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Structure dependence of ultrafast third-order optical nonlinearity for Ge–Ga–Cd sulfide glasses*

Wang Zhen-Wei(王振伟)[a], Wang Xue-Feng(王学锋)[b], Liu Chun-Ling(刘春玲)[a]†, Zhao Xiu-Jian(赵修建)[b], Xiang Hong(向 红)[a], Yu Jia-Guo(余家国)[c], Gong Qi-Huang(龚旗煌)[a]‡, and Gu Shao-Xuan(顾少轩)[b]

[a] *Department of Physics & State Key Laboratory for Mesoscopic Physics, Peking University, Beijing* 100871, *China*
[b] *Key Laboratory for Silicate Materials Science and Engineering (Wuhan University of Technology), Ministry of Education, Wuhan* 430070, *China*
[c] *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan* 430070, *China*

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Ultrafast third-order nonlinear optical responses of GeS_2–Ga_2S_3–CdS glasses have been measured by using femtosecond time-resolved optical Kerr effect (OKE) technique at the wavelengths of 820nm and 640nm respectively. The experimental results show that GeS_2–Ga_2S_3–CdS glasses have large femtosecond third-order optical nonlinear responses and their OKE signals vary considerably with the composition. The relationship of structure-property is discussed by means of Raman spectroscopy analysis, suggesting that the tetrahedron unit [GeS_4] or [GaS_4] plays an important role in the ultrafast third-order nonlinear optical response. In addition, the experimental results also reveal that the ultrafast third-order optical nonlinearity of these glasses does not obey the Miller rule.

Keywords: third-order optical nonlinearity, ultrafast spectroscopy, chalcogenide glasses
PACC: 4265, 4280W, 7865M

1. Introduction

The study of third-order nonlinear optical materials remains an interesting subject because of their potential applications in all-optical processing functional devices. Besides organic[1] and semiconductor[2] materials, glasses[3−10] seem to be preferable for optical devices due to their ease of fabrication, high transparency in a communication wave band, high chemical and thermal stability. According to the semiempirical Miller rule,[11] the third-order nonlinear optical susceptibility, $\chi^{(3)}$ can be enhanced with the increase of the refractive index n. As heavy-metal ions play an important role in enhancing the refractive indices of glasses, the third-order nonlinear optical responses of oxide glasses containing heavy-metal such as Bi, Pb, Tl, Nb, Ti have been widely investigated.[3−5] Recently, chalcogenide glasses[6−10] have been also reported to have large $\chi^{(3)}$ because of their high refractive indices.

Besides large $\chi^{(3)}$, an ultrafast response time is another necessary factor for a candidate of nonlinear optical materials. However, only a few reports on the ultrafast third-order optical nonlinearity of glasses can be found in the literature. Sugimoto *et al*[5,12] reported that oxide glasses containing Bi_2O_3 exhibited an ultrafast Kerr signal as large as that of the reference CS_2 at a wavelength of 810nm with a response time being less than 150fs. Yu *et al*[13] measured the ultrafast Kerr signal of a Pb–Bi–Ga oxide glass at a wavelength of 800nm, which was 2.3 times larger than that of the reference CS_2 with a response time being less than 350fs. In this paper, a series of Ge–Ga–Cd sulfide glasses is prepared and their ultrafast third-order nonlinear optical responses are measured by using the femtosecond time-resolved optical Kerr effect

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†E-mail address: clliu@pku.edu.cn;
‡E-mail address: qhgong@pku.edu.cn

(OKE) technique at the wavelengths of 820nm and 640nm respectively. These GeS_2–Ga_2S_3–CdS glasses have large femtosecond third-order nonlinear optical responses and $\chi^{(3)}$ can be about ten times larger than that of CS_2. The detailed structure-property relationship is discussed by means of Raman spectroscopy analysis. The tetrahedron unit $[GeS_4]$ or $[GaS_4]$ is found to play an important role in the ultrafast third-order optical response. Our experimental results also show that the ultrafast third-order optical nonlinearity of these sulfide glasses does not obey the Miller rule.

2. Experiments

2.1. Materials

The samples are listed in Table 1, which were prepared by use of the conventional melt-quenching technique from high-purity elements (Ge, Ga, S, all of 5 N-purity) and reagent-grade CdS (4 N purity). The batches were transferred to fused silica ampoules, which were sealed after having been evacuated, and then melted at 970°C for at least 12hrs in a rocking furnace. The melts were quenched to room temperature in water and then annealed near their glass transition temperatures. The annealed glass rods were cut and then polished to 0.6–0.8mm thickness with 0.05μm alumina aqueous suspensions. More details of the preparation and characterizations have been reported elsewhere.[14–16]

Table 1. Compositions and physical properties of GeS_2–Ga_2S_3 binary and GeS_2–Ga_2S_3–CdS ternary sulfide glasses.

Composition/(in mol%)	ρ/(g/cm^3)	n (at 633nm)	Absorption-edge/nm	OKE* at 820nm (640nm)
Binary (100-x)GeS_2–$x$$Ga_2S_3$ glasses				
x=10	2.78	2.15	484	15 (10)
x=15	2.82	2.18	488	9 (8)
x=30	2.92	2.25	492	3 (1)
Ternary 70GeS_2–(30-x)Ga_2S_3–xCdS glasses				
x=10	3.02	2.20	486	6 (4)
x=15	3.06	2.17	480	1 (1.5)
x=20	3.10	2.14	472	0.5 (1)
Other $x$$GeS_2$–$y$$Ga_2S_3$–$z$CdS glasses				
x=100; y= 0; z=0	2.68	2.01	446	4 (2)
x=90; y= 5; z=5	2.83	2.12	460	22 (11)

*OKE represents the ratio of Kerr signal intensity of glasses samples to that of CS_2, i.e. I_S/I_R

2.2. Absorption and Raman spectroscopy

Absorption spectra were recorded with an Agilent 8453 UV–Vis photodiode array spectrophotometer. Raman spectra were measured at room temperature using a back-scattering geometry with a solid-state laser (λ=532nm) as an excitation source. The scattered light was dispersed through a Jobin Yvon HRD1 monochromator and detected by a TE-cooled charge-coupled-device (CCD).

2.3. Third-order nonlinear optical response measurements

The third-order nonlinear optical response measurement was performed using a femtosecond time-resolved OKE technique.[17,18] The light source was a Ti:Sapphire laser (Mira 900F, Coherent, USA) or a dye laser (Satori, Coherent, USA) synchronously pumped by a CW mode-locked Nd:YAG laser (Antares, Coherent, USA). Both systems were operated at 76MHz and the wavelength was centred at 820nm or 640nm with the pulse duration of 120fs or 160fs respectively. The gating pump power at the samples was set to be 76mW at 820nm or 15mW at 640nm. And nonlinear absorption could be neglected because the transmission was in the linear region under such powers. The value of $\chi^{(3)}$ can be calculated from the following equation:[19]

$$\chi_S^{(3)} = \chi_R^{(3)} \cdot \left(\frac{I_S}{I_R}\right)^{1/2} \cdot \left(\frac{n_S}{n_R}\right)^2,$$

where the subscripts S and R represent the samples and the reference CS_2 respectively, I is the OKE signal intensity and n is the refractive index. $\chi_R^{(3)}$ of the reference CS_2 is taken to be 1×10^{-13} esu.[20]

3. Results and discussion

The absorption spectra of all samples are very similar to each other except for minor shifts of the absorption edge, which correspond to the difference of the band gaps given in Table 1. At a wavelength of 820nm or 640nm, the samples are all transparent. Taking the glass with the composition of $90GeS_2$–$5Ga_2S_3$–5CdS as an example, the experimental result is shown in Fig.1.

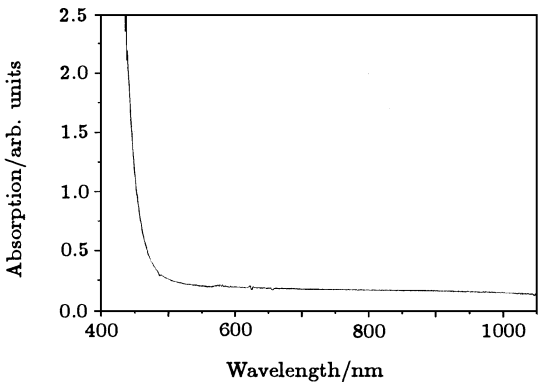


Fig.1. Absorption spectrum of the glass with the composition of $90GeS_2$–$5Ga_2S_3$–5CdS.

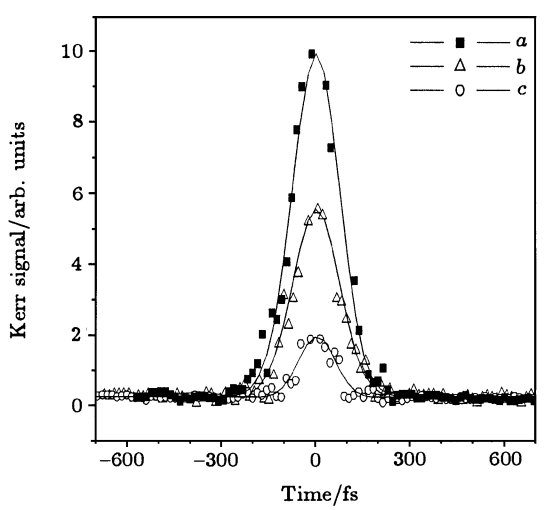


Fig.2. Kerr signals of the binary (100-x)GeS_2–xGa_2S_3 glasses at a wavelength of 820 nm. curve a: x=10; curve b: x=15; curve c: x=30.

Figure 2 shows the third-order nonlinear optical response of the binary (100-x)GeS_2–xGa_2S_3 (x=10,15,30) glasses at a wavelength of 820nm. The profiles of all the OKE signals are symmetrical with respect to the zero-delay time and the width of the signals is 150fs, which indicates that the third-order nonlinear optical responses of the Ge–Ga–Cd sulfide glasses are on the order of hundred femtosecond. The third-order nonlinear optical responses of the rest samples are also instantaneous and symmetrical. The values of I_S/I_R at 820nm and 640nm are listed in the last column of Table 1, which represent the ratio of the Kerr signal of the samples to that of the reference CS_2.

For the glass materials, the ultrafast third-order nonlinear optical responses originate from the distortion of electron cloud or the motion of nuclei. The former has a response time less than 10fs and the latter has a relaxation time lying between 100fs and 10ps.[21] Kang *et al*[22] have investigated the nuclear optical nonlinear contribution of a Ge-Ga sulfide glass using Z-scan technique with a 35fs laser and revealed that a damped ultrafast oscillatory response with a period of 98fs originated from the ν_1 breathing Raman mode of the tetrahedral [GeS_4]. In our experiment, the pulse duration is 120fs or 160fs and the nuclear optical nonlinear contributions can not be resolved. However, the nuclear optical nonlinear contribution is much smaller than the electronic part.[21,22] Therefore, it can be deduced that the third-order nonlinear responses of the Ge–Ga–Cd sulfide glasses are produced dominantly by the electronic contribution.

The basic structure units of GeS_2 glasses are tetrahedral [GeS_4], which are connected with each other through a bridging sulfur to form a three-dimensional network.[23] Four vibration modes of XY_4 tetrahedral unit give rise to four bands (ν_1, ν_2, ν_3, ν_4) in the Raman spectra. The separated bands by Lorentz fit to the Raman spectra of GeS_2 are shown in Fig.3. The bands of 342cm^{-1}, 110cm^{-1} and 150cm^{-1} are associated with the Raman vibration modes of ν_1, ν_2 and ν_4, respectively (the band associated with the mode of ν_3 is too weak to be seen). In addition, the bands of 430cm^{-1} and 370cm^{-1} are associated with the vibrations of corner-shared and edge-shared tetrahedral units respectively.[23]

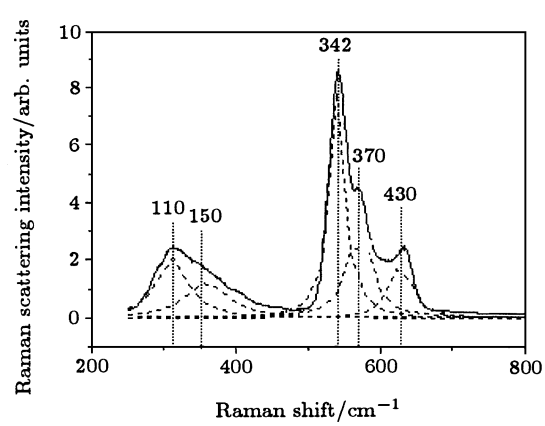


Fig.3. Separated bands by Lorentz fit to the Raman spectra of GeS_2 glass.

The Raman spectra of the (100-x)GeS_2–xGa_2S_3 (x=0, 10, 15, 30) glasses system are shown in Fig.4. The vibration strength at 263cm^{-1} increases with the addition of Ga_2S_3, which is associated with the metal–metal bonds. The sulfur deficiency is an important feature in the GeS_2–Ga_2S_3 glasses system because of the formation of [GaS_4] tetrahedral units from Ga_2S_3 with a S/Ga ratio being less than 2, then the emergence of the metal–metal bond $S_3Ge(Ga)$-(Ga)GeS_3 can compensate for the shortage of sulfur in the GeS_2–Ga_2S_3 network.[23]

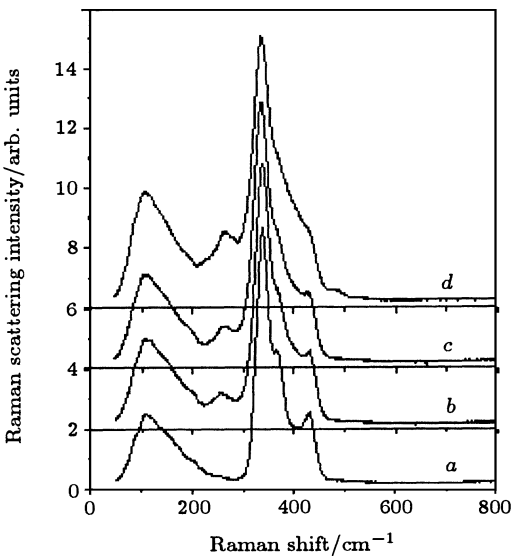


Fig.4. Raman spectra of the binary (100-x)GeS_2–xGa_2S_3 glasses. curve *a*: x=0; curve *b*: x=10; curve *c*: x=15; curve *d*: x=30.

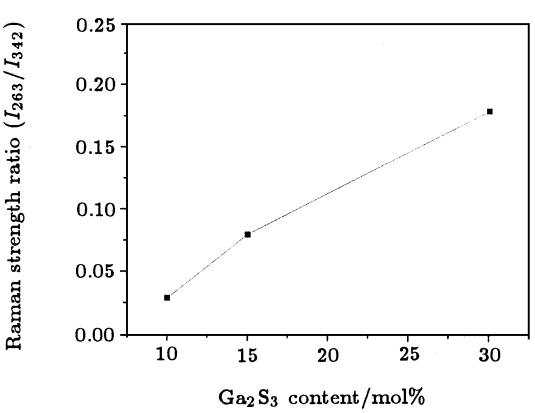


Fig.5. Ratio of Raman strength of the 263cm^{-1} band to that of the 342 cm^{-1} band for binary GeS_2–Ga_2S_3 glasses .

Figure 5 shows the ratio of Raman strength of the 263cm^{-1} band to that of the 342cm^{-1} band increases with Ga_2S_3. The corresponding Kerr signal becomes weaker when the number of metal–metal bonds in the glass network becomes larger. Because the formation of metal–metal bonds is at the expense of breaking the tetrahedral units, it is revealed that the [GeS_4] or [GaS_4] tetrahedral units play an important role in the ultrafast third-order nonlinear optical responses of these sulfide glasses. It means that the covalence bonds of S–Ge or S–Ga make much larger contribution to the ultrafast third-order optical nonlinearity than the metal–metal bonds. So the ultrafast third-order nonlinear optical responses mainly originate from the virtual electronic transition between the conduction and valence bands formed by the bonding and antibonding orbits of S–Ge or S–Ga.

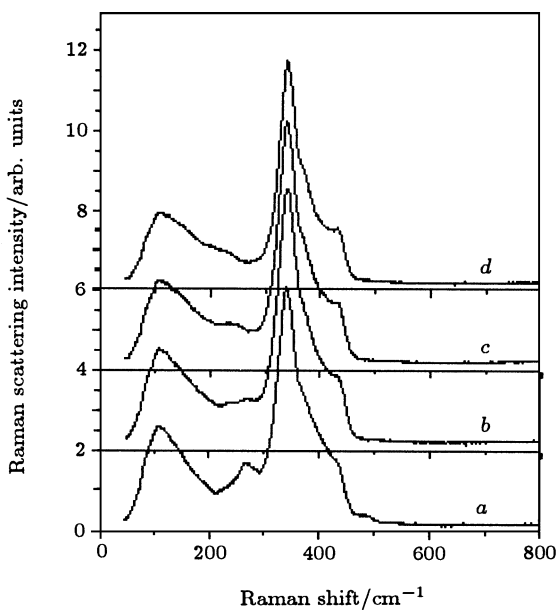


Fig.6. Raman spectra of ternary 70GeS_2–(30-x) Ga_2S_3–xCdS glasses. curve *a*: x=0; curve *b*: x=10; curve *c*: x=15; curve *d*: x=20.

The Raman spectra of the 70GeS_2–(30-x)Ga_2S_3–xCdS (x=0, 10, 15, 20) glasses are shown in Fig.6. Because sulfur carried by CdS can compensate for the shortage of sulfur and break metal–metal bonds $S_3Ge(Ga)$–(Ga)GeS_3 to form [GeS_4] ([GaS_4]) tetrahedrons, it is noted that the 263cm^{-1} band becomes weaker and almost disappears for 70GeS_2–20Ga_2S_3–10CdS. For third-order nonlinear optical measurements, the Kerr signal of the 70GeS_2–20Ga_2S_3–10CdS is much stronger than that of the 70GeS_2–30Ga_2S_3, which demonstrates that the ultrafast third-order optical nonlinear response is produced dominantly by the tetrahedral units of glass network. However, as shown in curves *c* and *d* of Figs.6, when the molar concentration of CdS is larger than 15%, a new band at about 230cm^{-1} emerges, which originates from the vibrations of Cd–S ionic bonds.[16,23,24] The Kerr signal of

the glass with x=15 or 20 becomes much weaker than that with x=10, which is ascribed to the decrease of the tetrahedral units. In addition, it suggests that the ionic bonds Cd–S make no considerable contribution to the ultrafast third-order optical nonlinearity.

According to the above analysis, it can be deduced that for Ge–Ga–Cd sulfide glasses, reducing the quantity of metal–metal bonds and increasing the formation of tetrahedral units can effectively enhance their ultrafast third-order nonlinear optical responses. So it is reasonable that the $90GeS_2$–$5Ga_2S_3$–5CdS glass has the largest OKE signal in this Ge–Ga–Cd sulfide glasses system.[25] According to Eq.(1), the value of $\chi^{(3)}$ for the $90GeS_2$–$5Ga_2S_3$–5CdS glass is obtained to be about 10^{-12} esu at 820nm. Compared with the reported heavy–metal oxide glasses,[4,12,13,26] the Ge–Ga–Cd sulfide glasses exhibit large ultrafast third-order nonlinear optical response.

It should be mentioned that the femtosecond time resolved third-order optical nonlinear responses of the glasses are not in accordance with the Miller rule, which is essentially due to the fact that the responses originate mainly from the instantaneous electronic contribution. In addition, with the gating power being higher than 300mw at 820nm, the Kerr signal intensity is increased with irradiation up to more than ten times, which may be attributed to the photo-induced localized change in structure[27] because of multiple photon absorption. This interesting photo-induced enhancement effect will be reported elsewhere.

4. Summary

The ultrafast third-order nonlinear responses of Ge–Ga–Cd sulfide glasses have been investigated by using femtosecond OKE technique. The experimental results show that Ge–Ga–Cd sulfide glasses have large ultrafast third-order nonlinear optical responses. By the analysis of Raman spectrum, it is suggested that the covalence bonds of S–Ge or S–Ga constituting the tetrahedral units $[GeS_4]$ or $[GaS_4]$, respectively, play an important role in the ultrafast third-order nonlinear optical responses of these sulfide glasses. In addition, the third-order ultrafast nonlinear optical responses do not obey the Miller rule.

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