OPTICS AND SPECTROSCOPY

PARAMETRICAL CONVERSION OF THE FREQUENCY OF ORGANIC LASERS INTO THE MIDDLE-IR RANGE OF THE SPECTRUM

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The possibility of parametrical conversion of visible radiation of solid-state organic lasers into the middle-IR range of the spectrum in nonlinear $GaSe_{1-x}S_x$ *(x = 0–0.13) crystals is investigated. Generation at the difference frequency (wavelength* $\lambda_3 = 9.43\ \mu m$*) of induced oxazine-1 (at* $\lambda_1 = 740\ nm$*) and rhodamine-800 (*$\lambda_2 = 803.4\ nm$*) radiation is excited. The conversion efficiency is estimated, and prospects for its further increase are demonstrated.*

Keywords: organic lasers, parametrical frequency conversion, nonlinear crystals.

To solve many scientific and applied problems on resonant influence of laser radiation on a substance in spectroscopy, remote sensing, isotope separation, etc., sources of coherent radiation with frequency tunable in various spectral ranges are required [1]. One of the most promising methods of mastering new spectral ranges is parametrical frequency conversion of radiation of the most efficient and technically developed lasers by the methods of nonlinear crystal optics [2, 3]. Many nonlinear crystals have been grown over the preceding period. They are widely used for parametrical frequency conversion of lasers operating in the UV, visible, and near-IR ranges of the spectrum. The middle-IR, submillimeter, and millimeter ranges of the spectrum have been mastered much weaker. The frequency converters of the middle-IR range, most promising for the spectral gas analysis because of the presence of intense isolated absorption lines, are only at the beginning of their commercial application. Radiation of gas and chemical lasers can efficiently be converted into other spectral intervals from the middle-IR range; however, the lasers themselves as sources of pumping radiation have low efficiency, big sizes, large energy consumption, and need cooling. Parametrical light generators (PLG) based on widespread nonlinear crystals of the middle-IR range have insufficiently high nonlinear properties and beam stability and do not allow narrow frequency-tunable lines to be generated with output energy parameters and operating time to failure suitable for practical applications. Due to the special features of the transparency spectrum of such crystals, only solid-state lasers with wavelengths exceeding 2–3 μm can be used for pumping, including cryogenic holmium and erbium lasers with low (≤10 Hz) pulse repetition frequency. Commercial PLG pumped by shorter-wavelength lasers and based on a number of nonlinear oxide crystals have been developed, but the spectral range of their generation is limited from above by wavelengths of 4–5 μm [4]. Such situation calls for a search of new pumping lasers and nonlinear crystals as well as of parametrical frequency converters to develop solid-state narrow-band frequency-tunable radiation sources for the entire middle-IR range with high output and operational parameters.

Significant progress achieved in the development of tunable organic lasers of the near-IR range pumped by radiation of Nd^{3+}:YAG lasers whose gain is sufficient for single-pass generation [5] enables us to consider these lasers

as the most promising pump sources for difference frequency generators (DFG) of the middle-IR range. Their high gain allows narrow frequency-tunable generation lines to be obtained, and the use of residual Nd^{3+}:YAG laser radiation for the second pump source allows narrow-band frequency-tunable radiation of the middle-IR range to be generated. By the present time, the solid-state organic lasers pumped by the second harmonic of the Nd^{3+}:YAG laser have been developed whose energy and service lifetime compare well with those of liquid active media. High-quality narrow-band (0.01 nm) radiation with small (~2 mrad) divergence, high (~15%) conversion efficiency, and high (~10^6 pulses) photostability was obtained for solid-state active media. The output radiation energy of the system master generator – preamplifier – amplifier was as great as 100 mJ [6].

The DFG have a number of advantages in comparison with the PLG. Being nonthreshold devices, they do not require high-quality dielectric feedback mirrors, and the requirements imposed on the optical crystal quality and quality of manufacturing nonlinear elements capable of operating without enhancement of their transmission are minimal. The same is true for mastering of submillimeter and millimeter ranges of the spectrum. In this approach, only one difficult problem, namely, a search for wideband nonlinear crystals transparent from the visible to far-IR range must be solved.

The present work studies the possibility of generation of radiation at different frequency of solid-state tunable organic oxazine-1 and rhodamine-800 lasers in the middle-IR range using nonlinear $GaSe_{1-x}S_x$ ($x = 0$–0.13) solid-solution crystals.

EXPERIMENT

Figure 1 shows the block diagram and the external view of the difference frequency generator and its unit with a nonlinear crystal.

For nonlinear crystals – difference frequency generators – we used GaSe crystals (the spectral transparency range is 0.62–20 µm) with modified physical properties, namely, the solid solution crystals with the chemical formula $GaSe:GaS \rightarrow GaSe_{1-x}S_x$ and the mixture ratio $0 \leq x \leq 0.13$. As is well known, the layered GaSe crystals are characterized by the unique physical properties and one very essential disadvantage, namely, extremely low mechanical properties caused by hardness in Mohs scale close to zero and easiness of cleavage. The modern technology of GaSe single crystal growth is characterized by high layer cleavage and as a result, a large number of cleavage defects that mask high natural nonlinear crystal properties ($d_{22} = 70$ pm/V) and determine relatively low optical quality (with the absorption coefficient $\alpha \leq 0.1$ cm^{-1}) of elements fabricated from the crystal [4, 7].

Preliminary investigations into the physical properties of layered $GaSe_{1-x}S_x$ ($x \leq 0.4$) solid solution crystals have demonstrated that they retain the main advantage of the GaSe crystals – the wide transparency range. Moreover, the short-wavelength boundary of the transparency spectrum is shifted toward a shorter wavelength of 0.56 µm as x increases to 0.4. This shift reduces the optical losses at dye laser wavelengths and the nonlinear two-photon losses. The hardness of solid-solution crystals linearly increases with x and is doubled for $x = 0.4$. Starting from $x = 0.09$ (a sulfur content of 2 wt%), crystals can be machined, cut with a diamond saw, and polished by a finely dispersed (0.5 µm) diamond powder with subsequent smoothing by finely dispersed polishers [8, 9]. After that the crystal cleavage decreases significantly compared to pure GaSe crystals, thereby eliminating the cleavage defects that mask high natural nonlinear crystal properties. It should be noted that with increase in the number of selenium atoms substituted by sulfur atoms, the nonlinear properties of the $GaSe_{1-x}S_x$ crystals are simultaneously deteriorated, which necessitates optimization of the mixture ratio x. The thermal properties also change with x: for $x = 0.4$, they increase 4 times in the direction orthogonal to that of layer growth and remain virtually constant in the direction of layer growth. Investigations of the optical properties and damage thresholds of the available crystal samples have allowed us to choose $GaSe_{1-x}S_x$ ($x = 0.13$) or $GaSe_{0.87}S_{0.13}$ crystals as those possessing the best physical properties for the modern technology of their growth.

The PÉP-558P pyroelectric detector without cooling and with nonselective sensitivity band of 2–20 µm and 8×8 mm receiving aperture having a response time constant of 1 ns was used as a detector of radiation at the difference frequency. Because the repetition frequency of Nd:YAG laser pulses was ≤10 Hz, a Unipan 233 nanovoltmeter with a Unipan 233.5 preamplifier operated in the nonselective mode with a 300-kHz transmission band and a measurement threshold of 0.03 µV. This transmission band determined the waveform of amplified radiation pulses and the regime of
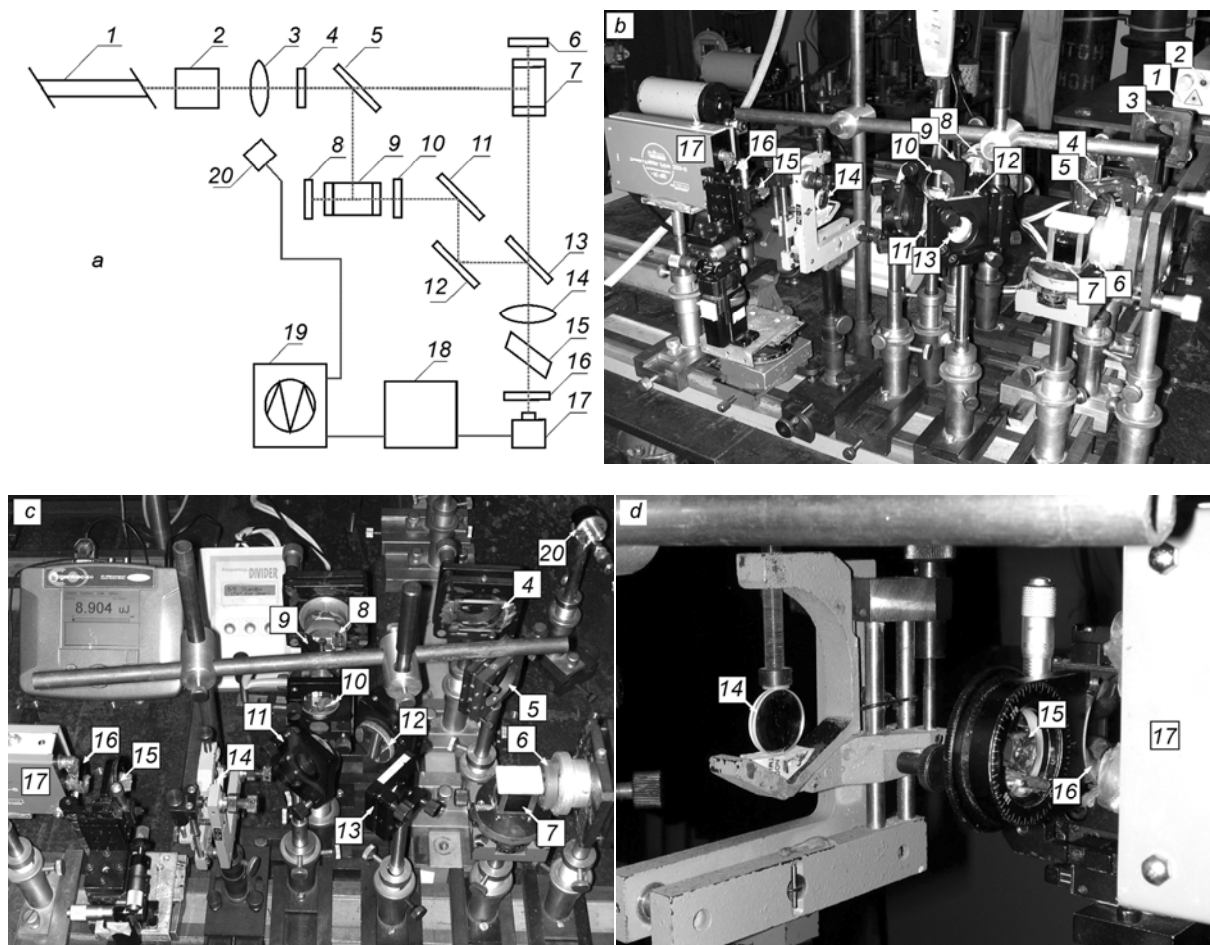
Fig. 1. Block diagram (*a*), side (*b*) and top views (*c*) of the difference frequency generator, external view of the difference frequency generator with the nonlinear crystal (*d*), and the nonlinear $GaSe_{1-x}S_x$ ($x = 0.13$) crystal. The generator comprises neodymium laser *1*, second-harmonic generator of the neodymium laser *2*, focusing cylindrical lenses *3* and *4*, splitting dielectric mirror *5*, 100% reflecting mirrors *6* and *8*, transmitter with $\lambda_1 = 740$ nm (oxazine 1) *7*, transmitter with $\lambda_2 = 803$ nm (rhodamine 800) *9*, output mirror (quartz plate) for $\lambda_1 = 740$ nm and $\lambda_2 = 803$ nm *10*, aluminum rotatable mirrors *11* and *12*, semitransparent dielectric mirror *13*, quartz lens *14*, nonlinear GaSe crystal *15*, GaAs blocking filter with thickness of 0.5 mm *16*, PÉP-558P pyroelectric detector with Unipan 233.5 preamplifier *17*, selective Unipan 233 nanovoltmeter *18*, TDS 224 Textronics oscillograph *19*, and reference silicon photodiode *20*.

energy rather than peak capacity measurements of pulses generated at the difference frequency. The pyroelectric detector with electronic registration channel was calibrated as an energy measuring instrument against an absolutely black body, a CO_2 laser, an IMO-2N laser radiation energy and power meter, and a set of calibrated attenuators – CaF_2 plates. The minimal measurement threshold was 0.3 µJ. The energy of organic laser pulses was measured with a Gentec DUO pyroelectric power meter produced by Gentec Electro-Optics, Inc. It was equipped with an ED-100A-UV V6 detector 3.8 mm in diameter having a measurement threshold of 10 µJ.

Difference frequency generation at a wavelength of 9.43 µm with energies per pulse up to 3.4 mJ was excited in the $GaSe_{0.87}S_{0.13}$ crystal pumped with radiation of organic oxazine-1 and rhodamine-800 lasers operating at wavelengths of 0.74 and 0.803 µm, respectively (Fig. 2*a*). Figure 2 shows the pulse waveform at the output from the detector of difference frequency radiation displayed on the oscillograph screen.
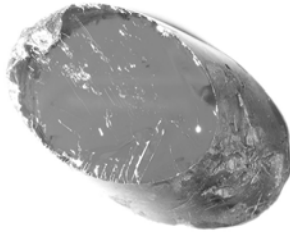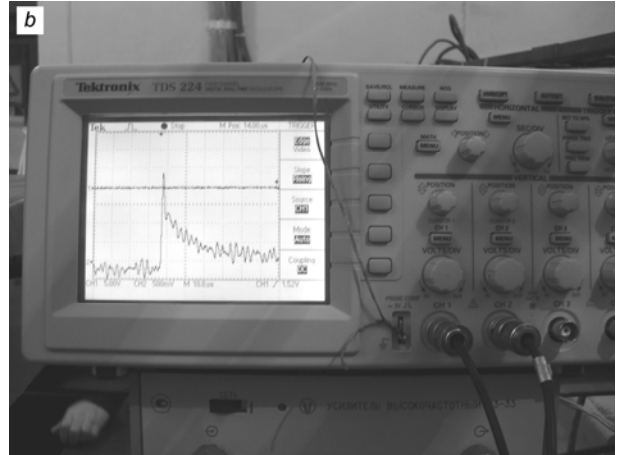
Fig. 2. External view of the GaSe$_{1-x}$S$_x$ ($x = 0.13$) crystal (*a*) and the waveform of the signal at the difference frequency with $\lambda = 9.43$ μm displayed on the oscillograph screen (*b*).
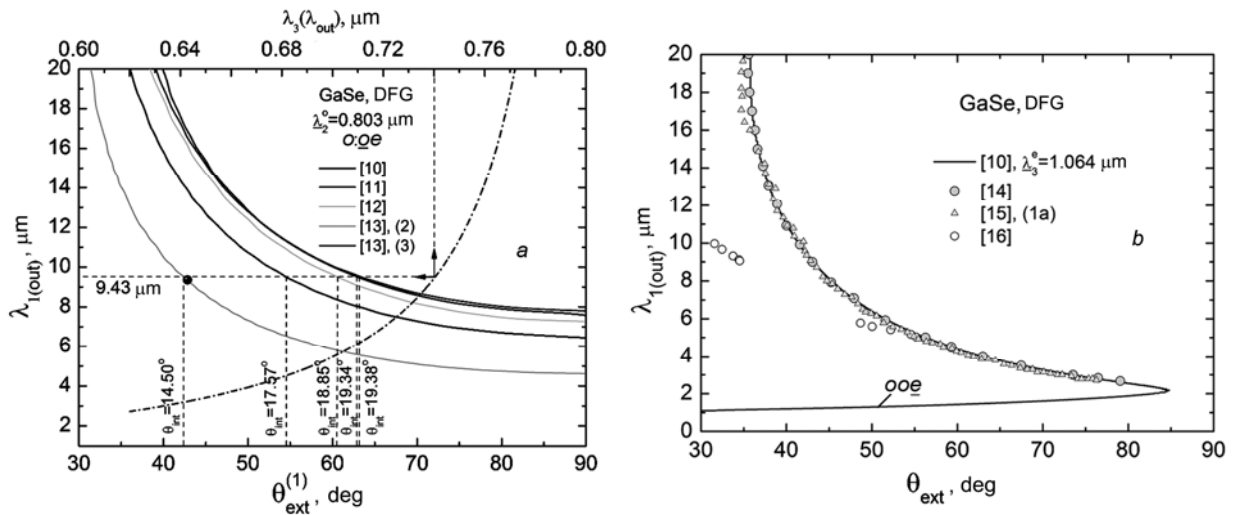

Fig. 3. Conditions of DFG phase matching through interactions of type I ($oo \rightarrow e$) in the GaSe crystal. Here solid curves show estimates from the available literature data indicated in the insert, the dashed curve shows coupling between IR wavelengths λ_1 and λ_3 when the condition of phase matching is satisfied, the filled circle illustrates the experimental result of the present work for DFG in the GaSe$_{0.87}$S$_{0.13}$ crystal (*a*) and for the DFG organic laser operating in the spectral range 0.61–1.01 μm and Nd:YAG laser; (*b*) shows the well-known experimental data. The parameters of the wave with a fixed frequency are underlined, and the serial numbers of calculation formulas are given in parentheses.

The conditions of phase matching for the difference frequency generator in the pure GaSe crystals (typically of ε polytype [7]) were calculated from the well-known data on the dispersive crystal properties [10–13]. It was found that difference frequency generation can be excited only through the $oo \rightarrow e$ interaction. The tuning curves illustrating the difference frequency generation of the rhodamine-800 laser with fixed wavelength λ_2 and of the oxazine-1 laser tunable in the range $\lambda_3 = 0.6$–0.8 μm are shown in Fig. 3*a*.

From Fig. 3*a* it can be seen that numerical estimates of the external phase matching angles $\theta_{ext}^{(1)}$ differ significantly, up to 20°. An analysis demonstrates that out experimental results on frequency conversion in pure ε-GaSe

crystals are in the best agreement with estimates performed in [10]. For a comparison, Fig. 3*b* shows the calculated and well-known experimental results on generation of radiation at the difference frequency of the Nd:YAG laser and lasers operating in the spectral range 0.61–1.01 µm in pure ε-GaSe crystals. It also indicates a wide scatter of the estimated and experimental data. As a whole, the results of investigations shown in Fig. 3 unambiguously indicate the necessity of determining the most reliable data on the dispersive properties of the pure ε-GaSe crystals or of their re-determination at least, for the short-wavelength part of the transparency spectrum. Though in the scientific literature there are data on the dispersive properties of the pure GaS crystals usually having the β-polytype structure [14], most of them, by analogy with the data on the dispersive properties of ε-GaSe crystals, cannot be used to estimate the dispersive properties (the spectral dependence of the refractive index $n_{o,e}$ for ordinary and extraordinary waves) of the $GaSe_{1-x}S_x$ solid solution crystals from the known expression [15]

$$n_{o,e}^2(\text{the solid solution crystal}) = (1-x) \cdot n_{o,e}^2(\text{the first crystal}) + x n_{o,e}^2(\text{the second crystal}).$$

The above expression is applicable for estimation of the dispersive properties of crystals with identical structures only, whereas all three crystals examined here are polymorphic, which makes their true structures uncertain. Nevertheless, we can assume that when the content of the second parental GaS crystal having any arbitrary polytype is small, the $GaSe_{1-x}S_x$ solid solution crystals will have the same crystal structure as the ε-GaSe crystals, and their dispersive properties will be determined mainly by those of the ε-GaSe crystals. The applicability of this approach was qualitatively confirmed by the estimated phase matching conditions for DFG in the $GaSe_{0.87}S_{0.13}$ solid solution crystal using the above expression and by the experimental external DFG matching angle $\theta = 42°$ (Fig. 3*a*). The shift of the phase matching condition for the $GaSe_{0.87}S_{0.13}$ crystal toward shorter wavelengths is in good agreement with the shift of the short-wavelength boundary of the transparency spectrum for the GaS crystals (0.48 µm) from the corresponding boundary of the GaSe crystals (0.62 µm). The coincidence of the matching conditions with those calculated in [13] (formula (2)) for pure GaSe crystal can be considered occasional.

As a consequence, a wide scatter of data on the dispersive properties of ε-GaSe crystals, the limited volume of data on the dispersive properties of the GaS crystals, the uncertainty in the polymorphic structure of the $GaSe_{1-x}S_x$ solid solution crystals, and the lack of an algorithm for estimation of the dispersive properties of solid solution crystals prepared from crystals with different polytypes have not allowed us to find a phase matching condition for DFG in the $GaSe_{1-x}S_x$ ($x = 0.0046$, 0.045, 0.09, 0.133, 0.216, 0.29 and 0.4) solid solution crystals. At the same time, experimental investigations of the possibility of the second harmonic generation by erbium and CO_2 lasers in the examined crystals were successful and demonstrated the high efficiency of frequency conversion that increased more than twice.

CONCLUSIONS

Thus, the most important results of our investigations are the following. With pumping by radiation of the solid-state oxazine-1 and rhodamine-800 organic lasers, generation of difference frequency radiation has been registered in the nonlinear $GaSe_{1-x}S_x$ ($x = 0.13$) crystal at $\lambda = 9.43$ µm for an external phase matching angle of 42°. The energy per pulse at the difference frequency was 3.4 µJ, which corresponded to external energy efficiencies of difference frequency generation of 0.68 and 0.34% and quantum efficiencies of 8.8 and 3.8%. The enhanced transparency of the nonlinear crystal and blocking filter will allow the quantum efficiency of difference frequency generation to be increased by a factor of 1.5, and the optimization of beam cross sections will allow it to be increased by a factor of 1.4. It has been established that the short-wavelength boundary of the $GaSe_{1-x}S_x$ ($x = 0.4$) crystal transparency spectrum is shifted toward shorter wavelengths from 0.62 to 0.58 µm. This allows shorter-wavelength radiation of organic lasers to be used.

From the known crystals, the nonlinear $GaSe_{1-x}S_x$ ($x = 0$–0.4) crystals are most promising for conversion of organic laser radiation. The problem of re-determination of the dispersive properties of GaSe and GaS crystals is very urgent. Of interest is the development of an algorithm for estimation of the dispersive properties of solid solution crystals grown from two parental crystals having different polytype structures.

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