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ULTRAFAST OPTICAL KERR EFFECT IN AMORPHOUS $Ge_{10}As_{40}S_{30}Se_{20}$ FILM INDUCED BY ULTRASHORT LASER PULSES

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The results of the femtosecond optical heterodyne detection of optical Kerr effect at 805 nm with the 80 fs ultrafast pulses in amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film is reported in this Letter. The film shows an optical nonlinear response of 200 fs under ultrafast 80 fs-pulse excitation, and the values of real and imaginary parts of nonlinear susceptibility $\chi^{(3)}$ were 9.0×10^{-12} esu and -4.0×10^{-12} esu respectively. The large third-order nonlinearity and ultrafast response are attributed to the ultrafast distortion of the electron orbits surrounding the average positions of the nucleus of Ge, As, S and Se atoms. This $Ge_{10}As_{40}S_{30}Se_{20}$ chalcogenide glass would be expected as a promising material for optical switching technique.

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1. Introduction

The development of materials with excellent nonlinear optical properties is a key for realizing the full potential of all-optical computing and signal processing[1-3]. Third-order nonlinear properties of optical media remained a subject of considerable theoretical and experimental efforts stimulated by the need of materials with large values of the nonlinear susceptibility $\chi^{(3)}$ for photonic devices. Meanwhile, nonlinear optical response speed is another most important property of materials for their applications in the photonic field. Many advanced techniques, including optical switching, modulating, optical information processing and ultrafast optical communications, need devices made from materials with fast optical nonlinear responses. Especially the rapid development of optical communication requires the novel materials with large and ultrafast nonlinear optical responses in the femtosecond domain for fabricating the ultrafast optical switching and processing devices[4-7]. For these purposes, research on measurement of femtosecond nonlinear optical properties of many materials has attracted much attention[1-3,8-10]. One of the essential problems here is that the third-order susceptibility $\chi^{(3)}$ must be defined as a complex quantity. In order to understand the dynamics of nonlinearity, it is essential to determine the magnitudes and signs of both the real and the imaginary parts of the nonlinearity. Chalcogenide semiconductors exhibit structural flexibility and are

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susceptible to photoinduced changes. So their nonlinearities should be large. In this paper, one kind of new amorphous semiconductor $Ge_{10}As_{40}S_{30}Se_{20}$ material was prepared and the optical nonlinear property was studied by the femtosecond optical heterodyned detection of optical Kerr effect (OHD-OKE)[10,11] method. A new nonlinear optical material for optical switching is expected.

2. Experimental

Firstly, bulk $Ge_{10}As_{40}S_{30}Se_{20}$ glass was prepared by standard thermal synthesis from Ge , As, S and Se of (99.999%), were mixed in a desired chemical ratio and heated in an evacuated quartz ampoules (10^{-3} Pa) at temperature of ~1000 ^{o}C for about 72 h. After that the melt was water-quenched, resulting in a bulk glass of the desired chemical composition. The $Ge_{10}As_{40}S_{30}Se_{20}$ thin films with thickness of ~300 nm were prepared from $Ge_{10}As_{40}S_{30}Se_{20}$ glass bulk powder by the vacuum evaporation technique at a rate of 15 Å/s in a 1×10^{-3} Pa vacuum.

The third-order susceptibility and the ultrafast response of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film were measured by the method of OHD-OKE. Fig.1 shows the OHD-OKE experimental set-up. The mode-lock Ti:Sapphire laser pumped by the Millennia Vs laser which provides 4.1 W of green 532 nm, is operated at 82 MHz and has an average output power of 680 mW, a wavelength of 805 nm and a pulse duration of 80 fs. The output beam is divided into a pump and a probe beam ($I_{probe} : I_{pump} = 1:10$) by a beam-splitter. The polarizer P1 is directed at 45° with respect to that of the pump beam. The pump and probe beams, with the average power 20 mW and 2 mW respectively, are focused into the sample, and their confocuse length is about 200 um. A polarization analyser is placed behind the sample at the crossed polarization direction to the input polarizer. A quarter-wave plate is inserted between the input polarizer and the focusing lens to measure the real part of $\chi^{(3)}$ in the OHD-OKE experiments. The optical axis of the quarter-wave plate is also directed at 45° to the polarization direction of the pumped beam.

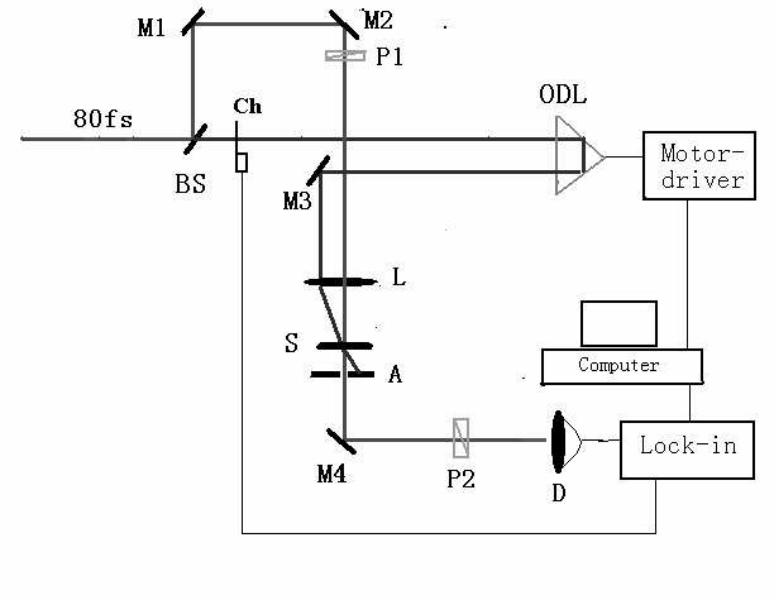

Fig.1. The OHD-OKE experimental set-up.

3. Results and discussion

The light absorption in amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film was performed in Perkin Elmer Landa 9UV/VIS/NIR spectrophotometer and the measurement range was 300~900 nm (Fig. 2). The absorption peak is situated under 500 nm. According to the wavelength of 805 nm of the mode-lock

Ti:Sapphire laser in the OHD-OKE experiments, amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film shows almost no absorption.

For measuring the third-order nonlinear susceptibility of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film, CS_2 was used as the reference sample and was firstly measured in the OHD-OKE experiments [12]. In the same time, we could use it to examine the reliability of our OHD-OKE experimental set-up. The OHD-OKE signal of CS_2 at two different heterodyning angles: 2° and -2° is shown in Fig. 3. The value of $(\chi^{(3)})_R$ (real part of $\chi^{(3)}$) for CS_2 is 0.67×10^{-13} esu (whose $\chi^{(3)}$ is positive)[13]. The OHD-OKE signal (real and imaginary parts) of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film is shown in Figs.4 and 5, respectively. From the symmetry of the signal, we can conclude that the response time of the sample should be less than 200 fs, which indicates that amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film shows a very fast response under ultrafast excitation.

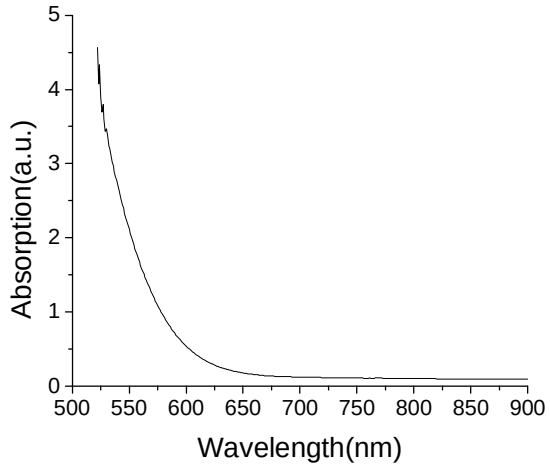

Fig. 2. Absorption spectrum of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film.

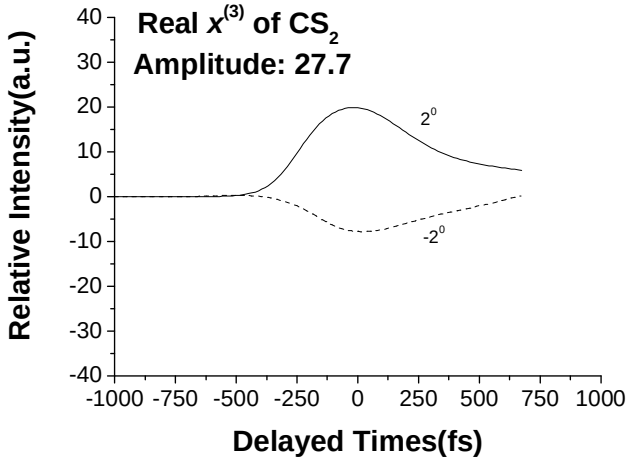

Fig. 3. OHD-OKE signals of CS_2 at two different heterodyne angles: -2 ° and 2 °.

In the OHD-OKE experiments, the combined effect of the pump intensity I_{pump} and probe electric field E_{probe} on the sample is to generate a nonlinear signal field E_s. Optical heterodyned detection of E_s is accomplished by coherently summing the signal field with a fraction of the probe electric field (the optical local oscillator, E_{lo}). The presence or absence of a phase retardation element establishes the phase relation between the Kerr signal and the local oscillator. The quarter-wave plate

imposed a fixed $\pi/2$ phase bias between the local oscillator and the Kerr signal through a slightly rotation ϕ of the first polarizer. Thus, without the quarter-wave plate, the local oscillator is E_{lo}=iϕE_{probe}. For $I \propto 2\mathrm{Re}\,[i\chi^{(3)} I_{pump}(E^{*}_{probe} E_{lo})]$, the out-of –phase local oscillator probes $(\chi^{(3)})_R$, the in-phase local oscillator probes $(\chi^{(3)})_I$ (imaginary part of $\chi^{(3)}$). Here $\chi^{(3)}$ is the effective third-order susceptibility of optical Kerr experiment, $\chi^{(3)} = \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyxy}$.

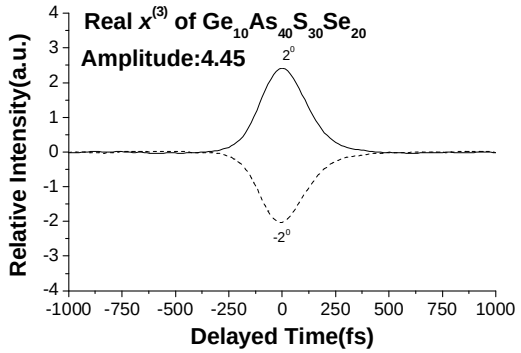

Fig.4 OHD-OKE signals of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film (real part) at two different heterodyne angles: -2° and 2°

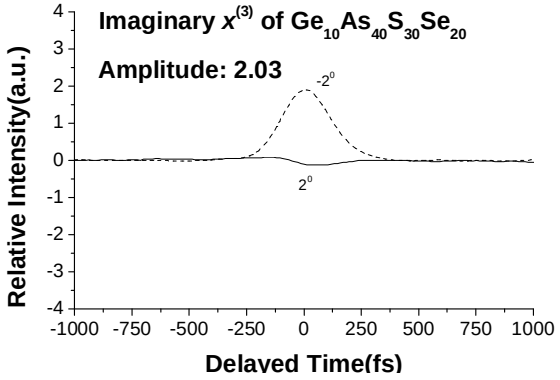

Fig.5 OHD-OKE signals of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film (imaginary part) at two different heterodyne angles: -2° and 2°

We carried out the measurements as a function of the angle ϕ and could fit the dependence of the heterodyned OKE signal with the form $I = z_1 + z_2\phi$. The coefficient z_2 is proportional to the real part

$$z_{2,R(\mathrm{Im})} = (4\pi^2\omega^2 L/\kappa_1 c^3) n^{-1/2} (\chi^{(3)})_{R(\mathrm{Im})} I_1 I_2 \quad (1)$$

where I_1, I_2 stand for the pump and the probe beam intensities respectively; L is the thickness of sample cell and κ_1 is the value probe beam's wave vector. The third-order susceptibility of the sample can be calculated by comparing with the reference CS_2

$$(\chi^{(3)})^{s}_{R(\mathrm{Im})} = (L^{ref} z^{s}_{2,R(\mathrm{Im})} / L^{s} z^{ref}_{2,R})(n^{s}/n^{ref})^{1/2} (\chi^{(3)})^{ref}_{R} = (L^{ref} A^{s} / L^{s} A^{ref})(n^{s}/n^{ref})^{1/2} (\chi^{(3)})^{ref}_{R} \quad (2)$$

The superscript ref denotes the reference CS_2 and $(\chi^{(3)})^{ref}_{R}$ is the effective third-order susceptibility of reference CS_2 for which we assume no imaginary part. L^{ref} and L^{s} are the effective path length of the thickness of sample respectively, and z^{ref} and z^{s} are the slopes of OHD-OKE signals at zero delay time in S-ϕ coordinates of CS_2 and the sample respectively. In our experiments,

we have taken the values $n^s = 2.5$ and $n^{ref} = 1.62$. Using Eq.(2), the $(\chi^{(3)})_R$ and $(\chi^{(3)})_I$ values of the amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film can be deduced. The value of $(\chi^{(3)})_R$ for CS_2 is 0.67×10^{-13} esu in our experiments. From Figs. 4 and 5, the real and imaginary parts of effective third-order nonlinear susceptibility of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film are calculated to be 9.0×10^{-12} esu and -4.0×10^{-12} esu, respectively. Since the signal of imaginary part is negative to CS_2, the value of $(\chi^{(3)})_I$ is negative. Its third-order optical nonlinearity is greater than oxide glasses[12], and As-S, Ge-S, Ge-Se and Ge-As-S chalcogenide glasses[14]. It is evident that the third order optical nonlinearity is ascribed to the electronic contribution due to nonlinear distortion of electron orbits surrounding the average positions of the nucleus of Ge, As, S and Se atoms.

Using Eq.(3),[15] the nonlinear refractive index n_2 can be obtained:

$$(\chi^{(3)})_R = (cn_0^2/160\pi^2)\gamma \tag{3}$$

Where c is the velocity of light and n_0 is the linear refractive index of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film. γ is calculated to be 7.5798×10^{-17} m^2/W and $n_2 = (cn_0/40\pi) = 4.52\times10^{-10}$ esu.

Generally, there are at least two processes that can contribute to nonlinear absorption, namely two-photon absorption and free carrier absorption. Since the pulse width (80 fs) is much shorter than the recombination time of free carriers (nanosecond or longer), the free carriers absorption is negligible. So the two-photon absorption may be considered as the main cause that leads to the nonlinear absorption.

The two-photon absorption coefficient β of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film can be determined from Eq.(4)[15]. Where λ is the wavelength of the laser. The obtained value of β is 0.5299×10^{-10} m/W.

$$(\chi^{(3)})_I = \lambda cn_0^2\beta/640\pi^3 \tag{4}$$

In the nonresonant case, far from any fundamental absorption, the optical nonlinearity is predominantly of electronic origin. These electronic effects exhibit subpicosecond response time with minimum heating, but the nonlinearities are small. However, in resonant case, when the operating wavelength is in the vicinity of a fundamental absorption, the electronic effects can be large and the nonlinearities are also large, but the response time is slower[16]. In the OHD-OKE experiments, the absorption edge of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film is less than 500 nm, almost no absorption is occurred in the operating wavelength of 805 nm. So amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film shows a very fast response time of less than 200 fs. Its third-order optical nonlinearity is greater than oxide glasses[12] and some chalcogenide glasses [14]. Such behaviour is well known in the nonlinear optical phenomena of glasses among phenomena such as the nonlinear refractive index, multiphoton absorption, and stimulated Raman and Brillouin scattering, where the glass itself is responsible for the nonlinearity (intrinsic effect). So the structure and composition of the glass are of primary importance in controlling the nonlinearity [16]. Chalcogenide semiconductors are structural flexibility and are susceptible to light-induced changes [17]. In amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film, the chalcogen elements (S and Se atoms) are only two-fold coordinated and possess lone pair electrons which are normally non-bonding. The non-bonding electrons lie at the top of the valence band and hence are preferentially excited by light and produce some short lived free electrons plasma and band filling effects. It is just the forming of the short lived electrons that makes amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film to show a very fast response time within 200 fs. It is also known in chalcogenide glasses that the valence band is formed by the interaction of the lone pair orbits and the conduction band is formed by the anti-bonding orbits. Therefore, in the case of OHD-OKE, inner core electrons can be excited, i.e. generation of inner core holes and short lived electrons takes place. The inner core holes can be immediately filled by outer electrons with Auger processes which can induce more holes in upper states (bonding and lone-pair states), since one Auger process creates two holes (vacancy cascade process). In this situation, bond-breaking or ionization of atoms is easy to occur. On the other hand, the nonlinear distortion of electron orbits, which undergoes light-induced reactions is easy to produce. So, a change in local structural order in the amorphous network occurrs, which induces a change of refractive index.

Further detailed researches on the optimization of experimental conditions and Ge-As-S-Se layer composition, especially chalcogenide glasses doped with heavy-metal atoms which improve the refractive index of glasses and make them to exhibit optical nonlinearities, are necessary to improve the value of third-order susceptibility and response time of amorphous Ge-As-S-Se glass films to make chalcogenide semiconductors meet the need for nonlinear optical devices.

4. Conclusions

The third-order nonlinear optical properties of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film were studied experimentally by the method of the femtosecond optical heterodyne detection of optical Kerr effect. The real and imaginary parts of complex third-order optical nonlinearity could be effectively separated and their values and signs could be determined. The results showed that the values of real and imaginary parts of third-order susceptibility of amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film were 9.0×10^{-12} esu and -4.0×10^{-12} esu respectively. Amorphous $Ge_{10}As_{40}S_{30}Se_{20}$ film showed a very fast response in the range of 200 fs under ultrafast excitation, which is promising for application in advanced techniques especially in optical switching.

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