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Compositional dependence of the optical properties of new quaternary chalcogenide glasses of Ge–Sb–(S,Te) system

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ABSTRACT

New quaternary telluride glassy materials with composition of $Ge_xSb_{40-x}S_{50}Te_{10}$ and $Ge_xSb_{40-x}S_{55}Te_5$ (x = 10, 20, and 27) have been synthesized and their optical properties have been studied by means of spectroscopic ellipsometry in the range of 400–820 nm. The optical constants, i.e. the refractive index, extinction coefficient, absorption coefficient, and the optical band gap energy are determined and their compositional dependence is considered. These parameters are characteristics for amorphous structure of the synthesized glasses, revealed from the neutron diffraction measurements.

1. Introduction

Chalcogenide glasses have unique properties for potential application in infrared optics, fiber optics, memory devices, inorganics photoresists and antireflection coatings [1–6]. These glasses are low phonon energy materials, and are light transparent in the visible and mid-infrared region. This underlines the importance of the characterization of these glassy materials through determination of their optical constants, such as refractive index and extinction coefficient, as well as the corresponding optical band gaps.

The ternary Ge–Sb–S glasses with nonstoichiometric compositions have been subject of intensive studies and their properties are well established [7–10]. Introduction of small amount of Te into these glasses alters the glassy structure, and leads to high refractive index values and photosensitivity. Therefore, telluride glasses from quaternary systems are potential candidates for integrated optics.

In recent years the number of papers dealing with telluride glasses from systems, such as Ge–Sb–Te [11–15], Te–As–Se [16–19], has increased reflecting the growing interest in these materials. Nowadays the attention is extended over quaternary systems as possible candidates for optoelectronic applications.

Recently we have synthesized new quaternary telluride glasses based on Ge–S system with addition of Sb and partial substitution of Te for S, and have considered the basic physicochemical parameters in dependence of glass composition [20]. To the best of our knowledge there is no data in the literature on glasses from a quaternary Ge–Sb–S–Te system. In general, the optical properties are closely related to the material's atomic structure, electronic band structure and electrical properties, which are strongly correlated with the glass composition. Thus the main goal of investigations of these materials is clarifying the influence of Te substitution for S on the optical properties of the glasses.

In this paper we present results on the ellipsometric study of the optical properties of glasses, synthesized by us, from the quaternary Ge–Sb–S–Te system, as the compositional dependence of the complex refractive index and optical band gap energy values are considered. These parameters have been obtained from the data analysis of ellipsometric measurements performed in the visible spectral range of light.

2. Experimental

The bulk glasses with four compositions, namely $Ge_xSb_{40-x}S_{50}Te_{10}$ (x = 10 and 27 at.%) and $Ge_xSb_{40-x}S_{55}Te_5$ (x = 20 and 27 at.%), were synthesized from 5 N purity elements by the conventional melt-quenching method. The synthesis was performed in a rotary furnace, as the glass components of a proper composition were placed in quartz ampoules, which was evacuated (10^{-3} Pa). The ampoules were heated up to 950 °C, and were kept at this temperature for 24 h, rotating the furnace for homogeneous melting. Ending the process, the ampoules were pulled out, and were quenched in air. Part of the samples was cut into ~4 mm thick slices with a diameter of ~10 mm and the slices were

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polished on one side for optical measurements. The other part of the samples was powdered for neutron diffraction measurement.

The elemental composition of the glasses was cross-checked by means of prompt γ-ray activation analyses (PGAA), the results of which are given in details elsewhere [21]. A good coincidence between the measured compositions and those calculated for the material synthesis is established.

The phase state of the glasses was examined by neutron diffraction (ND) measurements, carried out on a 'PSD' neutron diffractometer with a monochromatic wavelength of $\lambda_0 = 1.068$ Å. From the ND intensity data the total structure factor S(Q) was calculated after correction and normalization procedures, described in our previous work [22].

The ellipsometric measurements were done on a manual Rudolf Research ellipsometer with PCSA configuration in the spectral region of 400–820 nm (1.5–3.1 eV) and at an angle of light incidence of 50°. The accuracy of the polarizer, analyzer and incidence angles was within ±0.01°. The systematic errors in the experimental ellipsometric angles were eliminated through averaging the four zones measurements. From the SE data analysis, the complex refractive index ($\tilde{n} = n - jk$), where n is the refractive index and k is the extinction coefficient, absorption coefficient ($\alpha = 4\pi k/\lambda$) and optical bandgap energy (E_g) of the glasses were evaluated.

3. Results and discussion

In Fig. 1, the dispersion curves of the refractive index (1a) and extinction coefficient (1b) for the studied compositions are presented. The refractive index dependences (Fig. 1a) follow the ordinary dispersion behavior, namely in the weak absorption region the n value increases towards shorter wavelengths and below $\lambda \sim 480$ nm it starts to decrease due to the stronger absorption of light (Fig. 1b).

The shape of the dispersion curves of both quantities is similar but their values are compositionally dependent. Increasing the Ge content up to 27, correspondingly decreasing the Sb content, at constant amount of Te leads to reduction of the refractive index values throughout in the studied spectral region (Fig. 1a). Decrease of the Te content from 10 to 5 results in a further reduction in the n values. Similar tendency in the dispersion curves of k is observed (Fig. 1b).

In the dependence of the extinction coefficient on photon energy (Fig. 1b), a shift of the whole curve toward lower energy region (red shift) is observed when the Ge content decreases or Te content increases, as the latter has weaker influence on the observed displacement.

The observed compositional dependences of the optical constants n and k can be explained by the different polarizability of the glass constituent elements [23]. Since the Ge cations have smaller polarizability than the Sb cations, increase of their amount in the glass most probably causes the observed decrease of the refractive index. On the other hand, the Te ions, being larger than S ions, have higher polarizability and, hence, for 10 at.% Te the refractive index values are larger.

The absorption coefficient was determined from the k data by using the relationship $\alpha = 4\pi k/\lambda$. In the high absorption region ($\alpha > 10^4$ cm^{-1}), the absorption coefficient can be described by the relation $(\alpha h\nu)^{1/m} = B(h\nu - E_g)$ [24,25], where the parameter B is dependent on the electron transition probability, while the power m is an integer number characterizing the transition process. Plotting the $(\alpha h\nu)^{1/m}$ versus photon energy ($h\nu$) and assuming an indirect type electron transition ($m = 2$), as is the case for chalcogenide materials, the energy band gap (E_g) was determined by extrapolating the linear part of the curves toward zero absorption; the interception with the photon energy axis providing the E_g value. The results are summarized in Fig. 2, where the spectral dependence of α and the corresponding inserted plot of $(\alpha h\nu)^{1/m}$ versus ($h\nu$) are given for all compositions studied. By extrapolation, the E_g values were obtained with an accuracy of ±0.05 eV and are presented in Table 1. The tendency of the compositional dependence of E_g values is that the optical band gap energy increases with increasing Ge and it becomes smaller with increasing the amount of Te atoms.

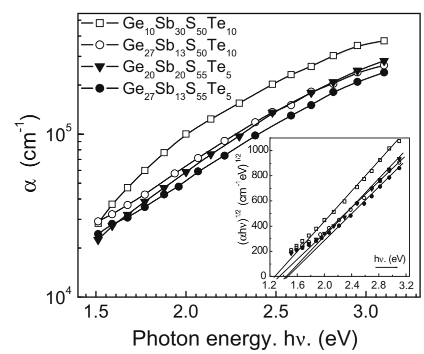

Fig. 2. Absorption coefficient α in dependence on photon energy of chalcogenide glasses with compositions, inserted. The corresponding plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ are also inserted.

Table 1
Optical band gap energy E_g, coordination number Z, heat of atomization H_s and the ratio H_s/Z of the synthesized chalcogenide glasses.

Composition	E_g (eV)	Z	H_s (kcal/g)	H_s/Z (kcal/g)
$Ge_{10}Sb_{30}S_{50}Te_{10}$	1.30	2.50	64.01	25.60
$Ge_{27}Sb_{13}S_{50}Te_{10}$	1.42	2.67	66.54	24.92
$Ge_{20}Sb_{20}S_{55}Te_5$	1.47	2.60	66.57	25.6
$Ge_{27}Sb_{13}S_{55}Te_5$	1.49	2.67	67.50	25.28

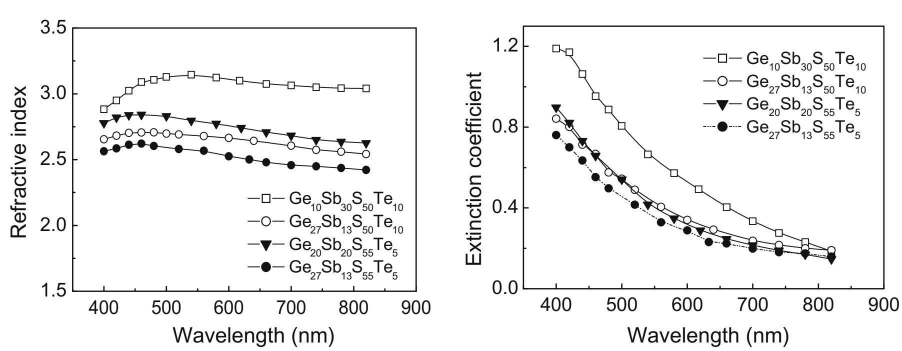

Fig. 1. Spectral dependences of the refractive index (a) and extinction coefficient (b) of chalcogenide glasses with compositions, inserted.