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

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A B S T R A C T
New quaternary telluride glassy materials with composition of GeSb_{40- x}S_{50}Te_{10} and GeSb_{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.

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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.

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 GeSb_{40– x}S_{50}Te_{10} (x = 10 and 27 at.%), and GeSb_{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
The glass constituent elements [23]. Since the Ge cations have lower energy (Fig. 1b), a shift of the whole curve toward lower energy remained displacement. Content increases, as the latter has weaker influence on the observation (red shift) is observed when the Ge content decreases or Te content up to 27, correspondingly decreasing the Sb content, at (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 dependence 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 $(\alpha^2 h^m)/(\epsilon m) = B(hv - E_g)$ [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 $(\alpha^2 h^m)/(\epsilon m)$ versus photon energy (hν) 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 intersection with the photon energy axis providing the $E_g$ value. The results are summarized in Fig. 2, where the spectral dependence of $\alpha$ and the corresponding inserted plot of $(\alpha^2 h^m)/(\epsilon m)$ versus (hν) 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.

### 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 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 in Fig. 1b).

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<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_g$ (eV)</th>
<th>Z</th>
<th>$H_s$ (kcal/g)</th>
<th>$H_s/Z$ (kcal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{10}$Sb$</em>{20}$S$<em>{50}$Te$</em>{10}$</td>
<td>1.30</td>
<td>2.50</td>
<td>64.01</td>
<td>25.60</td>
</tr>
<tr>
<td>Ge$<em>{20}$Sb$</em>{10}$S$<em>{50}$Te$</em>{10}$</td>
<td>1.42</td>
<td>2.67</td>
<td>66.54</td>
<td>24.92</td>
</tr>
<tr>
<td>Ge$<em>{20}$Sb$</em>{10}$S$<em>{50}$Te$</em>{5}$</td>
<td>1.47</td>
<td>2.60</td>
<td>66.57</td>
<td>25.6</td>
</tr>
<tr>
<td>Ge$<em>{20}$Sb$</em>{10}$S$<em>{50}$Te$</em>{5}$</td>
<td>1.49</td>
<td>2.67</td>
<td>67.50</td>
<td>25.28</td>
</tr>
</tbody>
</table>

![Fig. 1. Spectral dependences of the refractive index (a) and extinction coefficient (b) of chalcogenide glasses with compositions, inserted.](image1.png)

![Fig. 2. Absorption coefficient $\alpha$ in dependence on photon energy of chalcogenide glasses with compositions, inserted. The corresponding plots of $(\alpha^2 h^m)/(\epsilon m)$ versus hv are also inserted.](image2.png)
The increase in the $E_g$ values can be explained on the basis of the "density of states" model proposed by Davis and Mott [26]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous state. High concentration of localized states in the band structure narrows the energy gap and, therefore, broadening of energy gap, observed in our case, can be an indication for lesser degree of disorder and less defects in the studied glasses. In chalcogenide glasses containing a high concentration of group VI elements (Te and S in our case) the lone-pair electrons form the top of the valence band (bonding band) and the antibonding band form the conduction band [27]. The number of states in the conduction band depends only on the number of different bonds in the given composition, while the number of states in the valence band is determined by the number of lone-pair states related to the chalcogenide atoms. Since in the compositions considered by us the amount of chalcogenides is constant ($S_{50}Te_{10}$ or $S_{55}Te_{5}$), the valence band remains the same. Therefore, the increase of the optical band gap with the Ge content, keeping the S and Te contents constant, can be attributed to the narrowing of the conduction band tail caused by increasing the amount of stronger (53.5 kcal/mol) Ge–S bonds at the expense of the amount of weaker (47.6 kcal/mol) Sb–S bonds [28]. When the Te content decreases from 10 to 5 at.%, the increase of the number of the much stronger Ge–S and Sb–S bonds at the expense of weaker (35.5 kcal/mol) Ge–Te and (31.6 kcal/mol) Sb–Te bonds [28] leads to an increase of the average stabilization energy of chemical bonds and, therefore, to an increase of the gap energy, as was observed (Table 1).

The decrease of $E_g$ values with increasing the Te content can be also explained on the bases of the suggestion that the change of the band gap is caused by alloying effect, namely a compositional change in the host material itself [29] due to the change in bond angles and/or bond lengths modifying the glassy structure and disturbing the ordering. The lower value of the optical band gap for compositions with higher Te content can be related to the tendency of Te atoms to form chemical disordering and to create localized states in the band gap.

The energy band gap value is correlated with the physical parameters of the glasses, such as average coordination number ($\langle Z \rangle$) and average heat of atomization ($H_a$), the latter being a measure of cohesive energy and representing the relative bond strength. The average coordination number $Z$ is defined by the expression $Z = 4Q_x + 3Q_{Sb} + 2Q_S + 2Q_{Te}$, where $Q_x$ is the molar fraction of constituent elements and the numbers 4, 3, 2 and 2 are the coordination number of Ge, Sb, S, Te, respectively. The coordination number $Z$ characterizes the electronic properties of semiconducting materials, and shows the bonding character in the nearest-neighbour region [30]. The heat of atomization, $H_a$, for our quaternary glassy system Ge–Sb–S–Te can be calculated as $H_a = \langle xH^{e_x}_a + H^{e_{Sb}}_a + \gamma H^{e_{Te}}_a + \delta H^{e_{S}}_a \rangle / (x + \beta + \gamma + \delta)$ [31], where $H_a$ is the heat of atomization of constituent atoms, and corresponds to the average nonpolar bond energy of the Ge–Ge, Sb–Sb, S–S and Te–Te chemical bonds [28]: $x$, $\beta$, $\gamma$ and $\delta$ are the atomic percent of the corresponding elements. The calculated $Z$ and $H_a$ values, as well as their ratio are summarized in Table 1.

According to the constrain theory [32], the chalcogenide glasses can be organized into three different categories: (i) floppy, or under-coordinated glasses with $Z < 2.4$; (ii) optimally-coordinated or ideal glasses with $Z = 2.4$; (iii) stressed-rigid and over-coordinated glasses with $Z > 2.4$. In accordance with that, the glassy compositions studied by us are over-coordinated, stressed-rigid and with lower connectivity, as the values of $Z$ are larger than 2.4 (Table 1). The ratio of the heat of atomization and coordination number, parameter $H_a/Z$, given also in Table 1, is almost constant independently on composition and, therefore, one may conclude that the average heat of atomization has no essential influence on the band gap energy values.

The results from the neutron diffraction measurements of these Ge–Sb–S–Te glasses are summarized in Fig. 3. As is seen, there are no sharp peaks in the measured spectra of the structure factor $S(Q)$, which could be related to crystalline phase and, therefore, the synthesized glasses are fully amorphous. Based on these results we can conclude that all optical parameters considered here are characteristics for the amorphous glassy material with the given composition.

4. Conclusion

By spectroscopic ellipsometry, the optical constants of new amorphous quaternary telluride glassy materials with composition of Ge$_{x}$Sb$_{20-x}$S$_{50}$Te$_{10}$ and Ge$_{x}$Sb$_{20}$S$_{35}$Te$_{5}$ ($x = 10, 20, \text{and} 27$) have been defined in the spectral range of 400–820 nm. The observed increase of the optical band gap energy value with increase of Ge content or decrease of Te content is explained in terms of chemical bonds formation and density of states, both affected by compositional variation.

Acknowledgements

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References