Effect of CdS on the third-order nonlinearity in bulk GeS_2-Ga_2S_3-CdS chalcogenide glasses

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Effect of CdS on the third-order nonlinearity $\chi^{(3)}$ in bulk GeS_2-Ga_2S_3-CdS chalcogenide glasses was investigated using the Z-scan measurements. The $\chi^{(3)}$ increased with the increase of CdS content, which was strongly related to the addition of Cd, because it caused the appearance of non-briging sulfurs in glass, and the polarity of bonds in glasses was enhanced to lead serious distortion of atoms electron clouds to induce larger third-order nonlinear responses. The largest third-order nonlinear susceptibility of the glass containing 15% CdS (in mol) in our experiments was obtained as 9.17×10^{-13} esu.

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1. Introduction

Glasses with large third-order nonlinear susceptibility and ultrafast response has great potential application in optical information processing such as ultrafast optical switching and processing devices [1-3]. In the past few years, the chalcogenide/chalcohalide glasses and films as nonlinear materials have attracted much attention due to its advantages for optical application, such as larger Kerr nonlinearity [4,5], low two-photon absorption (TPA) and the fast intrinsic response for it owns large amount of defects and lone pair electrons.

In recent studying, Liu *et al* [6-9] have studied the nonlinear properties of a series of amorphous chalcogenide films using the method of the femtosecond optical heterodyne detection of the optical Kerr effect (OHD-OKE) with high value of $\chi^{(3)}$ (about 10^{-12}) and fast response (less than 200 fs). The third-order nonlinear susceptibilities $\chi^{(3)}$ of some chalcogenide/chalcohalide and oxide bulk glasses were also investigated [10-12]. Wang et al [13] have obtained a high Kerr response time (faster than 120 fs) and large third-order nonlinearity 1.0×10^{-12} esu caused by high content of $GeS_{4/2}$ tetrahedra structure unites in the $90GeS_2$-$5Ga_2S_3$-5CdS glasses. Troles et al [14] have fabricated chalcogenide photonic crystal fibers for near- and mid-infrared applications because chalcogenide glasses presented larger third-order optical properties than that of silica glass at 1.55μm. The nonlinear optical properties of various glass systems have been studies. However, the effect of CdS in the GeS_2-Ga_2S_3-CdS glass system has not been researched. And this is an important aspect to recognize the relation between the structural properties and optical properties of glasses.

In this paper, GeS_2-Ga_2S_3-CdS glasses was prepared by the melting-quenching method, and the third-order nonlinearity with varied CdS content was investigated by Z-scan method to clarify its effect on $\chi^{(3)}$.

2. Experiments

All investigated samples were fabricated by well-established melt-quenching method from high purity Ge (5N), Ga (5N), S(5N) and CdS in an evacuated quartz ampoules (10^{-2} Pa). The raw materials were melt at 950℃ for 12h and then cooled in the ice-water mixture. $10\times10\times1$ mm_3 glass plates were obtained from the bulk glasses and then polished to optical quality on both sides.

This system of GeS_2-Ga_2S_3-CdS has a relatively narrow glass-forming region which is mainly located in the GeS_2-rich region [15], and glass compositions chosen for our measurements are shown in Table 1. The transition temperature Tg of these three compositions is around 415 K [15].

Table 1. Compositions of GeS_2-Ga_2S_3-CdS glasses.

Samples	CdS (mol %)	GeS_2 (mol %)	Ga_2S_3 (mol %)
ggc-1	5	76	19
ggc-2	10	72	18
ggc-3	15	68	17

The optical transmission properties were characterized by a spectrophotometer (Shimadzu UV-1601) in the visible and near-IR region. The measurements of third-order optical nonlinearities were performed using a femtosecond Z-scan system with open- and closed-aperture (Spitfire, Spectra Physics). The femtosecond pulses from the spitfire have an average power of 300mW at 800nm, the pulse duration of 140fs and the repetition rate of 1KHz. The laser beam was focused on the sample by a lens of 140mm focal length. Samples driven by the step motor were gradually moved along the propagation direction of the Gaussian beam under the control of a PC (along the z-axis). A detector monitored the transmitted laser power and the signals were recorded and analyzed by a computer.

Raman spectroscopy was measured by the InVia Laser Confocal Raman Spectrometer. An Ar^{3+} laser was used as the exciting source with wavelength 514.5nm and power was less than 2 mW. There was no visible damage and structure detectable change by Raman spectroscopy during the laser irradiations.

3. Results and discussions

The transmission spectra of samples ggc-1, ggc-2 and ggc-3 in the visible and near-IR region were represented in Fig.1 and obviously red shift was observed with more contents of CdS contained in the glasses, but ggc-2 with 10% CdS showed good transmittance.

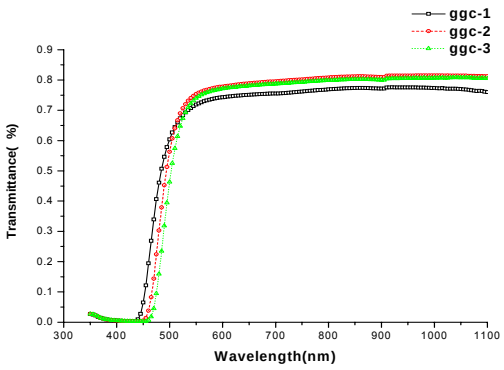

Fig. 1. The optical transmission spectra for the samples ggc-1 (black line and square), ggc-2(red line and circle) and ggc-3(green line and triangle).

With femtosecond Z-scan measurements, the closed- and open-aperture profiles for samples were shown in Figs.2, 3 and 4. Normalized transmittances with open-aperture Z-scan were displayed in Figs. 2(b), 3(b) and 4(b), and prefocal transmittance valleys followed by a postfocal transmittance maximum (peak) were observed, which indicated that the sample owned self-focusing properties and positive refractive nonlinearity [16], Using Z-scan method, the imaginary and real part of the third-order nonlinear susceptibility can be separated. The value of third-order nonlinear susceptibility can also be calculated by the following equation:

$$\chi^{(3)} = \sqrt{\left(\chi_{\mathrm{R}}^{(3)}\right)^2 + \left(\chi_{\mathrm{I}}^{(3)}\right)^2} \qquad (1)$$

where $\chi_{\mathrm{R}}^{(3)}$ and $\chi_{\mathrm{I}}^{(3)}$ refer to the real and imaginary part of third-order nonlinear susceptibility. The results and characteristics of samples by Z-scan measurement at 800nm were shown in Table 2.

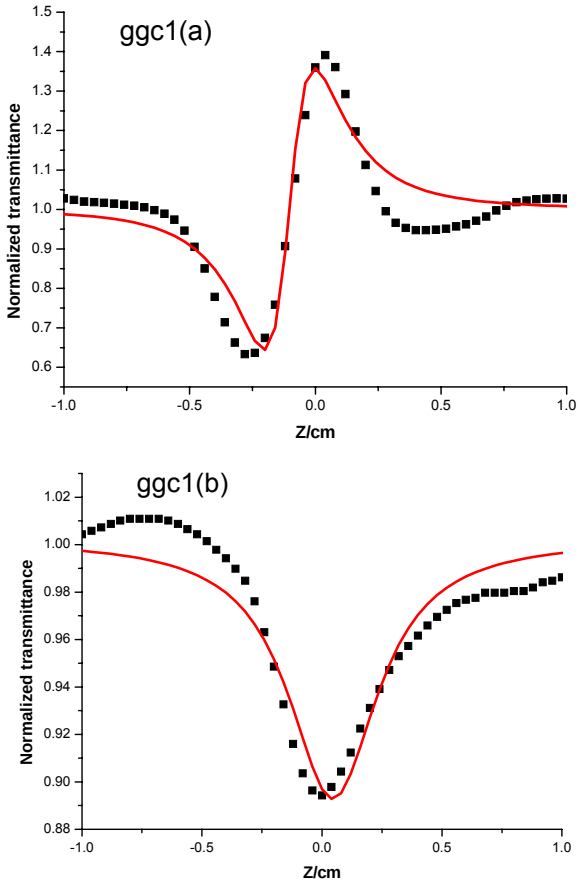

Fig. 2(a) The closed-aperture profile of ggc-1 (square) and its fit (red line).(b) The open-aperture profile of ggc-1 (square) and its fit (red line).

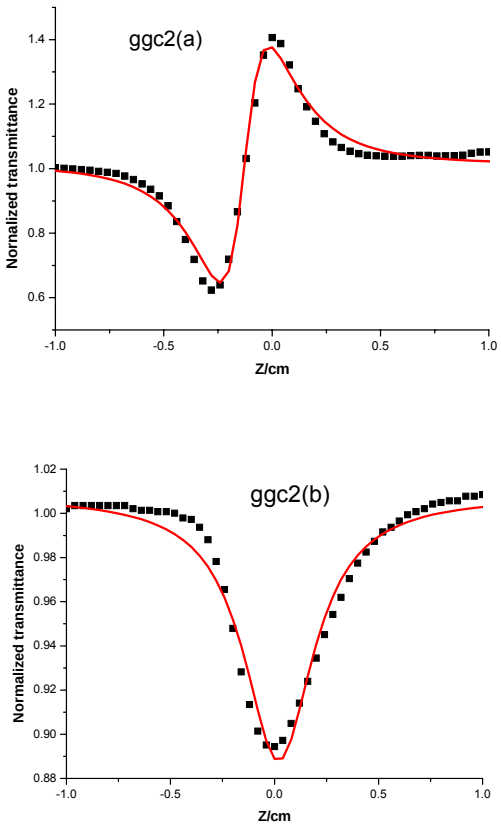

Fig. 3 (a) The closed-aperture profile of ggc-2 (square) and its fit (red line). (b) The open-aperture profile of ggc-2 (square) and its fit (red line).

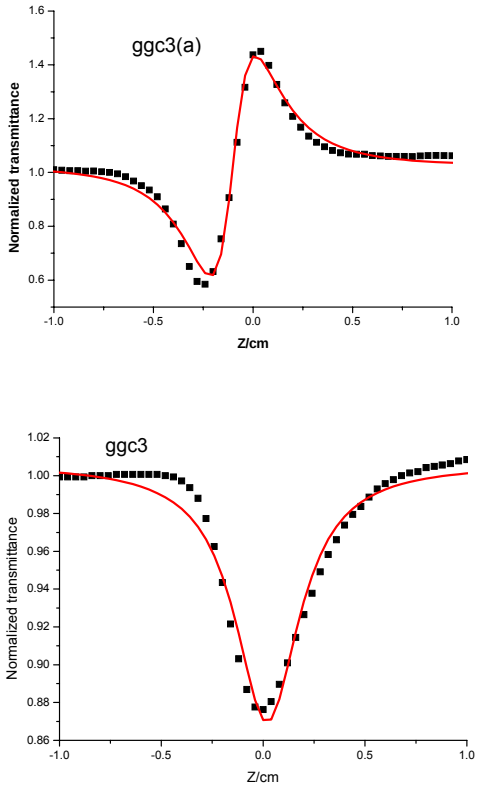

Fig. 4(a). The closed-aperture profile of ggc-3 (square) and its fit (red line). (b) The open-aperture profile of ggc-3 (square) and its fit (red line).

Table 2. The results and characteristics of samples by Z-scan measurement at 800nm.

Samples	$\chi_R^{(3)}$ (esu)	Characteristic	$\chi_I^{(3)}$ (esu)	$\chi^{(3)}$ (esu)
ggc1	4.60×10^{-13}	Self-focusing	6.56×10^{-14}	4.64×10^{-13}
ggc2	5.34×10^{-13}	Self-focusing	6.33×10^{-14}	5.38×10^{-13}
ggc3	5.89×10^{-13}	Self-focusing	7.03×10^{-13}	9.17×10^{-13}

Normally, optical nonlinear properties of glasses depend mainly on itself, such as nonlinear refractive index, multiple-photon absorption and so on. If we change the composition and structure of glasses, we can modify and control the optical nonlinearity of glasses. Fig. 5 showed the Raman spectra for ggc-1, ggc-2 and ggc-3 glasses with different CdS contents. In the GeS_2-Ga_2S_3-CdS system [17-19], the basic structure units are $GeS_{4/2}$ and $GaS_{4/2}$ tetrahedra. At the band 139cm^{-1}, there is a visible peak induced by symmetrical bending vibration of $GeS_{4/2}$ structure units. The high-frequency band at 341cm^{-1} shows the existence of symmetrical stretching vibration of Ge(Ga)$S_{4/2}$ tetrahedra. The shoulder observed at 372 cm^{-1} is a companion band of Ge(Ga)$S_{4/2}$ tetrahedra. Moreover, the band at 431cm^{-1} is due to the vibration of two corner-shared tetrahedral. The band at 250cm^{-1} will be discussed in the following sections.

When CdS content in glasses increased, some obvious vibrations were observed from Fig. 5. The amplitudes of the bands situated at 139cm^{-1}, 341cm^{-1}, 372cm^{-1} and 432cm^{-1} decreased with the increase of CdS content, which was related to the more addition of CdS in the samples and the less content of Ge and Ga contained which induced less number of $GeS_{4/2}$ and $GaS_{4/2}$ tetrahedra

formation. Cd plays a modifier role in the glass to break the tetrahedral structure unites (edge-shared and corner-shared) and also a charge–compensating role for non-briging sulfurs [16]. It has been reported that the Raman shift of 210~240cm^{-1} was described to the vibration of Cd-S band in the GeS_2-$Ga2S_3$-CdS system [16-18]. On the contrary, from Fig.5, at 240~250cm^{-1}, the amplitudes of these bands increased with the increase of CdS content. It is speculated that these bands were also associated with the vibration of Cd-S, not with the formation of ethane-like $S_3Ge(Ga)$-$(Ga)GeS_3$. If the latter was the origin of these bands, the amplitudes would decrease with the more CdS content because small amount of Cd in the glasses should decrease the number of metal-metal bonds [16].

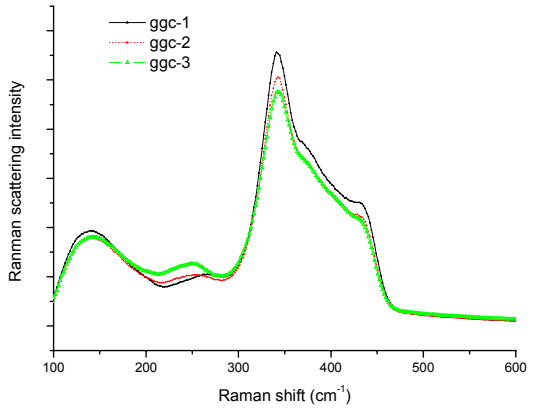

Fig. 5. The Raman spectra for the samples ggc-1(black line), ggc-2(red dot) and ggc-3(green triangle)

Therefore, the increased amplitudes indicated that the vibration of Cd-S caused these bands around 250 cm^{-1} in Fig. 5. The original reason of Raman shift vibration, as we proposed that we fabricated GeS_2-$Ga2S_3$-CdS glasses by the conventional melt-quenching method, it still existed some internal stress after annealing. The glasses were still in a metastable state. After we have placed the samples under the normal condition (room temperature) for a long period, they preferred to become stable and the internal stress disappeared gradually, which induced the structural change. As in the GeS_2-Ga_2S3-CdS glass system, $GeS_{4/2}$ and $GaS_{4/2}$ tetrahedra plays the role of network and network intermediate, respectively. They were relatively more stable and rarely influenced by the change of internal stress, which gave rise to the vibrations of Cd-S Raman Shift while the other Raman Shifts showed no vibrations.

The intrinsic $GeS_{4/2}$ tetrahedra structure units which possessed high hyperpolarizability had great influences on the enhancement of third-order optical nonlinearity[13], while the largest third-order susceptibility can be observed in the sample ggc-1. But in the ggc-3 sample which contained more CdS to break the tetrahedral (edge-shared and corner-shared) and the least number of structure unites $GeS_{4/2}$ and $GaS_{4/2}$ tetrahedra, the largest third-order susceptibility $\chi^{(3)}$ was obtained. As the irradiation power of femtosecond laser varied, neither saturation nor low time response appeared. The results of measurements can be reproduced. These results indicated that the thermal contribution could be neglected under the used scanning power intensity. With the increase of CdS, more non-briging sulfurs contained in tetrahedra of glasses appeared. Due to the existence of S^{2-} anions with lone electron pairs in the GeS_2-Ga_2S3-CdS glass, in case of light illumination, electrons would lie at the top of the valence band and hence were preferentially excited by laser illumination to induce structure change. Besides, inner core electrons could be excited and Auger process could be induced. In this situation, a change in local structural was easy to occur[20]. The degree of structure's symmetry and stability of glasses were declined when the polarities of bonds were enhanced. These results indicated that ultrafast optical nonlinearities in our investigated glasses were mainly originated from the electron polarization. Electron clouds of atoms in glasses with more CdS content, when accompanied by the interaction of femtosecond laser illumination, would become more distorted, so the largest value of $\chi^{(3)}$ as 9.17×10^{-13} esu was obtained in the ggc-3 sample, which indicated that the existence of $GeS_{4/2}$ tetrahedra structure unites was not the only one effective factor on the third-order optical nonlinearity, but also the quality of CdS when the third-order nonlinearity was mainly caused by the electron contribution.

Normally, the nonlinear absorption in materials arises from multiple-photon absorption, two-photon absorption, or dynamic free-carrier absorption. In the measurements of Z-scan, the magnitude of laser repetition rate was femtosecond scale which was less than the time for free-carrier coupling again. Therefore, the most reasons of nonlinear absorption for these samples are two-photon or multiple-photon absorption, and the thermal effect caused by nonlinear absorption could be neglected in our experiments.

4. Conclusions

Chalcogenide GeS_2-Ga_2S3-CdS glasses were fabricated by the conventional melt-quenching method. Comparing the$\chi^{(3)}$ of our performed samples by Z-scan measurements, we deduced that the quality of CdS was also an important factor to influence the value of $\chi^{(3)}$. More CdS contained in the glass will induce larger, which was related to that the addition of Cd caused the appearance of non-briging sulfurs, so the polarity of bonds in glasses were enhanced which led serious distortion of electron clouds of atoms to induce larger $\chi^{(3)}$. In our performed experiments, the largest third-order nonlinear susceptibility of the glass containing 15% CdS (in mol) was obtained as 9.17×10^{-13} esu with good optical

transmittance. Further investigation on optimizing the glass composition will induce larger $\chi^{(3)}$.

Acknowledgements

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