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RAMAN INVESTIGATION OF STRUCTURAL PHOTOINDUCED IRREVERSIBLE CHANGES OF $Ga_{10}Ge_{25}S_{65}$ CHALCOGENIDE GLASSES

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The influence of time exposure, when exposed to above band gap light (3,52 eV) and annealing, on $Ga_{10}Ge_{25}S_{65}$ glasses has been studied through their effects on the structure and optical properties. To evaluate the photostructural change infrared and Raman spectra for bulk $Ga_{10}Ge_{25}S_{65}$ glasses have been measured before and after exposure. The Raman spectra are interpreted in terms of models in which the Ge atoms are fourfold coordinated and the S atoms are two fold coordinated. The observed changes in the spectral region of (S-S) stretching vibration (470-490 cm $^{-1}$) is a direct evidence for the occurrence of important structural changes in local bonding configuration caused by optical irradiation. It is shown that the dominant photostrucural changes are chain formation tendency of the chalcogenide atoms under the laser irradiation rather than rings.

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Keywords: Chalcogenide, Photoexpansion, Raman spectra, GaGeS bulk glass

1. Introduction

Photoinduced changes of amorphous chalcogenide glasses have been the subject of extensive study from the point of view of both technological applications and also understanding of the nature of the phenomena [1-3]. These glasses, when illuminated by band-gap light, usually exhibit a blue or a red shift of the optical gap, namely photobleaching or photodarkening, respectively. Furthermore, such photoinduced changes can be in general irreversible, i.e., the changes are permanent after irradiation, or reversible in which case the changes can be removed by annealing to the glass transition temperature, T_g.

A number of different phenomenological models have been suggested to explain these experimental results as part of efforts to determine and understand the structures of chalcogenide glass networks [4-6]. In stoichiometric As_2S_3 glasses for example, where one expects just As-S bonds [7], it was concluded from Raman scattering studies that a number of the so-called "wrong" As-As bonds was created with light exposure. In our previous investigation of photoinduced changes in GaGeS glass [8] we have reported a UV induced photobleaching effect associated with a positive volume change (photoexpansion). Nevertheless, many photoinduced effects are still not understood and new photoinduced phenomena, such as photoinduced anisotropy, gyrotropy, etc. have emerged [9-12]. Behind all this effort is the need to describe and understand the physical and chemical properties of amorphous chalcogenides and their interaction with light.

As a part of the efforts to understand the structure of chalcogenide glasses network as well the structural change which can occur after illumination, Raman scattering continues to provide useful insights into the local structures of the vitreous state. The Raman spectra of GeS glasses have been discussed in terms of structural model in which the element of local order is a tetrahedral arrangement of S atoms about a central Ge atom, i.e., a GeS_4 tetrahedron. We used Raman scattering to determine as far as possible the structural change which can occur in this glass after illumination. We have observed diffusion of S atoms towards the illuminated area [8] and in this work we present more results on the characterization of the species so formed.

2. Experimental

Polycrystalline germanium, gallium and sulfur were weighted, mixed together and transferred to a silica ampoule. After vacuum sealing, a heat process with a heating rate 0.33 K/min up to 950° C was started. At 950° C the liquid was homogenized for 6 hours through a continuous horizontal rotation. Then the ampoule was withdrawn from the furnace and air-cooled. Annealing at 400° C for several hours followed.

These samples were illuminated at different exposure times (1 to 6 hours) with light from a cw Kr^+ ion laser (351 nm). The output power density of the laser was 5 W/cm^2.

The optical absorption edge was determined using a spectrophotometer (Cary 5). For this experiment, samples of 1 mm in thickness were measured in transmission in the wavelength range from 200 to 700 nm.

The morphology and composition were measured before and after exposure to U.V. light. Exposed and non-exposed surface areas were analyzed using a scanning electron microscope (SEM) (Zeiss 960) to which an Energy Dispersive X-Ray (EDX) analyzer (QX2000) is coupled. Compositional contrast of the exposed and non-exposed areas was determined by backscattered electrons (BSE).

The Raman scattering measurements were preformed with the normal back scattering configuration in the wavenumber region from 200 to 800 cm^{-1}. The 488 nm line of an Ar^+ ion laser was used as a light source.

3. Results

Fig. 1 shows a plot of absorption coefficient (α) against photon energy ($h\nu$) which illustrate the shift of the edges for $Ge_{25}Ga_{10}S_{65}$ exposed at to the UV light for different times. The optical absorption measurements reveal that the absorption edge of the glass sample shifted to shorter wavelengths after irradiation indicating a photobleaching effect. Nevertheless there is a significant difference between the shift of the edge for samples exposed and annealed at glass transition temperature (T_g). A photodarkening effect is observed in the last case. Unlike to exposure, it is observed that the annealing leads to darkening. We observed that E_g increases from E_g= 2.63 eV for non-exposed glass, to E_g =2.64 eV for exposure during 10 hours and E_g decreases to E_g= 2.55 eV for annealing at T_g.

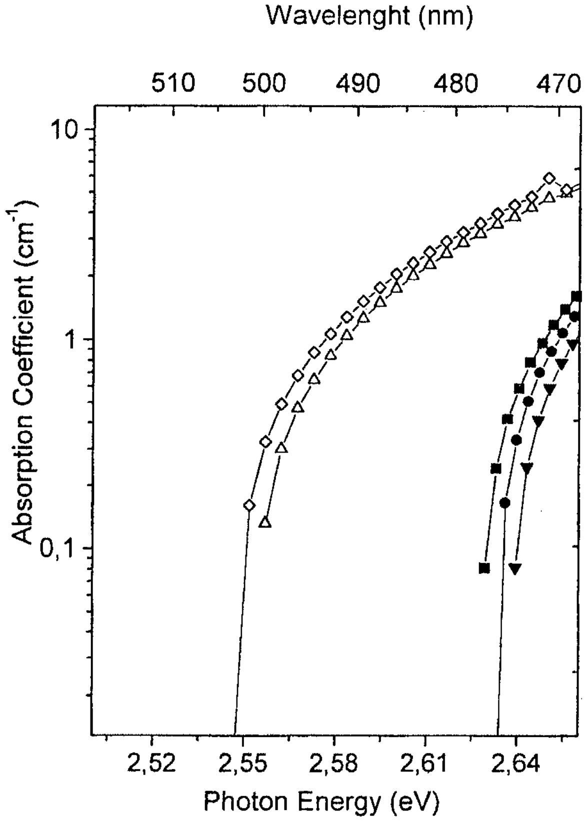

Fig. 1. Optical absorption spectra for $Ga_{10}Ge_{25}S_{65}$ exposed at different time: (■) non-exposed, (●) exposed 5 hours, (▲) exposed 10 hours, (□) exposed 5 hours and annealing at Tg, (◇) exposed 10 hours and annealing at Tg. Lines are drawn as guides for the eyes.

Fig. 2 shows morphological analyses of the exposed area by backscattering electrons (BSE). Local analysis of the glass surface area by backscattering electrons (BSE) images distinguishes two regions: a brighter area (non–exposed to UV light) and a darker area corresponding to the S-rich element (photoexpanded and photobleached).

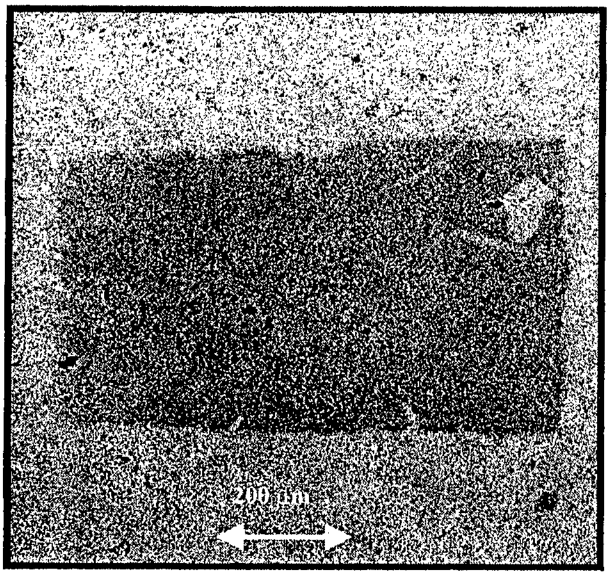

Fig. 2. Back scattering electron (BSE) of the irradiated surface area of the $Ga_{10}Ge_{25}S_{65}$, reveals a change in the glass composition, the brighter region representing non-exposed and the darker region is the photoexpanded and photobleached area.

As the image of (BSE) is built in contrast caused by element difference, the higher the atomic number, the more likely it is that backscattering will occur. Thus, as the electron beam passes to region of larger Z (atomic number), the signal due to backscattering, and consequently the image brightness increases. The gray levels, observed in Fig. 2, can be interpreted as regions of different composition with decreasing average atomic number corresponding to the decreasing brightness.

Irradiated samples (exposure time 2 hours, power density 5 W/cm^2) with 800 nm on thickness of the expanded area, have been treated at different temperature from room temperature to the glass crystallization temperature (T_g=470 °C). Fig. 3 shows a set of photographs of the samples at different temperatures.

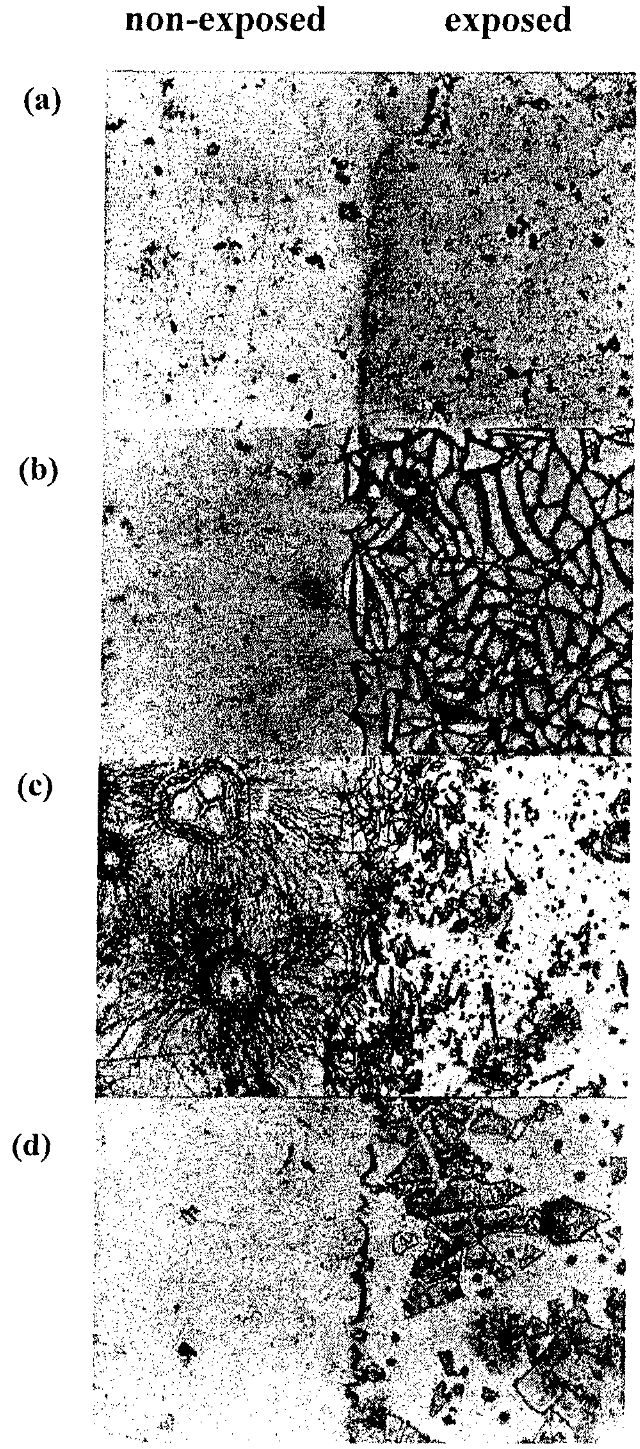

Fig. 3. Photographs of a evolution of the glass surface exposed at 5 W/cm^2 during 2 hours (right side) and non - exposed (left side) heat treated at different temperatures: (a) room temperature, (b) 420 °C, (c) 450 °C and (d) 470 °C.

When temperature reaches 420°C cracking of the glass surface is observed. Initial crystallization at the glass surface is noted at temperature around 450 °C and completed at 470 °C.

Fig. 4 presents Raman spectra performed in the spectrum 200-800 cm^{-1} range for the glass $Ga_{10}Ge_{25}S_{65}$ (a-GaGeS). Four bands at 273, 340, 430 and 475 cm^{-1} are observed. The Raman spectra obtained for crystalline sulfur (c-S) and GeS_2 (c-GeS_2) are also shown for comparison. Good agreement with spectra of GeS_2 crystal reported earlier by other research groups [13,14].

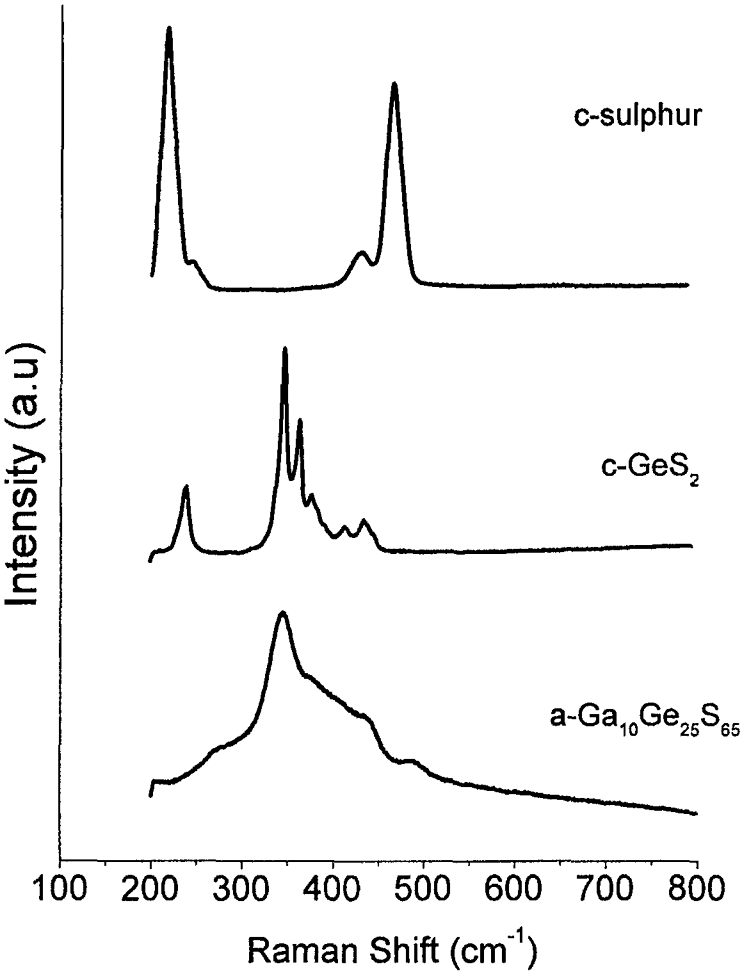

Fig. 4. Raman scattering spectra for Ga $_{10}Ge_{25}S_{65}$, c-GeS_2 and c-S taken with a 633 nm excitation energy at room temperature.

The first band at 273 cm^{-1} may be assigned to sulfur rings. The strong band at 340 cm^{-1} is due to a heteropolar bond, in this alloy system a Ge-S vibration assigned to bond-bending modes and the A_1-type bond-stretching mode of $GeS_{4/2}$ tetrahedra [13,14,15]. The band at 430 cm^{-1} is currently regarded following two ideas: one is to assign the band to vibrational modes of edge-sharing bi-tetrahedra, $Ge_2S_{2+4/2}$. This structure is known to exist in c-GeS_2, and its existence has also been demonstrated in a glassy phase [13] . On the other hand, some researchers have assigned the 430 cm^{-1} band to the S-S stretching mode, coming from cluster edges dimmers [16]. The band at 475 cm^{-1} is assigned to S_8 molecules [17].

Raman spectra of the samples irradiated for different times are presented in Fig. 5.

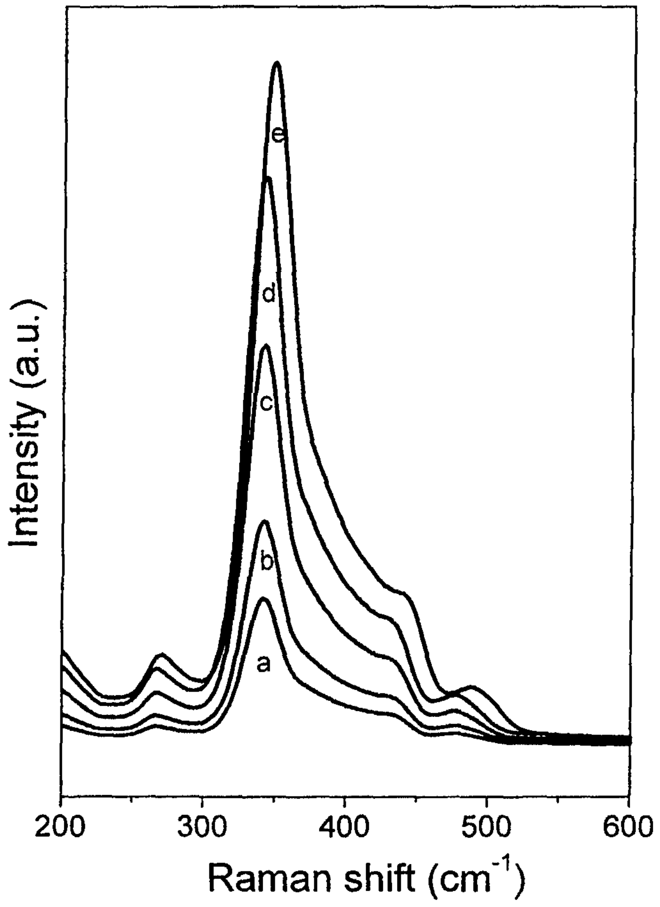

Fig. 5. Raman scattering spectra for $Ga_{10}Ge_{25}S_{65}$ illuminates at 5 W/cm^2 for different time exposure at room temperature. (a) non-exposed, (b) 1 hours, (c) 2 hours, (d) 4 hours and (e) 6 hours.

Finally the irreversible photobleaching of amorphous GaGeS glasses can be associated with a (i) an increase of the density of heteropolar bonds and (ii) increase of sulfur into the illuminated area of the Ge-S matrix surface.

5. Discussion

A large photobleaching effect is observed on samples exposed at different time using lower power density (I=5 W/cm^2). From Fig. 1, we may note the increase of the photobeaching with increase of time exposure and this process is irreversible, in the sense that annealing does not restore the original E_g to the initial value for non-exposed glass. It is known [18] that the absorption edge of an amorphous semiconductors shifts to lower energy if it contains mores defects. We think that the annealing at T_g could induce some defects through the weakens bond.

The present photobleaching effect differs from the one observed for As_2S_3 [19]. The Fig. 2 indicate a diffusion of sulphur atom into irradiated area. Consequently, we may assume that this diffusion will result in the creation of new S-S bonds in the irradiated area. Such polimerization may explains the effect of photobleaching which acompanies a glass network expasion in GaGeS glass.

With regards to the Raman spectra of the samples irradiated for different times (Fig. 5) an increase in intensity is observed for the whole spectrum. Moreover a blue shift is observed as the exposure time increases from 1 to 6 hours indicating that through the absorption of high energy photons, intramolecular covalents bonds are broken. The most obvious difference compared with non-exposed glassc is the dramatic shift of the band at 475 to 490 cm^{-1}. It is known that in S-rich composition there are additional absorption lines at 475 and 273 cm^{-1} correlated these with two of the three dominant absorption bands of S_8 molecules. According to the structural model of binary Ge-S glasses proposed by Lucovsky et al [17] glasses with S contents in excess of stoiciometry contain increasing number of S-S bond and ultimatly, at the largest level of S_8 rings. As a first assumption the photoexpansion of these glasses results from a microstructural transformation with the formation of new sulfide chains which may be confirmed by the shift bound from 470 to 490 cm^{-1}. G.J. Janz et al. have assigned the shift to higher frequency (from 400 to 490 cm^{-1}) to a diminution in the size of polysulfides anions from S_6 to S_3 [20]. At this stage, the dissociation of a S_8 ring molecule into smaller chains can be proposed from the spectroscopic observation. Messaddeq et al. [8] observed that following the absorption of light, the sulfur atoms difuses to the irradiated area from the non irradiated surrounding. This motion will result in the creation of new S-S bonds in the irradiated area. The same behaviour has been observed in cryobaric Raman scattering experiment on g-GeS_2 [21]. The appearence of 486 and 250 cm^{-1} modes are signature of S-rich (S_8 or S^n chains) and Ge- rich (GeS microphase). These results provide additional support for our identification of broken bonds after ilumination.

As we have observed from Fig. 1, the annealing leads to a darkening and cracking of the glass surface (Fig. 3). The tendency toward formation of crack verified for samples heat treat could result from the higher intensity of the internal stresses associated with photoexpansion. Due the stiffness of the glass surface, the shrinkage must occur only in the perpendicular direction of the surface and the photoexpanded area is constrained by the bulk glass. As a consequence, the average stress at photoexpanded area-bulk glass interface is proportional to the thickness of the expansion [22],i.e., the tendency to cracking increases with the thickness of the expanded area.

6. Conclusions

The pronounced changes observed in the Raman spectra obtained for UV illuminated $Ga_{10}Ge_{25}S_{65}$ glasses are related to structural changes in the local bonding configuration. The $Ga_{10}Ge_{25}S_{65}$ glass is essentially a solid solution consisting of a network of very short S chains cross linked by four-coordinated Ge atoms, and a monomer component of S_8 ring molecule. It has been shown that under laser irradiation, the bonding tendency of the chalcogenide atoms is to forms chains rather than rings. In addition it was demonstrated that in these glasses the photoexpansion and photobleaching are irreversible after heat treatment.

Acknowledgements

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