Comparative experiment on doubling the frequency of mini-TEA CO_2 lasers in $ZnGeP_2$, $AgGaSe_2$, and GaSe crystals

P.P. Geiko and Yu.M. Andreev

Institute of Optical Monitoring,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received October 20, 2000

Advantages of $ZnGeP_2$ crystals over $AgGaSe_2$ and GaSe have been demonstrated in the comparative experiment on second harmonic generation in a mini-TEA CO_2 laser. The mean power of the second harmonic achieved was 0.22 W at the conversion efficiency of 6%. It follows from the obtained data that the fundamental physical properties of laminar GaSe crystals are masked by low cleavage. Doping of GaSe crystals with indium significantly improves the cleavage and makes them potentially most attractive crystals for doubling the frequency of CO_2 lasers.

Mini-TEA CO_2 lasers are widely used in ecological monitoring of the atmosphere because of their high performance characteristics – capability of operating as a part of mobile systems, commercial availability, and low cost. Development of efficient crystal frequency converters can not only significantly extend the capabilities of existing systems, but also improve their parameters. In particular, frequency doublers of the 9-μm band extend the list of gases that can be monitored with a CO_2 lidar.[1,2] However, the choice of the most attractive crystal even for second harmonic generation of the CO_2 laser emission is obvious only at the first sight. Actually, it is an illusive prospect because of a number of factors. This follows from the table that gives the main parameters determining the efficiency of frequency doubling for the four most promising, in the common opinion, nonlinear crystals.

Table. Parameters of nonlinear crystals – frequency doublers of the CO_2 laser radiation

Crystal	$ZnGeP_2$	Tl_3AsSe_3	$AgGaSe_2$	GaSe
Second order non-linear susceptibility coefficient, pm/V	70–111	29–88	31–49	23–75
Figure of merit, $(pm/V)^2$	30–112	23–107	47–117	27–287
Spectral range of phase matching, μm	3.17–10.32	2.28–17	3.01–12.7	1.07–18
Optical damage threshold for TEA CO_2 laser radiation, MW/cm^2	50	35	40	35
Thermal conductivity, W/(cm·K)	0.36	0.0035	0.011	0.162
Birefringence	0.04	−0.18	−0.033	−0.375

Some of these parameters are given with a scatter in the available data. This scatter is one of the causes for vagueness in selecting crystals. As an illustration, Figure 1 shows the calculated spectral dependences of the figure of merit for the crystals under study. The figure of merit $M = d_{eff}/(n_1^2 n_2)$ is proportional to the conversion efficiency; here n_1 and n_2 are the refractive indices at the pump frequency and the second harmonic frequency, d_{eff} is the effective nonlinear susceptibility (taking into account the phase-matching angles and symmetries of the crystals).

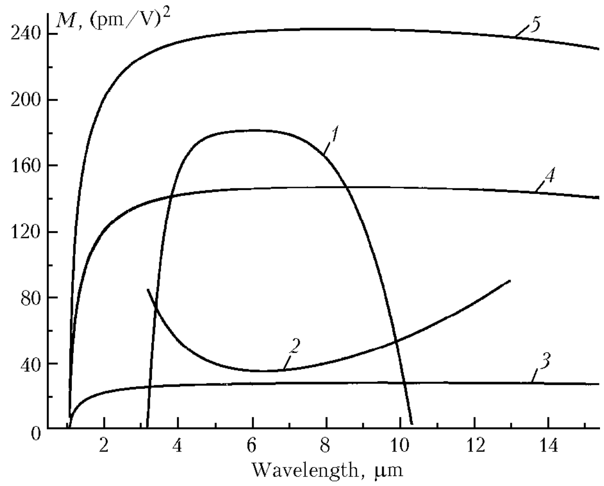

Fig. 1. Spectral dependence of the actual figure of merit for second harmonic generation of the crystals under study: $ZnGeP_2$ (*1*) and $AgGaSe_2$ (*2*); GaSe for different second-order nonlinear susceptibility coefficients: 23 (*3*), 54.4 (*4*), and 70 pm/V (*5*).

It is seen from Fig. 1 that $ZnGeP_2$ must surpass $AgGaSe_2$ in doubling the 9-μm band of the CO_2 laser, while being less efficient in the second harmonic generation of the 10-μm branch.

The situation with the GaSe crystal is most interesting. The literature data on the coefficient of the second-order nonlinear susceptibility range from 23 (Ref. 3) to 54.4 (Ref. 4) and even 75 pm/V (Ref. 5). The place of GaSe among other nonlinear crystals, as is seen from Fig. 1, changes from the last to the first as the value of nonlinear optical susceptibility (NOS) varies

0235-6880/00/12 1060-03 $02.00

within these limits. Other important parameters that determine, for example, the degree of development of distorting thermal processes (thermal conductivity) and walkoff of interacting radiation (birefringence) are now determined correctly. However, their values are significantly different for different crystals. This fact is often ignored in estimates, and just this is another one cause of the considered vagueness.

Upon solution of the known set of equations for amplitudes of interacting bound modes together with the equation of thermal conductivity, we have found the dependence of the second harmonic generation (SHG) efficiency on the parameters of the considered crystals.[6] This dependence demonstrates the potential advantages of GaSe crystals of rather high ($\alpha < 0.08$ cm^{-1}) optical quality over, for example, $AgGaSe_2$ crystals with even higher quality ($\alpha \approx 0.02$ cm^{-1}) on the assumption of the minimum value of the second-order NOS coefficient. Nevertheless, the overwhelming majority of experiments indicated the advantage of $ZnGeP_2$ crystals. However, Ref. 7 demonstrated the advantage of GaSe crystal over $ZnGeP_2$. In this situation, it is urgent to directly compare the efficiencies of the considered crystals under identical experimental conditions.

The comparative experiment has been conducted by the ordinary SHG scheme with $ZnGeP_2$, $AgGaSe_2$, and GaSe crystals of different length. The available Tl_3AsSe_3 crystals had low quality, and therefore they were rejected. The best results were obtained with the $ZnGeP_2$ crystal of 10.4 mm length and orientation $\theta = 72°$ and $\varphi = 0°$, $\alpha = 0.3$ cm^{-1} at the wavelength of pump at 9.3 μm and about 0.01 cm^{-1} at the second harmonic wavelength. Similar results were also obtained with $AgGaSe_2$ and GaSe crystals having close lengths of 10 and 9 mm and the absorption coefficients of 0.05 and 0.15 cm^{-1}, respectively. The $AgGaSe_2$ crystal had the orientation $\theta = 58°30'$, $\varphi = 0°$. As known, the GaSe crystal cannot be processed because of its layer structure and very low hardness. To be used in the experiment, it was detached along cleavage layers normal to the optical axis.

Mini-TEA CO_2 laser (model 143) was fabricated in the Special Design Bureau for Physical Instrument-Making of the Russian Academy of Sciences. The laser cavity is formed by a totally reflecting copper mirror with 10-m radius of curvature and a diffraction grating of 100 grooves/mm; the reflection coefficient in the backward direction is 50%. The radiation in the spectral region of 9.3–9.6 μm exits through a NaCl plate set at the Brewster angle. With the discharge zone of 6.8 × 6.8 × 430 mm, the laser operated in the repetitively pulsed mode at a pulse repetition rate up to 250–300 Hz, the pulse length was 50 ns, and the output energy was up to 20 mJ. The fundamental mode was selected, when needed, with an iris diaphragm. The beam divergence in that case was 1 mrad. The pump radiation was focused onto a crystal with a BaF_2 lens with $f = 473$ mm. The focal spot was 2 mm in size at multimode pumping and 1.2 mm at pumping by a single mode beam.

The threshold energy density of incident radiation, at which breakdown plasma arose, was determined for each type of the crystals. The measured damage threshold for the $ZnGeP_2$, $AgGaSe_2$, and GaSe crystals at a single mode pumping was 2.5, 1.5, and 0.8 J/cm^2, respectively. The $ZnGeP_2$ crystals had only surface damage mostly on the rear surface. This is indicative of the formation of a thermal lens inside the crystal. The $AgGaSe_2$ crystals were characterized not only by surface damage, but also by an intense bursting all over the volume due to low mechanic properties, whereas the GaSe crystals cracked mostly between the weakly bound layers. The external efficiency of frequency conversion was determined as the ratio $P_{2\omega}/P_\omega$, where $P_{2\omega}$ and P_ω are the peak powers of the second harmonic pulse and the pump pulse.

To obtain reliable results, the efficiency was measured at the power density two times less than the damage threshold. The efficiency of frequency doubling in the $ZnGeP_2$ crystals exceeded the level of 6%, and the mean power of the second harmonic achieved 0.22 W at the mean pump power of 5 W and the pulse repetition frequency of 250 Hz (single mode pumping). Figure 2 shows the peak efficiency of doubling the frequency of a mini-TEA CO_2 laser radiation at multimode (curve *1*) and single mode (*2*) pumping, as well as the calculated results for single mode pumping (*3*).

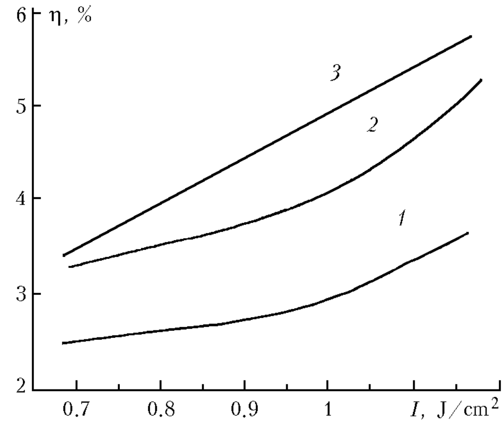

Fig. 2. Peak efficiency of doubling the frequency of a mini-TEA CO_2 laser radiation in $ZnGeP_2$ at multimode (*1*) and single mode (*2*) pumping; estimated efficiency for single mode pumping (*3*).

The transition to multimode pumping decreased the efficiency of the frequency conversion in accordance with Fig. 2 and led to its temporal instability. Therefore, this pumping was not used in our comparative experiments. The efficiency of frequency doubling in the $AgGaSe_2$ crystals was 1.5 times lower, and in the GaSe crystals it did not exceed 0.35%. In the latter case, the power of the second harmonic had a pronounced (up to 20%) "pedestal" at full detuning from the phase-matching direction.

The experimental results unambiguously point to the advantages of the $ZnGeP_2$ crystals as applied to doubling of the 9-μm band of the mini-TEA CO_2 laser radiation and the lowest capabilities of GaSe. According to the above table, the advantages of the former are largely determined by the high optical damage threshold and thermal conductivity, whereas the low capabilities of GaSe are caused by the low nonlinear susceptibility, low optical damage threshold, and large walkoff of the pump and second harmonic radiations. The walkoff was easily observed by the tracks of hot spots. The low damage threshold of the GaSe crystals can be explained by low cleavage leading to the inner breakdowns. It also causes the low nonlinear susceptibility. In this case, it is more correct to call this parameter the effective or actual susceptibility rather than the fundamental one. Objects, when viewed through the crystal, look blurred to a certain degree. This is indicative of local bending of the layers and the presence of microcavities. The presence of the pedestal on the experimental curve of phase matching also can be explained by low cleavage. We can assume that low cleavage causes the relatively low quality ($\alpha \geq 0.05$ cm^{-1}) of the produced GaSe crystals as well.

In this case, doping of GaSe crystals, as an easiest method to increase the cleavage, or growing of mixed crystals like $Ga_xIn_{(1-x)}Se$ may be an efficient way to realize their natural physical properties. Such crystals may have higher hardness, optical damage threshold, and thermal conductivity and be mechanically processable. Besides, what is more important, they may have higher nonlinear properties.

The results of foreign and our tentative studies of GaSe crystals doped with In up to the level less than 1% confirm these assumptions.[8,9] Doping allowed mechanical processing, in particular, cutting of GaSe crystals by a diamond saw in any direction. The coefficient of thermal conductivity in the direction normal to the cleavage layers increased by a factor of four – from 0.02 to 0.08 W/(cm·deg).

The dependence of the actual coefficient of nonlinear susceptibility on the length of doped and undoped crystals was found. This confirms the dominating influence of the cleavage on the experimentally observed physical properties. At short (up to 1 cm) lengths of crystals, the coefficients of nonlinear susceptibility differ by no more than several percent, and their absolute value is ~70 pm/V, i.e., it is close to the value of the corresponding coefficient of $ZnGeP_2$ crystals. For crystals of centimeter length, the difference is within tens of percent, and the absolute value of nonlinear susceptibility of undoped crystals drops down to the minimum level known from the literature (a little larger than 20 pm/V).

The obtained results allow the conclusion that $ZnGeP_2$ doublers of the CO_2 laser frequency have an advantage over $AgGaSe_2$ and, especially, over the widely used GaSe crystals. This fact is caused not only by physical properties of GaSe crystals, but also by the imperfect technology of their production. The advantage of the GaSe crystals that has been found by some investigators can be explained by uncontrolled growing of samples with high cleavage. Doping of GaSe crystals with indium at the concentration of 0.3–1% increased the coefficient of nonlinear susceptibility by 1.5 times and thus allowed partial realization of their potential capabilities. This gives us a hope that this coefficient can be increased up to the level typical of $ZnGeP_2$ crystals by improving the doping technology. According to estimates, the figure of merit of GaSe crystals for CO_2 laser second harmonic generation in this case will increase by 5.4–8.9 times depending on the wavelength, and the GaSe doubler will become most efficient frequency doubler among other crystals for the whole frequency range of the CO_2 laser emission. The spectral properties, high thermal conductivity, very high birefringence, and the possibility of changing it at technological stages of growing of mixed crystals like $Ga_xIn_{(1-x)}Se$ make these crystals promising for use in the mid-infrared nonlinear optics.

References

1. N. Menyuk, D.K. Killinger, and W.E. DeFeo, Appl. Opt. **19**, No. 19, 3282–3286 (1980).
2. V.E. Zuev, M.V. Kabanov, Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I. Grebenyukov, and V.V. Zuev, Izv. Akad. Nauk SSSR, Ser. Fiz. **52**, No. 6, 51–56 (1988).
3. D.N. Nikogosyan, Kvant. Elektron. **4**, No. 1, 5–25 (1977).
4. G.B. Abdullaev, L.A. Kulevskii, A.M. Prokhorov, A.D. Savel'ev, E.Yu. Salaev, and V.V. Smirnov, Pis'ma Zh. Eksp. Teor. Fiz. **16**, No. 3, 130–133 (1972).
5. J.L. Oudar, P.J. Kupecek, and D.S. Chelma, Opt. Commun. **29**, 122–125 (1979).
6. Yu.M. Andreev, P.P. Geiko, A.V. Vernick, V.G. Voevodin, and O.V. Voevodina, SPIE Proceedings **3983**, 450–457 (2000).
7. G.B. Abdullaev, K.R. Allakhverdiev, M.E. Karasev, V.I. Konov, L.A. Kulevskii, N.B. Mustafaev, P.P. Pashinin, A.M. Prokhorov, Yu.M. Starodumov, and N.I. Chapliev, Kvant. Elektron. **16**, No. 4, 757–763 (1989).
8. D.R. Suhre, N.B. Singh, V. Balakrishna, N.C. Fernelius, and F.K. Hopkins, Opt. Lett. **22**, No. 11, 775–777 (1997).
9. Yu.M. Andreev, S.A. Bereznaya, V.G. Voevodin, P.P. Geiko, L.G. Geiko, and M.V. Kabanov, in: *Proceedings of the II International Symposium on Monitoring and Rehabilitation of the Environment* (Tomsk, 2000), pp. 56–57.