Time-resolved non-linear optical response and photo-induced carriers trapping in glassy semiconductors

E Romanova¹, A Afanasiev², A Velmuzhov³, M Sukhanov³, Yu Kuzyutkina¹, A Nezdanov⁴, V Shiryaev⁵
¹ Saratov State University, 410012 Saratov, Russia
² Institute of Applied Physics of RAS, 603950 Nizhny Novgorod, Russia
³ Institute of Chemistry of High Purity Substances of RAS, 603600 Nizhny Novgorod, Russia
⁴ Lobachevsky State University of Nizhny Novgorod, 603950 Nizhny Novgorod, Russia
romanova@optics.sgu.ru

Abstract. Two realisations of the pump-probe method have been used to study the time-resolved non-linear optical response of glassy chalcogenides at frequencies near their single-photon and two-photon bandgaps. Photo-excitation of gap states has been revealed as a determining effect for structural, electronic, thermal and optical changes in a glass sample.

1. Introduction
Non-crystalline semiconductors have energy levels in their bandgaps (gap states) because of their lattice disorder. The gap states can be populated by sub-gap illumination or due to self-trapping of photo-excited carriers. The photo-induced carriers trapping at the gap states contribute to the non-linear optical response of a non-crystalline semiconductor illuminated by high-intensity femtosecond (fs) laser pulses.

Chalcogenide glassy semiconductors always contain one or more of the chalcogen elements: S, Se or Te. These inorganic glasses are transparent in the mid-infrared (IR). When illuminated by sub-gap light, chalcogenide glasses exhibit large photosensitivity. Photostuctural changes and the related photodarkening are phenomena unique to glassy chalcogenides and are not observed in amorphous group IV and V semiconductors (a-Si, a-As etc.), or in crystalline chalcogenides [1]. Changes of structural and optical properties induced by a sub-gap CW illumination in glassy chalcogenides were studied for applications such as optical memories and laser writing [1], but the mechanisms behind the glass-radiation interaction have not been fully understood. When using fs pulsed lasers, this interaction becomes highly non-linear allowing for creation of 3D structures [2].

In [3,4], we have presented the results of measurements of the non-linear optical response of chalcogenide glasses of the system As₄₀SₓSe₆₀₋ₓ with fs resolution in time. These experiments have revealed that structural, electronic, thermal and optical changes in a glass sample illuminated at a frequency in the range of its Urbach tail were determined by photo-induced single-photon excitations of the gap states. For microscopic mechanism underlying this type of charge carriers kinetics, the mechanism of valence-alternation pairs [5] with structural changes, which take place within a localized volume comparable with molecular bonds length has been proposed. In this work, we extend this research to analysis of the non-linear optical response near the two-photon bandgap frequencies of glass samples of the systems As₄₀SₓSe₆₀₋ₓ and As₄₀SeₓTe₆₀₋ₓ exposed to fs laser pulses at λ = 1570 nm.
2. Experimental methods

In the time-resolved interferometric pump-probe method [6], a phase shift $\Delta \varphi$ induced due to cross-modulation of a probe pulse by a pump pulse in a glass sample is recorded at each transverse coordinate for each time delay $\Delta t$ between the pump and probe pulses, both at $\lambda = 790$ nm. In our experiment [3], the pump pulse with energy $E$ ranging from 300 nJ to 15 $\mu$J was focused onto a glass sample that was moved transversally after each shot to avoid cumulative effects. As sign and magnitude of $\Delta \varphi$ were proportional to the pump pulse induced variation of the real part of refractive index, the time-resolved photo-refractivity and photo-conductivity were directly investigated.

In the spectrally resolved two-beam coupling technique [7], variation of a probe pulse spectrum due to cross-modulation of the probe pulse by a pump pulse in a glass sample is recorded. A spectral component power $T$ is detected at different $\Delta t$ with some offset with respect to pump pulse peak frequency. By using an approximation of $T$ dependence on $\Delta t$, non-linear refractive index $n_2$ and two-photon absorption coefficient $\beta_2$ are evaluated. In our experimental setup [8], a 100-fs fiber laser with repetition rate of 28 MHz operating near $\lambda = 1570$ nm has been used. Magnitude of $\Delta t$ was varying by a delay line with the total operating range of up to 30 ps. The pump and probe beams were focused onto a glass sample. Estimated peak intensity $I_1$ of the pump pulse was around $10^8$ W/cm$^2$.

3. Non-linear optical response dynamics

For analysis of the gap states contribution in the nonlinear optical response, several chalcogenide glass compositions of the systems As$_{40}$S$_x$Se$_{60-x}$ and As$_{40}$Se$_x$Te$_{60-x}$ were used in the measurements, so that the bandgap energy $E_g$ varied in the range of 1.8-2.4 eV (As$_{40}$S$_x$Se$_{60-x}$) and of 1.1-1.4 eV (As$_{40}$Se$_x$Te$_{60-x}$).

Glass samples were fabricated from synthesized glass rods, shaped as disks of ~1 mm thickness, polished to a 0.25 $\mu$m finish, hot pressed under vacuum, annealed and allowed to cool with the press. $E_g$ of each sample was evaluated by its absorption spectrum processing. Magnitudes of $n_2$ have been evaluated as described in [3,8], plotted as functions of $h\nu/E_g$ ($h\nu$ is a photon energy) and compared with the spectral function $G_s(h\nu/E_g)$ of $n_2$ (shown by solid line in figure 1) known from the theory of non-linear optical response of direct-gap crystalline semiconductors [9]. With the samples of the system As$_{40}$S$_x$Se$_{60-x}$ illuminated at $\lambda = 790$ nm (triangles), we have considered the spectral range of their Urbach tails ($0.7 < h\nu/E_g < 0.8$) [3]. With the same samples and with the samples of the system As$_{40}$Se$_x$Te$_{60-x}$, all pumped at $\lambda = 1570$ nm, our research has been extended to the range of frequencies near their two-photon bandgaps ($0.4 < h\nu/E_g < 0.6$).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Non-linear refractive index $n_2$ measured at $\lambda = 790$ nm (triangles) and at $\lambda = 1570$ nm (squares).

In figure 2, variation $\Delta T$ of the probe pulse transmittance measured near $\lambda = 1570$ nm at different $\Delta t$ is shown for the glass samples of the compositions: As$_{30}$S$_x$Se$_{70-x}$, with $x=10, 30$ (red squares in figure 1) and As$_{30}$Se$_x$Te$_{70-x}$, with $x=42, 50, 55$ (blue squares in figure 1). The fast non-linear optical responses of the samples As$_{30}$S$_x$Se$_{70}$ ($h\nu/E_g = 0.4$) and As$_{30}$Se$_x$Te$_{18}$ ($h\nu/E_g = 0.6$) shown in figure 2a,c by symbols develop similarly to the response of fused silica observed in [7] where it was described by a theoretical
model. We have used these analytical results to fit the data (solid lines) and evaluate \( n_e \). Similar response is observed in the samples of the systems \( \text{As}_{40}\text{S}_{50}\text{Se}_{10-x} \) with \( x > 30 \) and \( \text{As}_{40}\text{Se}_{55}\text{Te}_{5} \) with \( x < 42 \). Other samples in figure 2 demonstrate non-linear response of a different character. Instead of a fast decrease, a slow decrease of \( \Delta T \) at \( \Delta t > 0 \) is observed (figure 2 b,d). In spite of a noisy character of the data that is typical in measurements of the non-linear optical response, it is obvious that the maximum and decay time of \( \Delta T \) are greater in the samples with \( h\nu/E_g \) closer to 0.5 that is the two-photon bandgap, where direct two-photon transitions of electrons to the gap states are possible.

![Figure 2](https://example.com/image2.png)

**Figure 2.** Variation of the probe pulse transmittance measured at different delays of the probe pulse with respect to the pump pulse in the chalcogenide glass samples pumped at \( \lambda = 1570 \text{ nm} \).

In the samples of the system \( \text{As}_{40}\text{S}_{50}\text{Se}_{1-x} \) pumped at \( \lambda = 790 \text{ nm} \) (triangles in figure 1) in the range of their Urbach tails (samples with \( x \leq 30 \)), direct single-photon transitions to the gap states govern the kinetics [4]. The non-linear optical response develops together with the carriers trapping, and two-photon absorption is going on through two-step transitions of carriers to the conduction band. After some time, the conduction electrons can be trapped again at the gap states. This is a common way of trapping that happens in all samples under consideration. Due to the linear character of two-step transitions through the gap states, in this case there is no a threshold intensity \( F^0 \) for modification of a dielectric function upon the pump pulse illumination. If the photo-excitation develops as two-photon absorption, modification of a dielectric function is not observed if the pump intensity \( < F^0 \).

4. **Charge carriers kinetics**

In accordance with the Drude-Lorentz model, the following electronic populations induced in a sample by a pump pulse impact into the dielectric function variation: density of conduction electrons \( (n_e) \) and density of electrons \( (n_h) \) trapped in the bandgap. As was shown in [4], for the carriers excited to the gap states by single-photon transitions (like in \( \text{As}_{40}\text{S}_{50}\text{Se}_{1-x} \) samples with \( x < 30 \) pumped at \( \lambda = 790 \text{ nm} \)), these populations evolve as described by the system of equations:

\[
\begin{align*}
\frac{\partial n_e(t,z)}{\partial t} &= \sigma_s I_1(t,z) + \sigma_e n_e(t,z) I_1(t,z) - n_e(t,z) / \tau_e, \\
\frac{\partial n_h(t,z)}{\partial t} &= \sigma_s I_1(t,z) - \sigma_e n_e(t,z) I_1(t,z) + n_e(t,z) / \tau_e.
\end{align*}
\]

Here rate of increase of the trapped electrons density \( \sim I_1 \), \( \sigma_s = \beta/(2h\nu)/N_c, \sigma_e = \omega_0/(h\nu) \), \( \sigma_e = \sigma_s/(h\nu) \), \( \sigma_s \) is the cross-section of the single-photon absorption of trapped electrons, \( n_e \) and \( n_h \) are normalised to the critical plasma density \( N_c = \omega_0^2 \text{cm}^2/\text{e}^2 \), \( \omega_0 \) is the single-photon absorption coefficient; \( \tau_e \) is the time of conduction electrons trapping. If the gap states are populated by self-trapping of holes followed by
trapping of conduction electrons at the gap states (like in As$_{40}$S$_{60}$Se$_{40}$ samples with $x \geq 30$ pumped at $\lambda = 790$ nm), the system of kinetic equations can be written as [4]:

\[
\begin{align*}
\frac{\partial n_0(t, z)}{\partial t} &= \sigma_c I_1^2(t, z) - n_0(t, z) / \tau_h \\
\frac{\partial n_h(t, z)}{\partial t} &= n_h(t, z) / \tau_h \\
\frac{\partial n_e(t, z)}{\partial t} &= \sigma_c I_1^2(t, z) - \sigma_e n_e(t, z)(n_h(t, z) - n_e(t, z)) \\
\frac{\partial n_e(t, z)}{\partial t} &= \sigma_e n_e(t, z)(n_h(t, z) - n_e(t, z))
\end{align*}
\]

(2)

Here $n_h$ and $n_{th}$ are normalized densities of free and trapped holes, $\tau_h$ is the hole self-trapping time, $\sigma_c = \sigma_{cap} \cdot v \cdot N_e$, $\sigma_{cap}$ is the cross section of a hole trapping, $v$ is the average velocity of conduction electrons.

These kinetics were used to fit experimental data in [3,4] and find out magnitudes of basic parameters in (1) and (2). In figure 3a, the phase shift measured by using the interferometric pump-probe method [6] is shown by symbols in comparison with the results of the non-linear optical response modeling (solid blue curve) in the glass sample of As$_{40}$S$_{60}$Se$_{40}$ composition with charge carriers kinetics as described by (1). The modeling method has been described in details in [4]. The following magnitudes of parameters in (1) have been obtained: $\sigma_I = 0$, $\sigma_I = 6.65 \times 10^{-18}$ cm$^3$J$^{-1}$, $\sigma_h = 10^{-12}$ cm$^2$ J$^{-1}$, $\tau_e = 0.8$ ps. The calculated magnitudes of $n_e$ and $n_{te}$ at the front surface of the sample vary with time as shown by black lines so that at first the gap states are populated due to the single-photon absorption. The conduction electrons density grows due to single-photon exciton absorption rather than due to two-photon absorption as $\sigma_I$ is found to be close to zero.

With the same magnitudes of $\sigma_I$ and $\tau_e$, $n_e$ and $n_{te}$ have been calculated upon a single-pulse pumping on the same sample front surface for $\lambda = 1570$ nm by solution of the following system of equations:

\[
\begin{align*}
\frac{\partial n_e(t, z)}{\partial t} &= \sigma_e n_e(t, z)I_1(t, z) - n_e(t, z) / \tau_e \\
\frac{\partial n_{te}(t, z)}{\partial t} &= \sigma_e n_e(t, z)I_1(t, z) + n_e(t, z) / \tau_e - n_{te}(t, z)/ \tau_e
\end{align*}
\]

(3)

Magnitude of $\beta_2$ at this wavelength was obtained as described in [7,8] so that $\sigma_2 = 2 \times 10^{-26}$ cm$^2$W$^{-2}$s$^{-1}$, and $\sigma_1 \sim 0$. In this case, the rate of increase of the trapped carriers density $\sim I_1^2$. At $I_1=100$ GW/cm$^2$, the conduction electrons are populated at first due to two-photon transitions to the gap states followed by the single-photon exciton absorption. At $I_1=1$ GW/cm$^2$, the gap states are excited together with the conduction electrons and at $I_1= 0.1$ GW/cm$^2$, the gap states excitation is followed by the electrons appearance in the conduction band. In this case, which corresponds to the results shown in figure 3b,d, $n_e$ and $n_{te}$ are seven orders less than those obtained with $I_1=100$ GW/cm$^2$.

**Figure 3.** Non-linear optical response of the As$_{40}$S$_{60}$Se$_{40}$ sample pumped by a single pulse: phase shift measured (symbols) and calculated (solid blue line) at $\lambda = 790$ nm, charge carriers densities calculated by using (1), $I_1= 400$ GW/cm$^2$ (a); charge carriers densities calculated at $\lambda = 1570$ nm by using (3), $I_1= 100$ GW/cm$^2$ (red lines), 1 GW/cm$^2$ (blue lines), 0.1 GW/cm$^2$ (black lines) (b).
5. Summary
We have demonstrated that dispersion of the non-linear refractive index of the glassy chalcogenides of various compositions of the systems As$_{40}$S$_x$Se$_{60-x}$ and As$_{40}$Se$_x$Te$_{60-x}$ fits the spectral function of direct gap crystalline semiconductors obtained on the base of the non-linear Kramers-Kronig relation [9]. Magnitudes of $n_2$ increase with $h\nu/E_g$ in the range between the two-photon resonance and low-frequency limit, but decrease in the range between the two-photon resonance and the fundamental absorption band edge. However near the edge, magnitudes of $n_2$ are positive-valued that is different from those of direct gap crystalline semiconductors.

The results of the time-resolved non-linear optical response investigation obtained previously in [3,4] and results obtained in this paper demonstrate that photo-induced charge carriers kinetics develop in time in three different scenario depending on $h\nu/E_g$. 1) If a glass sample is illuminated at the red edge of its Urbach tail (0.7 < $h\nu/E_g$ < 0.8), charge carriers trapping is a result of photo-induced single-photon transitions to the gap states. 2) In the ranges 0.6 ≤ $h\nu/E_g$ ≤ 0.7 and 0.3 ≤ $h\nu/E_g$ ≤ 0.4, self-trapped excitons appear due to conduction electrons trapping by self-trapped holes. 3) Near the two-photon bandgap (0.4 < $h\nu/E_g$ < 0.6), the gap states can be populated by direct two-photon transitions. Kinetics 1) and 2) have been already proved by comparison with experimental data. For interpreting the scenario 3), the kinetics have been analyses via comparison with experimental data shown in figure 2b,d for the As$_{40}$S$_{20}$Se$_{40}$ sample. For the pump pulse intensity ~ 10$^8$ W/cm$^2$ in the sample, densities of the trapped carriers excited upon a single pulse pumping are quite small, so that their influence on the probe pulse phase is negligible. However the slow decrease of $\Delta T$ instead of a fast decrease in other samples shown in figure 2a,c reveals some variation of dielectric constant. This slow decrease of $\Delta T$ can be explained as induced by cumulative effect of pumping by multiple fs pulses at one point of the sample surface. In addition to excitons formation, a thermal lens effect can influence the probe pulse propagation in the sample and its registration with a spectrometer. For further understanding, it would be reasonable to investigate the non-linear optical response over all components of the pulse spectrum.

In conclusion, spatial distribution of modified dielectric function due to the gap states population and subsequent change of structural and optical properties of a glass sample depends on which type of kinetics is evolving. By a proper adjustment of $h\nu$ and $E_g$, an optimised regime of a glass modification can be found.

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