Q-Switched Laser Damage of Infrared Nonlinear Materials

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Abstract—Q-switched laser-damage thresholds have been determined for six materials (proustite—Ag_3AsS_3, pyrargyrite—Ag_3SbS_3, cinnabar—HgS, silver thiogallate—$AgGaS_2$, tellurium—Te, and gallium arsenide—GaAs) of interest for nonlinear optics in the medium infrared. Four TEM_{00} mode lasers were employed with outputs at wavelengths of 694 nm, 1.06, 2.098, and 10.6 μm. Damage has been found to be confined to the surface of the crystals and occurs for radiation intensities between 3 and 75 MW/cm^2. Particular care is needed in the cutting and polishing of tellurium crystals if a high-damage threshold is to be achieved.

Introduction

The question of laser damage is central to the design and operation of nonlinear optical devices, the reason being the large radiation intensities (power densities) to which the nonlinear crystals are normally subjected. Thus, for example, with optical parametric oscillators the interesting regimes of operation are commonly circumscribed by damage problems. The medium infrared (wavelengths 2.5–25 μm) is a spectral range where nonlinear devices are expected to find considerable practical application but one for which little systematic damage work has so far been done. We, therefore, set ourselves the task of determining damage limits for the principal nonlinear materials available for this range. We wished primarily to determine numerical values for damage thresholds that could be used in device design. The mechanism for damage has, therefore, been of secondary interest although some general facts have emerged.

The following phase-matchable crystals were studied; proustite—Ag_3AsS_3 [1], pyrargyrite—Ag_3SbS_3 [2], cinnabar—HgS [3], silver thiogallate—$AgGaS_2$ [4], and tellurium—Te [5]. Measurements were also made on gallium arsenide (GaAs), which since it is cubic cannot be phase matched, but is, however, widely used in the medium infrared as a standard of second-order susceptibility [6]. Damage thresholds have been found for four laser wavelengths spanning the range 694 nm to 10.6 μm. Q-switched lasers were used exclusively.

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Laser damage to the six materials has been found to be limited to the entrance and exit surfaces. For the intensities at which surface damage occurs, there is no evidence for any kind of bulk irreversible damage in the form of structural change, excess absorption, or reflective index variation. In the Q-switched time regime (10–100ns) the onset of surface damage is principally characterized by the level of instantaneous radiation intensity, i.e., the damage-threshold intensity. For accurate measurements of this quantity transverse electromagnetic (TEM_{00}) mode lasers must be used since only then can intensities be accurately calculated.

In the rest of the paper, consideration is given to the materials used and their preparation, to the lasers and measurement techniques, and to the results obtained.

Materials

All the materials studied were artificially grown single crystals. They were obtained from a variety of sources.[1] The crystals were cut into plates of thickness 1.5–5 mm, with no specific orientation relative to the crystallographic axes.

With the exception of tellurium, for which special techniques were used, the crystals were cut and polished mechanically and the surface thoroughly cleaned. The cleaning sequence was as follows; washing with Decon-75 detergent solution, deionized water, Analar, Aristar propan-2-ol, and finally drying in air.

Three methods were employed for producing the tellurim plates; mechanical cutting, cleaving, and chemical sawing. For the mechanical work, a conventional diamond saw was used followed by polishing with diamond paste. Cleavage along the [10$\bar{1}$0] faces was accomplished by cooling the crystal to liquid-nitrogen temperature and applying pressure with a warm blade. A Metallurgical Services, Ltd., thread saw was used for the chemical cutting, the solvent being prepared to the chromic-anhydride recipe of Stokes *et al.* [7]. The cut surfaces were also polished with the same mixture. The application of chemical sawing of tellurium crystals for optical work has previously been described by Kolb and Laudise [8]. Surface etching using the above solvent to remove polishing damage was found to raise the damage threshold of all tellurium crystals. Final cleaning was the same as for the other materials but with a concentrated

[1] The only commercial material used was tellurium bought from Wacker Chemie GmBh and from Métallurgie Hoboken. Further tellurium crystals were provided by the Centre National d'Etude des Télécommunications.

TABLE I
LASER PARAMETERS

Characteristics	Nd:YAG	CO_2	Ruby	Ho:YAG
Wavelength	1.06 μm	10.6 μm	694 nm	2.098 μm
Pulse length (full width half maximum)	17.5 ns	a) 220 ns b) 190 ns	14 ns	~200 ns
Peak power	390 kW	a) 2.4 kW b) 3.5 kW	375 kW	~10 kW
Spot radius W	0.65 mm	focused beam	0.52 mm	focused beam
Average	14 mW	~100 mW	3 mW	~400 mW
Peak intensity I_{max}	60 MW/cm^2	1) focused, 10-cm lens a) 19 MW/cm^2 b) 27 MW/cm^2 2) focused, 5-cm lens a) 76 MW/cm^2 b 107 MW/cm^2	88 MW/cm^2	>10 MW/cm^2
Pulse-repetition frequency	2 pps	a) 207 pps b) 190 pps	1 ppm	~200 pps
Spatial properties	TEM_{00}	TEM_{00}	TEM_{00}	substantially TEM_{00}
Temporal properties	some mode locked but not to baseline	no mode locking	no mode locking	unknown
Pumping	flash lamp	electric discharge	flash lamp	tungsten–iodine lamp

hydrochloric-acid wash replacing the detergent solution.

A limited number of measurements were made on plates having antireflection coatings.

Experimental Techniques

Only lasers operating in the lowest order transverse TEM_{00} mode are suitable for accurate measurements [9] of damage thresholds. With such lasers, the radial intensity pattern $I(r)$ of the output Gaussian beam is given by the equation:

$$I(r) = I_{max} \exp [-2r^2/W^2], \qquad (1)$$

where W is the spot radius, (it must be emphasized that W is the radius at which the electric field has fallen to e^{-1} of its value at the center of the beam [10]) and I_{max} = (total power over the beam)/$\frac{1}{2}\pi W^2$. Higher transverse modes of the laser or, even worse, mixtures of such modes result in complex intensity patterns frequently containing hot spots. Such hot spots will induce damage at low-beam powers. All four lasers used in our work were operated in the TEM_{00} mode.

With the well-defined intensity distribution of Gaussian beam radiation, at least two techniques are available for locating the radiation intensity at which damage occurs. In the first approach, I_{max} is varied through the use of filters or by focusing until damage just occurs at the very center of the beam. The damage threshold then equals I_{max}. For the second method, the intensity at the center of the beam is set well above threshold and the limiting value determined from the beam radius to which damage extends. Equation [1] is then used to calculate the threshold intensity. Both these techniques were used in our work and gave results in good agreement with each other.

Most of the measurements were made at one of two wavelengths; at 1.06 μm from a Nd:YAG laser and at 10.6 μm from CO_2 lasers. Brief experiments were also performed using a ruby laser at a 694-nm wavelength and and Ho:YAG laser at 2.09 μm. The properties of the lasers are summarized in Table I.

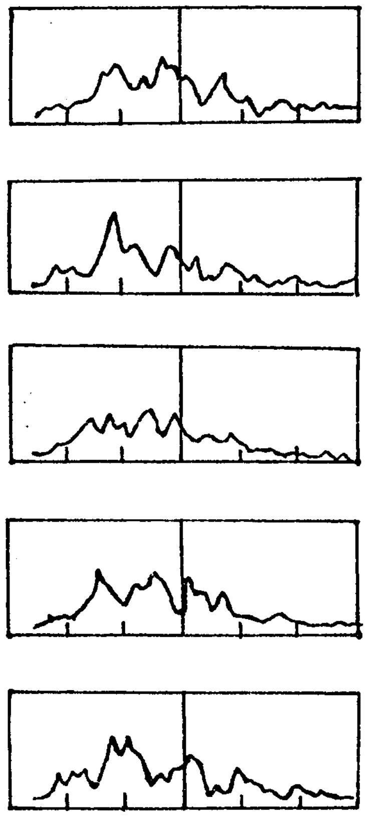

Fig. 1. Mode locking of the Nd:YAG laser. Time scale: 5 ns/div. Oscillograms of consecutive laser pulses.

The Nd:YAG laser was flash-lamp pumped at 2 pps and electrooptically Q switched. A lens and circular aperture were incorporated in the laser to ensure a TEM_{00} transverse mode. Operation on this mode was confirmed through burns on exposed Polaroid film and by scanning the beam profile with a slit and detector. The output pulse showed partial self-mode locking (see

Fig. 1; recorded using an ITT 4000 planar-vacuum photo diode and Tektronix-519 oscilloscope with a combined rise time of ~ 0.5 ns). However, the mode-locked structure appeared to have no effect on damage thresholds since these were consistent from pulse to pulse, whereas, the oscilloscope traces contained peaks of varying sizes. A conclusion to be drawn from this result is that the time constants characterizing the damage are at least a few nanoseconds long. The Q-switched power (averaged over mode locking) was 390 kW and the pulsewidth (3 dB) 17.5 ns. The diameter $2W$ of the beam was 1.3 mm and was used without focusing. The beam intensity was varied by transmission through various multilayer reflectors. This approach is preferred to using absorbing filters since the latter are prone to bleaching.

Two very similar CO_2 lasers were employed, these being of the conventional low-pressure type. They were spinning-mirror Q switched at ~ 200 pps. Transverse-mode selection was accomplished by the slit and edge technique of Arnold and Hanna [11]. The TEM_{00} mode was confirmed by thermal imaging and by slit scans. The peak powers and pulsewidths for the two lasers were 2.4 kW and 220 ns and 3.5 kW and 190 ns, respectively. Since the powers were much lower than for the Nd:YAG laser, focusing was required to produce damage. Two lenses were used giving focal-spot diameters of 90 and 180 μm, respectively. Additional variations of intensity were obtained by transmission through various transparent materials having different Fresnel reflectivities. When required, a camera shutter was used to isolate small numbers of pulses.

The ruby laser used [12] was dye Q switched using vanadium phthalocyanine in nitrobenzene and contained a circular aperture for TEM_{00} mode selection. The output pulse was examined with the same detection system used for Nd:YAG laser. The pulse envelope was quite smooth, showing no evidence of mode locking. The peak power was 375 kW and the pulse duration 14 ns. The beam was used without focusing and the power level was adjusted by using multilayer reflectors as before.

Laser radiation at 2.098 μm was obtained from an Ho:YAG laser. This laser [13] was continuously pumped and liquid-nitrogen cooled. A spinning-mirror Q switch was employed. The output was substantially in the TEM_{00} mode. 10-kW 200-ns pulses were obtained at 200 pps. Focusing was required for damage.

Laser peak powers were determined from the pulse energy and Q-switched pulse shape. A TRG cone calorimeter was used for energy measurement. This instrument had been previously calibrated by J. G. Edwards against a standard at the National Physical Laboratory. Energies (and peak powers) are estimated to have an absolute precision of ± 10 percent. (Comparison of the TRG calorimeter with two other commercial calorimeters yielded values consistent with ± 10 percent of the calibration.) The absolute intensities involve measurements of beam diameters and have a precision of approximately ± 20 percent. Relative accuracies are obviously somewhat better than the above figures.

Coincident with the surface damage, there was invariably a small visible plasma. The plasma was used as an indication that damage had occurred and this was confirmed by visual and microscope examination. In addition to an optical microscope, a secondary-emission Stereoscan electron microscope was used to study, in some detail, the damage region.

Results

Summarized in Table II are the results for all the damage measurements.

Proustite

The most detailed study of damage was made for this material with measurement at all four laser wavelengths. Much of this work was at 1.06 μm.

1.06 μm: In the initial experiment I_{max} was reduced until damage only just occured. It was thus found that a small region of damage was produced by ten pulses at I_{max} = 28 MW/cm². Damage was more apparent on the back surface of the crystal than on the front. Both surfaces showed a plasma on damaging.

For subsequent experiments, I_{max} was set above threshold and areas of damage created with one, three, and ten pulses, respectively. Fig. 2 shows examples of the damage regions created in this way. The regions are well defined following the circular form of the laser beam. The radii enclosing substantial damage were then measured and fitted to beam-intensity profiles (Fig. 3) to give damage thresholds. Good agreement is seen between the thresholds for three different values of I_{max} and the averages of these are given in Table II. The exit surface has a slightly lower threshold than the entrance surface. An increasing number of flashes, from one to ten, results in a reduction of threshold down to a value of 25 MW/cm² (exit face). However, a run of 1000 pulses at I_{max} = 12.5 MW/cm² produced no damage.

In an attempt to obtain more information on the reduction of damage threshold with the larger numbers of pulses, an experiment was performed with trains containing three pulses but increased time intervals between them. It was found that the three-pulse threshold became equal to the single-pulse threshold when the time interval was greater than about two minutes. This result indicates that some kind of damage-initiating center is induced at intensities below that for single-pulse damage and that these centers have lifetimes of a minute or two. Rapid visual inspection of the crystal after the first two pulses of a train did not reveal any extra absorption, etc., in the region illuminated by the laser beam.

The optical micrographs (Fig. 2) show damage occurring in small spots randomly located within the laser beam. Continued pulsing results in the spots merging together to form an area of massive damage. Examination of the edge of the damage region under the Stereoscan

TABLE II
DAMAGE THRESHOLDS

Laser Wave-length	Proustite	Pyrargyrite	Cinnabar
1.06 μm	2 pps: pulses — 1 = 44.5 MW/cm^2 pulses 3 = 37 MW/cm^2 pulses 10 = 28 MW/cm^2 pulses 1000 > 12.5 MW/cm^2 3 pulses: 2 pps = 37 MW/cm^2 1 ppm = 41.5 MW/cm^2 0.2 ppm = 44.5 MW/cm^2 Above for input surface; output thresholds ~ 3 MW/cm^2 lower	pulses — 1 = 25 MW/cm^2 pulses 10 = 25 MW/cm^2 pulses 1000 > 9 MW/cm^2 Damage thresholds for input and output surfaces within 1 MW/cm^2 of each other.	10 pulses ~ 40 MW/cm^2
10.6 μm	pulses — 1 < 76 MW/cm^2 pulses 100 = 53 MW/cm^2 pulses > 30 000 > 46 MW/cm^2	Pulses — 1 < 76 MW/cm^2 Pulses 300 = 53 MW/cm^2 Pulses > 30 000 > 46 MW/cm^2	— — —
694 nm	pulses —1 < 44 MW/cm^2 pulses 3 ~ 11 MW/cm^2 pulses 10 = 3 MW/cm^2 crystal with AR coating: 10 pulses ~ 15 MW/cm^2		— —
2.098 μm	10 000 pulses > 10 MW/cm^2	—	—

Note: For all tellurium samples occasional spots could be found on the crystal with substantially lower thresholds than above. See text for accuracies.

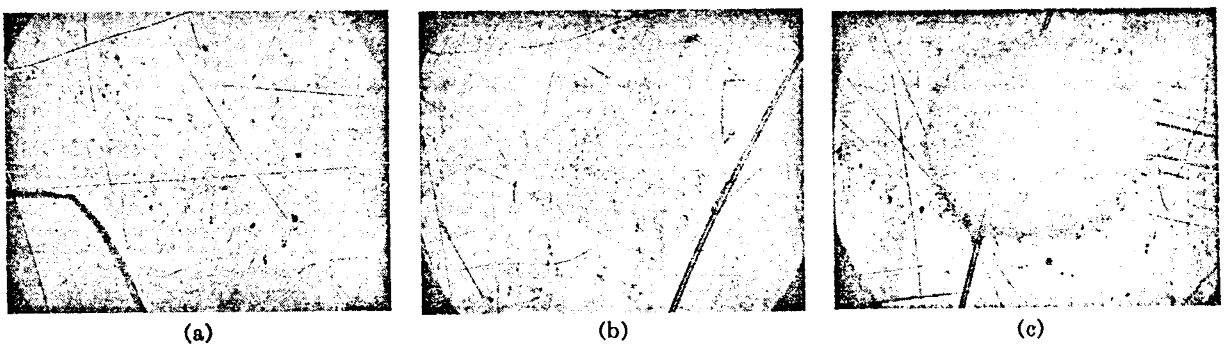

Fig. 2. Optical micrographs of entrance surface damage of proustite. The 1.06-μm intensity was I_{max} = 55 MW/cm^2 and damage regions are shown. (a) One shot. (b) Three shots. (c) Ten shots. Magnification is ×30.

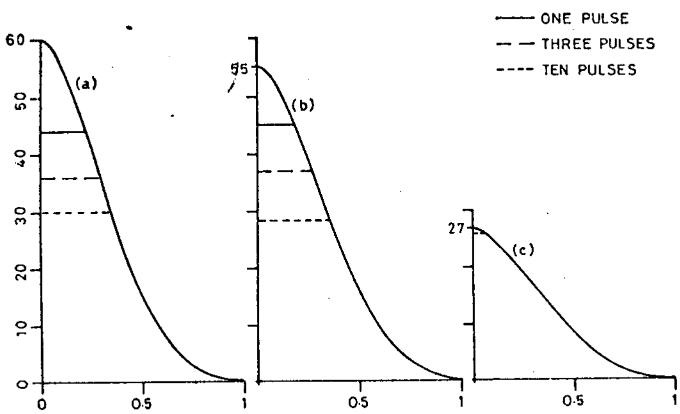

Fig. 3. Plots of the radii of proustite entrance surface damage on 1.06-μm beam profiles. (a) I_{max} = 60 MW/cm^2. (b) I_{max} = 55 MW/cm^2. (c) I_{max} = 27 MW/cm^2. Horizontal scale: Radius (millimeters). Vertical scale: Radiation intensity (megawatts per centimeter squared).

instrument reveals [Fig. 4(b)] that in the small spots, the surface has been removed to a depth of a fraction of a micron. The heavily damaged central region shows evidence of surface melting [Fig. 4(c)].

10.6 μm: Damage at this wavelength again occurs on the surface and is very similar in form, threshold, and accumulation to that at 1.06 μm (The diameter of the damage region is, due to the necessary focusing, ten times smaller.) A prolonged run at I_{max} = 46 MW/cm^2 again produced no damage. The short confocal parameter of the focused beam resulted in damage appearing on only one face at a time.

2.098 μm: The measurement at this wavelength was not as accurate as the others but the result fits the general pattern.

694 nm: The damage thresholds here are substantially

TABLE II (*Cont'd.*)

Silver Thiogallate	Gallium Arsenide	Tellurium
pulses – 1 ~20 MW/cm² pulses 1000 > 12.5 MW/cm²	pulses – 1 ~ 40 MW/cm²	
1000 pulses ~ 25 MW/cm²	Pulses – 1 < 107 MW/cm² Pulses 100 = 76 MW/cm² Pulses > 30 000 > 63 MW/cm²	*Wacker material* Mechanically cut: pulses – 1000 ~ 10 MW/cm² + etching:— pulses > 30 000 > 30 MW/cm² Cleaved: pulses – 1 < 43 MW/cm² pulses > 30 000 > 30 MW/cm² + etching:— pulses 100 = 43 MW/cm² pulses > 30 000 > 30 MW/cm² *Hoboken material* Chemically cut: pulses – 1000 = 43 MW/cm² + etching: pulses 1 < 63 MW/cm² pulses > 30 000 > 43 MW/cm² *CNET material* Mechanically cut, then etched: pulses – 10 000 = 63 MW/cm² pulses > 30 000 > 43 MW/cm² Crystal with AR coating: pulses – 10 000 ~ 20 MW/cm²
— —		
—	—	

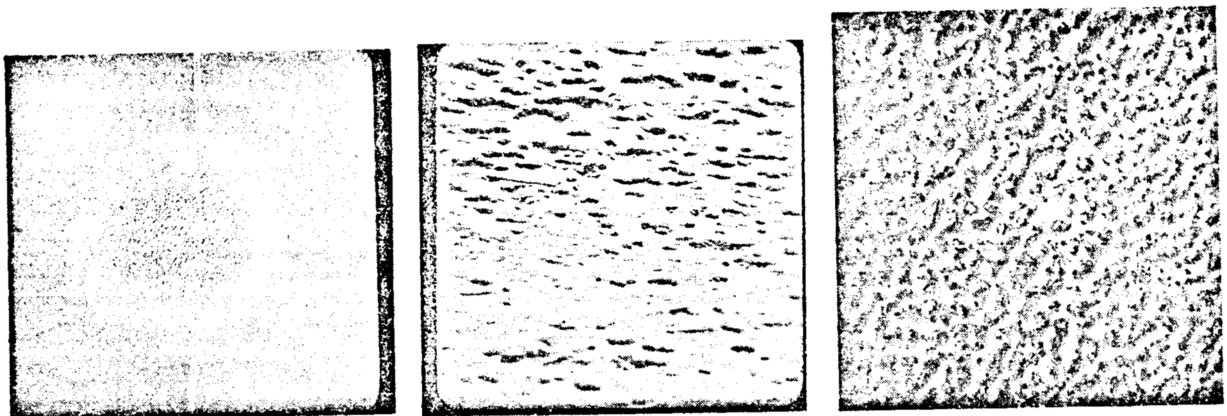

Fig. 4. Stereoscan micrographs of 106-μm proustite damage. The damage region is the same as Fig. 2(c). (a) Vertical view at ×30 magnification. (b) Slant view at ×1500 magnification of the edge of the damage region. (c) Vertical view at ×150 magnification of the center of the region.

lower than for the other wavelengths. However, the photon energy is close to the forbidden energy gap and there is measurable absorption to a few percent per centimeter (Proustite has negligible absorption at 1.06 and 2.098 μm. An absorption coefficient of ~ 0.5 cm⁻¹ applies to 10.6 μm [1].) Accumulation of damage is again apparent.

Pyrargyrite

1.06 μm: Damage to pyrargyrite closely resembles that of proustite except that the thresholds are a little lower and the input surface damages before the output surface. Of importance is the fact that accumulation (1–10 pulses at 2 pps) is absent.

10.6 μm: Similar to proustite.

Cinnabar

This crystal was of limited quality and the following results should therefore be treated with caution.

1.06 μm: Damage was found at ~ 40 MW/cm², very close to the values for the two previous materials. The entrance face had a lower threshold than the exit one. The central damage region was similar to that of the other materials; surrounding it, however were a number of small damage spots. These spots may have resulted from the poor crystal quality.

Fig. 5. Stereoscan slant view of 10.6-μm damage track on tellurium. $\times 34$ magnification.

Silver Thiogallate

1.06 μm: The results obtained are again similar to those for the previous materials. The back surface damages before the front surface. 1000 pulses at $I_{max} = 12.5$ MW/cm^2 failed to produce any damage.

10.6 μm: Nothing unusual.

Tellurium

10.6 μm: As for the other materials, surface damage to tellurium is accompanied by a clearly visible plasma. An accumulative effect is again apparent operating over the range 1–10 000 pulses. The damage threshold is somewhat dependent upon surface position, presumably due to local defects. It was found that once damage had started at a given place, a track could be formed as the crystal was moved across the laser beam (Since the CO_2 lasers ran at 200 pps they were essentially continuous for this test.)

Surface preparation has a large effect upon the intensity at which tellurium crystals damage. Etching of the crystal to remove the cut surface increases the threshold, enhancements of more than three times being found for aggressively cut crystals but only 10–15 percent for those prepared by cleaving or chemical cutting. The differences between the various cutting techniques only really show before etching. Crystal quality has a strong effect on damage as revealed by the fact that CNET crystals mechanically cut and then etched have twice the threshold of Wacker ones similarly prepared. In fact, with careful preparation, all samples of tellurium can withstand prolonged irradiation at 30 MW/cm^2.

Examination of tellurium damage with the Stereoscan microscope reveals a rather different picture from that of the other materials. Melting occurs, followed by flow of the liquid. Fig. 5 shows a track of continued damage formed by moving the crystal across the laser beam, as well as three spots (to the left of the main track) where only a few pulses were involved. The individual crater-like damage spots are similar to those formed on the surface of lithium niobate [14]. Also of interest in Fig. 5 is the bright region surrounding the damage track; the secondary emission has been enhanced here, possibly due to a scouring action of the plasma. Within this latter region a higher magnification revealed dislocation etch pits at $\sim 5 \times 10^{10}/\text{m}^2$.

The bulk absorption coefficient of tellurium at 10.6 μm is ~ 0.5 cm^{-1}.

Gallium Arsenide

1.06 μm: Surface damage occurred at approximately 40 MW/cm^2.

10.6 μm: This material is substantially more resistant to 10.6-μm laser damage than the other materials. Thus there is no damage at 63 MW/cm^2 after thousands of pulses and 100-pulse damage is only reached at 75 MW/cm^2. Whether this is due to a basic physical effect or simply to better crystal quality, cannot yet be determined.

General Remarks

Surface scratches did not appear to have a great effect on damage thresholds although damage in the region of a scratch is usually slightly enhanced (see Fig. 2 for examples). This general independence of damage threshold from surface finish is in agreement with Bass' results [15] for visible nonlinear materials.

Various parts of the damage region were frequently crossed by what were obviously interference fringes. These most likely arose from scattering at imperfections, etc. In one particular case, that of pyrargyrite sample, the whole damage region was covered with straight parallel fringes. It was demonstrated that these resulted from a finite wedge angle of the crystal plate giving near-field (Fizeau) fringes in the laser light.

No clear pattern could be deduced for the effect of antireflection coatings deposited on the surface. For one particular coating on proustite, the damage threshold was undoubtedly raised; another coating on tellurium resulted in a reduced threshold.

Conclusions

The most remarkable feature of the results reported here is the low values of intensity 3–75 MW/cm^2 at which surface damage is initiated in this range of materials. It is worth noting that all are semiconductors and that the thresholds for surface damage of dielectric nonlinear materials are at least an order of magnitude higher. This is not, however, the whole story as shown by the fact that germanium and silicon have 10.6-μm thresholds greater than 100 MW/cm^2.

No clear correlation emerges from our work between damage thresholds and bulk-absorption coefficients. However, it should be noted that the surface layers considered will fairly certainly have different absorptions from the bulk.

It is not possible to deduce much on the mechanism of damage from our measurements. For the compound materials there is evidence of a surface layer being stripped off before surface melting occurs. In contrast, damage to tellurium may have melting at the first stage. The role of the surface plasma, which seems to correlate with damage, is uncertain; whether it is the primary cause of damage or a secondary effect is not known. The fact that mode locking of the laser did not alter thresholds, indicates a buildup time for damage greater than a few nanoseconds. The reduction in proustite of damage threshold for pulse trains a few minutes long seems to show that a proportion of the damage-initiating centers remains for this time.

In a series of elegant experiments, Bass has recently shown [16] that under certain conditions (spot diameter $\sim$ 30 μm) surface damage has a statistical character; radiation intensities can then only be accorded probabilities of inducing damage. Brief experiments on proustite failed to show this statistical behavior, since damage always occurred after a well-defined number of pulses. Also the damage regions were of reproducible shape and dimension. If statistical effects exist for proustite and for some of our other materials, they are presumably associated with the micron-sized damaged pits [see Fig. 4(b)] rather than the overall damage region.

Proustite and tellurium are the only materials for which useful damage measurements have been reported by other workers. Fountain *et al.* [17] found, for proustite, a damage threshold (I_{max}) of 20 MW/cm^2 at 1.06 μm for 600 pulses at 10 pps and 10-ns duration. This value is not far from our own, especially when the possible effects of accumulation are considered. They also described damage occurring at 0.9 MW/cm^2 after several minutes of irradiation at 2000 pps. This result does not seem to fit the general pattern outlined above. We do not agree with their conclusion that surface melting is the dominant damage mechanism in proustite. For measurements on tellurium, Taynai *et al.* [18] used a Q-switched CO_2 laser similar to that used here but the resulting damage thresholds were much lower, only 2–4 MW/cm^2. Damage was in the form of 0.3-mm pits on the exit surface, the laser beam being gently focused. The most likely cause of their low thresholds is that they failed to etch the crystal surfaces to remove polishing damage. One single measurement of the damage threshold for gallium arsenide is known to us [19]. The value for a multitransverse-mode 1.06-μm laser is 9.5 MW/cm^2 for a single 1-μs pulse.

The type of damage discussed above concerns essentially the instantaneous level of radiation intensity. There is evidence for at least two other classes of effect. The first of these depends upon the average intensity. Thus for tellurium, Taynai *et al.* [18] found that the average intensity induced damage as craters on the entrance surface, the threshold being 150–200 W/cm^2. With proustite, surface oxidation that is enhanced by radiation [20] appears to be involved. It is noticeable after several minutes of continuous 694-nm irradiation at $\sim$ 1 W/cm^2 [21]. Surprisingly, this effect occurs only on proustite surfaces stored for a month or more after polishing. The damage layer can be removed by gentle cleaning with a lens tissue. The second class of effect involves reversible transmission changes having lifetimes ranging from approximately one minute for pyrargyrite [22] to fractions of a second of tellurium [23], [24].

In the past few months three further phase-matchable crystals have been found for potential use in the infrared; $ZnGeP_2$ [25], $CdGeAs_2$ [26], and CdSe [27]. For the first two materials the damage thresholds are low, being only a few MW/cm^2. In contrast, the much better quality cadmium-selenide crystals show the high threshold (I_{max}) of 60 MW/cm^2.

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