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Photo-induced effects in $Ge_{25}Ga_{10}S_{65}$ glasses studied by XPS and XAS

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Abstract

The present paper focuses on the structural, electronic, and compositional properties of $Ge_{25}Ga_{10}S_{65}$ glasses before and after UV illumination in air using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) techniques. The XPS Ge 3d spectra reveal the existence of Ge–O bonds in the surface region of illuminated glass. In the case of this sample, XAS O K-edge spectra showed the formation of an enriched region of oxygen atoms in the glass bulk, indicating a different bonding structure of oxygen at the surface and in the bulk of the glass. Moreover, the structural changes that occur after UV illumination in the glass sample are identified as the formation of a homogeneous germanium oxide surface layer followed by an intermediary $Ge_{25}Ga_{10}S_{65-y}O_z$ subsurface region.

Keywords: Chalcogenide glasses; Photo-induced effects; Oxygen; XPS; XAS

1. Introduction

The properties and structure of high band gap amorphous chalcogenide glasses are known to be sensitive to light incidence [1,2]. One of the most interesting photo-induced changes in the glass structure is the photoexpansion effect. In general, this phenomenon is accompanied by a reversible or irreversible shift in the optical absorption edge to lower (photodarkening) or higher (photobleaching) energy. These dimensional changes in the chemical bond structure are interesting (e.g., applications in focused laser beam-induced formation of optical microlenses) [3–5].

Recently, we reported on a photobleaching effect associated with a density decrease by dilatation (photoexpansion) of the $Ge_{25}Ga_{10}S_{65}$ glass structure [6]. The thickness of the illuminated region was increased after exposing the $Ge_{25}Ga_{10}S_{65}$ bulk glass to light with energy above the band gap of 3.3 eV. Moreover, it was detected that this was an irreversible photoexpansion effect [7]. Similar reversible and irreversible changes have been the subject of several studies. Some authors claim that a uniform expansion of the material is caused by photorelaxation, which is usually a starting mechanism of reversible photostructural changes [8]. Irreversible photo-induced phenomena have been attributed to glass interaction with the atmosphere during illumination [9,10].

Tanaka et al. observed that the magnitude of the photo-induced shift in the absorption edge of GeS_2 films is strongly dependent on the ambient oxygen pressure [11]. Other authors have associated the nature of the irreversible photo-induced phenomenon in these films to an increase in the density of heteronuclear bonds and incorporation of oxygen into the GeS glass matrix [12].

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Recently, we demonstrated that the magnitude of $Ge_{25}Ga_{10}S_{65}$ glass expansion depends on exposure conditions [13]. We observed that the thickness of the photo-expanded surface decreases with decreasing oxygen content of the ambient atmosphere. In order to understand the effect of exposure conditions and particularly the role of oxygen on the structure of $Ge_{25}Ga_{10}S_{65}$ glasses before and after illumination in air, a structural study was performed using X-ray absorption spectroscopy (XAS), Rutherford backscattering spectrometry (RBS), and infrared measurements [14]. According to the XAS analysis, there is a modification in the average coordination shell around Ge atoms in the illuminated sample due to formation of Ge tetrahedron with oxygen and sulfur atoms located at 2.01 Å and 2.20 Å, respectively. In contrast, the non-illuminated structure can be described by a Ge coordination shell of a distorted tetrahedron of sulfur atoms at around 2.20 Å. The existence of Ge–O bonds in the glass after illumination was also confirmed by infrared spectroscopy. For this sample, decrease on the oxygen content with increasing depth was also observed by RBS. As a possible explanation for this behavior, it was suggested that during illumination in air, GeS_2 (molecules) bonds are broken, forming an increasing concentration of dangling bonds at the surface. The interaction of the modified glass surface with atmospheric oxygen leads then to the formation of Ge–O bonds and, consequently, to an oxide surface layer. The fact that no photoexpansion was observed in vacuum suggests that illumination-induced oxidation at the glass surface is primarily responsible for the detected volume change.

In this paper, we report on structural and compositional changes detected in $Ga_{10}Ge_{25}S_{65}$ glasses before and after illumination in air using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) techniques.

XPS and XAS at low energies are suitable surface techniques providing atomic scale information regarding chemical bonding structure as well as chemical composition of the sample surface before and after illumination. Special attention was given to the interaction of the ambient oxygen with the glass species in order to evaluate the role of oxygen on glass photoexpansion upon illumination.

2. Experimental procedure

Polycrystalline germanium, gallium, and sulphur precursors were weighted, mixed, and transferred to a quartz ampoule. After vacuum sealing, a heating process up to 950 °C was started. At 950 °C, the liquid was homogenized for 6 h by continuous horizontal rotation. Then the ampoule was quickly removed from the furnace and air-cooled. Afterwards, the sample was annealed at 400 °C for several hours.

To improve the glass stability of germanium sulfide glasses, modification with gallium was used. We report that the $Ge_{25}Ga_{10}S_{65}$ composition lies at the center of the glass-forming region in the ternary system, Ge–Ga–S [15].

Characteristic temperatures (T_g, glass transition temperature; T_x, onset of crystallization; T_m, melting temperature) were determined using differential thermal analysis (DTA; Ta 3100 equipment). These temperatures were determined from DTA curves and the resulting values are reported in Table 1.

For the photoexpansion experiment, a part of the glass surface area was covered with a mask (1 cm^2) and exposed at room temperature to UV light (351 nm) with an intensity of 5 mW/cm^2 from a Kr^+ ion laser during 10 h in air.

The average penetration depth d of light depends on the value of the absorption coefficient (α) at this wavelength according to $d=1/\alpha$. In our glasses, this value is $d=0{,}02$ mm, which provides more surface information.

After illumination, the mask was removed and the exposed area was measured by means of an atomic force microscope (AFM Digital Instruments-Nanoscope 3A). The thickness increase of the exposed surface area was around 400 nm.

X-ray photoelectron spectroscopy (XPS) experiments were performed using a VG ESCA 3000 system and spectra were collected using Mg Kα radiation with an overall resolution of about 0.8 eV. Pass energy was set at 10 eV. Concentration of the surface elements was calculated using the system database after subtracting the background intensity. The C 1s peak set at 284.8 eV was used as reference value for calibration of the binding energy scale. Further analysis of the spectra was performed by a fitting procedure using Gaussian peak shapes.

X-ray absorption spectroscopy (XAS) measurements at the O K-edge were performed at LURE at the SuperACO storage ring (Orsay), operated at 800 MeV, with the current ranging from 215 to 400 mA. The XANES (X-ray absorption near-edge spectroscopy) spectra were measured at the SA22 beam line, which was equipped with a high-energy plane grating spherical mirror monochromator, with a resolution of about 100 meV at the O 1s edge (530 eV). The energy of the monochromator was calibrated at the oxygen K-edge using the weak absorption feature on account of the oxygen contamination of the optics. The $Ge_{25}Ga_{10}S_{65}$ bulk glass samples were measured before and after ex situ illumination. The spectra of glass samples and polycrystalline GeO_2 were collected at room temperature using fluorescence yield (FY) and total electron yield (TEY) modes. The XPS and XAS measurements were performed using glass samples obtained from the same batch.

Table 1
Characteristic temperature of the glass composition

Sample	T_g (°C)	T_x (°C)	T_m (°C)
$Ga_{10}Ge_{25}S_{65}$	400 ± 1	780 ± 1	815 ± 1