunable, near-infrared cw pump sources, as in case of AgGaS$_2$, or to use angle tuning.

90° Type I Phase Matching

The highest nonlinear frequency-conversion efficiency is achieved with 90° type I (noncritical) phase matching. Type II ($e \rightarrow o + o$) phase matching at $\theta = 90°$ in AgGaSe$_2$ is specifically ruled out by the combination of negative birefringence and 42$\pi$ crystal symmetry. The infrared wavelength-tuning characteristics for both AgGaS$_2$ and AgGaSe$_2$ for 90° type I ($e \rightarrow o + o$) phase matching based on the Sellmeier constants from Refs. 15 and 16 are shown in Fig. 1. This comparison of phase-matching curves indicates the respective infrared-wavelength-tuning ranges for DFG in AgGaS$_2$ and AgGaSe$_2$ using several different pump-laser sources. In the case of AgGaS$_2$, single-frequency lasers in the visible spectral region can be employed as pump sources. As the transparency, and in particular the dispersion range, of AgGaSe$_2$ is shifted toward longer wavelengths as compared to AgGaS$_2$, the phase-matching conditions imply that two tunable pump sources above 1 $\mu$m are necessary.

Table 1. Characteristics of Important IR Nonlinear Optical Crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>Transparency Range ($\mu$m)</th>
<th>Absorption (%) cm$^{-1}$</th>
<th>Damage Threshold (MW/cm$^2$)</th>
<th>Relative Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgGaS$_2$</td>
<td>0.5–13$^a$</td>
<td>1.0 (1 $\mu$m)</td>
<td>25 (10 ns)$^c$</td>
<td>42.3$^d$</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>0.71–18$^b$</td>
<td>0.4 (2 $\mu$m)</td>
<td>20–30 (10 ns)$^c$</td>
<td>245$^d$</td>
</tr>
<tr>
<td>ZnGeP$_2$</td>
<td>0.74–12$^c$</td>
<td>1.0 (5 $\mu$m)</td>
<td>50 (25 ns)$^c$</td>
<td>625$^d$</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>0.35–4.5$^d$</td>
<td>0.15 (1 $\mu$m)</td>
<td>300 (10 ns)$^c$</td>
<td>3.5$^d$</td>
</tr>
<tr>
<td>LiIO$_3$</td>
<td>0.31–6.5$^d$</td>
<td>0.08 (1 $\mu$m)</td>
<td>2000 (1 ns)$^c$</td>
<td>1.5$^d$</td>
</tr>
</tbody>
</table>

$^a$Ref. 30.  
$^b$Ref. 7.  
$^c$Ref. 9.  
$^d$Ref. 29.

Fig. 1. Infrared-wavelength-tuning characteristics with corresponding pump sources for (a) AgGaS$_2$ and (b) AgGaSe$_2$. The 90° type I phase-matching curves of AgGaS$_2$ and AgGaSe$_2$ are based on the refractive-index data given in Refs. 15 and 16, respectively.
to generate tunable infrared radiation in the 4–18-μm-wavelength range. The lack of tunable cw pump sources in this wavelength region (especially between 900 and 1400 nm) has limited the usefulness of AgGaSe₂ for parametric-frequency-conversion devices in the past. The progress in the development of reliable, tunable near-infrared solid-state lasers now offers several options for cw single-frequency pump sources for DFG in AgGaSe₂ as indicated in Fig. 1, e.g., Ti:sapphire lasers (Ti:s), color-center lasers, forsterite lasers (Cr⁺⁺:Mg₂SiO₄),¹⁷ Cr⁺⁺:YAG lasers,¹⁸ and single-frequency semiconductor laser diodes. Table 2 summarizes the main characteristics of these near-infrared pump sources. The last column indicates which portion of the optical transmission range of AgGaSe₂ each laser can generate in the DFG mixing process (either as a signal or a pump wave) if an appropriate second pump source is used.

The use of single-frequency laser diodes¹⁹ appears particularly attractive because these devices are able to generate the full infrared-wavelength-tuning range for DFG in AgGaSe₂. These lasers have been steadily improving in output power, wavelength coverage, reliability, and cost. Recently there have been important advances in spectral-control and frequency-stabilization techniques of diode lasers based on external cavities, optical feedback, injection locking, and electronic servo control.²⁰ Using laser diodes as master oscillators, high cw-output powers (up to several watts) have been obtained by injection-locking high-power broad-area diode lasers or diode-laser arrays and by using these devices as traveling-wave or double-path reflective amplifiers.²¹ Single-frequency diode lasers, each tunable over an ~15-nm range, have recently become available commercially in the 0.63–2.6-μm spectral region, with a bandwidth of < 500 kHz and output powers up to 25 mW.²² The utility of presently available single-frequency diode lasers for nonlinear frequency-conversion experiments has been demonstrated recently. Efficient frequency doubling of AlGaAs diode laser emission using a resonator for enhancement of the fundamental light field within the nonlinear material has been reported in KNbO₃.²³ In addition, efficient sum-frequency generation of blue light has been accomplished by mixing a Nd:YAG laser with a single-frequency AlGaAs diode laser in a monolithic KNbO₃ or KTP resonator.²⁴,²⁵ SFG employing a single-frequency diode laser has also been obtained without using an enhancement cavity.²⁴,²⁶ Recently, we demonstrated DFG in AgGaSe₂ utilizing cw single-frequency diode–Ti:sapphire and diode–diode pump-laser configurations.²⁷

The available IR power is of special interest for spectroscopic applications. To estimate the cw single-pass infrared DFG power using AgGaSe₂, an analysis was performed based on Refs. 28 and 29, assuming a lossless crystal and focused Gaussian input beams. In this case the DFG power can be expressed as

$$P_i = \frac{4\omega_0^4 k_s d_{eff}^2 l}{\varepsilon_0 \pi c n_p n_s (1 + \mu)} P_p P_s h(\mu, \xi).$$  \hspace{1cm} (1)

Here the subscripts $p$, $s$, and $i$ refer to the pump, signal, and idler beams, respectively; where $\omega_0$ is the IR angular frequency; $k$ is the wave vector, $d_{eff}$ is the effective nonlinear coefficient which equals $d_{36}$ for 90° type I phase matching in AgGaSe₂ and AgGaSe₄; $l$ is the crystal length, $\varepsilon_0$ is the free-space permittivity; $c$ is the speed of light in vacuo; $n_j (j = p, s$ or $i$) are the wavelength-dependent refractive indices; $\mu$ is the ratio of the input wave vectors ($\mu = k_i/k_p$); $\xi$ is the ratio of crystal length $l$ to confocal parameter $b$; and $h(\mu, \xi)$ is the focusing function given in Ref. 29.

The infrared DFG power calculated for mixing two cw tunable lasers (power 0.5 W each) in AgGaSe₂ and AgGaSe₄ utilizing 90° Type I phase matching and optimal focusing²⁹ ($l = 1.125b$) is depicted in Fig. 2. As can be seen from Eq. (1), the DFG power $P_i$ is proportional to the input-power product $P_p P_s$ of the pump and signal sources. This relation has been verified experimentally for even unbalanced signal-to-pump power ratios of up to 10:1.²⁶ For different input-power levels, the DFG output power can be predicted from Fig. 2 by properly scaling the input power product $P_p P_s$. It should be noted that the calculated data may be higher than the experimentally achievable IR power because of limitations in input-power density caused by surface damage, crystal absorption losses, imperfect spatial overlap of the pump and signal beams inside the nonlinear crystal, or deviations of pump and signal-beam modes from an ideal Gaussian TEM₀₀ mode. In the case of AgGaSe₂,⁶ our measured IR power was only approximately half of the predicted power mainly because of imperfect spatial overlap of the beam waists of the pump and signal beams inside the crystal. Unfortunately, no information is available on the cw-damage threshold of AgGaSe₂. However, for AgGaSe₂, up to 3 W of cw visible laser power (Ti:sapphire and DCM dye lasers at 740 and 650 μm, respectively) was focused down to a beam waist of 100 μm inside a 20-mm-long nonlinear crystal (10 kW/cm²) cut for 90° type I phase matching. After an exposure time of more than one hour, no damage to the front or rear crystal facet was visible with a 1-μm-resolution light microscope. Additionally, at these power levels the transmitted visible beams did not show any wavefront distortion.

| Table 2. Pump Sources in DFG Mixing with AgGaSe₂.⁶ |
|----------------|----------------|-----------------|
| Laser          | Tuning Range (nm) | Power (W) | Coverage |
| Ti:sapphire    | 660–1100          | 3⁺            | 13/40        |
| Cr⁺⁺:Mg₂SiO₄   | 1200–1350         | 1.8ᵇ          | 19/21        |
| Cr⁺⁺:YAG       | 1350–1560         | 1ᵇ           | 14/18        |
| Color Center   | 1400–3500         | 0.1ᵇ         | 36/14        |
| Diodes         | 630–2600          | 3⁺           | 100/100      |

ᵃSome tunable solid-state lasers that are useful as pump sources in AgGaSe₂-based difference-frequency generation (DFG) mixing.
ᵇRequires cryogenic operating conditions.
ᶜWhen a diode-laser amplifier is used.
²⁹Ref. 29
Table 3. Phase-Matchable DFG Wavelength Rangea

<table>
<thead>
<tr>
<th>Laser</th>
<th>Wavelength Range</th>
<th>DFG Range</th>
<th>Diode Range</th>
<th>Phase-Matchable Angle</th>
<th>Laser</th>
<th>Wavelength Range</th>
<th>DFG Range</th>
<th>Diode Range</th>
<th>Phase-Matchable Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:YAG</td>
<td>1.32 signal</td>
<td>10.3-18</td>
<td>1.17-1.23</td>
<td>84.7-57.7</td>
<td>Tm:YAG</td>
<td>2.01 signal</td>
<td>5.33-18</td>
<td>1.46-1.81</td>
<td>83.4-47.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tm, Ho:YAG</td>
<td>2.09 signal</td>
<td>5.07-18</td>
<td>1.48-1.87</td>
<td>83.7-48.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Er:YAG</td>
<td>2.94 signal</td>
<td>3.41-18</td>
<td>1.58-2.53</td>
<td>85.7-48.3</td>
</tr>
</tbody>
</table>

aWhen type I angle tuning is used with tunable diode lasers.

The Er:YAG laser at 2.94 µm is not phase-matchable as a pump wave in AgGaSe2.

Compact, fixed-frequency, all-solid-state lasers.

Phase Matching with Angle Tuning

An alternative approach for generating tunable infrared radiation is to mix one tunable and one fixed-frequency pump laser operating at wavelengths longer than 1 µm in AgGaSe2, and then to utilize angle tuning.31 The advantage of this approach is that it allows the combination of relatively powerful fixed-frequency lasers with the radiation of weak tunable laser sources. Table 3 gives the phase-matching ranges of several compact, fixed-frequency, all-solid-state lasers that can be used in combination with tunable III-V single-frequency diode lasers for this purpose. As an example, Fig. 3 shows the phase-matching angle as a function of DFG wavelength when mixing tunable single-frequency diode lasers as the signal wave with a fixed-frequency Nd:YAG laser at 1.32 µm as the pump wave. In practice, the effect referred to as the Poynting vector walk-off29 reduces the effective interaction length of the three waves in the crystal drastically. Owing to the birefringence of AgGaSe2, the Poynting vector of the e-ray pump beam behind the crystal, which indicates an absence of self-focusing effects. This lower limit for the cw-damage threshold of AgGaS2 should be transferable to AgGaSe2, as the damage thresholds for pulsed radiation are almost equal for both crystals. However, for high-input-power applications the surface damage threshold can be increased significantly by antireflection-coating the crystal.

Fig. 2. Calculated DFG output power for an input power product $P_p P_s$ of 0.25 W² as a function of the wavelength with (a) AgGaS2 and (b, c) AgGaSe2. In all cases, crystal length = 45 mm and confocal parameter = 40 mm. The case of focused Gaussian beams is considered in the calculation. Values of 12 and 33 pm/V are used for the nonlinear coefficient $d_{36}$ of AgGaS2 and AgGaSe2, respectively.10

Fig. 3. Wavelength dependence of the phase-matching angle $\theta$ and effective crystal length $l_{ef}$ for critical type I phase-matching in AgGaSe2 with a Nd:YAG laser (1.32 µm) as the fixed pump input and diode-laser input as the tunable signal (1.6-1.4 µm).
that is suitable for high-resolution spectroscopy and kinetic spectroscopy and is based on AgGaS\(_2\) is feasible. Equally promising is the application of such lasers to methods that require a compact, portable laser-based spectrometer, such as sensitive and selective environmental monitoring. This development is possible now only because of the recent advances in new nonlinear optical crystals and solid-state, infrared, electro-optic technology. Compact, tunable, single-frequency high-power diode lasers and subsequently diode laser amplifiers appear to offer particular promise as pump sources.

References


