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Nonlinear absorption measurements in proustite (Ag_3AsS_3) and CdSe

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Nonlinear absorption has been observed in proustite at 694 nm; however at 1.06 μm, in contrast to previous results, no nonlinear absorption could be detected at intensities up to the damage threshold. Measurements on CdSe at 1.06 μm and 1.32 μm show that the nonlinear absorption mechanism is two photon absorption followed by absorption by the photo-induced carriers. The implications of this for nonlinear mixing applications are discussed.

1. Introduction

Intensity-dependent absorption has been observed in many nonlinear optical materials, including proustite [1], $LiNbO_3$ [2], CdSe [3, 4], tellurium [5, 6] and GaAs, e.g. [4, 7, 8]. The absorption has usually been attributed to two photon absorption, but it has been pointed out, e.g. [5, 6, 8], that free carrier absorption by photo-induced carriers can also make a significant contribution. These absorption effects are of interest as far as nonlinear optical devices are concerned since they could affect the operation of parametric oscillators, and absorption by the free carriers could have a serious effect on long wavelength generation by down-conversion. Measurements of nonlinear absorption under nominally the same conditions have produced results with a wide spread in value of nonlinear absorption coefficient, some of which may be due to differences in the purity of the material used. The value of the two photon absorption coefficient reported recently by Berezovskii *et al.* for proustite [1] is such that this absorption should be readily observed under the operating conditions of a proustite parametric oscillator [9], where 1.06 μm pump intensities of up to 20 MW cm^{-2} have been used. It was therefore decided to repeat the measurements of Berezovskii using a high quality proustite crystal which had *actually been used* in a parametric oscillator. We found that no nonlinear absorption of 1.06 μm radiation could be detected in this crystal at intensities right up to the threshold for optical damage. Using 694 nm radiation from a Q-switched ruby laser, a small nonlinear absorption could however be detected. In addition, we have observed nonlinear absorption in CdSe of both 1.06 and 1.32 μm radiation from a Q-switched Nd YAG laser. Again, the crystal was of high quality, *having been used successfully* in a HF pumped parametric oscillator [10]. Evidence shows that this absorption is mainly due to free carriers excited by two photon absorption. It is shown that absorption by these free carriers would seriously limit the long wavelength power that could be generated in CdSe by down-conversion from wavelengths around 1.32 μm.

2. Proustite

Measurements on proustite at 1.06 μm were made using a Nd YAG laser. This was Q-switched electro-optically to give 20 ns pulses, and the output beam (TEM_{00}) was attenuated to give the required intensity at the crystal. A measurement was made of the power transmitted by the crystal with an attenuator placed after it, and compared with that when the same attenuator was moved to the front of the crystal, thus reducing the intensity on the crystal. This provides a simple way for detecting small changes in the transmission of the crystal. The parametric oscillator crystal used in these measurements had been grown at the Royal Radar Establishment, and was 10 mm long. Measurements were also made on a second crystal, 14 mm long, of

much poorer quality. The linear absorption coefficients of the two crystals at 1.06 μm were measured in a spectrophotometer to be 0.02 and 0.1 cm^{-1} respectively.

Despite the fact that the 1.06 μm intensity at the crystal was varied by a large factor, and taken up to the damage threshold (20 MW cm^{-2} for the pulses used [11]), no nonlinear absorption was seen in either crystal, for either polarization. From this result (taking into account the correction factors for pulse shape given by Kleinman *et al.* [7]) it can be calculated that the two photon absorption coefficient (β) for proustite at 1.06 μm is less than 0.003 cm MW^{-1}. This upper limit is a factor of ten lower than value reported by Berezovskii *et al.* [1].

Absorption measurements were also made in proustite using a ruby laser (694 nm), which gave 25 ns pulses in approximately a TEM_{00} mode. The same two crystals were used, their linear absorption coefficients being about 0.1 and 0.5 cm^{-1} at 694 nm. Nonlinear absorption was observed in both crystals at intensities approaching the surface damage threshold, which is about 10 MW cm^{-2} for the laser pulses used [11].

No change in this nonlinear absorption was seen when different directions of propagation and polarisation of the ruby beam were used. From the limited experimental data obtained, it is not possible to say which of several possible nonlinear absorption mechanisms [12] occurs in proustite. If the mechanism is simply two photon absorption then the value of β can be calculated to be 0.02 cm MW^{-1} for both crystals. This should be compared with the value of Berezovskii *et al.* [1] of 0.1 cm MW^{-1}. However, since the actual nonlinear mechanism is not known, it is not possible to estimate the magnitude of nonlinear absorption to be expected at higher intensities with shorter laser pulses.

3. Cadmium selenide

Nonlinear absorption measurements were also made in near intrinsic cadmium selenide. This crystal (28 mm long) had been compensated after growth to significantly reduce free carrier absorption at the long wavelength end of the transmission band. As a result, the material showed excess absorption near the band edge [13], with an absorption coefficient of 0.02 cm^{-1} at 1.06 μm and 0.01 cm^{-1} at 1.32 μm. Fig. 1 shows the transmission behaviour of the crystal at 1.06 μm as a function of input intensity. These measurements were taken with a small diameter pyroelectric detector measuring the energy at the centre of the laser beam. Similar results were obtained for both ordinary and extraordinary polarisation. If the nonlinear absorption mechanism were simply two photon absorption, the reciprocal transmission [curve (c)] would be a straight line, and the transmitted energy [curve (a)] would not show a decrease at high intensities. The shapes of these curves can however be accounted for by including the effect of absorption by carriers generated by the two photon process. Stimulated Brillouin scattering and thermal focussing could lead to similar effects to those observed, but independent checks showed that neither of these processes was occurring. The presence of free carriers was confirmed by observation of photoconductivity, and by observations of the transmission of a delayed probe pulse. These measurements indicated that the lifetime of the carriers is longer than the laser pulse duration. When the laser was operated on a single frequency [14], the observed nonlinear absorption for a given laser intensity was considerably reduced, thus giving evidence for two photon absorption rather than a two step absorption [12], as the mechanism responsible for carrier generation. The build up of the carrier concentrations can be seen by examining the real time transmission of the crystal. Fig. 2a shows the temporal shape of the transmitted pulses, taken with a fast vacuum

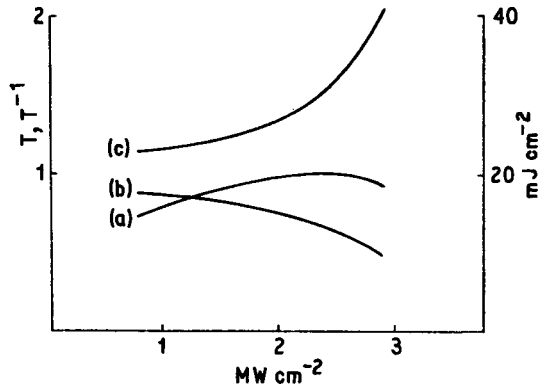

Figure 1 Energy transmission at 1.06 μm of the 28 mm A-R coated CdSe crystal as a function of input intensity for a 25 ns pulse length. (a) transmitted energy; (b) transmission (transmitted energy/input energy); (c) reciprocal transmission (input energy/transmitted energy).

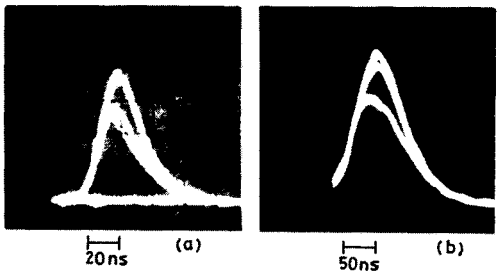

Figure 2 Temporal shape of input pulse (upper trace) and transmitted pulse (lower trace), monitoring the total beam energy. Each trace contains three shots. (a) 1.06 μm, ~ 3 MW cm^{-2} peak; (b) 1.32 μm ~ 4 MW cm^{-2} peak.

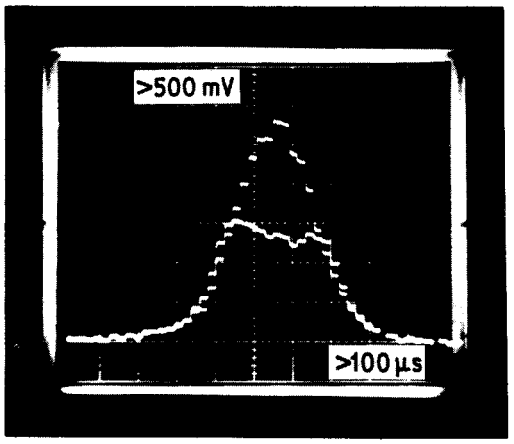

Figure 3 Spatial profile of 1.06 μm input beam energy (upper trace) and transmitted beam energy (lower trace) taken with scanning photodiode array. Peak intensity ~ 3 MW cm^{-2}, pulse length ~ 25 ns, diode spacing: 100 μm.

photodiode, at about 3 MW cm^{-2} peak intensity. The upper trace shows the transmitted pulse with the attenuator in front of the crystal, and the lower trace with the attenuator behind the crystal. Early in the pulse, these two traces overlap, but the build up of carrier concentrations leads to a drop in transmission of the trailing edge. Similar observations of the build up of free carriers and clipping of the latter part of the transmitted pulses have been reported for germanium by Gibson *et al.* [15]. The transverse spatial profile of the transmitted beam was also examined using a scanning photodiode array (Fig. 3). Besides being a rather simple way of observing nonlinear absorption, such measurements can also serve as a useful confirmation that thermal focussing effects are not significant. Again, the upper trace corresponds to the attenuator being in front of the crystal, and the lower, truncated trace with the attenuator behind the crystal.

The combined effect of two photon absorption and associated free carrier absorption was also seen in the same crystal at 1.32 μm. Fig. 2b shows the temporal shape of the transmitted pulses, which again show attenuation of the latter part of the pulses.

A simple analysis of the combined effects of two photon absorption and the consequent free carrier absorption shows that, to a first approximation, the transmission at low intensities is determined by linear and two photon absorption only, while at higher intensities, free carrier absorption becomes dominant, if carrier recombination can be neglected. In our measurements on CdSe, the observed carrier lifetime is such that the neglect of recombination is justified, thus making analysis of the situation simpler. The transmission at 1.06 μm (Fig. 1) was compared with that obtained from a computer solution of the differential equations describing absorption and carrier generation. This calculation takes into account the laser pulse shape, and the multifrequency operation of the laser. With β and the product $\beta\sigma$ as parameters (σ is the total absorption cross-section of a free hole and free electron), it was found that the best fit to the experimental data was obtained with $\beta\sigma = 5 \times 10^{-19}$ cm^3 MW^{-1}. The actual value of β (and hence σ) is more difficult to obtain. However, by examining the pulse shapes of Fig. 2a, an upper limit can be found for β, using the relation $I_{out}/I_{in} = 1/(1 + \beta l I_{in})$, which applies when two photon absorption is the sole absorption mechanism. Allowing for the multifrequency behaviour of the laser, and the Gaussian beam profile, leads to a value for β of less than 0.02 cm MW^{-1}. This value is considerably less than those reported by Bryukner *et al.* [3], and Ralston and Chang [4]. By comparison of the absorption in the trailing edges of the pulses shown in Figs. 2a and b, we estimate that at 1.32 μm, the value of $\beta\sigma$ is 10^{-19} cm^3 MW^{-1}, with β approximately 0.002 cm MW^{-1}. However, because of experimental uncertainties, the above figures can only be estimated to within a factor of two.

4. Effect on down-conversion

Optically excited free carriers have been shown to

have a limiting effect in second harmonic generation [5, 6] and difference frequency generation [16]. Since the free carrier absorption cross-section increases with wavelength as approximately λ^2, the longest wavelength involved in a parametric mixing scheme will be worst affected. We have analysed this limiting effect for a pulsed situation and with particular reference to difference frequency generation ($\omega_3 = \omega_1 - \omega_2$). If the simplifying assumptions are made that carrier recombination can be neglected, two photon absorption is suffered by only one of the input beams (ω_1), and free carrier absorption is only significant for the longest wavelength involved, it can then be shown that the energy per unit area generated at the difference frequency will saturate, and for square input pulses of duration T, the intensity I_1 (of the ω_1 beam) at which this saturation occurs is given by

$$I_1 = \left(\frac{2\hbar\omega_1}{\beta} \times \frac{2}{\sigma} \times \frac{1}{lT}\right)^{1/2}$$

where β is the two photon coefficient at ω_1, σ is the total free carrier absorption cross-section at the longest wavelength and l is the mixing crystal length. Maximum energy conversion to the difference frequency will therefore be obtained when beam ω_1 is focussed so as to have its intensity equal to I_1 given above. As an example, we have considered the case of difference frequency generation around 20 μm by mixing 1.32 μm (from a Nd YAG laser) with the idler of a 0.66 μm pumped OPO. For pulse lengths of 100 ns, crystal length of 3 cm, and using our value of β and a value of σ at 20 μm, estimated using the Drude formula [17], and the data of Hase and Onuki [18], I_1 is found to be about 300 kW cm^{-2}. This intensity is more than an order of magnitude smaller than the damage threshold of CdSe, and hence the maximum mixing efficiency is correspondingly reduced. For mixing wavelengths longer than 1.5 μm, two photon absorption should be negligible, and thus much greater mixing efficiencies are possible, e.g. [19].

These effects could also be of importance in other nonlinear infrared materials. Dewey and Hocker [16] have observed saturation of generated infrared radiation in ZnSe. Laser induced free carriers could also be a contributing factor in the unexpectedly low infrared powers generated in $AgGaS_2$ e.g. [20]. These results suggest that in assessing the potential of i.r. nonlinear optical materials, it is important to take account of their nonlinear absorption behaviour, and if necessary use pump or mixing wavelengths long enough to avoid two photon absorption.

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