Large and Ultrafast Third-Order Nonlinear Optical Properties of Ge-S Based Chalcogenide Glasses *

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We report ultrafast third-order nonlinear optical (NLO) properties of several chalcogenide glasses GeS_x ($x = 1.8$, 2.0, 2.5) measured by femtosecond time-resolved optical Kerr gate technique at 820 nm. The third-order nonlinear susceptibility of $GeS_{1.8}$ glass is determined to be as large as 1.41×10^{-12} esu, which is the maximum value of the third order nonlinear susceptibility $\chi^{(3)}$ for the three compositions investigated. The symmetric Gauss profiles of optical Kerr signals reveal the nature of ultrafast nonlinear response of these samples, which are originated from the ultrafast polarization of the electron clouds. By detailed microstructural analysis of these glasses based on the chain-crossing model (CCM) and the random-covalent-network model (RCNM), it can be concluded that $\chi^{(3)}$ value of GeS_x glasses can be enhanced greatly by S–S covalent bonds or S_3Ge–GeS_3 ethane-like units.

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Third-order nonlinear optical (NLO) materials have attracted a great deal of attention because of their potential applications in various optical telecommunication devices.[1−5] Glasses are important NLO materials. Among various glassy systems such as fluorides and oxides, chalcogenide glass presents the largest third-order optical nonlinearities.[6] According to the previous works,[7−9] the reported As and Se-containing glasses possess third-order optical nonlinearities 80–27000 times more than fused silica, and some of them have been used in optical switching devices. However, most of these glasses suffer from large nonlinear optical absorption at telecommunication wavelengths of 1.3 μm and 1.55 μm, which should be avoided.[10] Therefore, we turn to study the GeS_x-based glasses, with bandgap significantly shifted towards the short wavelength while still keeping relative high nonlinearities.

In this Letter, we report the third-order NLO properties of a series of GeS_x ($x = 1.8$, 2.0, 2.5) chalcogenide glasses measured by time-resolved femtosecond optical Kerr gate technique. The experimental results indicate that the glasses whose chemical composition is in non-stoichiometric proportion have third-order optical nonlinearities much higher than the stoichiometric one GeS_2. All the glasses have ultrafast response time.

The samples were prepared from particular high-purity elements by the well-established melt-quenching technique. The annealed glassy specimen was cut and then optically polished for the measurements of optical properties (for details see our previous works[11,12]). The linear refractive indices were measured by an MM-16 spectroscopic ellipsometer (Jobin Yvon Lt. Co.). Some parameters of our samples are listed in Table 1.

The linear absorption spectrum of our samples were measured using an Agilent 8453 UV-Vis spectroscopy system. The ultrafast third-order optical nonlinearities of the samples were measured by the time resolved femtosecond optical Kerr gate technique.[13] The femtosecond laser pulse train with repetition rate of 76 MHz and with central wavelength

Table 1. Parameters of GeS_x chalcogenide glasses. Here n is the linear refractive index, l is the thickness of the sample, α is the linear absorption coefficient, I_s/I_R is the ratio of the maximum value of the OKE signal of the sample to that of CS_2 at 820 nm, and $\chi^{(3)}$ is the third-order nonlinear susceptibility calculated at 820 nm.

Sample	Composition	Bandgap (nm)	n	l (mm)	α (cm^{-1})	I_S/I_R	$\chi^{(3)}$ (10^{-13} esu)
A	$GeS_{1.8}$	550	2.45	0.84	2.65	14.41	14.1
C	GeS_2	460	2.14	0.64	3.48	3.50	5.33
B	$GeS_{2.5}$	500	2.21	0.70	5.14	4.23	7.08

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of 820 nm came from a Ti:sapphire laser (Mira 900F, Coherent). The pulse train was split into two beams with intensity ratio of 10:1. The stronger one with the power of 20 mW passing through the variable delay line was used as the pump beam; the weaker one acted as the probe beam. The pulse intensity of the pump beam was 0.1 GW/cm^2 when focused down to the sample. The polarization of the probe beam was rotated 45° with respect to the pump one by a polarizer. Then the two beams were parallel aligned to each other before focusing down to the sample by a single piece of convex lens. After the sample, the probe one passed through an analyser (polarizer) with transmission axis perpendicular to the original polarizer. The generated optical Kerr signal was detected by a photodiode detector. In order to improve the signal-to-noise ratio, a dual-beam chopping configuration was applied with a beam chopper in front of the sample. The signal detected from the photodiode was transferred to a lock-in amplifier (SR830, Stanford, USA). A computer program was used to control the step motor and to collect the data from the lock-in amplifier. The zero delay point was determined by replacing the sample with a 0.3-mm-thick BBO crystal. The width of the laser pulse was measured to be 120 fs. In order to remove the uncertainty factors in our experiment, for example, the overlap of the pump beam and the probe one at focus, a reference sample, CS_2, whose third-order nonlinear susceptibility has been determined to be 1.3×10^{-13} esu,[14] was used. The signal of our samples and the reference were measured under the same experimental conditions. The third-order NLO susceptibilities $\chi^{(3)}$ of the samples can be calculated by

$$\chi_s^{(3)} = \chi_{\mathrm{R}}^{(3)} \left(\frac{I_{\mathrm{S}}}{I_{\mathrm{R}}}\right)^{1/2} \left(\frac{I_{\mathrm{S,pump}}}{I_{\mathrm{R,pump}}}\right)^2 \cdot \left(\frac{n_{\mathrm{S}}}{n_{\mathrm{R}}}\right)^2 \frac{\alpha l}{e^{-\alpha l/2}(1 - e^{-\alpha l})}. \quad (1)$$

The subscripts S and R refer to samples and reference, respectively; I is the peak intensity of the acquired optical Kerr signal; n is the linear refractive index; $I_{\mathrm{S,pump}}$ and $I_{\mathrm{R,pump}}$ represent the pump beam intensities on the sample and the reference, respectively; α is the absorption coefficient; and l is the thickness of the sample.

The results of the linear absorbance of our samples are shown in Fig. 1. They clearly indicate that there are no absorption structures at the wavelength of 820 nm for all of these three samples. To figure out the nonexistence of two-photon absorption, we measured the absorption towards the pump intensity. The results are present in Fig. 2. When the power of the pump beam is below 200 mW, there is mainly linear absorption, and no two-photon absorption clearly can be observed. Then the two-photon resonance contribution can be ignored in our experiment since the pump beam is only 20 mW.

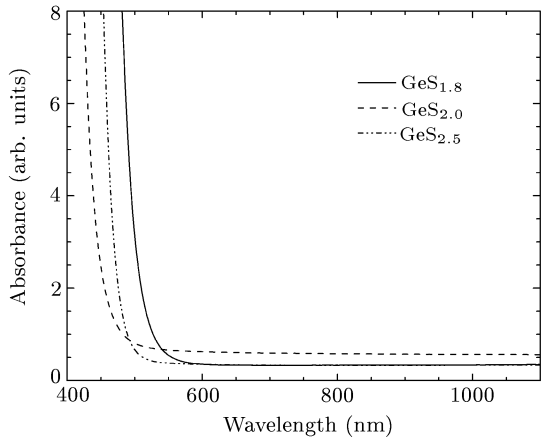

Fig. 1. Absorption spectra of the GeS_x glasses.

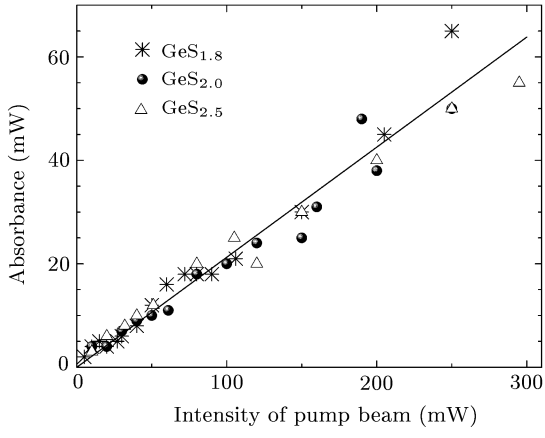

Fig. 2. Relationship between the absorbance and the intensity of pump beam in the GeS_x glasses.

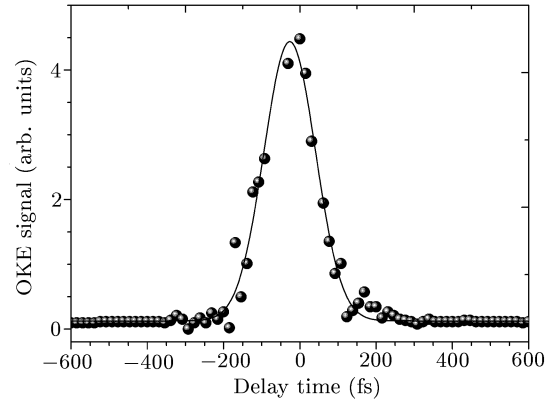

Fig. 3. The Kerr signal of GeS_2.

Figure 3 shows the optical Kerr effect (OKE) signal of GeS_2, others are of the similar profile with different peak values. The OKE signals of our samples

are symmetrical and their full widths at half maximum are about 120 fs, which is equal to the width of the laser pulse, implying that the third-order NLO responses of our samples are instantaneous. Therefore, the third-order optical nonlinearities we obtained can be attributed to the electronic contribution due to nonresonant distortion of the electron clouds.

Using Eq. (1), third-order nonlinear susceptibilities of our samples are calculated. The results are listed in Table 1. The $\chi^{(3)}$ value of $GeS_{1.8}$ is larger than that of $95GeS_2$-$5Ga_2S_3$-5CdS, which was investigated by our group previously.[15] All these $\chi^{(3)}$ values are higher than that of heavy-metal oxide glass measured by the same method recently.[16–18]

In GeS_x glasses, the $\chi^{(3)}$ values of both $GeS_{2.5}$ and $GeS_{1.8}$ are larger than that of GeS_2. These results indicate that glasses, which are out of stoichiometric proportion, possess higher third-order NLO susceptibilities. As discussed by Lucovsky *et al.*[19] together with our previous works,[20,21] the structure of GeS_x can be interpreted in terms of models based on covalent bonding in which the 8-N rule is satisfied. For the GeS_2 glass, its basic structure is mainly $[GeS_4]$ tetrahedral units despite a few quantities of ethane-like units S_3Ge-GeS_3 and multi-S bonds. These tetrahedral structure units are connected with each other through a bridging sulfur to form a three-dimensional network.[22] In S-rich alloys, that is, $2 < x < 9$, a generalized chain-crossing model (CCM) is preferable, which assumes that Ge atoms incorporated into amorphous S can crossly link the twofold coordinated chains through a fourfold coordinated Ge site. In the CCM model, no Ge–Ge bonds exist. It allows a second species of S_8 rings to be in solution of the $[GeS_4]$ tetrahedral network. Therefore, the S–S covalent bonds may be the reason of larger nonlinear response in $GeS_{2.5}$, which was also expected by Cardinal *et al.*[23] and Hajto *et al.*[24] However, in Ge-rich alloys, that is, $x < 2$, they satisfy the random-covalent-network model (RCNM). In this model, it allows Ge–Ge and Ge–S bonds, but no S–S bonds exist. Therefore, the local order can be characterized in five types of tetrahedral, GeS_4, $Ge(S_3Ge)$, $Ge(S_2Ge_2)$, $Ge(SGe_3)$, and $Ge(Ge_4)$. All of these types of tetrahedral unit have a central Ge atom, and the other four atoms are then attached to the central Ge atom. In $GeS_{1.8}$, the concentration of $Ge(S_3Ge)$ is up to 40%,[19] which is the most one among these five types, so the larger NLO properties of $GeS_{1.8}$, which has $\chi^{(3)}$ nearly three times of GeS_2, come from the ethane-like units of S_3Ge–GeS_3.

In summary, ultrafast third-order nonlinearities of several GeS_x chalcogenide glasses have been determined by employing femtosecond time-resolved optical Kerr gate technique. According to detailed analysis on the evolution of microstructure of these glasses based on the CCM and RCNM models, it is clear that the $\chi^{(3)}$ values of GeS_x glasses are increased effectively by S–S covalent bonds or S_3Ge–GeS_3 ethane-like units. They share a key light in the development of third-order nonlinear optical materials.

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