Non-linear optical response of bulk chalcogenide glasses near the fundamental absorption band edge

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Abstract. Magnitudes of the non-linear coefficients of absorption and refraction have been evaluated near the bandgap wavelengths of chalcogenide glasses of the system As-S-Se by using the interferometric pump-probe method and are compared with literature data. Photo-excited plasma dynamics and long-time scale variation of the dielectric constant have been studied by comparison with the results of numerical modelling of the behaviour of the glasses when heated by the ultra-short laser pulses.

1. Introduction

As other amorphous semiconductors, chalcogenide glasses have a disordered lattice and localised states of electrons in their bandgaps. Due to these specific structural and electronic properties, fundamental absorption band edge of amorphous semiconductors is not sharp. It has a spectral range of exponential decay of the single-photon absorption coefficient $\alpha$ that is usually referred to as the Urbach tail. Chalcogenide glasses have also weak absorption tails with $\alpha < 1 \text{ cm}^{-1}$ [1].

Using of chalcogenide glasses, as highly non-linear materials transparent in the mid-infrared, can enhance non-linear optical effects and reduce the dimensions of integrated and fibre optical devices. However a theory of the non-linear optical response of chalcogenide glasses has not yet been fully developed. For direct-gap crystalline semiconductors, the values of non-linear refractive index $n_2$ in the low-frequency limit have been obtained by using the bond-orbital approximation [2]. The non-linear Kramers-Kronig relation has been applied to obtain spectral dependencies of $n_2$ and of the two-photon absorption coefficient $\beta_2$ near the bandgap frequencies of the direct-gap and indirect-gap crystalline semiconductors in [3] and [4], respectively, by using two-band models. For amorphous semiconductors, only some experimental results of measurements of $n_2$ and $\beta_2$ are currently available. In particular, for chalcogenide glasses, these parameters have been measured mostly in the spectral range above their two-photon bandgap wavelengths [5-8].

In this paper, we study the non-linear optical response of chalcogenide glasses of the compositions As$_{40-x}$Se$_{60-x}$S$_x$ ($x = 0,10,15,20,30,40,45,60$) (atomic %) by using the time-resolved interferometric pump-probe method [9]: evaluate $n_2$ and $\beta_2$ near their bandgap wavelengths and characterise plasma dynamics at the Urbach tail. Different compositions fit the pump pulse peak wavelength of 790 nm (the photon energy is shown in figure 1 as a dashed line) at different points of their Urbach tails.

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2. Non-linear optical response at low energies of the pump pulse

In the experiment, a glass sample (hot pressed between two precision aligned tungsten carbide plates with flatness of 0.08 µm and a surface finish of 0.009 µm at ~25 °C above its glass transition temperature in an in-house-built vacuum rig) was probed with two collinear 50 fs pulses separated by a fixed time delay. When a high intensity pump pulse was focused on the sample (by a lens with a focal distance of 300 mm after a 3 mm aperture) at some time between the two probe pulses, the second probe pulse experienced a disturbed dielectric constant. The induced phase shift $\varphi$ and absorbance were measured by a spectrometer as a function of time by changing the delay $\Delta t$ between the pump pulse and the second probe pulse. At relatively low pump energies $E$, the phase shift was induced by non-linear refraction and two-photon absorption (figure 2a) or single- and two-photon absorption (figure 2b) of the pump pulse. The effect of cross-phase modulation is described by the system of differential equations for the pump pulse intensity $I_{pu}$ and the probe pulse intensity $I_p$:

$$\frac{\partial I_{pu}}{\partial z} = -(\alpha + \beta_2 I_{pu})I_{pu}; \quad \frac{\partial I_p}{\partial z} = -(\alpha + 2\beta_2 I_{pu})I_p; \quad \frac{\partial \varphi}{\partial z} = 2kn_2I_{pu}$$

(1)

Parameters $n_2$ and $\beta_2$ evaluated by solution of Eqs.(1) are shown in figure 3 for some compositions (filled circles at 790 nm). For comparison, the wavelength dependencies of $n_2$ and $\beta_2$ have been plotted by using the spectral function obtained in [3] for direct-gap crystalline semiconductors.

Figure 1. Logarithm of the absorption coefficient of the compositions $\text{As}_x\text{Se}_{60-x}\text{S}_x$, $x = 0$ (1), 10 (2), 20 (3), 30 (4), 40 (5), 60 (6). The linear parts of the curves correspond to the Urbach tails, $\alpha_0 = 1 \text{ cm}^{-1}$.

Figure 2. Time-resolved non-linear optical response of the compositions:
(a) $\text{As}_{40}\text{Se}_{60}, E = 1.0 \mu\text{J}$ and (b) $\text{As}_{40}\text{Se}_{50}\text{S}_{10}, E = 0.7 \mu\text{J}$. 
The curves in figure 3b were obtained by fitting the values of $n_2$ calculated in the low-frequency limit [2]. Each curve ends at the bandgap wavelength $\lambda_g$ of a particular composition. In some range of wavelengths near $\lambda_g$, these curves exhibit negative values of $n_2$. In our measurements, only positively-valued $n_2$ have been obtained for all the glass compositions. In estimations of $n_2$ and $\beta_2$, maximum magnitudes of the measured phase shift and absorbance at the probe beam axis have been used.

3. Non-linear optical response at high energies of the pump pulse

At higher energies, the effect of plasma formation due to the single- and two-photon absorption is to be taken into account. In [10], three basic scenarios of the plasma dynamics have been distinguished depending on the ratio $P=\hbar \nu/E_g$ of the irradiating photon energy to the bandgap energy. In figure 4, the positive-valued maximum corresponding to the self-induced refraction of the pump pulse is followed by the fast phase shift decrease in $\text{As}_{40}\text{S}_{60}$ sample ($P=0.65$) due to plasma formation and a subsequent slow phase shift increase due to the recombination of carriers. The effect of plasma formation is weakening when partially replacing S by Se. For the $\text{As}_{40}\text{S}_{20}\text{Se}_{40}$ sample, $P=0.74$ and for the $\text{As}_{40}\text{S}_{15}\text{Se}_{45}$ sample, $P=0.77$. In the latter sample, there were no free electrons after the pump pulse.

Permanent positive variation $\Delta n_p$ of the refractive index observed at the long-time scale and associated with photodarkening or the formation of excitons, has been compared with the results of numerical simulations of the glass heating [11]. A correlation with a sample surface heating above the glass transition temperature ($T_g$) and energy threshold of $\Delta n_p$ observation has been revealed (figure 5).
4. Conclusions
Study of the non-linear optical response of chalcogenide glass samples of the system As-S-Se has demonstrated that all the samples have the positive-valued $n_2$ unlike the direct-gap crystalline semiconductors having the negative-valued $n_2$ near their bandgap wavelengths. By comparison with the available literature data we have shown that the spectral curve obtained in [3] for the direct-gap crystalline semiconductors, agrees with the spectral dependence of the non-linear coefficients of chalcogenide glasses at wavelengths more than the two-photon bandgap wavelength.

A scenario of the photo-excited plasma dynamics depends on the ratio of the photon energy to the bandgap energy. If $P > 0.75$, fast trapping of carriers results in the lack of free electrons after the pump pulse. By numerical simulation of the glass sample heating in the irradiated zone, we have found a correlation between the permanent change of the dielectric constant at the long-time scale and glass heating above the glass transition temperature.

Acknowledgments
The research leading to these results has received funding from LASERLAB-EUROPE (grant agreement no. 284464, EC's Seventh Framework Programme) and The Royal Society (IES-2013/R2). E.Romanova and S.Guizard are grateful to S.Klimentov for taking part in the measurements.

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