PACS numbers: 42.55.Px; 42.60.Jf
DOI: 10.1070/QE2001v031n12ABEH002101

Radiation resistance of nonlinear crystals at a wavelength of 9.55 μm

Yu M Andreev, V V Badikov, V G Voevodin, L G Geiko, P P Geiko, M V Ivashchenko, A I Karapuzikov, I V Sherstov

Abstract. **The results of radiation resistance measurements for twelve nonlinear crystals are presented. The crystals include the well-known nonlinear $CdGeAs_2$, $ZnGeP_2$, $AgGaSe_2$, GaSe, $AgGaS_2$, and Ag_3AsS_3 crystals operating in the middle IR range, new mixed $AgGaGeS_4$ and $Cd_{0.35}Hg_{0.65}Ga_2S_4$ crystals, two-phase (orange and yellow) $HgGa_2S_4$ crystal, and the doped GaSe:In crystal. The mixed crystals and the two-phase $HgGa_2S_4$ crystal are transparent in the range from 0.4 – 0.5 to 11.5 – 14.5 μm. The measurements were performed using a pulsed single-mode highly stability TEA CO_2 laser with an output pulse duration of $\sim$ 30 ns. The damage thresholds of new nonlinear $AgGaGeS_4$ and $Cd_{0.35}Hg_{0.65}Ga_2S_4$ crystals and of the $HgGa_2S_4$ crystal (the orange and yellow phases) were found to be 1.5 – 2.2 times higher than for the crystals operating in the middle IR range.**

Keywords: *nonlinear crystals, radiation resistance, TEA CO_2 laser*.

1. Introduction

The efficient frequency conversion of radiation from TEA CO_2 lasers significantly widens the scope of their application. In practice, however, the seemingly trivial task of choosing the best crystal for some specific type of a frequency converter proves to be by no means a simple one. The reason is a significant scatter in the available data on such parameters of nonlinear crystals as nonlinear susceptibility and thermal characteristics. As for the summary data on radiation resistance collected in Ref. [1], for a variety of reasons they also show an extremely wide scatter. This is explained by the fact that the damage threshold is commonly determined by the method of visual indication, when the subjective factor plays an important part, whereas quantitative criteria are seldom used.

Because in some cases the details of the experimental conditions and results are not reported, it is impossible to reevaluate quantitatively the data presented. For example, in the description of an internal damage, the depth of their occurrence is quite often omitted. The difference between the resistance of the working crystal surface to the pump radiation and the radiation resistance of the nonlinear element itself are often ignored, when the exit surface is damaged due to the thermal self-focusing of the interacting radiation beams. In this case, the radiation resistance depends on the crystal length, resulting in a difference of the measurement data obtained under identical conditions with crystals of different length.

In many studies of the radiation resistance [1], commercial TEA CO_2 lasers without an electrooptical shutter were used, which exhibit a significant spread of output parameters. Typically, their output pulse contains a leading peak with a duration of 60 – 250 ns at half maximum and a low-intensity 'nitrogen tail' with a duration of 1 – 3 μs and over. This 'tail' contains from 25 % – 30 % to 60 % – 80 % of the total pulse energy. Such lasers are characterised by significant variations in the pulse shape and energy, as well as in the intensity and duration of leading radiation peaks, which increase measurement errors. The variations in the total output pulse energy are sometimes greater than 10 % – 20 %.

Note that the damage threshold of commonly used $ZnGeP_2$ crystals, like the efficiency of frequency conversion in them, increases nonlinearly as the pump pulse duration becomes shorter [2]. Conversion efficiencies ranging into the tens of percent acceptable from the practical standpoint are achieved when the pump pulse duration is made shorter than 40 – 50 ns. This statement is also true for other nonlinear crystals operating in the middle IR range.

The aim of this work is to determine the resistance of the entrance surfaces of the $CdGeAs_2$, $ZnGeP_2$, $AgGaSe_2$, GaSe, GaSe : In (the weight concentration of In was 0.5 %), CdSe, $HgGa_2S_4$ (the orange and yellow phases), $AgGaS_2$, Ag_3AsS_3, $AgGaGeS_4$, and $Cd_{0.35}Hg_{0.65}Ga_2S_4$ nonlinear crystals to the radiation of a parametrically stable short-pulse 9.55-μm TEA CO_2 laser under identical experimental conditions. This laser was chosen because of the favourable conditions for the generation of the second harmonic of its radiation in most of the above crystals and the wide use of this laser with frequency doubling for the remote gas analysis in the atmosphere.

Yu M Andreev, L G Geiko, P P Geiko Institute of Optical Monitoring, Siberian Branch, Russian Academy of Sciences, Akademicheskii prosp. 10/3, 643055 Tomsk, Russia, e-mail: andreev@iom.tomsknet.ru;
V V Badikov Laboratory for Novel Technologies, Krasnodar State University, ul. Stavropol'skaya 149, 350040 Krasnodar, Russia;
V G Voevodin V D Kuznetsov Siberian Physicotechnical Institute, Tomsk State University, pl. Novosobornaya 1, 634050 Tomsk, Russia;
M V Ivashchenko, A I Karapuzikov, I V Sherstov Institute of Laser Physics, Siberian Branch, Russian Academy of Sciences, prosp. akad. Lavrent'eva 13/3, 630090 Novosibirsk, Russia

Received 15 May 2001; revision received 18 September 2001
Kvantovaya Elektronika **31** (12) 1075 – 1078 (2001)
Translated by E N Ragozin

2. Experimental

To improve the accuracy of measurements of the radiation resistance of the nonlinear crystals, we used a repetitively pulsed TEA CO_2 laser with stable parameters of the output pulses optimised for frequency conversion. The basic version of this laser was described in paper [3]. Its specific feature is the combination of the intense symmetric preionisation of the discharge gap, the optimal delay of initiation of the main discharge, the bipolar pulsed power supply with an amplitude of 80 kV, and a low-inductance regime of energy input into the gas discharge. This enables laser operation with gas mixtures at high pressures up to 1 bar. In this case, in the discharge cell with a volume of ~ 10 L there forms a homogeneous discharge in a 0.44-L volume (2 cm $\times$ 3 cm $\times$ 73 cm). The active laser medium is excited by high-voltage current pulses with a duration of 240 ns at half maximum. The stable laser cavity 1.3 m in length was formed by a reflection 100 mm^{-1} diffraction grating operating in the autocollimation mode and a semitransparent output mirror with a transmittance of $\sim 75\,\%$. Fig. 1 shows the output pulse shapes for the basic TEA CO_2 laser and for the same laser with a working mixture of the $CO_2:N_2:H_2 = 56:14:30$ composition in the cases of multimode and single-mode lasing.

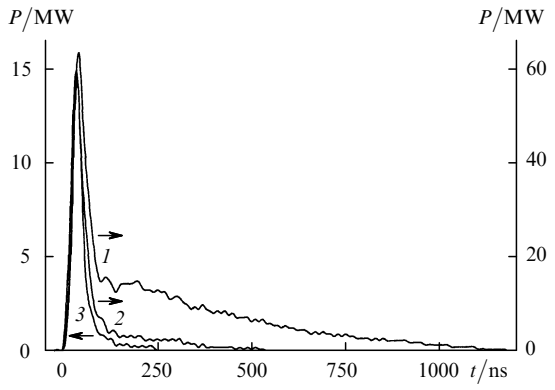

Figure 1. Temporal shapes of the output pulses of the basic TEA CO_2 laser (*1*) and the same laser with the $CO_2:N_2:H_2 = 56:14:30$ working mixture operating in the multimode (*2*) and single-mode (*3*) regimes.

The maximum energy of output laser pulses at the 10*P*(20) line in the multimode regime was 10 J and the peak power was 100 MW for a duration of the leading peaks of $\sim 40 - 50$ ns and a 'tail' duration of ~ 1 μs. As revealed by subsequent investigations, a helium-free molecular gas mixture of the $CO_2:N_2:H_2 = 56:14:30$ composition at a pressure of 0.7 bar is well suited to this laser for the production of shortened pulses devoid of the 'nitrogen tail' [4]. The use of this mixture ensures the most acceptable combination of the output energy, the peak power, the pulse duration, the energy contribution of the leading peak, and the service life with one filling with the mixture.

When operating in the multimode regime at the same laser line, the pulse energy amounts to 3.5 J for a peak output power up to 60 MW, the $\sim 30 - 35$-ns leading peak accounting for as much as 80 % of the pulse energy. Two apertures 10 mm in diameter were mounted inside the laser cavity to ensure the single-mode regime of laser operation. Upon lasing at the 9.55-μm 9*P*(20) line, the duration of the leading peak was ~ 30 ns (Fig. 1) and the energy contribution of the 'tail' lowered to $\sim 10\,\%$ of the total pulse energy, which amounted to 560 mJ. The transverse intensity distribution in the pump beam at entry into the focusing lens at a distance of ~ 1 m from the laser is given in Fig. 2. One can see that the transverse beam intensity distribution is close to the Gaussian distribution with a diameter of 6 mm at the e^{-2} level.

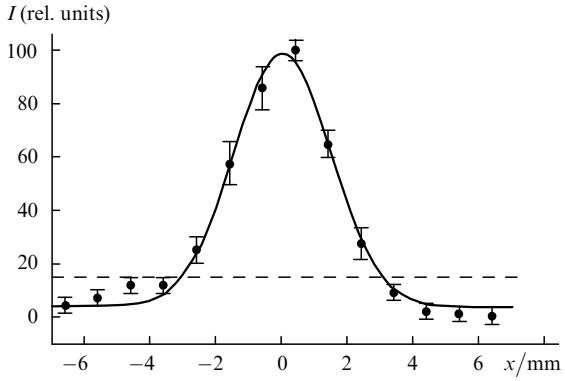

Figure 2. Spatial intensity distribution of the laser beam *I* in the lateral section at entry into the focusing lens. The points represent the experiment, the solid line is the Gaussian approximation of the lateral intensity distribution in the beam, and the dashed line corresponds to the intensity $e^{-2}I_{max}$.

In our experiments, the energy of output laser pulses was monitored with an IMO-2N calorimeter. The pulse shape was recorded with a Ge detector combined with an S9-27 digital storage oscilloscope ($\Delta f = 50$ MHz, a sampling time of 10 ns) connected to a computer or to a TDS-210 oscilloscope ($\Delta f = 60$ MHz, a sampling time of 1 ns). The measured energy values and the stored oscilloscope traces of the pulse shape were employed to determine the average values and rms deviations of the energy and peak power, the energy contribution of the leading peak, and the pulse duration. In the course of one measurement series, the variations of output pulse energy were within 3.5 %, the variations of the leading pulse duration within 2 ns, and the variations of their contribution to the total pulse energy within 2 %. No fine structure of the pulses was recorded. Therefore, the stability of the energy parameters of output pulses and their duration inherent in the laser elaborated was more than five times superior to the stability of these parameters in conventional TEA CO_2 lasers.

All the crystals investigated for radiation resistance, with the exception of two crystals, were mechanically polished. The $CdGeAs_2$ crystal was polished using a chemicodynamic technique, while the GaSe crystal was obtained by cleavage. The optical loss factor α for the $AgGaSe_2$, GaSe, $AgGaS_2$, and Ag_3AsS_3 crystals did not exceed 0.1 cm^{-1}. For the 3.1-mm thick $HgGa_2S_4$ crystal (its greater part corresponded to the orange phase and the remaining part to the yellow phase) and the 2.1-mm thick $AgGaGeS_4$ and $Cd_{0.35}Hg_{0.65}Ga_2S_4$ mixed crystals we determined the upper bound for α, which was no higher than 0.2–0.3 cm^{-1}. For the $ZnGeP_2$ crystals, the loss factor was $\alpha =$ 0.26 cm^{-1}; for the uncooled $CdGeAs_2$ crystal we have $\alpha =$ 0.42 cm^{-1}. The GaSe : In crystals cut out from a specially

grown boule were noticeably inhomogeneous in colour. The orientation of all the crystals, excepting GaSe and CdSe, corresponded to the phase matching for the generation of the second harmonic of the $\lambda = 9.55$ μm radiation. The working surface of GaSe crystals obtained by cleavage was orthogonal to the crystal optical axis, and the CdSe crystal had an orientation whereby $\theta = 80^\circ$ [1].

3. Experimental results and discussion

The radiation resistance was determined by calculating the peak radiation intensity of a TEA CO_2 laser at the front crystal surface upon the optical breakdown, which was detected by the same operator in darkness. The radiation was focused with a lens with a focal length $f = 673$ mm. The radiation intensity was varied by displacing the crystal along the beam axis. An aperture 1.25 mm in diameter was placed in front of the crystal at a distance of 20 mm from its front surface to pass the central part of the radiation beam. This afforded a rational use of the crystal surface under investigation by inflicting optical breakdown-induced defects on very local surface regions. The high stability of the energy parameters of output pulses ensured a reliable detection of damage threshold as the pump laser energy was continuously increased.

The optical-breakdown intensity I_d was calculated in the Gaussian beam approximation using the formula

$$I_d^{-1} = (2E)^{-1}\pi w_d^2 \int_0^\infty \frac{\psi(t)}{\psi_{max}}\,dt, \qquad (1)$$

where E is the pulse energy and $\psi(t)/\psi_{max}$ is the normalised pulse shape. The beam radius w_d at the point of occurrence of the optical breakdown was calculated by the expression

$$w_d = w_{02}\left[1 + \left(\lambda\frac{f - L_d}{\pi w_{02}^2}\right)^2\right]^{1/2}, \qquad (2)$$

where λ is the radiation wavelength, L_d is the distance between the lens and the crystal, $w_{02} = \lambda f/(\pi w_{01})$ is the beam radius at the lens focus, and w_{01} is the beam radius at entry into the lens [5].

For each of the crystals under study, 10–20 independent series of measurements were made of the distance L_d at which the optical surface breakdown was detected. The effect of fine-structure pump-pulse variations, which arise from spontaneous self-mode-locking of the longitudinal modes, on the accuracy of measurements was compensated for by the statistical processing of the stored data array and the spline approximation in the construction of the averaged shape of radiation pulses. Note that special efforts were made to maximise the relative accuracy of the damage threshold measurements on different crystals. The absolute measurements of the energy of 30-ns pump pulses were not conducted separately.

The results of measurements of the crystal damage thresholds I_d and the distances L_d at which the optical breakdown was observed are presented in Table 1. Also specified here are the average values and the rms deviations of the energy E and peak power P of the output laser pulses measured at the exit of the focusing lens; the E_1/E energy ratio (where E_1 is the energy that fell within the initial 100-ns long time interval); and the pulse lengths determined at levels of 50 % ($\tau_{0.5}$), 10 % ($\tau_{0.1}$), and 1 % ($\tau_{0.01}$) of the peak power P. The pulse durations $\tau_{0.5}$ and $\tau_{0.01}$ are in essence the duration of the leading peaks at half maximum and the total pulse lengths, respectively. The energy E_1 corresponds to the total energy of the leading radiation peaks. The data collected in Table 1 allow an objective comparison of the radiation resistance of the crystals investigated here.

The data obtained suggest that the damage thresholds of the $CdGeAs_2$, $ZnGeP_2$, $AgGaSe_2$, CdSe, $AgGaS_2$, and Ag_3AsS_3 crystals fall within a relatively narrow value range. A somewhat higher radiation resistance of the Ag_3AsS_3 crystals is attributable to the minimal duration of the pump pulses and a relatively high measurement error in this case. The low (in comparison with the crystals considered) radiation resistance of the GaSe crystals is most likely attributable to the poor layer cleavage, which in principle can be eliminated by doping. The low radiation resistance of the doped GaSe crystals is undoubtedly related to the imperfection of their production technology and the consequential visible inhomogeneity of the crystals.

Since the working laser mixture was periodically renewed in the course of the measurements, the duration of pump radiation pulses changed significantly from one measurement cycle to another. In our view, the radiation resistance for some reduced pulse duration can be obtained in the following way. The dependence of damage-inducing pulse power P_d on the pulse duration τ will be assumed to obey the equation given in Ref. [2]:

$$\lg P_d = 5.1 + 0.053\lg\tau(1 + \lg\tau). \qquad (3)$$

For a small spread in pump pulse duration, this depen-

Table 1. Summary measurement data for the radiation resistance of the nonlinear crystals.

Crystal	I_d/MW cm^{-2}	L_d/mm	E/mJ	P/MW	E_1/E (%)	$\tau_{0.5}$/ns	$\tau_{0.1}$/ns	$\tau_{0.01}$/ns	I_d'/MW cm^{-2}
$CdGeAs_2$	163 ± 14	396 ± 15	203 ± 16	5.1 ± 0.51	88 ± 4	29 ± 2	82 ± 5	275 ± 40	157
$ZnGeP_2$	142 ± 9	386 ± 6	195 ± 13	4.7 ± 0.3	90 ± 2	31 ± 2	85 ± 4	263 ± 34	142
$AgGaSe_2$	145 ± 6	310 ± 5	273 ± 10	7.03 ± 0.3	90 ± 2	29 ± 1	82 ± 4	226 ± 36	139
CdSe	127 ± 7	306 ± 11	219 ± 8	5.06 ± 0.32	85 ± 2	30 ± 1	84 ± 2	301 ± 13	130
GaSe	121 ± 11	358 ± 13	189 ± 6	4.62 ± 0.36	89 ± 3	31 ± 1	125 ± 6	266 ± 37	121
GaSe:In (0.5 %)	66 ± 3	256 ± 5	163 ± 6	4.09 ± 0.23	93 ± 2	32 ± 2	81 ± 1	284 ± 67	68
$AgGaS_2$	176 ± 7	415 ± 5	183 ± 6	3.34 ± 0.15	84 ± 1	31 ± 1	129 ± 3	285 ± 18	146
Ag_3AsS_3	183 ± 20	402 ± 13	234 ± 12	5.53 ± 0.57	85 ± 2	27 ± 2	89 ± 3	289 ± 34	169
$AgGaGeS_4$	234 ± 9	446 ± 6	215 ± 1	5.46 ± 0.13	89 ± 2	30 ± 1	73 ± 2	268 ± 19	230
$HgGa_2S_4$ (orange)	294 ± 32	502 ± 19	201 ± 5	4.8 ± 0.1	88 ± 2	31 ± 1	84 ± 3	291 ± 28	294
$HgGa_2S_4$ (yellow)	310 ± 35	510 ± 20	201 ± 5	4.8 ± 0.1	88 ± 2	31 ± 1	84 ± 3	291 ± 28	310
$Hg_{0.65}Cd_{0.35}Ga_2S_4$	281 ± 53	505 ± 33	181 ± 8	4.46 ± 0.24	89 ± 1	29 ± 2	85 ± 2	300 ± 7	271

dence can be taken to be linear and, on this basis, we can estimate the resistance I'_d of the crystals under investigation to pump pulses of equal length. The corresponding estimates of the resistance I'_d to pulses with a duration of 31 ns, which is equal to the average pulse length in the experiments conducted, are given in the last column of Table 1.

In this case, the scatter in the damage threshold data for different crystals lowers to ±15 %, which is well below the scatter in the well-known data of Ref. [1]. During the measurements in the ~ 1-cm long Ag_3AsS_3 and GaSe crystals, internal breakdown was observed due to thermal self-focusing. Damage of the output surface was observed with the $ZnGeP_2$ crystals of the same length. Unlike the results of Ref. [6], we observed a clear correlation between the optical quality of $ZnGeP_2$ crystals and their radiation resistance. The radiation resistance of the new $AgGaGeS_4$ crystals turned out to be 1.6 times higher than that of the $ZnGeP_2$ crystals. On reducing the measurement data to similar conditions, the respective damage thresholds for the $Cd_{0.35}Hg_{0.65}Ga_2S_4$ and $HgGa_2S_4$ (the orange and yellow phases) crystals were found to be 1.9, 2.1, and 2.2 times higher than for the $ZnGeP_2$ crystals.

Assuming that the second-order nonlinear susceptibility coefficient for $ZnGeP_2$ is $d_{36} = 75$ pm V^{-1}, for the generation of the second harmonic of CO_2-laser radiation ($\lambda = 9$ μm) we obtain the effective coefficient $d_{\rm eff} = d_{36} \times \sin(2\theta)\cos(2\varphi) \leqslant 30.5$ pm V^{-1}. Similarly, for $AgGaGeS_4$, considering that $d_{32} = 13$ pm V^{-1} and $d_{31} = 8$ pm V^{-1}, we obtain $d_{\rm eff} = d_{32}\cos^2\varphi + d_{31}\sin^2\varphi = 9.8$ pm V^{-1}. For the $HgGa_2S_4$ crystals we have $d_{36} = 32$ pm V^{-1}, $d_{31} = 12$ pm V^{-1}, and $d_{\rm eff} = d_{36}\sin(2\varphi) + d_{31}\cos(2\varphi) = 33$ pm V^{-1}. Taking into account the refractive indices of the $ZnGeP_2$, $AgGaGeS_4$, and $HgGa_2S_4$ crystals at wavelengths in the 9-μm region (3.1, 2.3, and 2.45) and the phase-matching angles (70, 50, and 65°), the ratio between the figures of merit of the above-listed crystals for the generation of the second harmonic of CO_2-laser radiation becomes 1 : 0.81 : 2.5.

The efficiency of second harmonic generation with neglect of optical losses is proportional to the product of the figure of merit and the damage threshold. Since the optical losses in the $AgGaGeS_4$ and $HgGa_2S_4$ crystals are not higher than those in the $ZnGeP_2$ crystals, the expected ratio between the efficiencies of frequency doubling with the above crystals is 1 : 1.4 : 5.5. In other words, these crystals offer advantages or at least are competitive in the generation of the second harmonic of CO_2-laser radiation. Such is the case with the analysis of other frequency conversions in the medium-IR spectral range. We note that, unlike the well-known crystals, the transmittance spectra of the new mixed crystals and both $HgGa_2S_4$ crystal phases permit the widely used near-IR (Nd : YAG lasers) and even visible (copper vapour lasers) range lasers to be employed as pump sources for a middle-IR optical parametric oscillator.

4. Conclusions

We have studied the radiation resistance of a large number of nonlinear crystals, including the well-known $CdGeAs_2$, $ZnGeP_2$, $AgGaSe_2$, GaSe, $AgGaS_2$, and Ag_3AsS_3 crystals operating in the middle IR range and also the new mixed $AgGaGeS_4$ and $Cd_{0.35}Hg_{0.65}Ga_2S_4$ crystals, the doped GaSez: In (0.5 %) crystal, and the two phases (orange and yellow) of the $HgGa_2S_4$ crystals under identical experimental conditions.

The measured damage thresholds of the $CdGeAs_2$, $ZnGeP_2$, $AgGaSe_2$, GaSe, $AgGaS_2$, and Ag_3AsS_3 crystals lie in a narrow (±15 %) interval. The damage thresholds of the new $AgGaGeS_4$, $HgGa_2S_4$ (the orange and yellow phases), and $Cd_{0.35}Hg_{0.65}Ga_2S_4$ nonlinear crystals exceed those of the widely used $ZnGeP_2$ crystals by factors of 1.6, 2.1, 2.2, and 1.9, respectively. Our data suggest that the new mixed crystals and the $HgGa_2S_4$ crystals are competitive with the well-known crystals for operating in the middle IR range. These crystals can also be employed for the frequency conversion of Nd : YAG and copper vapour lasers operating in the near-IR and visible spectral ranges.

References

1. Dmitriev V G, Guzadyan G G, Nikogosyan D N *Handbook of Nonlinear Crystals* (New York, Berlin, Heidelberg: Springer-Verlag, 1999)
2. Churnside J H, Wilson J J, Andreev Yu M, Grybenyukov A I, Shubin S F, Zuev V V *Frequency Conversion of a CO2 Laser with ZnGeP2, NOAA Technical Memorandum ERL WPL-224* (Boulder, Colorado: Wave Propagation Laboratory, 1992)
3. Karapuzikov A I, Malov A V, Sherstov I V *Infrared Phys. Technol.* **41** 77 (2000)
4. Ivashchenko M V, Karapuzikov A I, Sherstov I V *Kvantovaya Elektron.* **31** 965 (2001) [*Quantum Electron.* **31** 965 (2001)]
5. Svelto O *Principles of Lasers* (New York: Plenum, 1989; Moscow: Mir, 1990)
6. Peterson R D, Schepler K L, Brown J L *J. Opt. Soc. Am. B: Opt. Phys.* **12** 2142 (1995)