Optical properties and CO_2 laser SHG with $HgGa_2S_4$

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Optical properties and nonlinearity on phase-matching (PM) of two (yellow and orange) phase $HgGa_2S_4$ crystals were investigated in details. Damage threshold was determined in comparison with middle infrared (IR) crystal at identical experimental conditions. Second harmonic generation (SHG) of 30 ns TEA CO_2 laser pulses was realized with 5% efficiency in energy and 6.9% in peak power.

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Frequency conversion with nonlinear crystals transparent from $0.4-0.5$ to $11.5-14.0$ μm spectral range has been very attractive in recent years. It provides possibility to realize high efficiency second harmonic generation (SHG) of middle IR lasers and possibility to change all near infrared (IR) solid state lasers into middle IR sources. And high efficiency up-conversion of middle IR emission into near IR and even visible range also becomes possible, as well as inverse process. It is regrettable that efficient middle IR nonlinear crystals are either not transparent or deeply absorptive at CO_2 or solid state laser wavelengths, and so can not be used in these cases.

Considering available data, this crystal is a potential candidate for laser devices mentioned above. Though results on growth and optical properties of $HgGa_2S_4$ were first reported in 1979[1], due to its poor optical quality, limited size and distribution, it has not been investigated carefully thus far and so restricted in applications. Now with the development in growth technology, $HgGa_2S_4$ with good optical quality has been developed and large size single crystal like $\phi 20 \times 50$ mm^2 is available[2,3].

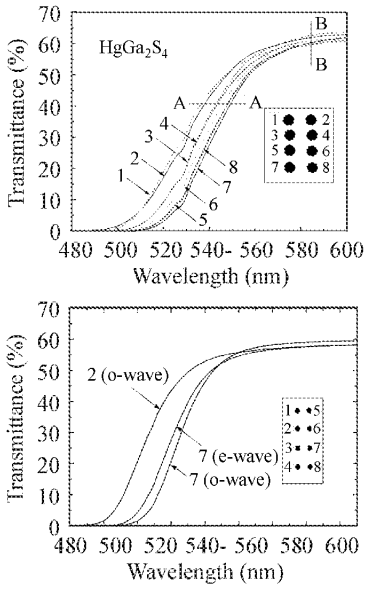

Fig. 1. Short-wavelength transmission spectra at 1 to 8 local regions at the entrance surface (see internal map) for unpolarized (a) and polarized (b) beam.

Negative uniaxial crystal $HgGa_2S_4$ possesses $\overline{4}$ point group symmetry ($d_{ooe} = d_{36}\sin\theta\sin 2\varphi + d_{31}\sin\theta\cos 2\varphi$, $d_{eoe} = d_{oee} = d_{31}\sin(2\theta)\sin(2\varphi) - d_{36}\sin(2\theta)\cos(2\varphi)$) with melting temperature 880°C, 3 – 3.5 hardness in Moohs and density of 4.95 g/cm^3. And transparency range at "0" level is $0.5-13.0$ μm with energy band gap 2.84 eV in accordance with known data[1−7].

$10 \times 12 \times 3.1$ mm^3 sized two phase (yellow and orange light) $HgGa_2S_4$ crystal is used in our investigation. Point chemical microanalyses carried out with e-emission spectrophotometric microscope of Joel, Japan shows that maximum variations of crystal composition in local volumes are $Hg_{(1\pm0.100)}Ga_{(2\pm0.085)}S_{(4\pm0.067)}$. Local volumes are 1×1 mm^2 on surface and 5 nm in depth. And short-wavelength transparency is measured with a Shimazdu UV 3101PC (operation range $0.3-3.2$ μm) while the long wavelength transmission with a Specord 80 IR ($2.5-25$ μm) spectrophotometer (Figs. 1 and 2). Points 1 and 2 correspond to yellow phase while 3 to 8 to orange phase (region around point 2 is most transparent, regions around points 7 and 8 are most deep colored). From Fig. 1(a) short-wavelength cut-offs in yellow and orange phase are 490 and 507.5 nm at 0% level, 510 and 525 nm at 10% level respectively. It can be proposed that the shifting of short-wavelength cut-off to long wavelength in orange

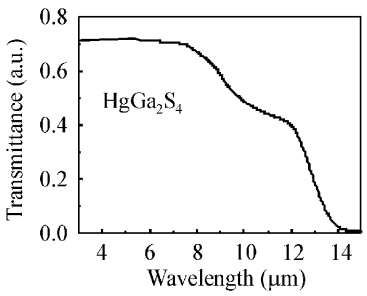

Fig. 2. Long wavelength transmission spectrum.

phase arises from point defects. The long-wavelength (Fig. 2) cut-offs are almost the same down to 14.3 μm. Transparency variations at different regions (cross section B-B) are within 5% with optical losses coefficients $\alpha \leq 0.1 - 0.2$ cm^{-1} at the maximum transparency range $0.9 - 8.5$ μm. From the cross section A-A in Fig. 1(a) it is clear that pairs of local regions 1-2, 3-4, 5-6, and 7-8 have close but orderly increased cut-offs. It means crystal's stoichiometry changes significantly from small number pairs to bigger ones i.e. along growth direction. Furthermore, this difference can be used as reference mark value of $HgGa_2S_4$ stoichiometry. Optical losses at CO_2 laser wavelengths $\alpha \leq 0.2 - 0.57$ cm^{-1} induced by phonon absorption are comparable with or locally less than $ZnGeP_2$ and best samples of $LiInS_2$. And transmission spectra weakly depend on beam polarization.

Refractive indices of $HgGa_2S_4$ are developed by minimum deviation technique with 5 mm-side prisms at room temperature and measurement accuracy is better than 10^{-3}. We also fit the measured data in the form of Sellmeier equation $n^2_{o,e} = A_{o,e} + B_{o,e}\lambda^2/(\lambda^2 - C_{o,e}) + D_{o,e}\lambda^2/(\lambda^2 - E_{o,e})$. Different Sellmeier coefficients are given in Table 1.

Sellmeier equation in the form $n^2_{o,e} = A_{o,e} + C_{o,e}/(B_{o,e} - \lambda^2) + E_{o,e}/(1 - D_{o,e}/\lambda^2)$ was accepted by Badikov[1] and $n^2_{o,e} = A_{o,e} + B_{o,e}/(\lambda^2 - C_{o,e}) - D_{o,e}\lambda^2$ by Takaoka[5]. PM diagrams for three frequency interactions, OPO pumped by Nd:YAG and Cu:vapor laser, and type I SHG according to above Sellmeier coefficients are represented in Fig. 3.

It is seen that $HgGa_2S_4$ is suitable for frequency conversion of visible, near and middle IR lasers. In difference to other efficient middle IR crystals it is useful even for design of OPO pumped by second harmonic of Nd:YAG, Cu-vapor and dye lasers. We can also see almost the same results on SHG PM considering Sellmeier coefficients given by Badikov[1], us for yellow phase and Takaoka[5] for unidentified phase, but see significant difference for orange phase. Wide spectral (about 0.05 μm) and angular (about 0.86°) bandwidth of SHG, which $HgGa_2S_4$ possesses, is another good property of this crystal from practical point of view.

Newly determined non-zero tensor components of second order nonlinear susceptibility coefficients are $d_{31} = 11.7 \pm 1.8$ and $d_{36} = 35.2 \pm 5.3$ pm/V, respectively, different with previous results[1–7]. According to that, figure of merit ($M \approx d^2_{eff}/n^3$) of $HgGa_2S_4$ in proportional to frequency conversion efficiency is simulated versus wavelength for type I and II SHG on PM conditions ($\varphi = 35°48'$ and $81°06'$ for two types), as presented in Fig. 4 together with M values of other crystals. It is easily seen that from Fig. 4, $HgGa_2S_4$ crystal is superior to wide used $ZnGeP_2$, $AgGaSe_2$, and GaSe crystals on SHG of 2-μm solid-state holmium and 3-μm erbium lasers. It also outperforms $AgGaSe_2$ and GaSe in CO_2 laser SHG. Whether $HgGa_2S_4$ is able to compete with $ZnGeP_2$ or not in CO_2 laser SHG depends on ratio of their damage thresholds.

Damage threshold of $HgGa_2S_4$ is redetermined with known procedure[8] by original TEA CO_2 laser for the first time in comparison with a number of known and new crystals with close optical quality at maximal transparency range, and at identical experimental conditions.

Table 1. Sellmeier Coefficients in Accordance with Known and Determined Data

Crystal Phase	Coefficient	$A_{o,e}$	$B_{o,e}$	$C_{o,e}$	$D_{o,e}$	$E_{o,e}$	Reference
Yellow Phase	n_o	9.8040442	1500	−5797.5001	0.09216865	−0.24624395	Badikov[1]
	n_e	9.5181294	1500	−5702.0814	0.08526369	−0.22510314	
Orange Phase	n_o	6.2081522	225	−63.706298	0.09568646	−0.23698804	
	n_e	6.0090267	225	−63.280659	0.09214633	−0.21489656	
Not Identified Phase	n_o	5.9405	0.2361	0.0929	0.00257	–	Takaoka[5]
	n_e	5.7412	0.2138	0.0897	0.00247	–	
Yellow and Orange Phase	n_o	2.31327	3.59424	0.07619	0.34109	225	This Paper
	n_e	1.9801	3.71269	0.06777	0.32711	225	

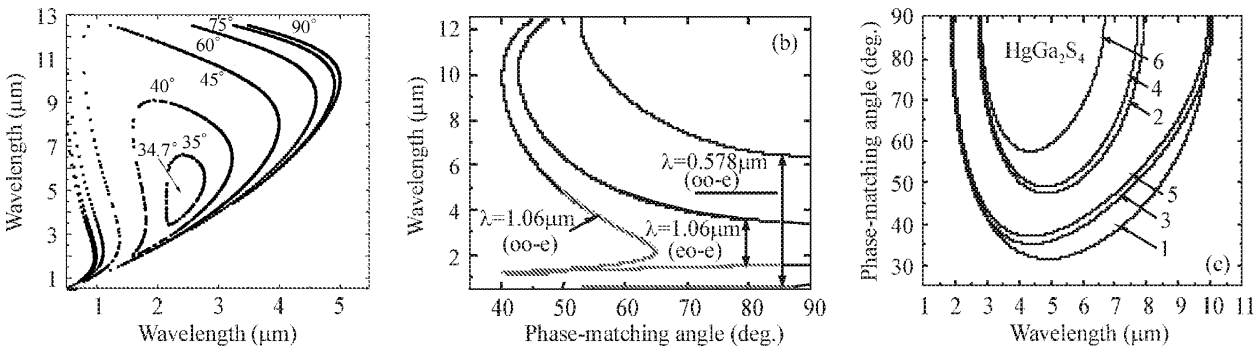

Fig. 3. PM diagrams for three frequency oo-e interactions (a), optical parametric oscillator (OPO) pumped by Nd:YAG (1.06 μm) and Cu-vapor lasers (b), and type I SHG (c) in accordance with the data of Ref. [1] (1, 2), of this paper data (3, 4) and of Ref. [5] (5, 6), see also Table 1.

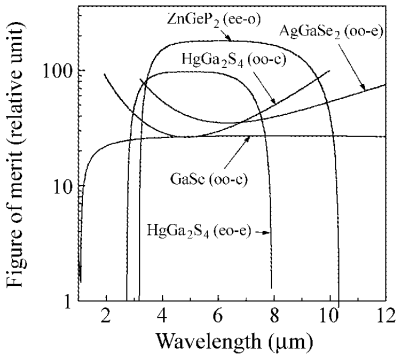

Fig. 4. Efficient figure of merit versus wavelength for SHG.

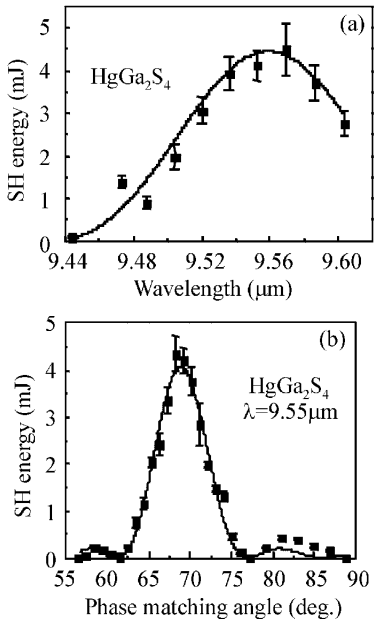

Fig. 5. CO_2 laser SH energy versus wavelength (a) and angular mismatch (b).

The laser emits $\sim$ 30 ns (FWHM) pulses up to 560 mJ in TEM_{00} mode at $9P(20)$ emission line (9.55 μm) with 90% energy in leading peak and less than 10% in low intensity "tails". It is found that damage threshold of yellowish phase $HgGa_2S_4$ is 310 MW/cm^2 (more credible due to its stoichiometry) which is a little bit higher than 294 MW/cm^2 of orange phase. Both phases of the crystal have about 2.2 to 2.3 times higher damage level than the known and widely used $CdGeAs_2$ (157 MW/cm^2), $ZnGeP_2$ (142), $AgGaSe_2$ (139) and $AgGaS_2$ (149).

SHG of CO_2 laser is then performed for all lines of 9-μm emission band of CO_2 laser, as shown in Fig. 5(a). The crystal is cut for type I interaction with $\theta = 75°, \varphi = 45°$. Two 5-mm-thick LiF plates accounting for 81% transmittance for SH and $< 0.04\%$ for fundamental wave are placed between the crystal and a thermal detector connecting to 2835-c energy meter (Coherent). SHG efficiency of $4.7 \pm 0.4\%$ in energy is fixed at pumping 431 ± 10 mJ/cm^2 and 6.9% in peak power at pumping 13.2 ± 0.6 MW/cm^2. In our knowledge it is the highest efficiency that has ever been realized in $HgGa_2S_4$ crystal at nanosecond pulse pumping. Pump intensity worked here, is much less than damage threshold for excluding influence of heating on SHG and that is why SH energy is well in agreement with the theoretical estimation. It is surprise to find the same results of SH energy and PM angle in the yellow and orange phase of the crystal. For yellow phase $HgGa_2S_4$ experimental PM angles at 9.55 μm pumping are 68°[1], 69° (this paper), 74°[8] and estimated 72.65°[8], respectively. While, estimated angle for orange phase is 62°[1]. It is evident that all the experimental PM data and the estimated data on SHG in yellow phase $HgGa_2S_4$ can be in close coincidence within acceptive discrepancy. This is one more confirmation that both yellow and orange phase have identical physical properties and crystal parameters, and that the only difference in short wavelength cut-off can be caused by point defects. The same conclusion can be obtained from spectral dependences of SH energy and angular mismatch on wavelength that is also in well coincidence with the yellow and orange phases, as shown in Fig. 5(b).

With $10 \times 12 \times 3.1$ mm^3-sized two-phase $HgGa_2S_4$ crystal sample, its linear and nonlinear optical properties are further investigated. Newly determined Sellmeier coefficients and damage threshold make $HgGa_2S_4$ outstanding in frequency conversion of CO_2, Nd:YAG and visible lasers into middle IR competing with other counterparts. Carrying out CO_2 laser SHG shows indistinguishableness between the yellow and orange phases of $HgGa_2S_4$. It is proposed that point defects determine the crystal colors (yellow and orange) which mean only single phase does exist in physical state.

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