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LETTER

Ultrafast nonresonant third-order optical nonlinearity of the $0.64GeS_2$–$0.16Ga_2S_3$–0.2CsCl chalcohalide glass

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Over the last few years, great efforts have been made about the research and development of highly nonlinear optical materials for applications such as all-optical switching devices in the optical telecommunication field. In particular, among the materials available to date, chalcogenide glasses are emerging as the promising candidates for future compact and high efficiency all-optical switching devices due to their large electronic nonlinear refractive indices and high abilities to drawing fibers with them [1–5]. Early in 1992 Masaki et al. have demonstrated that ultrafast all-optical switching with 14 W of switching power can be realized utilizing an only 48-cm long single-mode As_2S_3-based glass fiber according to an optical Kerr shutter configuration [6]. And the large nonlinear refractive index (n_2) of the As_2S_3-based glass, which was estimated to be 4×10^{-14} cm^2/W, two orders larger than that of silica glass fibers, has been confirmed by switching characteristics. However, succeeding researches found that at the communication wavelength of 1,300 nm, the large nonlinearity of the As_2S_3-based glasses was coupled with the drawback of photo-darkening initiated by two-photon absorption (TPA) [7]. And to prevent from the optical damage of the glass fiber at 1,300 nm, TPA should be avoided in the fast or high bit-rate telecommunication systems in operation. Due to the distinct blue shift of the absorption edge compared with the As_2S_3-based glasses [8], many GeS_2-based chalcohalide glasses will not exhibit TPA at the telecom wavelengths. So much basic research about this sort of chalcohalide glasses has been done in our lab [9–14].

In this letter, utilizing the femtosecond time-resolved optical Kerr effect (OKE) technique, we reported the ultrafast third-order optical nonlinearity of the GeS_2–Ga_2S_3–CsCl chalcohalide glasses in order to find out a larger optical nonlinear material with ultrafast response time and no TPA at the optical telecommunication wavelengths.

The chalcohalide glasses with the composition $0.64GeS_2$–$0.16Ga_2S_3$–0.2CsCl (in mol%) were prepared according to the well-established melt-quenching technique in our lab. Within a N_2 gas-filled glove box, batches of Ge, Ga and S of 99.999% purity and CsCl of 99.99% purity were weighted and shifted into the 10 mm ID by 12 mm OD fused quartz tubes which were then sealed under vacuum with 10^{-1} Pa and inserted into a rocking furnace. The homogeneous glasses were obtained through air quenching and subsequently annealing at the temperature a few degrees below the glass transition temperature (T_g). And then the annealed glasses were cut and optically polished for the measurements of optical properties. According to the results of the energy-dispersive XRF analyzer, the reasonable difference in composition between the batch and the prepared one was confirmed. Homogeneity and amorphous characteristics of the prepared bulk samples were confirmed by optical and electron microscopy and X-ray diffraction (XRD) patterns. The characteristic temperatures T_g = 330 °C and

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T_x = 435 °C (onset of crystallization) were determined by differential scanning calorimeter (NETZSCH STA 449C). The difference between T_x and T_g is larger than 100 °C, indicating its high fiber-drawing capability that must be considered when preparing the optical switching devices as the optical fibers provide large interaction lengths. The main microstructural units of these glasses were considered to be [GeS_4] and [$GaS_{4-x}Cl_x$] tetrahedra through Raman scattering investigations. More details about the microstructure see the Refs. [10, 11].

Figure 1 represents the linear absorption spectrum of the studied sample at room temperature recorded by a UV–VIS-near IR spectrophotometer (Shimadzu UV-1601) in the region 400–1,100 nm, which show a high transparency window for wavelengths larger than ≈450 nm. The visible absorption edge, λ_{vis}, defined as a wavelength at which 50% of the transmission at longer wavelength is obtained, is at about 430 nm for this sample much shorter than the As_2S_3-based chalcogenide glasses. Based on the report of Prof. Jha and coworkers [8], it can be anticipated that for the present chalcohalide glass, the photo-darkening will be absent and four/five photon absorptions will be observed at the communication wavelength of 1,300 nm that dose not affect their performance at all as all-optical switching devices. In addition, the long-wavelength cut-off edge λ_{IR} (defined as a wavelength at which 50% of the transmission at shorter wavelength is obtained) of this sample is at about 11.5 μm (see insert in Fig. 1). When considering the practical applications, further efforts should be made to remove the distinct absorption bands at about 1,600, 2,500 and 3,500 cm^{-1}

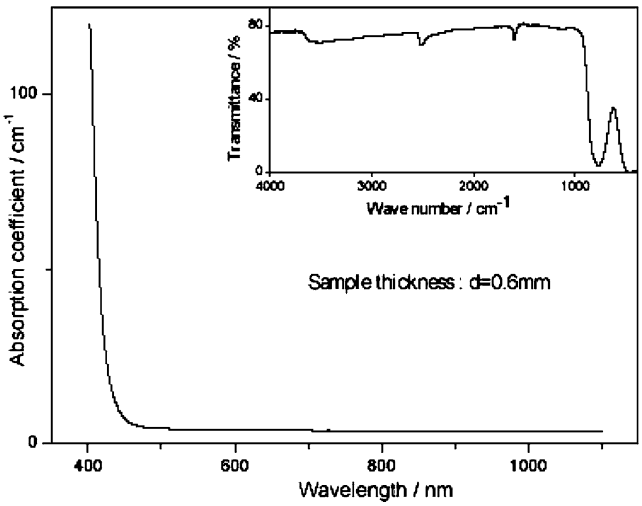

Fig. 1 Absorption coefficient α_o and FTIR transmittance spectrum of the studied chalcohalide glass: $0.64GeS_2$–$0.16Ga_2S_3$–0.2CsCl (in mol%)

attributed to the hydroxide contamination during the process of preparation. The linear refractive index of the studied sample was measured to be 1.91 at 830 nm using the Ellipsometry (Type: JY-UVISEL).

The ultrafast third-order optical nonlinear measurements were performed by a time-resolved homodyne-detection optical Kerr gate (OKG) technique utilizing the femtosecond pulses (the repetition rate is 76 MHz) from a Ti:Sapphire laser (Mira 900F, Coherent, USA) centered at the wavelength of 830 nm. Utilizing a 0.3 mm thickness BBO crystal, the pulse duration was determined to be 115 fs. The experimental arrangement is shown schematically in Fig. 2. To adjust the optical path difference between the probe and the pump beams during the measurement, the pump beam was led through an optical delay line (ODL) driven by a step-by-step motor. The pump and probe beams were polarized at 45° with respect to each other and focused (F_1) on the same spot of the sample (S) with a diameter of 20 μm with an intensity ratio of 12:1. The pump pulse induced third-order nonlinearity within the sample, which allowed the detecting of an orthogonal optical Kerr signal through the two perpendicular polarizers P_1 and P_2 utilizing the probe beam. To improve the signal-to-noise ratio, the pump beam passes through a chopper to facilitate lock-in detection. All measurements were controlled by a computer program. Liquid CS_2 in a quartz cell with a thickness of 1 mm was used as a reference. To avoid the saturation effect and the nonlinear absorption, the gating pump power on the sample was set to be 360 mW or less in this experiment. Under the same experimental condition, the third-order nonlinear optical susceptibility, $\chi^{(3)}$, can be calculated from the following equation [15]:

$$\chi_S^{(3)} = \chi_R^{(3)} \left(\frac{l_R}{l_S}\right) \left(\frac{I_S}{I_R}\right)^{\frac{1}{2}} \left(\frac{n_S}{n_R}\right)^2 \frac{\alpha l_S}{e^{-\alpha l_S/2}(1 - e^{-\alpha l_S})} \quad (1)$$

where I, n, α and l denote the OKE signal intensity, the linear refractive index, the absorption coefficient and the effective length of the sample, respectively and the subscripts S and R represent samples and the reference CS_2, respectively. In addition, the ultrashort lifetimes of the excited states of samples were measured by the standard pump-and-probe method utilizing the same setup. In this technique, the populations of the relevant states are first altered with a strong pump pulse and the subsequent population change in the states is probed by a suitably delayed weak probe pulse that does not significantly perturb the population change being measured.

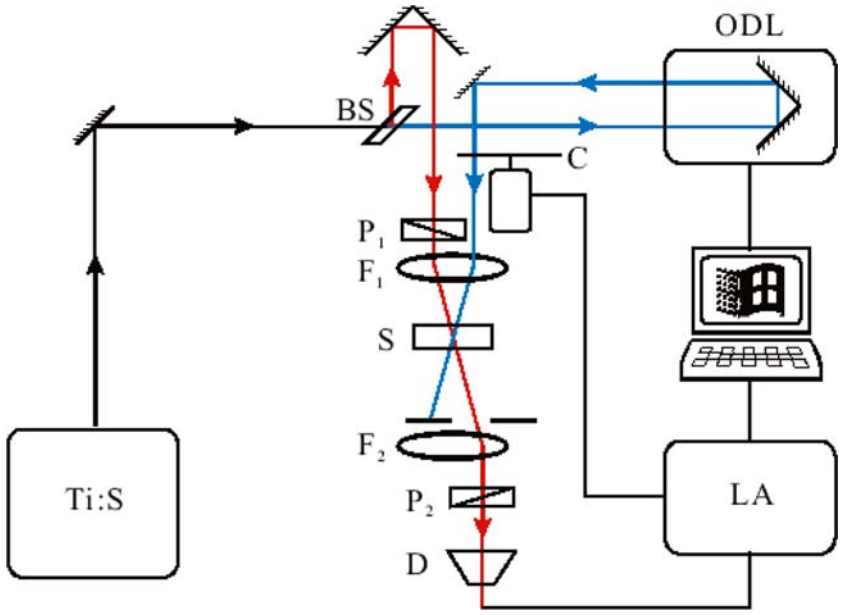

Fig. 2 The experimental setup schematic for the Kerr shutter system Ti:S, Ti-sapphire femtosecond laser; ODL, optical delay line; BS, beam splitter; C, chopper; P, polarizer; D, detector; F, focusing lens; S, sample; LA, lock-in amplifier

The OKG signal of the reference sample CS_2 is shown in Fig. 3 (top). Because of the negligibly small absorption coefficient in CS_2 at 830 nm, only the real part of the nonlinear susceptibility is to be considered. The curve has an asymmetrical decay tail. That's to say, the relaxation of the population of the excited states is not governed by a single exponential process but by, for example, a fast process superimposed on much slower processes. According to the references [16, 17], the temporal profile of CS_2 can be reproduced by the sum of the instantaneous electronic response and the two exponential decays which are molecular origins. Furthermore, the $\left|\chi^3_R\right|$ of the reference CS_2 has been measured to be 1×10^{-13} esu on the femtosecond time-scale by Minoshima et al. [16] and the refractive index of CS_2 is 1.62.

Under the same experimental conditions, a typical temporal behavior of the optical Kerr signal observed for the present chalcohalide glass was also shown in Fig. 3 (bottom). The salient feature of the figure indicates that the temporal profile of the OKG signal in the present chalcohalide glass is Gaussian symmetrical, and the response time, i.e., the full width at half maximum (FWHM) of the Kerr signal, is as fast as 195 fs only which is similar to the autocorrelation signal of laser itself. Under the present experimental gating power density, neither saturation effect nor any slow decay component was detected for the present chalcohalide glassy sample. No damage on the sample surface appeared at the highest gating intensity. These findings indicated that the thermal effect that originated from the two-photon absorption or other slow processes, which is intrinsically of ''nuclear'' origin did not occur under the present experimental conditions. These results indicate the ultrafast optical nonlinearity in the $0.64GeS_2$–$0.16Ga_2S_3$–0.2CsCl glass comes from

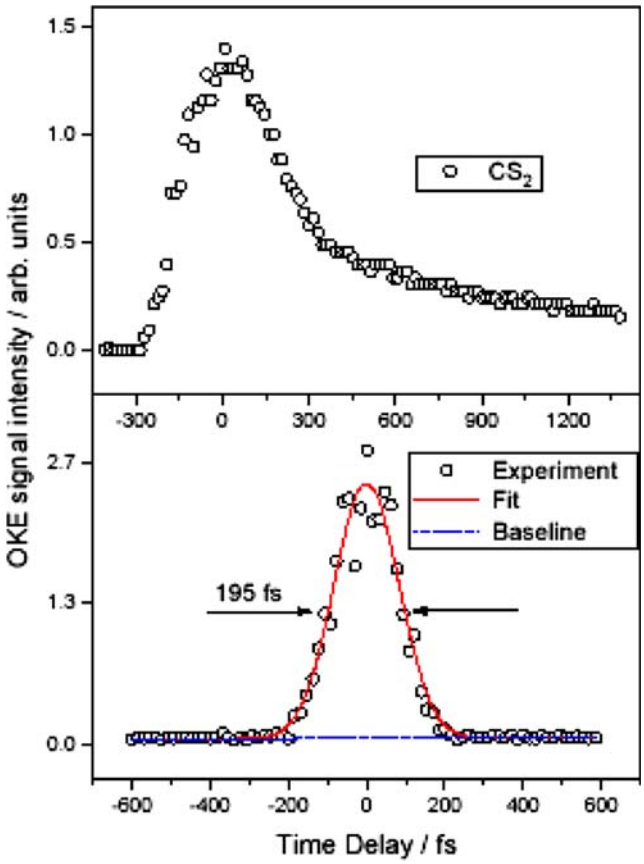

Fig. 3 Time-resolved optical Kerr signals of the chalcohalide glass ($0.64GeS_2$–$0.16Ga_2S_3$–0.2CsCl) (bottom) and the reference CS_2 (top)

an instantaneous process, i.e., a ''purely electronic'' process mainly originated from the nonlinear distortion of the electrons around a fixed nuclear configuration of the molecules. According to Eq. 1, the third-order nonlinear optical susceptibility of the present chalcohalide glass was estimated to be $3 \pm 0.5 \times 10^{-13}$ esu at the incident laser wavelength of 830 nm. Furthermore, when changing the power of the pump beam, the third-order nonlinear optical susceptibility $\chi^{(3)}$ keeps the same magnitude which suggests the $\chi^{(3)}$ of the present glass free of any intensity dependent effects.

Based on the relationship of conversion between n_2 and $\chi^{(3)}$ [3], n_2 (cm^2/W) $\approx 0.04\chi^{(3)}$ (esu)$/n_0^2 \approx 3 \times 10^{-15}$ cm^2/W. This value is about three times smaller than the nonlinear refractive index of As_2S_3 glasses, but the nonlinear absorption of the present glass is much smaller at telecommunication wavelengths originated from the much higher band edge compared with that of As_2S_3 glasses. Widely transparent wavelength range, higher $\chi^{(3)}$ and off-resonant electronic ultrafast OKG response coupled with lower nonlinear absorption make the present glasses having the potential applications in the current photoelectric fields such as all-optical switching devices.

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