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Two-photon absorption in arsenic sulfide glasses

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Abstract. **The two-photon absorption coefficient of 1047-nm light in $As_{35}S_{65}$ chalcogenide glass has been measured. CW probe radiation has been used to observe the linear absorption in glass induced by two-photon excitation. The induced absorption lifetime was found to be ~2 ms.**

Keywords: *two-photon absorption, chalcogenide glass.*

1. Introduction

Nonlinear optical phenomena occurring in crystals and glasses, in particular, two-photon absorption [1], continue to be of interest for researchers. Many efforts are aimed at studying the nonlinear optical properties of glasses containing chalcogens (S, Se, and Te). Chalcogenide glasses, which have transparency windows in the wavelength range of 0.7–20 μm (depending on the glass composition), are the most appropriate materials for nonlinear optics devices operating in the mid-IR spectral range [2]. The progress in the fabrication technology of semiconductor chalcogenide crystals and glasses with low optical loss led to the development of high-quality optical fibers for near- and mid-IR ranges [3, 4]. Chalcogenide glasses of the As–S, As–Se, As–S–Se, As–Se–Te, and Ge–As–Se–Te systems are most popular in fiber optics.

Chalcogenide glasses differ from the glasses of other types by high third-order nonlinearity. The nonlinear refractive index, absorption coefficient, and Raman scattering gain of chalcogenide glasses in the near-IR range exceed the corresponding parameters of quartz glass by two to three orders of magnitude [2].

There are data in the literature on studying the stimulated Raman scattering (SRS) and measuring the Kerr refractive index in chalcogenide glasses near the fundamental absorption edge (see review [2] and references therein). At the same time, we believe that the nonlinear process of two-photon absorption (TPA), which leads to a significant transformation of laser radiation and limitation of its power, has not been comprehensively studied. In particular, measurements of the two-photon absorption coefficient at different wavelengths have not been performed.

In this paper, we report the results of experimental determination of the two-photon absorption coefficient β in $As_{35}S_{65}$ glass. The TPA coefficients in glasses of the As–S system were measured in [5–10]. Previously we proposed an express method for studying and analysing the dynamics of interband TPA in crystals upon their excitation by a train of picosecond laser pulses with a gradually changing intensity [11, 12]. A passively mode-locked Q-switched Nd:YLF laser with a radiation wavelength $\lambda = 1047$ nm was used as an excitation source.

2. Measurement of the two-photon absorption coefficient

Figure 1 shows the transmission spectrum of one of the $As_{35}S_{65}$ glass samples in the wavelength range of 500–1200 nm. The short-wavelength limit of the glass transparency window is near the wavelength $\lambda_g \approx 580$ nm. The TPA coefficient was measured at $\lambda = 1047$ nm, assuming that the necessary condition for the interband two-photon absorption ($2h\nu > E_g$) is satisfied at this wavelength.

In the case of two-photon absorption, the change in light intensity I along the propagation axis z is determined by the equation

$$\frac{dI}{dz} = -\alpha I - \beta I^2, \tag{1}$$

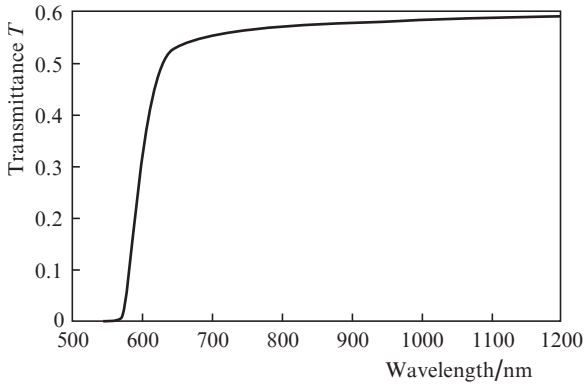

Figure 1. Transmission spectrum of $As_{35}S_{65}$ glass, measured with a Carry 5000 spectrometer.

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where α is the linear absorption coefficient and β is the TPA coefficient (see [10]). The solution to this equation is given by the formula

$$I(z) = \frac{I_0 \exp(-\alpha z)}{1 + (\beta/\alpha) I_0 [1 - \exp(-\alpha z)]}, \quad (2)$$

where I_0 is the light intensity at $z = 0$. Then the reduction of the light intensity transmitted through a medium of length L is given by the expression

$$\frac{I_0}{I} = e^{\alpha L} + \beta \frac{e^{\alpha L} - 1}{\alpha} I_0. \quad (3)$$

In the case of two-photon absorption, the attenuation of light intensity linearly increases with increasing input intensity I_0. The plot of this dependence is a straight line with a slope $b = \alpha^{-1}\beta(e^{\alpha L} - 1)$. Measuring this slope, one can find coefficient β.

To obtain the dependence of attenuation I_0/I on incident light intensity I_0, we used picosecond pulses of a passively mode-locked Q-switched Nd:$YLiF_4$ laser with a working wavelength $\lambda = 1047$ nm [11, 12]. The laser generated trains (total duration ~100 ns) of picosecond pulses with a gradually changing amplitude (Fig. 2). Laser pulse duration τ at half maximum was 25 ps. The light beam was focused into a glass sample using a lens with a focal length $f = 40$ cm. The laser beam power distribution was close to Gaussian, and the spot radius in the lens focus was measured to be $w_0 = 77$ μm (at the I_{max}/e level). The waist length in the Gaussian beam was [12] $l_G = 4\pi w_0^2/\lambda = 7.0$ cm. Since the length of the $As_{35}S_{65}$ glass sample under study ($L = 1.0$ cm) is much shorter than the waist length, the laser beam cross section can be considered constant along the sample length.

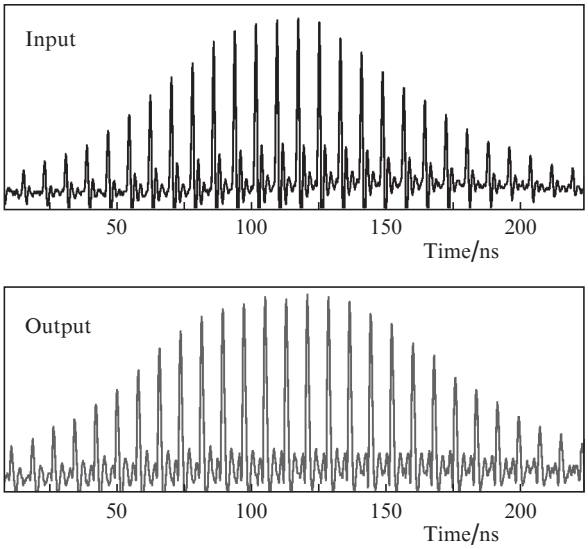

Figure 2. Oscillograms of trains of laser excitation pulses with $\lambda = 1047$ nm at the input (I_0) and output (I) of an $As_{35}S_{65}$ glass sample of length $L = 1.0$ cm.

The oscillograms of radiation at the input and output of the glass sample were recorded during one laser shot in real time (see Fig. 2). The amplitudes of pulses in a train were measured using LFD-2 avalanche Ge photodiodes and Tektronix DPO-4104 digital oscilloscope with a gain band of 1 GHz. The photodiodes were calibrated with respect to energy of the light incident on the sample and transmitted through it; thus, the energies at the input and output of the sample (E_{in} and E_{out}, respectively) were known for each picosecond pulse. The radiation energy was measured by a Molektron J3-05 pyroelectric joulemeter. The absorption nonlinearity can clearly be seen in the oscillogram: the more intense pulses are attenuated more strongly than the less intense ones (Fig. 3).

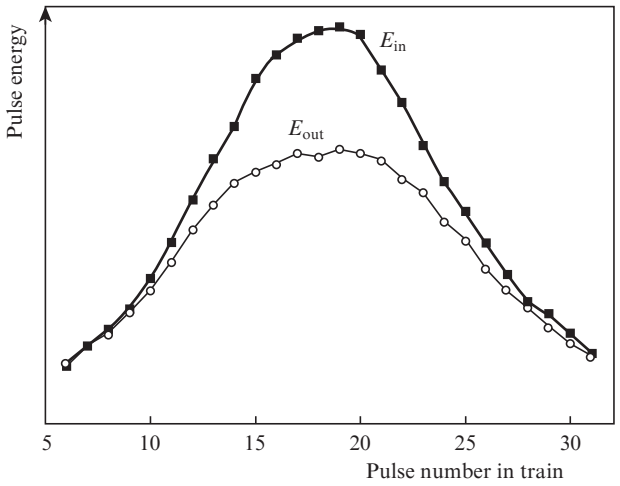

Figure 3. Transformation of the shape of laser pulse trains as a result of nonlinear two-photon absorption.

In the case of pulsed radiation, expression (3) is transformed into the formula for the pulse energy attenuation [13, 14]. For a pulse with a Gaussian temporal profile, the dependence of the attenuation on the energy at the sample input is given by the formula

$$\frac{E_{in}}{E_{out}} \approx \frac{e^{\alpha L}}{T_{in} T_{out}} + \frac{1}{\sqrt{2}} \frac{2}{\sqrt{\pi}} \sqrt{\ln 2} \frac{\beta}{S_{eff}\tau} \frac{1}{T_{out}} \frac{e^{\alpha L} - 1}{\alpha} E_{in}, \quad (4)$$

where T_{in} and T_{out} are the transmittances of the air–glass interfaces at the input and output of the sample, respectively, and $S_{eff} = 2\pi w_0^2$ is the effective cross-sectional area of the beam.

Transmittances T_{in} and T_{out} are calculated from the Fresnel formula: $T_{in} = T_{out} = 4n/(n+1)^2$, where n is the refractive index of the glass. The high refractive index of the glass ($n \approx 2.4$ [15]) is responsible for the high Fresnel reflectivity; $T_{in} = T_{out} = 83\%$, and the linear transmittance of the samples is $T_{lin} = T_{in} T_{out} = 69\%$.

Figure 4 shows the measured dependence of the attenuation of the light energy transmitted through a sample with a length $L = 1$ cm on the incident pulse energy. Since the laser emits a train of picosecond pulses with a gradually changing intensity, this dependence is measured in a single laser shot. Two sets of references correspond to an increase and decrease in intensity within the pulse train. While energy E_{in} increases, the light attenuation is more pronounced due to the enhancement of the two-photon absorption. The slope of this dependence in our experiments was found to be $b \approx 0.09–0.11$ μJ^{-1}.

The calculation formula for the two-photon absorption coefficient,

$$\beta = \sqrt{2} \frac{\sqrt{\pi}}{2} \frac{\tau}{\sqrt{\ln 2}} S_{eff} \frac{\alpha}{e^{\alpha L} - 1} T_{out} b \quad (5)$$

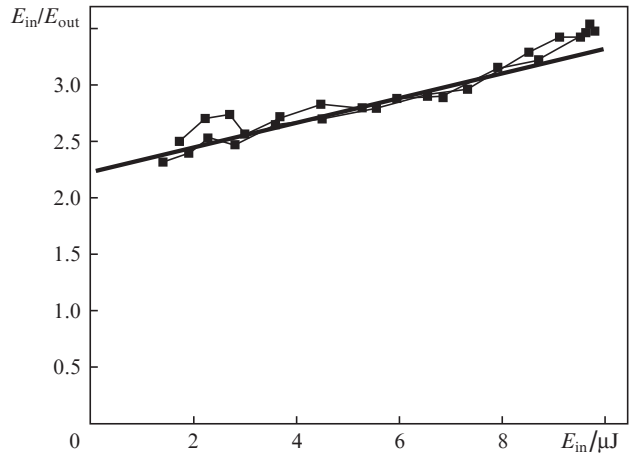

Figure 4. Dependence of the attenuation of the light energy transmitted through a sample on the incident pulse energy.

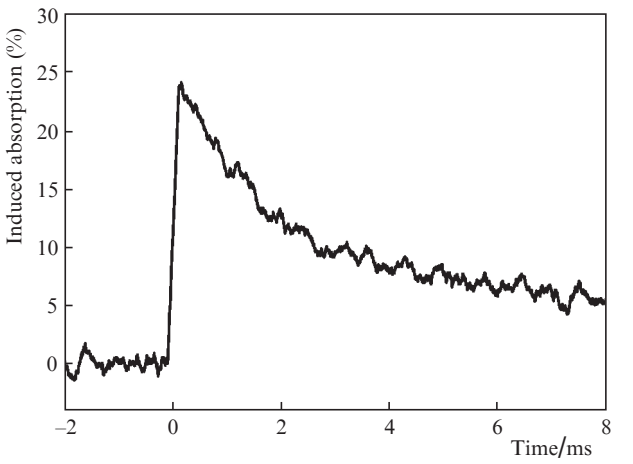

Figure 5. Room-temperature rise and relaxation kinetics of the induced absorption in an $As_{35}S_{65}$ glass sample of length $L = 2$ mm, measured at $\lambda = 632.8$ nm upon picosecond laser excitation at a wavelength of 1047 nm.

yields $\beta = 0.83-1.0$ cm GW^{-1}. An excitation pulse with a duration $\tau = 25$ ps and energy $E_{in} = 10$ μJ corresponds to peak power $P = E/\tau = 0.4$ MW and power density at the centre of focal spot $I_{max} = P/\pi w_0^2 = 2.2$ GW cm^{-2}. At this intensity, nonlinear additive βI to the linear absorption coefficient $\alpha = 0.40$ cm^{-1} is approximately 1.8 cm^{-1}.

3. Kinetics of the generation and relaxation of electronic excitations at two-photon interband absorption in $As_{35}S_{65}$ glass

The two-photon absorption of light in solids leads to the excitation of electronic states in the conduction band. It was experimentally shown in [11, 12, 16, 17] that the occupation of conduction-band states upon two-photon excitation of a medium by high-power laser pulses is accompanied by induced absorption from excited states. A method for investigating the kinetics of the rise and subsequent relaxation of induced absorption, based on the use of cw probe radiation, was proposed in the aforementioned studies. We also used this technique (applying a cw probe beam) to measure the relaxation kinetics of optical excitations in $As_{35}S_{65}$ glass.

To this end, along with the intense picosecond radiation, collinear probe cw He–Ne laser radiation with $\lambda = 632.8$ nm was introduced into a 2-cm-long glass sample using a beam-splitting plate. The probe beam transmitted through the glass sample was directed to a photoelectron multiplier FEU-76 and then analysed using an oscilloscope. The time resolution of this detection scheme (~12 ns) was determined by the photoelectron multiplier characteristic.

Figure 5 shows the room-temperature induced-absorption kinetics, measured at $\lambda = 632.8$ nm upon picosecond laser excitation ($\lambda = 1047$ nm) in an $As_{35}S_{65}$ glass sample. The plot exhibits a stage of induced absorption rise with a duration of about 150 ns, which is followed by a relaxation stage. The width of the induced-absorption leading edge (~150 ns) is determined by the duration of the excitation-pulse train. The shape of the absorption relaxation kinetics is similar to that of a single-exponential dependence with a time constant of about 2 ms.

The transmittance of a 2-mm-long glass sample decreases by about 20% upon induced-absorption excitation. In this case, the linear induced-absorption coefficient $\alpha_{ind} \approx 1.1$ cm^{-1}. With the nonlinear absorption coefficient known ($\beta = 0.83$ cm GW^{-1}), one can estimate the energy absorbed by a unit volume of the medium in a single picosecond pulse of high-power excitation radiation:

$$W = \beta I^2 \tau. \tag{6}$$

The maximum excitation-pulse energy in our experiments was 10 μJ, a value corresponding to a peak power density of 2.2 GW cm^{-2}. Then, the energy absorbed in a unit volume of the medium is $W \approx 0.1$ J cm^{-3}. The number of excitations per unit volume can be found from the relation

$$N = \frac{1}{2}\frac{W}{h\nu}, \tag{7}$$

where $h\nu = 2\times10^{-19}$ J is the photon energy at the excitation wavelength. For the W value obtained in this study, the number of excitations per unit volume is $N \approx 0.25\times10^{18}$ cm^{-3}. In this case, one can estimate the transition cross section at the probe cw radiation wavelength: $\sigma = \alpha_{ind}/N = 0.44\times10^{-17}$ cm^2 (a value of $\sigma = 10^{-16}$ cm^2 was obtained in [16] upon TPA excitation in As_2S_3 glass at $\lambda = 610$ nm).

Thus, we measured the two-photon-absorption parameters in chalcogenide glass $As_{35}S_{65}$, the TPA coefficient and induced-absorption relaxation time, upon picosecond excitation of electron levels in the conduction band of glass.

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