Measurement of Nonlinear Coefficient and Phase Matching Characteristics of $AgGaS_2$

P. Canarelli, Z. Benko, A. H. Hielscher, R. F. Curl, and F. K. Tittel

Abstract—**The nonlinear optical characteristics of $AgGaS_2$ were investigated by measuring visible parametric fluorescence with a pump wavelength of 600 nm. A value of d_{36} [$AgGaS_2$] = $31 \pm 5\ 10^{-12}$ m/V for the nonlinear coefficient was determined. The temperature dependence of phase matching up to 100°C was studied. A significant temperature effect, although much smaller than for $LiNbO_3$, was found and results in a change in the infrared difference frequency generated of $\sim 0.6\ cm^{-1} \cdot °C^{-1}$.**

I. Introduction

SILVER thiogallate ($AgGaS_2$) is a very promising infrared nonlinear optical material. Its birefringence and high optical transmission from 0.5 to 13 μm make it possible to generate infrared radiation over a wide spectral range using various pump sources. Furthermore, it exhibits a large nonlinear coefficient, a high damage threshold, and is chemically stable. Several nonlinear optical devices in the infrared have been demonstrated with this crystal including second harmonic generation (SHG) [1], difference frequency generation (DFG) [2], [3] and optical parametric oscillator (OPO) [4]. Recent availability of $AgGaS_2$ crystals of high optical quality and in large dimension has led to a renewed interest in that crystal [5].

This letter reports on a measurement of the nonlinear coefficient of $AgGaS_2$, its 90° phase matching characteristics, and the temperature dependence of the output infrared frequency. Several measurements have been carried out on phase matching in $AgGaS_2$ but only Seymour *et al.* [6] have reported on 90° phase matching conditions. Optical interaction based upon 90° phase matching operation is of special interest since it optimizes the interaction length in the nonlinear crystal resulting in the highest effective nonlinear mixing possible. Bahr *et al.* [7] have made some refractive index measurements at different temperatures and deduced a dispersion formula for thermooptic coefficients, but no investigation of the dependence of phase matching upon temperature has been reported.

Nonlinear coefficient measurements have been reported by Boyd *et al.* [1]. A value of $18 \pm 30\%\ 10^{-12}$ m/V was found employing a SHG wedge technique at 10.6 μm. Kato [2] deduced a value of $14 \cdot 10^{-12}$ m/V from DFG conversion efficiency at 6 μm. Others have reported a nonlinear coefficient of $57 \pm 33\%\ 10^{-12}$ m/V (Chemla *et al.* [8]) and $20 \pm 20\%\ 10^{-12}$ m/V (Kupecek *et al.* [9]) at 10.6 μm. More recently Yodh *et al.* [10] measured a value of $9.2 \pm 20\%\ 10^{-12}$ m/V at 5 μm. These values present a considerable experimental discrepancy, even taking into account the frequency dependence of the nonlinear coefficient through Miller's delta [11]. Therefore, we reexamined the nonlinear coefficient of $AgGaS_2$ in order to provide reliable data for design of a tunable CW infrared DFG laser spectrometer for high resolution absorption spectroscopy [12].

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II. Nonlinear Coefficient Measurement

Silver thiogallate has 42 m point group symmetry. In that class the coefficients d_{14} and d_{36} are nonzero and equal if the Kleinman symmetry condition is assumed. Here, this coefficient is deduced from measurement of the signal generated by spontaneous parametric emission (SPE). Byer *et al.* [13] have studied SPE experimentally and theoretically. If a pump beam is incident on a nonlinear crystal, there exists a certain quantum-mechanical probability that a pump photon will split into signal and idler photons such that $\nu_p = \nu_s + \nu_i$. The result is a generated signal polarization which can in principle radiate in all directions and at all frequencies. However, the signal will be amplified significantly only when velocity phase matching exists between the three frequencies. The signal power radiated into an angle θ can be expressed

$$P_s = \frac{2\hbar\omega_s^4 \omega_i n_s l}{4\pi^2 \epsilon_o c^5 n_i n_p b} d_{36}^2 \pi\theta^2 P_p \qquad (1)$$

where the subscripts p, s, i represent the pump, signal, and idler, respectively, ω is the angular frequency, $\hbar$ is Planck's constant, n is the refractive index, ϵ_o is the permittivity of the free space, and c is the velocity of light. The factor of dispersion b is given by

$$b = \frac{\partial k_s}{\partial \omega_s} - \frac{\partial k_i}{\partial \omega_i}$$

and l is the crystal length.

The measurement of the nonlinear coefficient by means of SPE has certain advantages over methods that employ either the SHG or DFG conversion efficiency measurement. First, it is only necessary to measure the power ratio of the pump radiation and the generated fluorescence

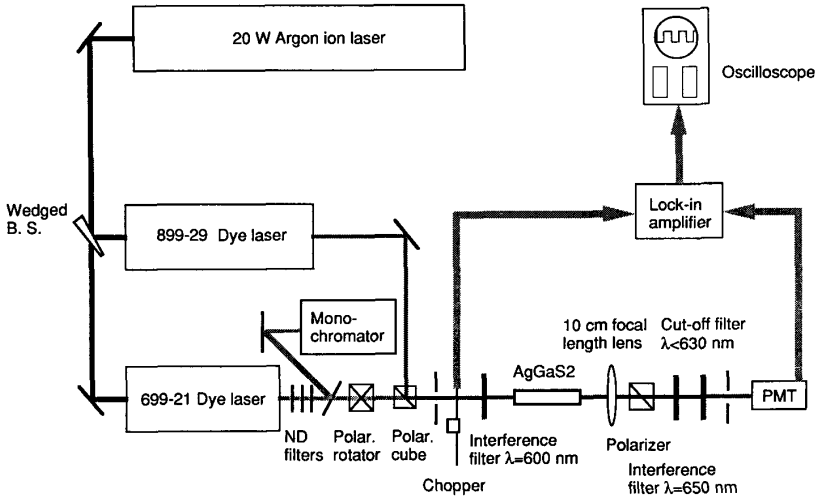

Fig. 1. Schematic diagram of the parametric fluorescence experimental setup used to measure the $AgGaS_2$ nonlinear coefficient.

in the visible spectrum. The difficult determination of the pump beam diameter is not necessary, and the angular alignment or temperature of the crystal are far less critical. Finally, the method is not dependent upon beam mode or focusing and a higher accuracy in the measurement can thus be expected.

The experimental setup used to monitor the spontaneous parametric fluorescence is shown in Fig. 1. A ring dye laser (Coherent model 899-29 employing Rhodamine 6*G*) operating at 600 nm is used as the pump source. The vertically polarized beam is chopped and then enters the $AgGaS_2$ crystal. The $4 \times 4 \times 20$ mm^3 crystal was antireflection (AR) coated for the 600–900 nm on its input side and AR coated for the 3.8–9.1 μm on its output side. An interference filter centered at 600 nm (transmission bandwidth ~ 10 nm) is placed in front of the crystal in order to eliminate all other frequencies particularly those near the phase matched signal frequency at 650 nm. The horizontally polarized signal generated in the nonlinear material is then collected by a 10 cm focal length lens f and directed to a cooled photomultiplier (PMT) through an aperture whose radius r defines the angle θ by the expression

$$\theta = \frac{r}{n_s \cdot f}.$$

The pump beam exiting after the crystal is attenuated first by a polarizer, followed by an interference filter centered at 650 nm (transmission bandwidth ~ 10 nm) and a cutoff filter. The output signal of the PMT is then monitored by a lock-in amplifier. The signal power is deduced by making a comparison measurement of the beam at 650 nm from a second dye ring laser (Coherent 699-21 operating with DCM dye) using calibrated neutral density filters to attenuate the probe beam. Care was taken to align the DCM dye laser beam collinearly with the Rh6*G* pump beam so that the probe beam and the generated fluorescence were incident on the same area of the crystal and PMT surface. The transmission at the signal wavelength of the optical path between the crystal and the PMT were measured using the unattenuated probe laser beam in order to deduce the signal power at the exit of the crystal. The typical pump to signal power ratio was $\sim 10^9$.

Numerous measurements were performed with different input powers and angles (θ) (accomplished by changing the aperture radius). The reproducibility of the measurements was good within about 30%. The main sources of error were the aperture radius determination, the fluctuation of the input power, and the calibration of the neutral density filters. This value is then corrected by taking into account the transmission losses of the beams through the crystal (the absorption coefficient was deduced from a calorimetric method to be $\sim 4\% \cdot \text{cm}^{-1}$ at 600 and 650 nm) and the $\sim 17\%$ reflection of the signal on the output side of the crystal. The value of d_{36} [$AgGaS_2$] obtained after these corrections is $31 \pm 5\ 10^{-12}$ m/V.

The most detailed results published previously together with the value reported here are summarized in Table I. The various results involve different frequencies and are compared using Miller's delta rule. Miller [11] suggests that nonlinear coefficients be expressed in the form

$$d_{36} = \chi_p \chi_s \chi_i \delta_{36}$$

where $\chi_{p,s,i} = n^2 - 1$ are the linear optical susceptibilities at the three frequencies and δ_{36} is Miller's delta. Various theories of nonlinear coefficient [11], [14] assume that the frequency dependence of d_{36} is only contained in the product of the susceptibilities, δ_{36} being constant. Table I shows that our experimental value of δ_{36} [$AgGaS_2$] $= 0.23 \pm 0.04\ 10^{-12}$ m/V agrees with the values found by Boyd *et al.* [1] and Kupecek *et al.* [9] employing SHG methods. These values are significantly larger than the

TABLE I
SUMMARY OF THE PUBLISHED RESULTS ON THE NONLINEAR COEFFICIENT OF $AgGaS_2$

λp (*np*)	λs (*ns*)	λi (*ni*)	d_{36} (10^{-12} m/V)	δ_{36} (10^{-12} m/V)	Method	Ref.
10.6 μm (2.347)	10.6 μm (2.347)	5.30 μm (2.341)	57 ± 17	0.62 ± 0.19	SHG Maker fringe relative to GaAs	[8]
10.6 μm (2.346)	10.6 μm (2.346)	5.30 μm (2.341)	18 ± 6	0.20 ± 0.07	SHG wedge relative to GaAs	[1]
1.06 μm (2.451)	1.06 μm (2.451)	5.30 nm (2.606)	34 ± 5	0.23 ± 0.04	SHG Maker fringe relative to SiO_2	[9]
10.6 μm (2.347)	10.6 μm (2.347)	5.30 μm (2.341)	20 ± 4	0.22 ± 0.05	SHG Maker fringe relative to GaAs	[9]
1.06 μm (2.378)	1.30 μm (2.436)	6.0 μm (2.337)	14	0.13	DFG conversion efficiency	[2]
880 nm (2.412)	1.06 μm (2.451)	5.1 μm (2.396)	9 ± 2	0.08 ± 0.02	DFG conversion efficiency	[10]
600 nm (2.531)	650 nm (2.544)	7.8 μm (2.377)	31 ± 5	0.23 ± 0.04	SPE	This work

values established by Kato [2] and Yodh *et al.* [10] obtained from DFG data. For the calculation of refractive indexes for $AgGaS_2$ at different wavelengths we used the Sellmeier equations given by Fan *et al.* [4]. The experiments performed by Chemla *et al.* [8], Boyd *et al.* [1], and Kupecek *et al.* [9] are based on relative measurements of $d_{36}[AgGaS_2]$ with respect to $d_{14}[GaAs] = 134.1 \cdot 10^{-12}$ m/V and $d_{11}[SiO_2] = 0.46 \cdot 10^{-12}$ m/V. More recently, available data for $d_{14}[GaAs]$ and $d_{11}[SiO_2]$ may lead to revision of their value of $d_{36}[AgGaS_2]$ [15].

III. Phase Matching Measurement

The phase matching characteristics were investigated in an experimental setup developed for DFG and described in detail in [12]. Type I 90° phase matching was investigated for three different temperatures, 20, 60, and 100°C. The resulting tuning curves are shown in Fig. 2. Wavelength tuning of the pump and signal lasers from 580 to 610 nm and 620 to 680 nm, respectively, for the crystal at room temperature leads to infrared generation from 7 to 9 μm. Bahr *et al.* [7] previously investigated the dependence of refractive index on crystal temperature up to 90°C. The thermooptic coefficients deduced for both ordinary and extraordinary waves were fitted in the form of a dispersion formula. The results of phase matching calculations using the refractive index data given in [4] corrected by this temperature dependence and applied to our experimental conditions are shown as the solid lines in Fig. 2. Clearly the dependence of the infrared wavelength on temperature we observe is less than that predicted. Quantitatively, the infrared generated frequency deduced from the previous measurements on index of refraction data a shift of ~ 1.5 cm$^{-1} \cdot$ °C^{-1} for a pump wavelength of 600 nm, our measured value is ~ 0.65 cm$^{-1} \cdot$ °C^{-1}. This value is over an order of magnitude smaller than the one obtained for $LiNbO_3$ [13] at 488 nm

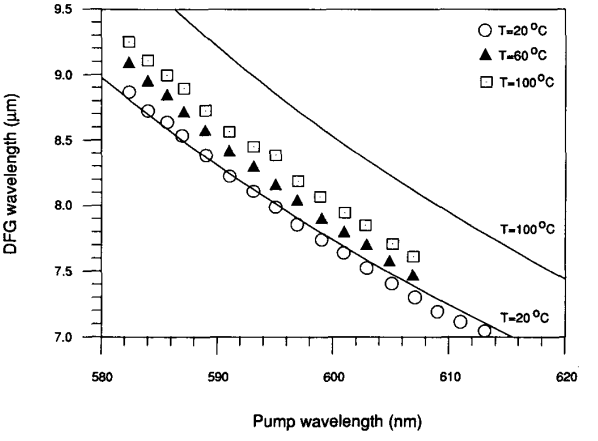

Fig. 2. 90° type I phase matching tuning curves for T = 20, 60, 100°C. The solid lines correspond to the characteristics deduced from refractive index data given in [4] and [7].

(~ 9.5 cm$^{-1} \cdot$ °C^{-1}). In addition, the experimental and calculated phase matching tuning curves at room temperature show a smaller discrepancy which is explained in part by the limited accuracy of the monochromator (±0.15 nm) employed to measure the 699-21 dye laser wavelength although we cannot rule out slight differences between different crystals.

IV. Conclusion

The nonlinear coefficient and phase matching characteristics of $AgGaS_2$ have been investigated. The nonlinear coefficient of $AgGaS_2$ was determined to be d_{36} [$AgGaS_2$] = 31 ± 5 10^{-12} m/V using a SPE technique and accounting for the losses in the crystal. The deduced Miller's delta δ_{36} [$AgGaS_2$] = 0.23 ± 0.04 10^{-12} m/V agrees with the measurements performed by groups employing

SHG methods. However, this value is about twice as large as the value found by groups using DFG measurements.

The 90° type I phase matching tuning curve has been studied for three different temperatures up to 100°C. A small temperature dependence was found corresponding to a sensitivity of the infrared DFG radiation frequency of $\sim 0.6\ \mathrm{cm}^{-1} \cdot {}^{\circ}\mathrm{C}^{-1}$. This sensitivity is twofold smaller than that predicted from previous published refractive index measurements and is much smaller than the temperature sensitivity of $LiNbO_3$.

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