Abstract

Irreversible photoexpansion effect has been observed in amorphous Ga$_{10}$Ge$_{25}$S$_{65}$ glasses when its surface was exposed to light with energy greater than the band gap, 3.52 eV. A volume change of about 5% was reached in bulk samples by controlling illumination time and the laser power density. To understand the atomic scale processes of the photoexpansion effect, extended X-ray absorption fine structure (EXAFS) spectroscopy has been used as a local probe of the germanium environment in the glass samples before and after illumination. Modifications are observed in the average coordination shell around Ge atoms in the illuminated sample compared to the non-illuminated one. For the non-illuminated sample, the Ge coordination shell is described by a distorted tetrahedron of sulfur atoms at around 2.20 Å. After illumination, the EXAFS signal can be explained by introducing an additional contribution to this average environment. Based on an analysis of the EXAFS data we proposed a two-shell model of 0.5 oxygen atoms at 2.01 Å and 3.6 sulfur atoms at a 2.20 Å. The existence of Ge–O bonds in the glass after illumination was confirmed by infrared measurements. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Photostructural changes have been subject of research for several years because they not only reveal interesting properties about the structure of disordered solids but may have technological potential as well [1]. In chalcogenide glasses these changes are induced by exposing a sample to near band gap light. They include changes in the density [2], rheological properties [3], etching, and, in some cases, photocrystallization [4]. Depending on experimental conditions, these changes can be 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, $T_g$.

In our previous investigation of the photoinduced changes in GaGeS glass, we reported an induced decay of refractive index associated with a decrease in the density through dilation which increased volume when samples were exposed to laser light with $\lambda = 351$ nm and power density
of 5 W/cm² [5]. Moreover, we found that this photoexpansion effect was irreversible [6]. Several mechanisms have been proposed for the irreversible changes, in which the interaction with light induces bond breaking and structural changes. Irreversible changes, which are most reported in as-deposited films [7,8], have been explained in terms of bond breaking models [9]. In this work, exposing the Ga₁₀Ge₂₅S₆₅ samples to light having above band gap energy increased the thickness of the illuminated region.

The main network of germanium based chalcogenide glasses is described as GeO₄ tetrahedral units connected to each other by corners and edges [10]. The volume change during the irradiation should be correlated to structural changes in this glassy network. The objective of the present study was to investigate these changes, by using EXAFS as a structural probe of the local environment around the germanium atoms.

2. Experimental

Glass samples were prepared by melting elements (Ga, Ge, and S) in a quartz ampoule evacuated to 10⁻³ Pa. All procedures including synthesis, distillation and sample production were carried out in a closed system. After melting at 900 °C during 6 h the ampoule was removed, quenched in water and annealed at the glass transition temperature, T_g, of the sample around 400 °C. Rods about 60 mm in length and 10 mm in diameter were obtained after cutting the quartz ampoule. Slices of around 1 mm in thickness were cut and polishing by a pad charged with polishing particles (CeO₂, mean diameter of 0.5 μm).

Before the extended X-ray absorption fine structure (EXAFS) measurements, the glass surface area, 10 mm in diameter and 1 mm thick, was exposed through a mask that was in contact with the sample surface. For the photoexpansion experiment, the sample was exposed to ultra-violet (UV)-light (351 nm) from a Kr⁺ ion laser at room temperature. After 5 and 10 h illumination, the mask was removed from the samples and the elevation of the exposed area was measured using a 3D perfilometer instrument (Tencor, TF1). An image of the exposed area was obtained using an atomic force microscope (AFM – Digital Instruments-Nanoscope 3 A).

EXAFS measurements at the Ge K-edge (11 104 eV) were performed at the XAS beam line of at the LNLS facility (Campinas, Brazil) with an average beam voltage of 150 mV [11]. The monochromatization of the incident beam was made using a double Si(1 1 1) crystal [11].

Firstly, we measured the EXAFS spectra of the reference compounds, crystalline GeS₂ (c-GeS₂) and amorphous GeS₂ (a-GeS₂), in which the Ge sulfur surroundings are quasi tetrahedral and the local structure is well known. The reference compounds were than ground to powder and sieved to obtain powders having a grain size between 15 and 20 μm. For the EXAFS measurements, the sieved powders were than deposited on a polymeric membrane. The data collection was then performed in the transmission mode using ionization chambers as detectors. Each sample was subjected to; at least, five different scans, which were averaged to increase the quality of the experimental data.

The EXAFS spectra of a Ga₁₀Ge₂₅S₆₅ sample (slices of 10 mm in diameter and 1 mm of thickness) was then collected in samples before and after illumination (exposed 5 and 10 h). The intensity of the incident beam was measured by an ionization chamber whereas the beam originated by the sample was collected using the total electron yield mode [11]. Each sample was subjected at least, to five different scans, which were averaged to increase the quality of the experimental data.

The EXAFS spectra were analyzed by a standard procedure of data reduction [12], using WinXAS code [13]: extraction of the EXAFS signal, γ(κ), the oscillatory part of the absorption coefficient, then Fourier transformed which was obtained after a k³ EXAFS weighting and a Bessel apodization function (coefficient of 4) over 2.8–12.0 Å⁻¹. The Fourier transforms give a radial distribution function, modified by the phase shifts due to the absorber and backscattered atoms. The contribution of each shell is then backtransformed into k-space. Structural parameters, N (coordination number), R (interatomic distance), and σ (Debye Waller term) are obtained from least squares fitting in k-space, using theoretical phase
and amplitude functions obtained from FEFF6.01 software [14].

The IR spectrum of the surface of GaGeS samples (slices of 10 mm in diameter and 1 mm of thickness) before and after illumination, was measured in the reflection mode using a spectrophotometer Perkin–Elmer 684.

3. Results

3.1. AFM measurements

Fig. 1 shows the result of three-dimensional profile performed on the surface of a Ga$_{10}$Ge$_{25}$S$_{65}$ sample after irradiation exposed 5 h. As can be seen in Fig. 1, the exposed part of the glass surface is higher than their surroundings that were not illuminated by the laser. The elevation of the exposed surface, compared to the unexposed region of the same sample, was measured as 250 nm.

3.2. EXAFS spectra of the reference samples

Fig. 2 shows normalized experimental EXAFS spectra, $\chi(K)$, of the c-GeS$_2$ and a-GeS$_2$ references, together with that of the Ga$_{10}$Ge$_{25}$S$_{65}$ powder. We observe that EXAFS spectra of the three samples are similar.

The Fourier transforms of the EXAFS spectra presented on Fig. 2 are shown in Fig. 3. The first peak in the Fourier transform, situated at approximately 1.98 Å, is due to the first coordination shell around germanium. We should note that the Fourier transforms are not corrected for phase shift parameters, so that the peak positions are shifted to smaller distance compared to the real distances. The corrected distances are found after the fitting procedure. The structural parameters for the first coordination shell is presented in Table 1, where $N_1$ represents the coordination number and $R$ the Ge–S distance for the edge sharing GeS$_4$ tetrahedra. It is well known from X-ray diffraction measurements [15] and spectroscopic studies [16] that in c-GeS$_2$, Ge atoms are bonded to four sulphurs located at the corner of a distorted tetrahedron with an average Ge–S bond length of 2.0 Å. The crystalline structure is a layered structure built up from chains of GeS$_4$ corner-sharing tetrahedra, these chains being connected through links of two GeSe$_4$ edge-sharing tetrahedra [17].

![Fig. 1. Three-dimensional representation of profile measurement of GaGeS showing the effect of the photoexpansion on the surface structure of glass exposed during 5 h.](image-url)
This structure is known to exist in c-GeS$_2$, and its existence has also been demonstrated in an a-GeS$_2$ phase [18]. The second neighbouring sphere of Ge atoms is composed of a short Ge–Ge distance (2.5 Å) and a longer Ge–Ge distance (3.0 Å) forms the third Ge neighbouring shell.

3.3. EXAFS measurements of Ga$_{10}$Ge$_{25}$S$_{65}$ glass before and after illumination

EXAFS spectra of the Ga$_{10}$Ge$_{25}$S$_{65}$ samples are shown in Fig. 4 as a function of exposure time. A decrease of the amplitude of EXAFS signal is observed as the exposure time increases.

Fig. 5 shows the radial distribution function obtained from Fourier transform of the normalized signal EXAFS presented in Fig. 4. The modification in the amplitude of the EXAFS signal is associated to a decrease of the amplitude of the first peak in the FT, which indicates modifications of the average coordination shell around germanium atoms after the illumination.

During the fitting of the spectra of the non-illuminated sample, the best fitting was achieved when the first coordination shell around Ge atoms was performed assuming the existence of four sulfur atoms located at approximately 2.2 Å. Concerning the illuminated samples, to take into

<p>| Table 1: Fit results concerning the S shell around Ge atoms |
| Sample | First coordination shell |</p>
<table>
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<tr>
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<th>$N_1$ (±0.2)</th>
<th>$R_1$ (±0.01)</th>
</tr>
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<tbody>
<tr>
<td>c-GeS$_2$</td>
<td>4.0</td>
<td>2.20</td>
</tr>
<tr>
<td>a-GeS$_2$</td>
<td>4.0</td>
<td>2.21</td>
</tr>
<tr>
<td>GaGeS powder</td>
<td>4.1</td>
<td>2.21</td>
</tr>
</tbody>
</table>
account the amplitude decrease observed in the Fourier transform first peak, the number of sulfur scattering atoms and their average distance, R, from the germanium central atom were allowed to vary, as well as the width of the distribution of these neighbours (Debye Waller term, σ). Nevertheless, no fit was achieved with any single shell model. Actually, for the illuminated samples, the only way to fit the EXAFS signal in a satisfactory way is to introduce an additional backscattering contribution. A fit to within ±10% was obtained assuming the existence of a contribution of O atoms at a distance of around 2.0 Å. Although in the fitting procedure we assume the existence of Ge–O and Ge–S bonds, only one peak is observed in the Fourier transform first peak. This fact is due to the intrinsic limitation in the EXAFS measurements that reduces the resolution at such a small distance resolution. However, in the EXAFS fit (Fig. 6) the best fit was obtained only when the contribution of the O atoms was included. The structural parameters obtained for the illuminated samples are also presented in Table 2, where N₁, R₁ and N₂, R₂ correspond to Ge–S and Ge–O atomic pairs, respectively.

To confirm the presence of oxygen in the illuminated samples, infrared spectra of non-illuminated and illuminated glasses was measured. The results are shown in Fig. 7. The features in the spectral region studied are the vibrational bands at 3500, 870 and 727 cm⁻¹. Comparing the infrared spectra, the intensity of the peak at 870, which was attributed to the Ge–O–Ge stretching [19], is much smaller for the non-illuminated sample when compared to the sample illuminated during 10 h. This fact indicates that the number of Ge–O bonds increases with illumination duration.

Fig. 4. Normalized XAFS oscillations extracted at germanium K-edge for Ga₁₀Ge₂₅S₆₅ samples as function of time glass illumination: (□) non-illuminated, (○) illuminated 5 h and (△) illuminated 10 h.

Fig. 5. Radial distribution function around the Ge atoms for Ga₁₀Ge₂₅S₆₅ samples as function of time exposure: (□) non-illuminated, (○) illuminated 5 h and (△) illuminated 10 h.
4. Discussion

From the data of the reference samples, we conclude that in the Ga$_{10}$Ge$_{25}$S$_{65}$ sample before illumination both the local and the medium range order around Ge are similar to that observed in the layered crystalline form of c-GeS$_2$. Loireau–Lozac’h et al. [20] have reported that the incorporation of Ga$_2$S$_3$ in GeS$_2$-based glasses forms GaS$_4$ tetrahedral units with Ge–S distances of 2.22 Å in GeS$_4$ tetrahedral units. The insertion of gallium in the structure may maintain the global structure, but distorting it through edge or corner sharing linkage of GaS$_4$ tetrahedra substituted for GeS$_4$ units [20].

Concerning the structure of Ga$_{10}$Ge$_{25}$S$_{65}$ glasses as function of the illumination time, an interesting change was noted. The amplitude decrease of the Ge first peak in the Fourier transform was a function of exposure time. This decrease in the first peak of the Fourier transform was attributed to presence of an additional contribution. The fitting procedure gives to a contribution of Ge–O atomic pairs at a distance on the order of 2.0 Å. This distance is in agreement with the usual Ge–O distances in oxides [21]. The decreases of the EXAFS signal can be then explained by destructive interference between photoelectron waves backscattered by O and S.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur neighbours Ge–S</th>
<th>Oxygen neighbours Ge–O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N$_1$ (±0.2)</td>
<td>R$_1$ (±0.01)</td>
</tr>
<tr>
<td>Non-exposed</td>
<td>3.8</td>
<td>2.20</td>
</tr>
<tr>
<td>Exposed 5 h</td>
<td>3.7</td>
<td>2.21</td>
</tr>
<tr>
<td>Exposed 10 h</td>
<td>3.5</td>
<td>2.21</td>
</tr>
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Fig. 6. $k^2 \chi (k)$ curves fit (solid line = experimental, dotted line = modelization) for Ga$_{10}$Ge$_{25}$S$_{65}$ bulk sample.

Fig. 7. Infrared spectra of Ga$_{10}$Ge$_{25}$S$_{65}$ samples non-illuminated (a) and illuminated glass during 10 h (b).
The presence of oxygen in illuminated samples was also confirmed by infrared measurements (Fig. 7). Murth et al. [19] assigned the band at 870 cm\(^{-1}\), observed in GeO\(_2\) glass, as being due to the Ge–O–Ge stretching. We assume that the vibrational band for the illuminated sample due to the Ge–O interactions could be a product of photooxidation of the glass surface. In fact, the origin of the vibrational band at 727 cm\(^{-1}\) observed in the illuminated sample, was assigned by others [22] to the Ge–O stretching mode in S\(_3\)GeO–GeO\(_x\)S\(_3\) clusters formed on the surface of a sample. Similar results, i.e., dependence of the exposure condition and appearance of absorption in the region 800–870 cm\(^{-1}\) (indicating presence of Ge–O bonds), were also observed in glassy Ge\(_{30}\)S\(_{70}\) [22].

Thus, EXAFS spectra collected at the germanium K-edge for Ga\(_{10}\)Ge\(_{25}\)S\(_{65}\) glass samples before and after irradiation shows that for the non-illuminated sample, the first coordination shell is formed by four sulfur atoms at a mean bond length of 2.21 Å, as observed in the a-GeS\(_2\). After illumination, a change is observed in the amplitude of the Fourier transform first peak, which is related to the Ge first coordination shell. To account for this change, an additional contribution is introduced in the fitting procedure. This contribution is related to oxygen atoms situated at around 2.0 Å. Infrared measurement confirmed the presence of Ge–O bond in the glass samples after illumination.

5. Conclusions

These experimental results showed that glass illumination leads to an introduction of oxygen in the glass structure breaking Ge–S intermolecular bonds. This structural study will now be extended to the other two atoms (sulfur and gallium) to have a complete overview of the photoexpansion effect in the glass structure.

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References