Two-photon absorption of an intense femtosecond pulse in glasses doped with microscopic semiconductor crystals at a photon energy greater than the band gap

I. V. Bezel', Yu. A. Matveets, A. G. Stepanov, S. V. Chekalin, and A. P. Yartsev

Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia

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The nonlinear transmission of glasses doped with semiconductor crystallites has been measured over a broad intensity range (4×10^8–3×10^{12} W/cm^2) with the help of femtosecond laser pulses. In the interval 10^{11}–10^{12} W/cm^2 the absorption by the samples is due primarily to a two-photon absorption of the semiconductors. The coefficients of this two-photon absorption, β, have been found for RG-4 and RG-8 glasses: $(3.8\pm1.9)\times10^{-10}$ and $(5.3\pm2.7)\times10^{-10}$ cm/W.

Glasses doped with semiconductor crystallites have been the subject of applied and fundamental research for a long time. Of particular interest are the nonlinear optical characteristics of these materials, because of (for example) the promising outlook for the use of these glasses as fast, efficient optical switches. The nonlinear properties of a material, which are associated with the fastest electronic response, can be studied by measuring the two-photon absorption of laser light. In order to eliminate the intense linear absorption, it is customary to use laser light with a photon energy smaller than the width of the band gap. It thus becomes possible to measure the two-photon absorption coefficient in fairly thick samples by means of laser pulses in the nano- and picosecond ranges. The two-photon absorption of light with a photon energy greater than the width of the band gap (i.e., in the region of intense linear absorption) can be studied only at fairly high intensities, at which the probabilities for one- and two-photon absorption become comparable. Here one must deal with the danger of damage to the samples by the laser pulse. Damage can be avoided by shortening the pulse. Femtosecond laser pulses are thus preferable for studying two-photon absorption in the region of intense linear absorption of the semiconductors.

In this letter we are reporting a study of the transmission of test samples of glasses doped with semiconductor crystallites which differ in the width of the band gap (RG-4 and RG-8 glasses, from Jenaer Glaswerke GmbH). The transmission was studied as a function of the intensity of femtosecond laser pulses at the entrance to the sample. The semiconductor crystallites in the samples constitute "ternary solid solutions," in which the difference in the width of the band gap stems from a difference in the concentrations of the semiconductors (of a common type) which make up the solution.[1] Figure 1 shows spectra of the linear transmission of the RG-4 and RG-8 samples used in these experiments. The thicknesses of these samples were 0.014 and 0.013 cm, respectively. The absorption near 2 eV (the energy of the exciting photon) is due to interband

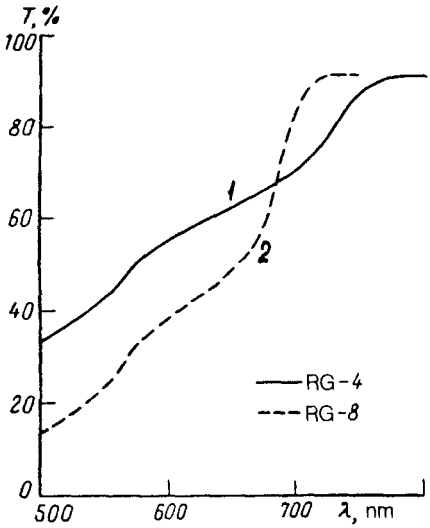

FIG. 1. Transmission spectra of crystals doped with semiconductor crystallites in the visible region. 1—RG-4; 2—RG-8.

transitions in the semiconductor. The reason for the more rapid increase in the absorption in the RG-8, for samples of essentially equal thickness, is apparently a greater volume fraction of the semiconductor in this sample. The absorption edge of the RG-8 sample is at a longer wavelength than in RG-4, because of the difference in the width of the band gaps of these semiconductors. Since these crystallites are fairly large, the spectra have no features stemming from a quantum size effect.[1] The transmission of the samples at the excitation wavelength (610 nm) is 41% for the RG-8 and 57% for the RG-4. The energy of the exciting photon is greater than the width of the band gap by 0.2 and 0.3 eV, respectively. The relatively weak absorption leads to a fairly uniform distribution of the intensity of the laser light in the sample along the propagation direction of the exciting pulse.

The test sample was illuminated by pulses from a femtosecond-range dye ring laser after an amplification to 20–40 μJ in a four-stage amplifier with pumping by a Xe–Cl laser.[2] The output pulses, with a wavelength of 610 nm, a length of 300 fs, and a repetition frequency of 3–5 Hz, were focused onto the sample in a spot with a half-width of 50 μm. The energy incident on the sample could be reduced with calibrated neutral filters. In the experiments we measured the energy incident on the sample and the energy transmitted through it. We calculated their ratio, i.e., the reciprocal transmission $1/T$, as a function of the peak intensity of the light incident on the sample, I_0. For this purpose we used two photodiodes, whose output signals were digitized by S9-8 digital storage oscilloscopes, and then entered into a computer memory. To improve the signal-to-noise ratio, we sampled the energy; the resulting values turned out to lie within $\pm 10\%$ of the average value. Each experimental point in Figs. 2 and 3 is an average of data obtained in 100 laser shots. Measurements of the optical density of the sample during this series of experiments made it possible to detect irreversible changes which occurred. In determining I_0 we assumed that the spatial

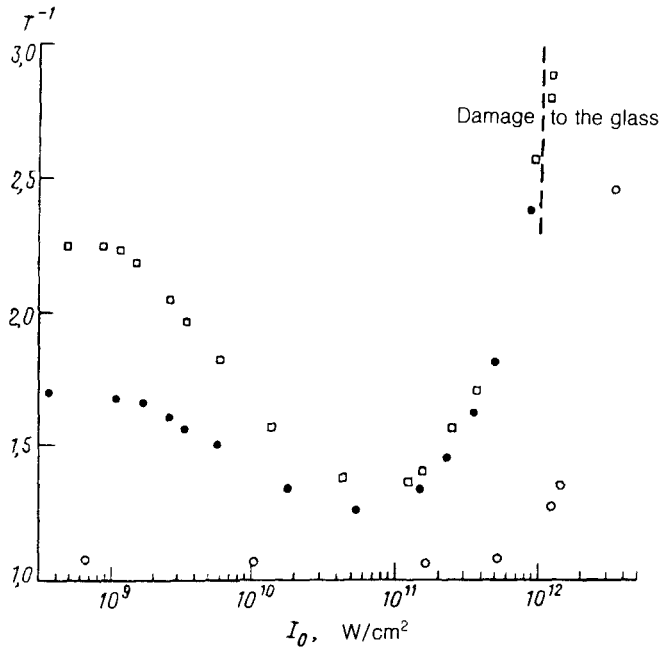

FIG. 2. Reciprocal transmission of the test samples versus I_0. ●—RG-4; □—RG-8; ○—K-8 glass (the I_0 scale is logarithmic).

distribution of the light was approximately Gaussian and that the temporal shape could be described by the square of a hyperbolic secant.

Figure 2 shows that the transmission of the samples is not a monotonic function of I_0. As I_0 increases from 10^9 to 5×10^{10} W/cm^2, the transmission of the sample increases (this is the familiar bleaching). A further increase in the intensity from 10^{11} to 10^{12} W/cm^2 reduces the transmission. Pulses with I_0 above 10^{12} W/cm^2 cause irreversible changes in the samples. At lower intensities, no irreversible or accumulating changes are observed.

The increase in the transmission at $I_0=10^9$–5×10^{10} W/cm^2 results from a filling of states at the excitation level in the semiconductor. The absorption which arises at higher values of I_0 leads to an approximately linear dependence of $1/T$ on I_0 (Fig. 3). The reason may be either two-photon or two-step absorption. In the latter case, there might be a one-photon interband absorption in the first step, while the second step might be (for example) an absorption by photoexcited carriers and traps (defects or impurities), at which part of the energy of the excited carriers relaxes even during the pulse.[3] A saturation of one of the steps would have the result that the resultant absorption would be determined primarily by the linear absorption of the unsaturated step. It can be seen from Fig. 2 that the interband absorption in both glass samples reaches saturation at intensities $\leqslant10^{11}$ W/cm^2. Consequently, the two-step absorption

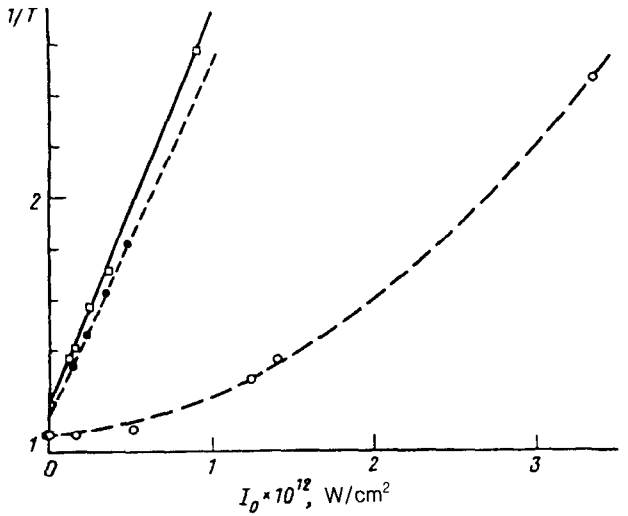

FIG. 3. Reciprocal transmission of the samples versus I_0 (the I_0 scale is linear). The notation is the same as in Fig. 2. Shown as guidelines are linear plots for a glass doped with semiconductor crystallites and a quadratic plot for K-8 glass.

does not have any substantial effect on the absorption increase observed at $I_0 = 10^{11}$–10^{12} W/cm^2.

The absorption increase at high intensities is again unrelated to matrix effects. A study of the nonlinear transmission of a plate of K-8 glass showed that, as I_0 is varied from 10^9 to 5×10^{11} W/cm^2, the transmission of this plate is determined (at the experimental accuracy) by Fresnel reflection. A significant decrease in transmission is observed only at $I_0 \geqslant 10^{12}$ W/cm^2 (Fig. 2). In addition, the absorption coefficient of the matrix is not described by a linear function of I_0; the functional dependence is more complicated: $\kappa \simeq I_0^k$, $k > 2$ (Fig. 3).

In the intensity range $I_0 = 10^{11}$–10^{12} W/cm^2 the nonlinear absorption coefficient κ can be written

$$\kappa = \alpha + BI, \tag{1}$$

where β is the two-photon absorption coefficient, and the coefficient α reflects the presence of an absorption which does not vary in this intensity interval (more on this below). The ratio of the peak intensities of the incident light and of the light transmitted through the sample is then[4]

$$I_0/I = (i-R)^{-2} e^{\alpha l} + \beta (e^{\alpha l} - 1) I_0 / \alpha (i-R), \tag{2}$$

where l is the thickness of the sample, and R is its reflection coefficient. A numerical approximation of the experimental results on $1/T$ by expression (2), with allowance for the temporal shape and spatial distribution of the intensity of the incident pulse, yields the following values for the coefficient β (in units of cm/W):

$(3.8\pm1.9)\times10^{-10}$ for the RG-4 glass and $(5.3\pm2.7)\times10^{-10}$ for the RG-8 glass. An extrapolation of these values with allowance for the volume fraction of the semiconductor in the glass yields the values $\beta=(3.8\pm1.9)\times10^{-7}$ and $\beta=(1.8\pm0.9)\times10^{-7}$ cm/W, respectively, for the bulk semiconductors. The error in the determination of β is due primarily to the error in the I_0 measurements. In the numerical approximation, the smallest standard deviation from the experimental results was achieved with $0 \leqslant \alpha \leqslant 2$ cm^{-1} for the RG-4 and with $0 \leqslant \alpha \leqslant 3$ cm^{-1} for the RG-8. These values of α agree well with the absorption cross sections of free carriers in glasses doped with semiconductor crystallites.[5,6]

It can thus be concluded that two-photon absorption in semiconductors is the primary mechanism for the absorption of glass doped with semiconductor crystallites when excited in the interband-absorption region by pulses with intensities of 10^{11}–10^{12} W/cm^2.

The difference between the values of β, extrapolated to the bulk semiconductors, for the two glasses can be interpreted as a spectral dependence of the two-photon absorption, according to Ref. 1. The density of states in the bands corresponding to two-photon absorption with quasimomentum conservation is higher in the RG-4 (the band gap is narrower). Comparison of (on the one hand) the values which we found for β with (on the other) the values 2×10^{-8} cm/W measured for corresponding bulk semiconductors at a photon energy smaller than the width of the band gap[7–9] demonstrates that in the case of two-photon excitation the absorption increases near the band edge. In addition, we may be seeing here an increase in the probability for a two-photon transition in a situation in which there is an intermediate resonance for one photon.

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