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Photoexpansion and photorefraction in oxysulphide glasses

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ABSTRACT

Oxysulphide glasses have been prepared in the pseudo binary system $GeS_{2.6}$–Ga_2O_3. The effect of addition of gallium oxide has been evaluated in term of thermal and optical properties. Structural behavior has been studied using Raman spectroscopy. Samples have been exposed above band gap energy (3.52 eV) varying power density and exposure time. Giant photoexpansion and photorefraction is obtained for samples containing 20% of Ga_2O_3.

1. Introduction

The chalcogenide glasses have been studied due to the large possibility of applications in photonic area. They are good candidates for integrated optics because they present low band-gap energy, high sensitivity and been identified as possible materials for applications in nonlinear optics [1]. These glasses also are known to be sensitive to the absorption of electromagnetic radiation that results to several photoinduced phenomenons.

Among the various models proposed to explain the origin of photoinduced effects in chalcogenide glasses, the diffusion of oxygen from atmosphere within the glass associated with interaction with the sulfide glassy network and to strain formation [2,3] have been proposed for GeS_2. Tanaka et al. [4] observed a photobleaching induced under irradiation of a normally deposited $Ge_{35}S_{65}$ film and which magnitude depends on the air pressure.

Moreover, in our previous studies a modification with gallium sulphide was used to improve the stability of binary glasses Ge–S. Results already published in $Ga_{10}Ge_{25}S_{65}$ glasses [5–7] had shown the effect of oxygen in photoinduced phenomenon.

However, few papers in the literature report the study of photoinduced effects in oxysulphide glasses. In this direction, we report in the present paper the combination of sulphide and oxides glasses and studied the oxysulphides glass system. We have mainly prepared glasses in the pseudo-binary system $GeS_{2.6}$–Ga_2O_3 and study their thermal and optical properties. We have evaluated the effect of addition of Ga_2O_3 to the $GeS_{2.6}$ glasses and studied the photoinduced effect by exposing the sample above bandgap energy.

2. Experimental procedure

2.1. Preparation of the glasses

$GeS_{2.6}$–Ga_2O_3 belong to the group of substances that possesses a different melting temperature with a high vapor pressure and are susceptive to the oxidation and hydrolysis. Therefore, the synthesis of these must be carried through evacuated quartz tube (3–5 mTorr).

In the preparation of $GeS_{2.6}$–Ga_2O_3 oxysulfide glasses germanium sulfide (II) has been used as the starting compound. GeS (II) has been selected because of relative simplicity of its preparation (low temperature of its synthesis (~800 °C) and no danger of its explosion during melting of the compounds). Starting GeS (II) is a black crystal compound (rombic pyramidal) with melting temperature $T_m = 530$ °C.

Oxysulfide glasses were prepared by addition of corresponding quantities of Ga_2O_3 and elemental sulphur to crystalline GeS(II). The silica tube was placed in a rocking furnace and heated at 1 °C/min to 900°–1100 °C (depending on the amount of Ga_2O_3 concentration) held during 8 h, and then quenched in air. Several glass compositions have been prepared varying the percentage of Ga_2O_3 and keeping the ration [S]/[Ge] = 2.6. We have selected this ration in order to compare with our previous reported study on the effect of addition of Ga_2S_3 to Ge–S glass system [8].

In order to eliminated residual stress, samples have been annealed at different temperatures depending on the glass composition.

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2.2. Thermal and optical characterization

The characteristic temperatures (T_g, glass transition temperature; T_x, onset of crystallization; and T_m the melting temperature) were determined using Differential Scanning Calorimetry (DSC) 2910 Modulated TA Instruments. 20 mg of glass powder (45–53 μm) was loaded into an aluminium pan and hermetically sealed under dry nitrogen inside the glove box. The samples were then heated from 100 to 600 °C using 10 °C/min.

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 range from 200 to 700 nm.

The optical bandgap can be represented by the relation,

$$\alpha h\nu = B(h\nu - E_g)^p \quad (1)$$

where B is constant, $E = h\nu$ is the energy of incident photons, E_g is the bandgap and p is theoretically equal to ½ for direct allowed transitions. The usual method for determining the value of the E_g, involves plotting a graph of $(\alpha E)^2$ versus photon energy, in accordance to Eq. (1).

2.3. Raman scattering

Raman spectroscopy was carried out using a He–Ne laser with a wavelength of 633 nm and the power was limited to less than 5 mW to avoid sample damage. The laser beam was focused on a sample surface by a (100×) microscope objective and then recorded from 100 to 800 cm^{-1} with a resolution of 2 cm^{-1}.

2.4. Photoexpansion and photorefractive experiments

The bulk samples were covered with a mask and exposed to Multiline UV of an Ar^+ laser at room temperature, varying the laser power density (0.6–5 mW/cm^2) and exposure time (30–120 min).

The surface expansion profile after illumination was measured using a profilometer (FORMTRACER model SV-C525 from Taylor Hobson Precision). Refractive index and the absorption spectrum were obtained using a prism-coupling technique [9], before and after illumination. The present experimental technique allowed us to measure the refractive index of the films along polarization directions in the film plane (that propagation constants measured from TE-optical modes) and perpendicular to it (from TM-modes).

3. Results

The composition of the prepared glasses has been determined using EDS. Good agreement between the nominal composition and EDS analysis. Table 1 reports the glass compositions prepared including melting and annealing temperatures with their acronyms.

The characteristic temperatures for the glasses samples are reported on Table 2. We have also included in this table the value of $(T_x - T_g)$ used as an estimate of glass stability against devitrification.

It is observed from Table 2 that the value of the glass transition temperature and the temperature of crystallization increase with the increase of the gallium oxide concentration (313 to 417 °C and 591 to 619 °C, respectively).

Table 1
Glass compositions prepared with their acronym, melting and annealing temperatures.

Samples	Ga_2O_3 (mol%)	Melting (T_m)	Annealing temperature (T_a)	Acronym
$Ge_{28}S_{72}$	0%Ga_2O_3	950	340	GaO0
$Ge_{26}Ga_2S_{67}O_4$	5%Ga_2O_3	950	340	GaO5
$Ge_{24}Ga_5S_{63}O_8$	10%Ga_2O_3	950	340	GaO10
$Ge_{22}Ga_8S_{60}O_{12}$	15%Ga_2O_3	1100	360	GaO15
$Ge_{21}Ga_{10}S_{54}O_{15}$	20%Ga_2O_3	1100	360	GaO20

Table 2
Characteristic temperatures of the glass compositions.

Sample	T_g (°C)	T_x (°C)	$T_x - T_g$ (°C)
GaO_0	313 ± 2	591 ± 2	278
GaO_5	361 ± 2	637 ± 2	276
GaO_{10}	340 ± 2	607 ± 2	267
GaO_{15}	367 ± 2	625 ± 2	258
GaO_{20}	417 ± 2	619 ± 2	202

The criterion of thermal stability ($T_x - Tg$) used as a parameter of the degree of thermal stability against crystallization is relatively high (>200 °C) in comparison with tellurium and selenide glass system (~100 °C) [10]. This thermal stability is favorable for the production of optical fiber and an optimum value is obtained for low gallium oxide concentration.

Fig. 1 present the optical absorption edge versus photon energy. We can observe that increasing the concentration of Ga_2O_3, the absorption edge is shifted to higher energies (blue shift). The valence band of these glasses is formed by pairs of free electrons of atoms of oxygen or chalcogen. Increasing the gallium oxide concentration we can assume that we are increasing the binding energy which is in accordance with the data obtained through the values of the glass transition temperature (T_g).

Raman spectroscopy measurements are performed from 100 to 800 cm^{-1} for the glass compositions including the references samples as sulphur (S_n) gallium oxide (Ga_2O_3) and germanium sulphide (GeS_2) (Fig. 2). The intense band at 344 cm^{-1} is assigned to the stretching vibration mode $GeS_{4/2}$. The shoulder at 370 cm^{-1} is attributed to the vibration of two tetrahedrons with shared edges. The band at 433 cm^{-1} is assigned to the symmetrical stretching mode of the Ga–O–Ga linking tetrahedral GaO_4. The centered band at 206 cm^{-1} is attributed to the vibration of the $S_3Ge(Ga)$–$Ge(Ga)S_3$ types connections.

Addition of Gallium oxide into GeS_2 resulted in pronounced changes in the Raman spectra as illustrated in Fig. 2. When the concentration of gallium oxide increases, the bands at 370 and 440 cm^{-1} increase and shift to lower frequency. The intensity of the band at 480 cm^{-1} decreases progressively with an increase of gallium oxide content above 15% (in mol%). The formation of new oxysulfide structural units is in accordance with the previous study in the Ge–Ga–As–S–O system [11].

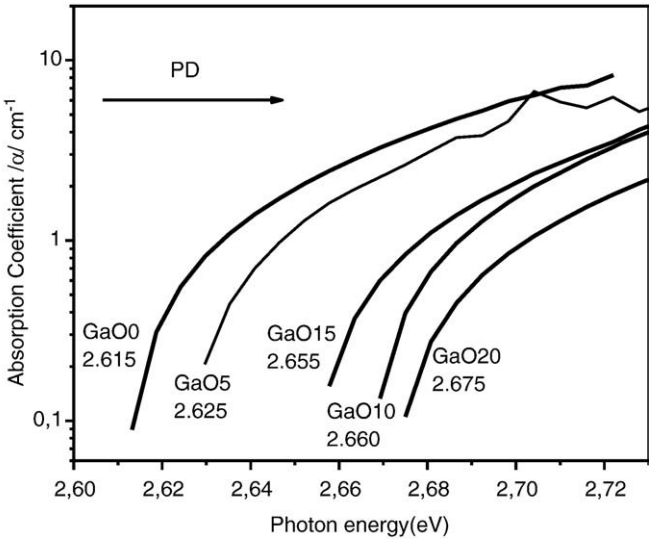

Fig. 1. Absorption coefficient α (cm^{-1}) versus photon energy (eV).