Generation of second harmonic of TEA CO_2 lasers in $Cd_xHg_{(1-x)}Ga_2S_4$

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The composition of new mixed nonlinear crystals $Cd_xHg_{(1-x)}Ga_2S_4$ grown at the initial mixing ratio $x = 0.35$, as well as the transmission spectrum, disperse properties, and coefficient of second-order nonlinear susceptibility, is determined. The damage threshold of 271 MW/cm^2 for 30 ns pump pulses of the TEA CO_2 laser is 1.7–2.0 times higher than that of $ZnGeP_2$. For the first time, parametric frequency conversion, i.e., second harmonic generation of CO_2 lasers is realized. The external SHG efficiency is threefold as high as the SHG efficiency in $ZnGeP_2$ and equals to 0.12% in energy and 0.22% in peak power at the pump intensity amounting to 10% of the damage level intensity.

Introduction

The creation of efficient second harmonic generators (SHGs) for CO_2 lasers on the basis of well known nonlinear $CdGeAs_2$ crystals (transmission region of 2.4–18.0 μm) is difficult due to the presence of significant optical losses at the second harmonic (SH) wavelengths, characterized by the attenuation coefficient $\alpha = 0.3$–0.5 cm^{-1}. The efficiency of SHG on the basis of $ZnGeP_2$ crystals (0.74–12.0) is limited due to the high losses at the wavelength of the fundamental radiation, $\alpha = 0.8$–1.2 cm^{-1}. Because of the low damage threshold, relatively low nonlinear properties, and low thermal properties, $AgGaSe_2$ (0.71–19.0) and Tl_3AsSe_3 (1.28–17.0) crystals also do not allow this problem to be solved. The poor cleavage of laminar GaSe crystals causes the extremely low mechanical properties and low thermal conductivity in the direction orthogonal to growth layers and masks the high natural nonlinear properties, thus preventing the creation of efficient SHG CO_2 lasers on their basis.[1] The spectral position of shortwave boundaries of the transmission spectra of the crystals and their features mentioned above do not also permit the creation of mid-IR optical parametric oscillators (OPO) pumped by the widely used Nd:YAG lasers. Though Nd:YAG lasers can be used to pump OPO on the basis of $AgGaS_2$ (0.47–13.0) [Ref. 1], $LiInS_2$ (0.4–12.5) [Ref. 2], and $LiInSe_2$ (0.6–12.2) crystals [Ref. 3], the efficient parametric generation in them is not obtained because of the clearly low nonlinear and thermal properties.[4]

New nonlinear $HgGa_2S_4$ crystals (0.49–14.3 μm) possess experimentally proved advantages over all the crystals mentioned above both in the creation of SHG CO_2 lasers and in the potential efficiency of mid-IR OPO pumped by Nd:YAG laser radiation.[5,6,11–14] The damage threshold of these crystals exceeds by two to three times that of $CdGeAs_2$, $ZnGeP_2$, Tl_3AsSe_3, $AgGaSe_2$, and GaSe crystals. Because of high nonlinear properties ($d_{36} = 35$ pm/V and $d_{31} = 15$ pm/V) at the lower values of the refractive indices, as well as the more optimal phase matching conditions in comparison with the crystals mentioned above, they occupy the second place in the SHG efficiency of CO_2 lasers (after the $CdGeAs_2$ crystals, operating at cryogenic temperatures) and the first place in the potential efficiency of mid-IR OPO pumped by the radiation of near-IR solid-state lasers in general and the Nd:YAG laser in particular.[6] On the other hand, $HgGa_2S_4$ crystals do not provide for the noncritical 90° phase-matching conditions (NPLCs) for SHG and OPO, which lift the restrictions on the length of the used crystal samples (restrictions are caused by the "walk-off effect" of the interacting radiations). Note that the efficiency of frequency conversion is proportional to the square length of the used crystal samples. For $HgGa_2S_4$ crystals, NPLCs provide for the maximum possible value of the effective coefficient of nonlinear susceptibility.

In Refs. 7 to 10, to overcome the problem of achieving NPLCs, solid solutions of two nonlinear crystals of the $A^{I}B^{III}C_2^{VI}$ group and crystals of the $A^{IV}B_2^{VI}$ group were developed and studied. One of the crystals of the $A^{I}B^{III}C_2^{VI}$ group[11] had low or zero

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birefringence. The noncritical phase-matching conditions in these mixed crystals were obtained by the selection of the mixing ratio x of the two initial crystals. It was assumed that the mixed crystals should be more efficient in the frequency conversion as compared to the initial anisotropic crystals, if the second crystal, which may be isotropic, is characterized by higher figure of merit $M = d^2/n^3$, where d is the second-order nonlinear susceptibility coefficient; n is the mean value of the refractive index at the wavelengths of the interacting radiations. Nevertheless, the investigations of the frequency converters based on mixed crystals such as $CdGe(As_xP_{1-x})_2$ [Ref. 7], $AgGa_xIn_{1-x}S_2$ [Ref. 8], $AgGa_xIn_{1-x}Se_2$ [Refs. 9, 10], and $AgGa(S_xSe_{1-x})_2$ [Ref. 7] confirmed this assumption only in the case of $AgGa_xIn_{1-x}Se_2$ crystals used for SHG of CO_2 lasers.

This paper presents some results of investigation of the optical properties, composition, and damage threshold of a new mixed crystal, obtained by the scheme $HgGa_2S_4$:$CdGa_2S_4 \rightarrow Cd_xHg_{(1-x)}Ga_2S_4$, as well as the parameters of CO_2 laser frequency doublers on the basis of this crystal.

1. Linear optical properties

The initial negative birefrigent $HgGa_2S_4$ crystal has a point symmetry group $\bar{4}$, a melting point of 880°C, the Mohs hardness of 3–3.5, and the density of 4.95 g/cm^3. The width of its forbidden zone is 2.84 eV, and the transmission region of the studied crystal sample having yellow color and the length of 3.1 mm is 0.51–14.3 μm at the 0.1 level.[5,6,11–14] Another initial crystal, $CdGa_2S_4$, has the same point symmetry group, the transmission region of 0.4–13.0 μm at the 0.1 level, the melting point of 984°C, the density of 3.97 g/cm^3, the second-order nonlinear susceptibility coefficient 10% lower than that of the $HgGa_2S_4$ crystal, and the birefringence $B \le 0.006$ [Refs. 15 and 16].

The studied sample of the mixed $Cd_xHg_{(1-x)}Ga_2S_4$ monocrystal was cut off a tail piece of an ingot, grown by the vertical Bridgman method from the initial material characterized by the mixing ratio $x = 0.35$ at the stage of preparation of the growth process. The chemical microanalysis by an electron-emission microscope (M/S Joel, Japan) with a Link spectrophotometric attachment (Germany) has confirmed its stochiometric composition. The maximum variations in the content of the components are reflected in the chemical formula: $Cd_{0.1\pm0.06}Hg_{0.9\pm0.06}Ga_{2\pm0.12}S_{4\pm0.09}$. The data on the mean content of Cd in this sample differ considerably from the results of the previous analysis – Cd (0.35 ± 0.07) [Ref. 17]. This is indicative of a more significant change in the mixing ratio of the crystals due to the interaction with walls of a growth container and, as expected, over the length of the ingot grown. Note that the difference between the expected Cd content and that determined from the experimentally found values of the phase-matching angles were also noticed in Ref. 18.

The short-wave part of the transmission spectrum of the 2.1-mm thick sample studied was recorded with a Shimazdu UV 3101PC spectrophotometer (0.3–3.2 μm) (Fig. 1*a*), while the long-wave one (Fig. 1*b*) was recorded with a Specord 80M IR spectrophotometer (2.5–25.0 μm) and then the spectrum was compared with the transmission spectrum of $HgGa_2S_4$.

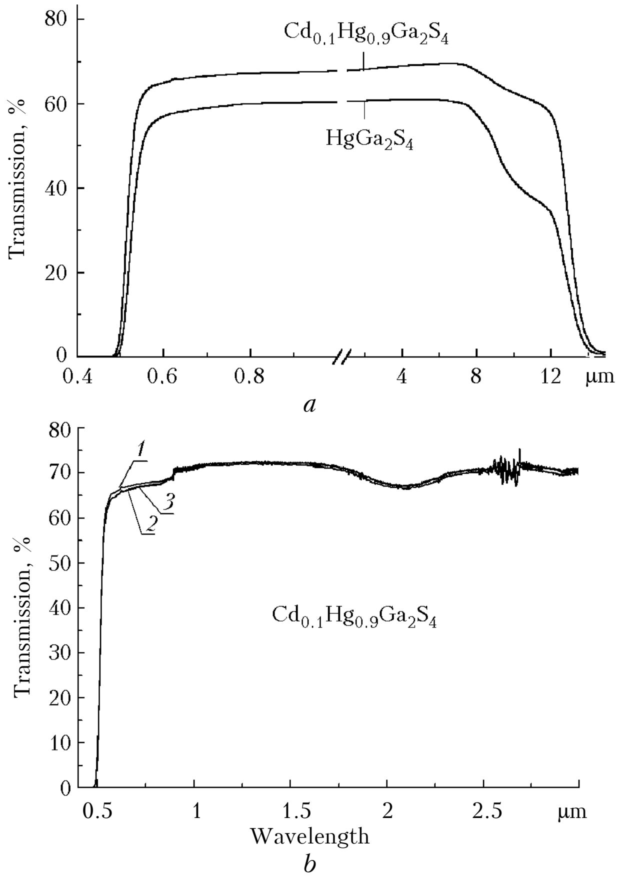

Fig. 1. The transmission spectrum of a 2.1-mm thick $Cd_{0.1}Hg_{0.9}Ga_2S_4$ crystal and of a 3.1-mm thick $HgGa_2S_4$ crystal (*a*) along with the short-wave part of the transmission spectrum of a $Cd_{0.1}Hg_{0.9}Ga_2S_4$ crystal in detail for 3 points (*1, 2, 3*) on input surface (*b*).

It is seen from Fig. 1 that the short-wave part of the transmission spectrum of the mixed crystal is shifted, as compared to the $HgGa_2S_4$ crystal, to shorter wavelength region from 510 to 495 μm, while the longwave part is almost identical for both of the crystals and lies in a range of 14.3 μm at the zero level. These results are in a good agreement with the results of previous investigations[17] and with the data from Ref. 18. It has been found that the boundaries of the transmission spectrum are almost insensitive to the radiation polarization. The absorption coefficient, caused by the phonon absorption, in the CO_2 laser wavelength range is somewhat lower than for $HgGa_2S_4$ crystals due to the presence of light Cd atoms (as compared to Hg atoms) in the crystal lattice. It was found to be ≤ 0.2 cm^{-1}. In Fig. 1*b*, one can see a weak absorption peak at the wavelength of 2.07 μm, which is possibly caused by point defects.

Thus, the mixed crystal has a somewhat wider transmission spectrum than the initial anisotropic $HgGa_2S_4$ crystal.

These properties of new crystals allow us to predict the possibility of using solid-state Nd:YAG, holmium, and erbium lasers for pumping of these crystals in order to convert the radiation into the mid-IR region. The realization of SHG of CO_2 laser is possible as well.

2. Damage threshold

In practice, the upper limit of the efficiency of frequency conversion is restricted by the damage threshold of crystals being determined by the product $M \times I_d$, where I_d is the damage threshold of a crystal; $M = d_{eff}{}^2/n^3$ is the figure of merit of a crystal, which is proportional to the efficiency of frequency conversion; d_{eff} is the effective second-order nonlinear susceptibility coefficient. The damage threshold of the $Cd_{0.1}Hg_{0.9}Ga_2S_4$ crystals was determined with the use of a TEA–CO_2 laser, operated at the 9P(20) line with the wavelength of 9.55 μm and compared with that of some other nonlinear crystals under the identical experimental conditions. The measurement procedure is described in Ref. 4. The laser emitted the energy up to 560 mJ in a (30 ± 2)-ns duration pulses (FWHM) in the TEM_{00} mode with about 90% of the total energy contained in the leading peak. The generation of short pulses was obtained by use of the original active-gas mixture $CO_2:N_2:H_2$ = = 56:14:30 and a carefully developed power supply.

The damage threshold appeared to be (271 ± 51) MW/cm^2, which is 13% lower than that of the initial straw colored $HgGa_2S_4$ crystal [(310 ± 35) MW/cm^2], although we expected higher damage threshold because of the 20% higher damage threshold of another initial $CdGa_2S_4$ crystal compared to that of $HgGa_2S_4$. Most probably, the low damage threshold of the mixed crystal is caused by the imperfect production technology. Nevertheless, this damage threshold is 1.7–2.0 times higher than that of such widely used crystals, as $CdGeAs_2$ [(157 ± 13) MW/cm^2], $ZnGeP_2$ (142 ± 9), $AgGaSe_2$ (139 ± 6), and $AgGaS_2$ (149 ± 6), and 20% higher than the damage threshold of the $AgGaGeS_4$ crystal (230 ± 9). The data on the damage threshold of $HgGa_2S_4$ are in a good agreement with the data from Ref. 11.

3. Phase matching conditions

The dispersion dependences of the refractive indices n for the ordinary (n_o) and extraordinary (n_e) waves, determined with a GS-5 goniometer-spectrophotometer for the initial crystals, are approximated by the Sellmeier equations: $n_{o,e}{}^2 = A_1 + A_3/(A_2 - \lambda^2) + A_5/(A_4 - \lambda^2)$, whose coefficients are tabulated below.

The dispersion properties of the mixed $Cd_{(x)}Hg_{(1-x)}Ga_2S_4$ crystals for the current values of x were estimated by the weighted average method as

$$n^2(\text{mixed crystal}) = xn^2(HgGa_2S_4) + (1-x)\,n^2(CdGa_2S_4).$$

The phase-matching curves for SHG by the type I of three-frequency interactions, calculated from these values of x, are shown in Fig. 2. It can be seen that NPLCs for SHG of the 9-μm band of the CO_2 laser radiation by the type I of three-frequency interactions can be realized in mixed $Cd_{(x)}Hg_{(1-x)}Ga_2S_4$ crystals by selecting the mixing ratio within the range of x from 0 to 0.28. The estimates have shown that, with the use of Sellmeier equations for $HgGa_2S_4$, obtained by Takaoka,[11] the corresponding values of x range from 0 to 0.2. Note that, according to Fig. 2, at high values of the mixing ratio, NPLCs can be realized for the radiation of chemical HF and DF lasers.

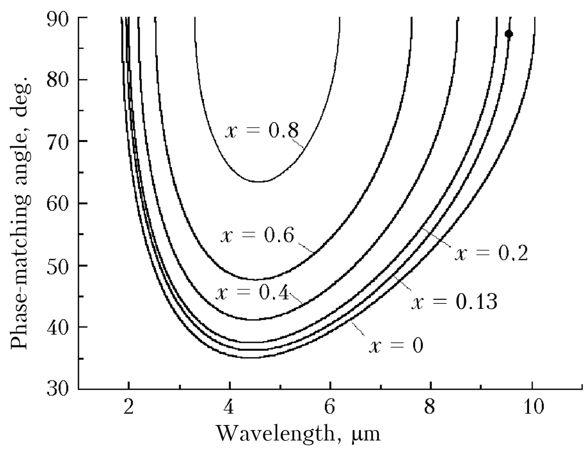

Fig. 2. Phase-matching curves for SHG in $Cd_{(x)}Hg_{(1-x)}Ga_2S_4$ crystals by the type I of three-frequency interactions. The dot indicates the experimental value of the phase-matching angle for SHG of the 9P(20) line of a CO_2 laser with the wavelength of 9.55 μm.

In addition, it follows from the estimates that the mixed crystals, as well as the initial $HgGa_2S_4$ crystals, are suitable for creation of mid-IR parametric oscillators pumped by the radiation of Nd:YAG lasers and lasers of the visible region, which cover the spectral region at least up to 12 μm.

Sellmeier coefficients of nonlinear straw colored $HgGa_2S_4$ and $CdGa_2S_4$ crystals

Crystal	n	A_1	A_2	A_3	A_4	A_5
$HgGa_2S_4$	n_o	9.8040442	1500	–5797.5001	0.09216865	–0.24624395
	n_e	9.5181294	1500	–5702.0814	0.08526369	–0.22510314
$CdGa_2S_4$	n_o	5.4973700	200	–46.488100	0.05875540	–0.17048600
	n_e	5.4818700	200	–48.185400	0.06180010	–0.17116300

4. Experimental investigation of the second harmonic generators for converting CO_2 laser radiation

The second harmonic of all lines of the 9-μm band of the CO_2 laser radiation described above and of a mini-TEA–CO_2 laser[4] was obtained by pumping the $Cd_{0.1}Hg_{0.9}Ga_2S_4$ crystal 2.1 mm in length, cut for the realization of NPLCs by the type I of three-frequency interactions (Fig. 3*a*). The pump intensity did not exceed 10% of the damage threshold in order to exclude the effect of thermal processes on the measurement results. For a pump wavelength of 9.5 μm, the phase-matching angle was 87° (Fig. 3*b*), that is, close to NPLCs. It varied within 1° as the pumping went from one point of the crystal entrance surface to another. During this process, at some point of radiation entrance into the crystal, we observed distortions of the converted radiation, typical of the inexact angular tuning to the phase-matching direction, as well as distortions caused by the point defects in the crystal.

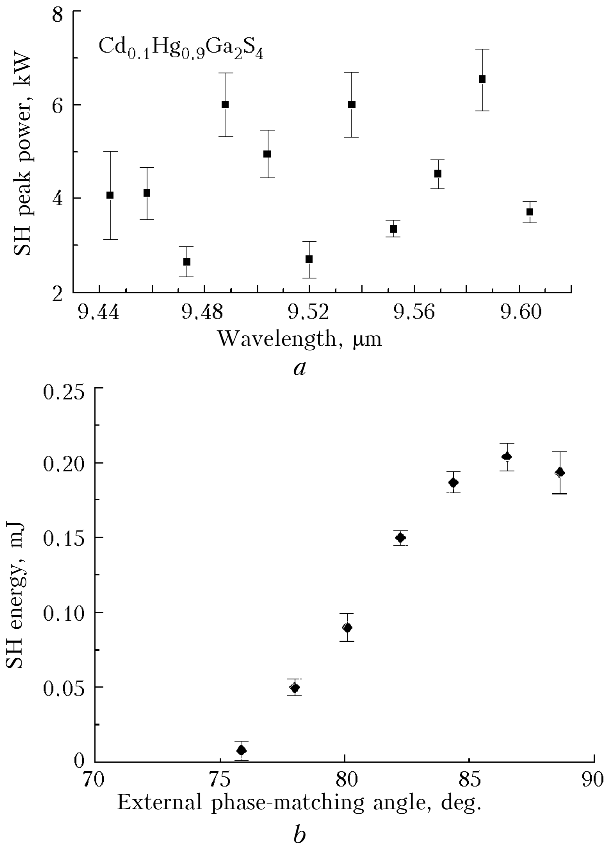

Fig. 3. Dependences of the second harmonic peak power on the pump wavelength (*a*) and of the pulse energy of second harmonic of the 9*P*(20) line with the wavelength of 9.55 μm on the angular tuning to the phase-matching direction (*b*).

Using the above technique of estimating the dispersion properties of mixed crystals, it was found that the experimentally determined conditions of noncritical phase-matching for SHG of the 9*P*(20) lines take place as the mixing ratio $x = 0.13$ if the Sellmeier–Badikov equations[5] are used for $HgGa_2S_4$ and $x = 0.09$ if the equations obtained by Takaoka[11] are used. The comparison of the estimates and the experimental results shows that the latter equations better describe the phase-matching conditions for SHG of the CO_2 laser radiation in $Cd_{0.1}Hg_{0.9}Ga_2S_4$, and, consequently, in $HgGa_2S_4$. Variations of the SH peak power at different wavelengths can be explained by the interference phenomena in the thin crystal sample used of a rather high optical quality.

The large angular width of phase matching (Fig. 3*b*) well agrees with the estimates. The maximum external efficiency of the SHG was 0.12% at the pump energy density of 518 mJ/cm^2 and 0.22% in the peak power. The direct comparison has shown a threefold improvement over $ZnGeP_2$ crystals. However, possibly due to the imperfect technology of crystal growth, the efficiency of the studied crystals did not exceed that of $HgGa_2S_4$ crystal. The maximum SH energy amounted to 0.21 mJ, and the peak power was 6 kW.

Conclusions

It has been found that the mixing ratio of materials in the process of growth of mixed nonlinear crystals can vary significantly with respect to the initial one: from $x = 0.35$ to $x = 0.1$ due to the interaction with the container walls and the change in the composition of the loading in the process of growth. The linear and nonlinear properties along with the phase matching conditions in the mixed nonlinear $Cd_{0.1}Hg_{0.9}Ga_2S_4$ crystals have been studied. It has been established that at $x = 0.1$ the conditions of noncritical phase matching have been realized for the second harmonic generation of the 9-μm band of the CO_2 laser radiation. In this case, the SHG efficiency exceeds by 25% that of the initial $HgGa_2S_4$ crystal. The damage threshold of the $Cd_{0.1}Hg_{0.9}Ga_2S_4$ crystal (271 MW/cm^2) 1.7–2.0 exceeds that of $CdGeAs_2$, $ZnGeP_2$, $AgGaSe_2$, and $AgGaS_2$ crystals. The external SHG efficiency (0.22% in peak power and 0.12% in energy), realized in the sample of the mixed 2.1-mm long crystal, threefold exceeded the efficiency of the $ZnGeP_2$ crystals.

The estimates obtained have shown that, selecting the mixing ratio of crystals, it is possible to realize the conditions of noncritical phase matching for many other types of frequency conversion, in particular, for the parametric generation of light in the mid-IR region with the pumping by radiation of Nd:YAG lasers and lasers operating in the visible spectral region.

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