90° phase-matched parametric frequency conversion in AgGa$_{1-x}$In$_x$S$_2$

S. BANERJEE$^{1,2,3}$
K. MIYATA$^1$
K. KATO$^1$
N. SAITO$^2$
S. WADA$^2$

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ABSTRACT AgGa$_{1-x}$In$_x$S$_2$ with $x = 0.14 \pm 0.01$ was found to be 90° phase-matchable for type-I difference-frequency generation (DFG) by mixing the dual-wavelength pulses emitted from an electronically tuned Ti:sapphire laser. Infrared radiation continuously tunable over the range of 4.80–6.98 μm was generated by independently varying the two wavelengths in the 705–932 nm spectral range, and 4.04 μm radiation by mixing a Nd:YAG laser with the Ti:sapphire laser. In addition, this material was found to be noncritically phase-matchable for the second harmonic generation (SHG) of CO$_2$ laser radiation at 10.591 μm at 203°C. Sellmeier equations that reproduce well these experimental data are presented.

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1 Introduction

Birefringence tailoring by means of mixing ternary chalcoprite semiconductors offers a unique advantage for achieving noncritical phase-matched (NCPM) parametric interactions in the mid-IR. Several mixed quaternary crystals such as AgGa(S$_{1-x}$Se$_x$)$_2$ [1], CdGe(P$_x$As$_{1-x}$)$_2$ [1], AgGa$_{1-x}$In$_x$Se$_2$ [2], AgGa$_{1-x}$In$_x$S$_2$ [3] and Hg$_x$Cd$_{1-x}$Ga$_2$S$_4$ [4] have been grown for nonlinear device applications. Noncritical phase-matched second and third harmonics of CO$_2$ laser radiation have been achieved in AgGa$_{1-x}$In$_x$Se$_2$ [2,5]. Temperature-tuned type-2 noncritical phase-matched SHG of CO$_2$ laser radiation at 9.27124–10.5910 μm was reported in CdGe(P$_x$As$_{1-x}$)$_2$ [6], while a Nd:YAG laser pumped optical parametric oscillation (OPO) in the 2.85–3.27 μm range was recently demonstrated in Hg$_x$Cd$_{1-x}$Ga$_2$S$_4$ [7].

The solid solution of AgGa$_{1-x}$In$_x$S$_2$ appears to be an attractive material for OPO and DFG in the mid-IR region when pumped by the commercially available short wavelength lasers because of its noncritical phase-matchability and high transparency in the visible range. We have studied the phase-matching properties of this material by difference-frequency generation (DFG) and by second-harmonic generation (SHG) in the mid-IR. Here, we report on the 90° phase-matched type-I DFG in AgGa$_{1-x}$In$_x$S$_2$ with $x = 0.14 \pm 0.01$ in the 4.04–6.98 μm spectral range and temperature tuned type-I noncritical SHG of CO$_2$ laser radiation at 10.591 μm, together with the Sellmeier equations that reproduce well these experimental results and the previous data given by Saito et al. [8] for DFG at 5.4–7 μm when a 5.2° correction is made for the crystal orientation.

2 Experiments and discussion

The 5 mm thick, 15 mm long uncoated AgGa$_{1-x}$In$_x$S$_2$ crystal ($\theta = 84.8°$, $\varphi = 45°$) used in the experiment was supplied by the High Technologies Laboratory of Kuban State University in Russia. The transmission curves of this crystal, measured with a Fourier transformed IR spectrometer are shown in Fig. 1. As reported by Badikov et al. [3], the transparency range of this mixture crystal shifted towards the longer wavelengths compared to the pure AgGa$_2$S$_2$. The short and long cutoff wavelengths were 0.53 μm and 14.2 μm, respectively.

Figure 2 shows the experimental setup used in the DFG measurements. The basic pump source was an electronically tuned dual-wavelength Ti:sapphire laser operated by two-
frequency-driven acousto-optics device as reported in the Ref. [9]. The Ti:Al₂O₃ crystal was pumped by a Q-switched frequency-doubled Nd:YLF laser at 2 kHz with an average output power of 280 mW. Dual-wavelength oscillation was achieved by feeding two different radio-frequencies (RFs) to the acousto-optic tunable filter (AOTF) and by controlling their powers. The system generated two synchronized pulses of 60 ns duration at 2 kHz in the 700–950 nm range with a total average output power of 25 mW. The wavelengths of these two pulses were independently tunable by varying the RF frequencies applied to the acousto-optic device via a computer program. The spectral bandwidth (FWHM) of the Ti:sapphire laser was approximately 3 cm⁻¹ near 800 nm. Since the two pulses had the same polarization direction owing to the Brewster-angle cut Ti:Al₂O₃ crystal, a polarization rotator was used to rotate the polarization by 45° for both pulses to achieve type-I DFG. A germanium filter, having a 46% transmission in the mid-IR, was used to block the pump and signal waves. By focusing the output from the dual-wavelength oscillator into the AgGa₁₋ₓInₓS₂ crystal with a 20 cm focal length lens and by tuning the RF frequency, we were able to generate continuously tunable mid-IR radiation in the 4.80–6.98 μm range. Additionally, an LD pumped acousto-optically Q-switched Nd:YLF laser operating at 2 kHz with a pulse width of 90 ns was synchronized with the Ti:sapphire laser and was used to generate the 90° phase-matched DFG at 4.04 μm in this sample.

Neutral-density filters and a half-wave plate were used to reduce the Nd:YLF output power to 15 mW to avoid the possible damage to the crystal and to adjust the polarization direction for type-I phase-matching. The difference-frequency radiation generated was detected by a liquid nitrogen cooled HgCdTe detector (Infrared Associates, Inc, FTIR-13-1.00) and the Ti:sapphire wavelengths were measured by Burleigh wavemeter. The DFG wavelengths were indirectly determined from the input wavelengths. These data are shown in Fig. 3 together with the theoretical curves. The dashed curve (B) is computed from the Sellmeier equations given by Badikov et al. [3] at x = 0.2, which differs significantly from our experimental points, while the dashed curve (S) is the theoretical curve calculated with the following Sellmeier equations for x = 0.14:

\[
\begin{align*}
n_0^2 &= 5.7931 + \frac{0.2583}{\lambda^2 - 0.00662} - 0.00262\lambda^2, \\
n_e^2 &= 5.5625 + \frac{0.2541}{\lambda^2 - 0.0973} - 0.00270\lambda^2,
\end{align*}
\]

where \(\lambda\) is in micrometer, and correctly reproduces the experimental results. These equations were constructed by using the refractive indices measured by a prism cut at an apex angle of 18.06° at 0.6328, 1.0642 and 10.591 μm, and were iteratively adjusted by assuming that the variation in the refractive indices due to the indium doping in AgGa₁₋ₓInₓS₂ is identical to that of AgGa₁₋ₓInₓSe₂ [5].

It should be pointed out that a chemical analysis made at Sumitomo Metal Mining company gave the value of x = 0.14 ± 0.01, in contrast to the crystal grower’s value of x = 0.2 as is shown in Fig. 4, where we have plotted the values given by Badikov et al. [3] at x = 0.08, 0.2 and 0.6 and our measured value at x = 0.14.

![FIGURE 3](https://example.com/fig3.png)

**FIGURE 3** 90° phase-matching curves for type-I difference-frequency generation in AgGa₁₋ₓInₓS₂ with x = 0.14 ± 0.01. (S) is the theoretical curve calculated with the Sellmeier equations presented in this text, (B) is the theoretical curve calculated with the Sellmeier equations given by Badikov et al. [3] at x = 0.2 ● are the experimental points

![FIGURE 4](https://example.com/fig4.png)

**FIGURE 4** The variation of the refractive index due to the change in the indium concentration for 1.0642 μm and 10.591 μm. ● are the data points from [3], ○ are the measured refractive index at x = 0.14