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Two-photon absorption in GaSe and $CdGeAs_2$

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Abstract

We measured two-photon absorption (TPA) coefficients, at room temperature, for two noteworthy mid-infrared nonlinear-optical crystals, namely GaSe and $CdGeAs_2$ in the wavelength range corresponding to $E_g/2 < \hbar\omega < E_g$. We used the nonlinear transmittance technique, employing different types of nano- and picosecond lasers with wavelengths ranging from 0.68 to 2.8 μm, and the dynamic range of laser intensities spanning 6 orders of magnitude. TPA coefficients were found to be $\beta = (6 \pm 1.2) \times 10^{-9}$ cm/W for GaSe (at $\lambda \approx 700$ nm) and $\beta = (2.5 \pm 0.5) \times 10^{-7}$ cm/W for $CdGeAs_2$ (at $\lambda \approx 2.8$ μm).

1. Introduction

GaSe and $CdGeAs_2$ belong to the class of the most promising nonlinear-optical crystals for middle-infrared frequency conversion [1]. For example a III-VI GaSe crystal has a very broad transmission range, 0.62–20 μm, high nonlinear-optical coefficient d_{NL} (see Table 1) and is phase-matchable (due to its extremely high birefringence) for most of three-wave nonlinear-optical processes over its transparency range. These processes include: efficient second harmonic generation, sum- and difference-frequency generation [1] (see also the comprehensive review of Fernelius [2]), and superluminescent optical parametric generation [3].

The chalcopyrite structure of the $CdGeAs_2$ crystal, on the other hand, has a bandgap almost four times smaller, as compared to GaSe, with its transmission window lying predominantly in the mid-IR (2.4–20 μm, Table 1). Its major merit, however, is the highest known nonlinear-optical coefficient for a phase-matchable crystal, with the exception of tellurium. So far $CdGeAs_2$ was used for mid-IR sum- and difference-frequency generation and for second harmonic generation [1]. Recently highly efficient frequency doubling of CO_2 laser radiation [4] and difference frequency generation in the 7–20 μm spectral range [5] in this crystal have been reported. Potentially $CdGeAs_2$ is also a very promising material for optical parametric oscillators/amplifiers pumped at $\lambda > 2.4$ μm [6].

Due to remarkable progress in the crystal growth technology in the last decade it became possible to grow defect-free GaSe and $CdGeAs_2$ crystals of appreciable sizes, and with low absorption, < 0.1–0.2 cm^{-1}, in the middle of their transmission window.

The purpose of the present work is to study two-photon absorption (TPA) in GaSe and $CdGeAs_2$, a phenomenon of fundamental nature, which can set the limit to the performance of nonlinear-optical devices (both TPA and parametric gain are intensity-dependent and give contributions of opposite sign), based on these crystals. The two-photon absorption, corresponding to band-to-band transition, is non-zero when the laser photon energy $\hbar\omega$ is larger than half of the bandgap of the crystal ($\hbar\omega > E_g/2$).

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2. TPA in GaSe

The phenomenon of two-photon absorption in GaSe was first observed by Abdullaev et al. [7,8] via two-photon photoconductivity, luminescence, and superluminescence (Nd laser with $\lambda = 1.06$ μm was used for excitation), although no estimates were made on the TPA absorption coefficient. Baltramiejunas [9,10] found that two-photon Nd laser (1.06 μm) excitation in GaSe may cause dramatic induced absorption (e.g. due to inter-valence-subband absorption by nonequilibrium free carriers generated by TPA of laser radiation) and spectra of this induced absorption were studied. For example it was found that irradiation of GaSe with laser pulses of 6 MW/cm^2 intensity caused induced absorption of 0.75 cm^{-1} near $\lambda = 1$ μm at room temperature. Adduci and co-workers [11] measured TPA in GaSe with the nonlinear transmittance method using a Nd laser (1.06 μm). TPA coefficient was found to be 1.1×10^{-7} cm/W (see Table 1).

For the study of TPA in GaSe we used several types of lasers to match the condition $E_g/2 < \hbar\omega < E_g$ (here the bandgap E_g corresponds to $\lambda_g = 0.62$ μm). The lasers used were: (i) Flashlamp-pumped Alexandrite laser (PAL 101 from Light Age), with $\lambda = 800$ nm, pulse duration of 60 ns, close to TEM$_{00}$-mode beam quality, and repetition rate of 20 Hz; (ii) Raman-shifted (using high-pressure H_2 cell) second harmonic (SH) of a Nd:YAG laser (Spectra Physics – Quanta Ray GCR-230), with $\lambda = 683$ nm, pulse duration of 6 ns, TEM$_{00}$-mode, repetition rate of 20 Hz; (iii) Fourth harmonic (FH) of a mode-locked Er,Cr:YSGG ($\lambda = 2.8$ μm) laser, λ(FH) = 700 nm, pulse duration of 70 ps, TEM$_{00}$-mode, repetition rate of 3 Hz.

The GaSe crystal was cleaved along the (001) plane (the principal c-axis is normal to the surface, ''z-cut''), was $L = 13$ mm long, and had linear absorption $\alpha_0 \approx 0.1$ cm^{-1} at 700–800 nm. The laser radiation was focused onto the crystal using a $f = 10$ cm glass lens and the Z-scan method was employed to measure the crystal's transmission as a function of the peak incoming laser intensity (I_L). The pyro-detector which was used to register the transmitted laser radiation in the Z-scan method had sufficiently large aperture (10 mm) and was sufficiently close to the crystal (so-called open aperture Z-scan) to neglect the effects of nonlinear refraction.

With nanosecond laser pulses (Alexandrite and Raman-shifted SH of Nd:YAG) we did not observe noticeable changes in the transmission (Fig. 1) upto the maximum I_L, set by the GaSe surface damage threshold (10–100 MW/cm^2, see below). With picosecond laser pulses at 700 nm (FH of an Er-laser) we observed a clear (and reversible) decline of the crystal's transmission with increasing intensity, as can be seen in Fig. 1. Again, the limit for the highest achievable laser power density I_L was set by the GaSe crystal's surface damage threshold.

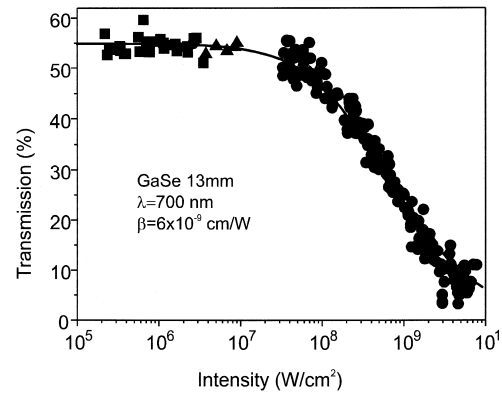

Fig. 1. GaSe transmission versus incident peak laser intensity, obtained using the Z-scan method. Squares – Alexandrite laser ($\lambda = 800$ nm, 60 ns); triangles – Raman-shifted SH of a Nd:YAG laser ($\lambda = 683$ nm, 6 ns); circles – fourth harmonic of an Er, Cr:YSGG laser ($\lambda = 700$ nm, 70 ps). Solid line – TPA theoretical fit.

We found in our experiments that the GaSe surface damage, within the range of laser durations used, depends solely on the fluence (energy density) of laser radiation, and not on its intensity. The damage threshold fluence (for the typical exposure of 100 laser shots) was found ($\lambda =$ 700–800 nm) to be approximately 1 J/cm^2. This corresponds to the damage threshold intensity $I_L = 7$ GW/cm^2 for pulses with 70 ps duration, 82 MW/cm^2 for 6 ns pulses, and, correspondingly, 8 MW/cm^2 for 60 ns pulses.

3. TPA in $CdGeAs_2$

The TPA phenomenon in $CdGeAs_2$ was studied by Guha et al. [12], where the authors utilised 75 ns pulses at $\lambda = 4.6$ μm and have shown that the TPA process is dominantly dependent on the free-carrier concentration, so that improving the linear absorption properties of the material by decreasing the free-carrier concentration reduces the TPA effect. For the best samples, with room temperature carrier concentration of 0.4×10^{16} cm^{-3} and

Table 1

Crystal	E_g (eV)	Transparency range (μm)	d_{NL} (pm/V)	β from literature (cm/W)	β measured (cm/W)
GaSe	2.0	0.62–19	54	1.1×10^{-7} at 1.06 μm [11]	6×10^{-9} at 0.7 μm
$CdGeAs_2$	0.52	2.4–20	247	$(0.7–3.5) \times 10^{-7}$ at 4.6 μm [12]	2.5×10^{-7} at 2.8 μm

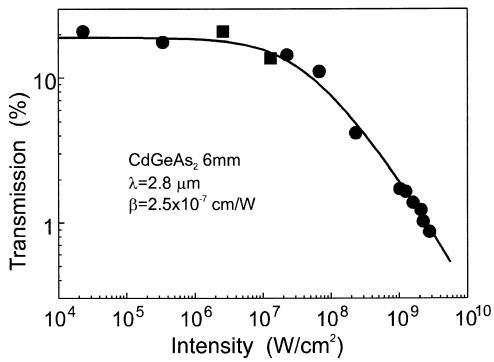

Fig. 2. $CdGeAs_2$ transmission versus peak incident laser intensity at $\lambda = 2.8$ μm, 100 ps in the *Z*-scan method. Solid line – TPA theoretical fit.

a linear absorption of ~ 1 cm^{-1} at 4.6 μm, the TPA coefficient was found to be in the range $(0.7–3.5) \times 10^{-7}$ cm/W.

For the study of TPA in $CdGeAs_2$ (E_g corresponds to $\lambda_g = 2.4$ μm) we have used the fundamental wavelength, $\lambda = 2.8$ μm, of a mode-locked, Q-switched and cavity dumped Er,Cr:YSGG laser [13], emitting single pulses of approximately 100 ps duration in a TEM_{00} mode. The $CdGeAs_2$ crystal (cut at 41° with respect to the principal *c*-axis, no AR-coating), was $L = 5.8$ mm long, and its linear absorption was $\alpha_0 \approx 1.5$ cm^{-1} at 2.8 μm (and ~ 0.2 cm^{-1} at 10 μm). The crystal was kept at room temperature. We have used a $f = 10$ cm BaF_2 lens to focus the laser beam (polarized perpendicular to the crystal's *c*-axis, i.e. ''o-wave'') onto the crystal. Fig. 2 shows the results of the *Z*-scan measurement of the transmission versus intensity dependence. Similar to the GaSe case, a pronounced reversible decrease of the transmission with intensity, due to interband two-photon absorption, can be observed, up to the crystal's surface damage threshold of ~ 2.7 GW/cm^2 for 100 ps $\lambda = 2.8$ μm pulses.

4. Results

To find best fitted TPA coefficients β from our experimental data we modelled the nonlinear transmission behaviour in Figs. 1 and 2 by numerical integrating the differential equation

$$\mathrm{d}I_L = -I_L(\alpha_0 + \beta I_L)\,\mathrm{d}z \qquad (1)$$

over time, *z*-coordinate (along the beam) and transverse *xy*-coordinates. Here α_0 is the low-signal absorption, and β the TPA coefficient. We took into account Fresnel reflection losses and assumed Gaussian distribution of the laser intensity $I_L = I_L(t, x, y, z)$, both in time and in transverse coordinates.

Solid lines in Fig. 1 and Fig. 2 represent the best fitted curves (with a single adjustable parameter β) for both GaSe and $CdGeAs_2$ crystals with TPA coefficients $\beta = (6 \pm 1.2) \times 10^{-9}$ cm/W for GaSe and $\beta = (2.5 \pm 0.5) \times 10^{-7}$ cm/W for $CdGeAs_2$. One can see (Figs. 1 and 2) that in both cases the local dependence (1) accounts very well for the observed nonlinear transmission. A small deviation from the theoretical curve at > 2 GW/cm^2 for GaSe in Fig. 1 is likely to be the result of thermal effects emerging when I_L becomes too close to the surface damage threshold (7 GW/cm^2). We estimate the accuracy of the measurement of TPA coefficients in our experiment to be 20% which is mainly set by uncertainties in the measurements of the laser intensity.

Our experimental TPA coefficient β for GaSe is 18 times smaller than the value of $\beta = 1.1 \times 10^{-7}$ cm/W determined by Adduci et al. [11] for 20 ns pulses at $\lambda = 1.06$ μm. This discrepancy is likely to be the result of poor quality of the samples used in Ref. [11] (so that the role of impurities, free-carrier absorption and surface effects might have played a role); small sample length (2.5 mm), reducing the accuracy of the measurements; and small dynamic range (< 2 orders of magnitude) of the laser intensities. On the other hand, our measured TPA coefficient for GaSe is much closer to those measured for other materials with a similar bandgap, e.g. $\beta = 1.4 \times 10^{-9}$ cm/W at 1.06 μm ($AgGaSe_2$, $E_g = 1.75$ eV) [14] and $\beta = 5.8 \times 10^{-9}$ cm/W at 0.53 μm (ZnSe, $E_g = 2.5$ eV) [15].

As far as $CdGeAs_2$ is concerned, our measured TPA coefficient fits well into the range given in Ref. [12] (see Table 1).

5. Conclusion

We found experimentally TPA coefficients to be $\beta = (6 \pm 1.2) \times 10^{-9}$ cm/W (GaSe) and $\beta = (2.5 \pm 0.5) \times 10^{-7}$ cm/W ($CdGeAs_2$) using nonlinear transmittance measurements in the dynamic range of 6 orders of magnitude of laser intensity.

The practical implication of the results presented in this work is that, although the TPA losses in GaSe would be small ($< 1\%$) for pulsed nanosecond OPO applications, with pump intensities typically ~ 10 MW/cm^2, it may become a serious obstacle when pulsed pico- and femtosecond parametric down-conversion schemes are used, where pump intensities may be larger than 1 GW/cm^2. The result of TPA in this case may not only be absorption at shorter ''pump'' wavelengths, but also induced losses, due absorption by nonequilibrium free carriers generated by TPA, at longer (e.g. signal and idler) wavelengths. As far as $CdGeAs_2$ is concerned, the two-photon effects can be substantial even at $I_L \sim 1$ MW/cm^2 (corresponding to TPA losses of 25% at $L = 1$ cm); thus pump radiation with lower photon energies, $\hbar\omega < E_g/2$ (corresponding to $\lambda > 4.8$ μm), should be employed.

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References

[1] V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikogosyan, Handbook of Nonlinear Optical Crystals, Springer, Berlin, 1997, pp. 166–179.
[2] N.C. Fernelius, Prog. Crystal Growth Character. Materials 28 (1994) 275.
[3] K.L. Vodopyanov, V. Chazapis, Optics Comm. 135 (1997) 98.
[4] P.G. Schunemann, in: Conf. on Lasers and Electro-Optics, Vol. 9, 1996 OSA Technical Digest Series, Optical Society of America, Washington, DC, 1996, p. 230.
[5] K.L. Vodopyanov, P.G. Schunemann, Efficient difference frequency generation of 7–20 μm radiation in $CdGeAs_2$, Optics Lett., in press.
[6] R.L. Byer, H. Kildal, R.S. Feigelson, Appl. Phys. Lett. 19 (1971) 237.
[7] G.B. Abdullaev, M.K. Alieva, B.R. Mirsoev, S.M. Ryvkin, V.M. Salmanov, I.D. Yaroshetskii, Sov. Phys. Semicond. 4 (1971) 1187.
[8] G.B. Abdullaev, M.K. Alieva, B.R. Mirsoev, S.M. Ryvkin, V.M. Salmanov, I.D. Yaroshetskii, Sov. Phys. Semicond. 4 (1971) 1189.
[9] R. Baltramiejunas, Yu. Vaitkus, V.I. Gavryushin, Bull. Acad. Sci. USSR Ser. Phys. 42 (1978) 66.
[10] R. Baltramiejunas, V. Gavryushin, G. Raciukaitis, Solid State Comm. 80 (1991) 303.
[11] F. Adduci, I.M. Catalano, A. Cingolani, A. Minafra, Phys. Rev. B 15 (1977) 926.
[12] S. Guha, M.C. Ohmer, P.J. Hood, P.G. Schunemann, in: Conf. on Lasers and Electro-Optics, Vol. 11, 1997 OSA Technical Digest Series, Optical Society of America, Washington, DC, 1997, p. 486.
[13] K.L. Vodopyanov, J. Opt. Soc. Am. B 10 (1993) 1723.
[14] A. Miller, G.S. Ash, Optics Comm. 33 (1980) 297.
[15] A.A. Said, M. Sheik-Bahae, D.J. Hagan, T.H. Wei, J. Wang, J. Young, E.W. Van Stryland, J. Opt. Soc. Am. B 9 (1992) 405.