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Study of nonlinear-optical characteristics of $AgGa_{1-x}In_xSe_2$ crystals

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***Abstract*. The nonlinear-optical characteristics of $AgGa_{1-x}In_xSe_2$ crystals with $x = 0.25 - 0.34$ are studied. The experimental dependence of the wavelength of noncritical phase matching on the indium concentration is obtained upon second-harmonic generation by pumping the crystal by a CO_2 laser. The quadratic nonlinear susceptibility is measured by the absolute method. The radiation resistance threshold for pulsed radiation from the CO_2 laser is determined.**

Keywords: *nonlinear-optical crystals, quadratic nonlinear susceptibility, radiation resistance.*

1. Introduction

The mid-IR wavelength range from 3 to 20 μm can be covered for solving some scientific and applied problems by using nonlinear-optical frequency conversion in crystals (sum and difference frequency mixing and optical parametric oscillation). Mixed chalcopyrite crystals are quite promising for these purposes. Solid-solution crystals first of all attract interest because their birefringence depends on their composition. This opens up broad possibilities to optimise them for the type of interaction required to achieve noncritical phase matching.

The $AgGa_{1-x}In_xSe_2$ crystals are well known and the outlook for their use for obtaining nonlinear three-wave mixing with noncritical phase matching has been demonstrated in papers [1 – 6]. At the same time, the main problem encountered in the growing of solid-solution crystals is to obtain samples of the homogeneous chemical compositions. This problem cannot be solved in principle because of the existence of liquid and solid phases with different chemical compositions in the region of crystallisation temperature. For this reason, nonlinear elements cut of $AgGa_{1-x}In_xSe_2$ crystals have the indium concentration that differs from its concentration in the charge [6]. This can introduce uncertainties to the calculations of dispersion dependences for a specific concentration x and, hence, to the calculations of noncritical phase matching wavelengths or other characteristics. For example, the wavelength dependence of the pump wave for second-harmonic generation (SHG) with noncritical phase matching at which the refractive indices n_o and n_e are identical (isotropy point) was experimentally determined in [7] and compared with the dependence calculated based on the data [4 – 6]. This comparison showed that the assumption about a linear dependence of the coefficient of the Sellmeyer equation on x [6] allows a more accurate calculation of the SHG noncritical parameter than it can be done by using results [4]. The inhomogeneity of the chemical composition, which cannot be eliminated in principle, also affects the real efficiency of nonlinear conversion.

In this paper, we studied $AgGa_{1-x}In_xSe_2$ crystals with $x = 0.25 - 0.34$ grown by the Bridgman – Stockbarger method. We found the relation between the chemical composition of the crystal and the pump wavelength at which the noncritical phase-matched SHG can be realised. In addition, the component d_{36} of the nonlinear susceptibility tensor was determined by the absolute method from the measured SHR efficiency and the laser damage threshold of the nonlinear element surface was measured.

2. Experimental

The setup and measurement method are described in detail in [8]. We carefully controlled spatiotemporal characteristics of the TEA CO_2 laser used in experiments. The laser resonator had a diaphragm of diameter 10 mm to obtain the Gaussian intensity distribution over the pump-beam cross section. The radiation was polarised in the vertical plane. Upon lasing at the extreme lines, when a mixture with a low amount of nitrogen was used in the presence of the diaphragm in the laser resonator, a pulse of the CO_2 laser consisted of only a front peak with the FWHM ~ 70 ns. The radiation was focused using a lens with a focal distance of 90 cm. The crystals of length from 14 to 20 mm under study were placed on an optical rotation stage in the lens caustics. The caustics length was ~ 5 cm and the typical beam diameter was ~ 1 mm. Therefore, the energy density over the crystal length was virtually constant, which allowed the use of the plane-wave approximation in calculations.

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2.1 Tuning characteristics and the spatial homogeneity of $AgGa_{1-x}In_xSe_2$ crystals

The $AgGa_{1-x}In_xSe_2$ crystal boule for experiments was grown in the form of a cylinder of diameter 25 mm and length 70 mm. The concentration x of indium changed monotonically over the crystal length. The boule was machined to obtain an element with faces oriented parallel to the cylinder generatrix. The normal to the input face was oriented so that the cut angle was $\theta = 90^\circ$ and the azimuthal angle was $\varphi = 45^\circ$. The input face and optical axis were oriented perpendicular to the CO_2 laser beam.

For a fixed wavelength of the CO_2 laser, the element aperture was scanned by the laser beam along the input face and the coordinates of the region were determined where SHG was detected. These coordinates were later used to manufacture crystalline samples and for chemical analysis. The elemental composition of the samples was studied by the method of optical emission spectrometry with inductively coupled plasma. The stoichiometric composition was calculated from three measurements of concentrations of elements.

Figure 1 shows the dependence of the pump wavelength at which SHG is realised with the 90° phase matching on the concentration x of indium in a crystal. Also, the results of calculations [3, 4, 6, 9] are presented. The results of calculations [3, 4] [curves (*1*) and (*2*)] virtually coincide because the authors of both papers assumed that the squares of refractive indices n_o^2 and n_e^2 were linearly related to the indium concentration. However, the calculated curves are noticeably shifted to the high-concentration region compared to the experimental values. Curve (*3*) from paper [6], where the coefficients of the Sellmeyer equation were related linearly to the concentration x, is much closer to the experiment. Curve (*4*) from [9] is most close to the experiment. Unfortunately, the original data used in the calculation of the theoretical dependence were not presented in [9].

Later on, we used a smaller sample of length 14.6 mm, width 21.8 mm, and height 17 mm of the composition $AgGa_{0.75}In_{0.25}Se_2$. In this case, we expected the realisation of noncritical SHG at the pump wavelength $\lambda_p = 10.7$ μm. The normal to the input aperture (21.8×17 mm) of the crystal was oriented as for the sample with variable x ($\theta = 90^\circ$ and $\varphi = 45^\circ$). The input face was oriented perpendicular to the CO_2 laser beam, while the optical axis lied in the horizontal plane. We measured the second-harmonic energy by scanning the element aperture by the CO_2 laser beam along the horizontal and vertical axes. The horizontal scan showed that the 90° phase matching is realised only in the middle part of the crystal (Fig. 2). One can see from Fig. 2 that the noncritically phase-matched SHG occurs with almost constant efficiency over the crystal length ~ 8 mm. This indicates to a high homogeneity of the chemical composition in this region. The 'plateau' of the dependence of the second-harmonic energy on the laser beam position at a distance of 10 mm from the left edge of the crystal exhibits a minimum of width ~ 1 mm, where the SHG efficiency deceases approximately by one third. This is probably caused by the local inhomogeneity inside the crystal. Upon scanning the aperture by the CO_2 laser beam along the vertical over the length 8 mm, the SHG efficiency continuously changed no more than by ~ 30 %.

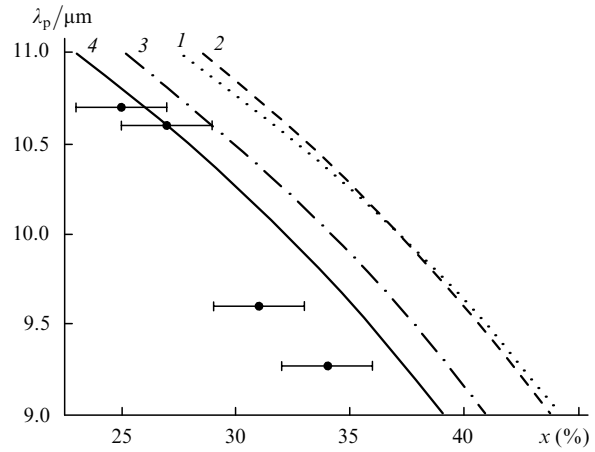

Figure 1. The CO_2 laser pump wave λ_p for which the noncritically phase-matched SHG is realised as a function of the indium concentration x in the crystal. Circles are the experiment, the curves are calculations taken from [3] (*1*), [4] (*2*), [6] (*3*), and [9] (*4*).

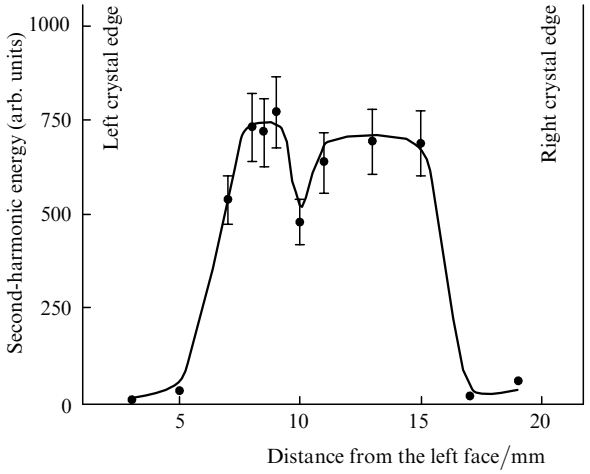

Figure 2. Dependence of the second-harmonic energy on the laser-beam position along the horizontal of the $AgGa_{0.75}In_{0.25}Se_2$ crystal aperture for the normal incidence of laser radiation on the input face of the crystal. The laser beam is located at a height of 9 mm. The pump laser wavelength is $\lambda_p = 10.7$ μm.

The two-dimensional scan of the element aperture clearly illustrates the complexity of growing chemically homogeneous solid-solution crystals. Nevertheless, the homogeneity achieved in our experiments can be considered sufficiently high because upon a change in the indium concentration only by 1 %, the frequency of the 90° phase matching for SHG changed by ~ 10 cm^{-1} (see Fig. 1). For example, when the pump frequency was shifted by 12.8 cm^{-1} in our experiments [the 10P(16)] line, the 90° phase matching could not be achieved at all. Because the external angle of incidence of pump radiation at the 10P(16) line for which the maximum SHG efficiency is achieved was $10^\circ - 30^\circ$ for different points over the aperture width, while the half-width of the angular dependence was $10^\circ - 7^\circ$, we can conclude that the experimental conditions considerably differ from the noncritical phase matching condition. Therefore, the change in the indium concentration in the $AgGa_{0.75}In_{0.25}Se_2$ of size $\sim 14 \times 8 \times 8$ mm is probably of the order of 0.1 %.

The dependence of the SHG efficiency on the rotation angle of the crystal was obtained by irradiating the middle of the crystal aperture by the CO_2 laser at 10.7 μm. The angular phase-matching FWHM was 24°. This value is in good agreement with the estimate of the 90° phase-matching half-width performed by using the corresponding expression from [10]. The values of n_o and n_e required for the estimate were calculated from the Sellmeyer equations with coefficients taken from [3]. The obtained result distinctly demonstrates the realisation of uncritical SHG with a large angular phase-matching width in $AgGa_{1-x}In_xSe_2$ crystals. For comparison, the angular phase-matching width for SHG in an $AgGaSe_2$ of the same length is an order of magnitude smaller.

2.2 Quadratic nonlinear susceptibility

The quadratic nonlinear susceptibility of an $AgGa_{0.75}In_{0.25}Se_2$ crystal (see section 2.1) was measured by the absolute method using the second harmonic of the CO_2 laser. To calculate the nonlinear susceptibility from the measured SHG efficiency, it is necessary to fulfil certain experimental conditions and to select the corresponding model of nonlinear interaction and the adequate method of calculations. Only in this way the required accuracy of the calculations can be obtained. Obviously, the best calculation accuracy can be obtained by solving the system of equations for the amplitudes of interacting waves by the numerical method taking into account different experimental factors, as for example, has been proposed in [11]. On the other hand, if the accuracy of measuring experimental data and (or) the difference between the real parameters of a nonlinear medium and the ideal parameters do not correspond to the accuracy of the model, the simpler calculation methods can be used, as has been done in our paper [8] for calculating the quadratic nonlinear susceptibility of $HgGa_2S_4$ crystals.

The component d_{36} of the tensor of quadratic nonlinear susceptibility was calculated assuming that the mixed crystal belongs to the same point symmetry group D_{2d} as pure crystals $AgGaSe_2$ and $AgInSe_2$. Therefore, the effective nonlinear susceptibility for SHG is $d_{\text{eff}} = d_{36}\sin\theta\sin 2\varphi$, and for $\theta = 90^\circ$ and $\varphi = 45^\circ$, we obtain $d_{\text{eff}} = d_{36}$.

The mathematical expression for the calculation of d_{eff} was obtained by solving the system of shortened equations for coupled plane waves in the fixed-field approximation. The equations took into account the linear absorption of pump fields and second harmonic in the crystal. The final expression for d_{eff} was derived taking into account the following experimental facts: the Gaussian shape of the pump and second-harmonic beams; the difference between the spatial and temporal distributions of the second-harmonic and CO_2 laser radiations; and a decrease in the energy of the pump wave incident at the phase-matching angle on a crystal surface due Fresnel losses. The real shape of the CO_2 laser pulse, the increase in the cross section, propagation length, and absorption of the CO_2 laser and second-harmonic radiation due to their non-perpendicular incidence on the input face, the losses of second-harmonic radiation in a LiF filter and Fresnel losses on the output crystal surface were also taken into account. The walk-off of the second-harmonic radiation with respect to the pump beam and the presence of longitudinal modes in the pump radiation were neglected. As a result, we obtained

$$d_{\text{eff}} = \left\{ \frac{n_1^2 n_2 \lambda^2 c (2S\cos r/\cos i)\Delta t}{512\pi^2 k_f (1-R_2^p)(1-R_1^s)^2} \times \frac{\left[\sum_i \left(f_i \Big/ \sum_i f_i\right)^2\right]^{-1}}{(e^{-2k_1 L'} - e^{-k_2 L'})^2/(k_2 - 2k_1)^2} \frac{E_2}{E_1^2} \right\}^{1/2}. \quad (1)$$

Here, $n_{1,2}$ are the refractive indice of the crystal for the pump wave (o-wave) and second-harmonic wave (e-wave); λ is the pump wavelength; c is the speed of light; S is the pump-beam cross section at the 1/e level; 2 is a factor that takes into account a decease in the cross section of the second-harmonic beam for a Gaussian pump beam by half compared to S; i and r are the angle of incidence on the crystal and the corresponding refraction angle of the pump beam for which the second-harmonic pulse energy is maximal; $k_{1,2}$ are the linear absorption coefficients of the crystal at the pump and second-harmonic waves; k_f is the transmission coefficient of LiF filter at the second-harmonic wavelength; $E_{1,2}$ are the pump and second-harmonic energies measured at the maximum of the angular dependence of the lasing intensity; $L' = L/\cos r$; L is the crystal length; R_1^s and R_2^p are the reflection coefficients for the pump wave (s-polarisation) and second-harmonic wave (p-polarisation) calculated by the Fresnel formulas taking into account the oblique incidence of pump radiation of the crystal; $\Delta t = t_{i+1} - t_i$ is a digitisation step of the temporal shape of the pump pulse; f_i is the value of the function $f(t)$ describing the time dependence of the pump-pulse energy at points t_i.

The real shape of the laser pulse was taken into account as was proposed in [10]. In the case of SHG, it can be rigorously shown that this can be achieved by introducing the factor

$$F \equiv \Delta t\left[\sum_i \left(f_i \Big/ \sum_i f_i\right)^2\right]^{-1},$$

which accurately takes into account the temporal shape of the pulse and is calculated numerically. The term $(e^{-2k_1 L'} - e^{-k_2 L'}) \times (k_2 - 2k_1)^{-1}$ describes the linear absorption of pump and second-harmonic beams and is similar to that obtained in [12]. In our case, it is virtually equal to L' because absorption in $AgGa_{1-x}In_xSe_2$ crystals can be neglected [9].

The average value of d_{36} measured at different points of the central part of the aperture for the $AgGa_{0.75}In_{0.25}Se_2$ crystal was $(29 \pm 5) \times 10^{-12}$ m V^{-1} or $(70 \pm 12) \times 10^{-9}$ esu. Taking into account a change in the SHG efficiency along the crystal aperture vertical, the value of d_{36} achieves $(37 \pm 5) \times 10^{-12}$ m V^{-1} or $(88 \pm 14) \times 10^{-9}$ esu.

Let us compare the obtained value of d_{36} with the values reported in the literature. In [2], the relative measurements of the SHG efficiency were performed in $AgGa_{0.6}In_{0.4}Se_2$ and $AgGaSe_2$ crystals. It was reported that the SHG efficiency in the $AgGa_{0.6}In_{0.4}Se_2$ crystal was higher by a factor of 1.5. However, this result was explained in [2] by the violation of the phase-matching condition for the $AgGaSe_2$ crystal due to the angular mismatch and the aperture effect caused by a high divergence of the pump beam. In [3], the ratio $d_{36}(AgInSe_2)/d_{36}(AgGaSe_2) = 1.133 \pm 0.16$ of the components of nonlinear susceptibility of pure crystals was determined from data [13] and, taking the known value $d_{36}(AgGaSe_2) = 39.0 \times 10^{-12}$ m V^{-1} [14] into account, the values of d_{36} were calculated for mixed crystals with

different x. It was found in [3] that $d_{36} = 40.3\times 10^{-12}$ m V^{-1} for $x = 0.25$. In [9], the value $d_{36} = 34.2 \times 10^{-12}$ m V^{-1} is reported without indication of the indium concentration. Therefore, the maximum value of $d_{36} = (37 \pm 5)\times 10^{-12}$ m V^{-1} measured in our paper is in good agreement within the experimental error with the values of d_{36} reported in [3] and [9].

At the same time, taking into account the error in measuring the ratio $d_{36}(AgInSe_2)/d_{36}(AgGaSe_2)$ and a significant scatter in the values of $d_{36}(AgGaSe_2)$ [$(32.4-57.7) \times 10^{-12}$ m V^{-1}] [15] reported in the literature, we can say definitely only that the components d_{36} for real mixed crystals can be comparable with d_{36} for $AgGaSe_2$, which has been confirmed by our measurements.

2.3 Radiation resistance

We measured the radiation resistance of the $AgGa_{0.75}In_{0.25}Se_2$ sample described above. For comparison, the surface damage threshold was also measured for an $AgGaSe_2$ crystal. Both these crystals were grown at the Laboratory of Novel Technologies, Kuban State University and mechanically polished at the same optical workshop to the degree of surface finish between III and IV. The crystal surface was oriented perpendicular to a beam of the CO_2 laser emitting a 10.7-μm 10P(30) line. The fluence of the laser beam could be varied from 1 to 5 J cm^{-2} by using CaF_2 plate attenuators of different thickness. The laser-beam cross section at the 1/e level was 0.83 mm^2. Because the spatial energy distribution over the beam cross section was Gaussian, the damage thresholds presented below were measured at the maximum of the Gaussian distribution.

The appearance of the damage on the sample surface was determined visually by a plasma flash near the surface with the help of a tenfold magnifying glass. Each crystal region was irradiated one time, 8 – 10 different regions on the crystal surface being irradiated at the same energy density. The damage probability P_d was calculated as the ratio of the number of irradiated regions where the damage was produced to the total number of regions. The damage threshold Φ_d was determined by plotting the curve $P_d(\Phi)$ and determining the region where $P_d > 0.5$.

The experiment showed that the damage threshold $\Phi_d = 2.6 \pm 0.3$ J cm^{-2} for the $AgGa_{0.75}In_{0.25}Se_2$ crystal was lower by a factor of 1.6 than that for the $AgGaSe_2$ crystal ($\Phi_d = 4.2 \pm 0.5$ J cm^{-2}). Because the total laser-pulse energy was concentrated in a 70-ns pulse, the intensity damage threshold I_d can be calculated from Φ_d. It was 37 ± 4 and 60 ± 7 MW cm^{-2} for the $AgGa_{0.75}In_{0.25}Se_2$ and $AgGaSe_2$ crystals, respectively.

Let us discuss in more detail the values of damage thresholds I_d obtained in our experiment. It is known that the damage threshold substantially depends on the sample quality (concentration of absorbing impurities and defects) and the quality of their surface determined by the methods of machining and storage, and can vary from sample to sample [16]. In addition, the damage threshold also depends on the irradiation regime; the pulse duration, the mode composition and laser-beam cross section [17]. Taking all this into account, the damage threshold $I_d = 60$ MW cm^{-2} for the $AgGaSe_2$ measured in our experiments well agrees with thresholds reported in [18] for laser pulses of duration $30 - 150$ ns in the region from 9.27 to 10.6 μm. According to [18], the thresholds lie in the range $10 - 150$ MW cm^{-2}, most of them being within $10 - 50$ MW cm^{-2}.

It is important to emphasise that we measured the radiation resistance under the same experimental conditions for crystals grown and polished with the same quality. Therefore, the decrease in the damage threshold for $AgGa_{1-x}In_xSe_2$ crystals by a factor of 1.6 compared to that for $AgGaSe_2$ crystals can be considered a reliable experimental fact. The reduction in the TEA CO_2 laser damage resistance of mixed crystals by ~ 20 % compared to pure $AgGaSe_2$ crystals was pointed out in [3].

Note also that the absolute thresholds were measured for one-shot irradiation of crystal surfaces by a 0.83-mm^2 single-mode laser beam. The damage threshold can considerably decrease upon repeated irradiation of the same region of the crystal surface by a multimode laser beam of a greater diameter [17, 19].

3. Conclusions

We have studied some nonlinear-optical characteristics of $AgGa_{1-x}In_xSe_2$ solid-solution crystals for $x = 0.25 - 0.34$. The pump wavelength for which the 90° phase-matched SHG is realised is measured as a function of the indium concentration x. The quadratic nonlinear susceptibility has been measured by the absolute method, its maximum value for a particular crystal being $(37 \pm 5) \times 10^{-12}$ m V^{-1}. The surface damage threshold for pulsed CO_2 laser radiation was measured to be 37 ± 4 MW cm^{-2}.

We have shown that the nonlinear-optical characteristics of solid-solution $AgGa_{1-x}In_xSe_2$ crystals are comparable to those of the efficient mid-IR frequency converters such as $AgGaSe_2$ crystals. At the same time, $AgGa_{1-x}In_xSe_2$ crystals have a substantial advantage allowing the realisation of the 90° phase matching for a particular type of interaction by selecting a proper concentration of indium.

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