Single-oscillator description of spectral dependence of the refractive index of new chalcogenide Ge-Sb-(S,Te) glasses

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Abstract. New quaternary telluride glasses based on Ge-S system with addition of Sb and partial substitution of S by Te have been synthesized and their optical properties in dependence on composition have been studied by spectroscopic ellipsometry in 400-820 nm spectral range. The dispersion behavior of the refractive index of these glasses with composition of GeSb40-S50Te10 and GeSb40-S55Te5 (x= 10, 20, and 27) was examined applying the single-oscillator theory and using the Wempel-DiDomenico’s model. From the data analysis the optical constants (n, k, ε), optical bandgap energy \( E_{og} \) and film thickness, as well as the oscillator energies \( E_0 \) and \( E_d \) have been determined. The observed increase of \( E_0 \) and decrease of \( E_d \) with increasing the Ge content or decreasing the Te content are explained by the change of amount and strength of heteropolar chemical bonds and by the less covalent character of chemical bonding in these materials. Correlation between the oscillator energy \( E_0 \) and optical band gap energy \( E_{og} \) is established.

1. Introduction
Telluride glasses from quaternary systems are potential candidates for integrated optics due to their high refractive index and photosensitivity as well as their transparency in the infrared spectral region. This explains the growing interest in these semiconducting materials for manufacturing filters, anti-reflection coatings and, in general, a wide range of optical devices [1-3]. In recent years the number of papers, dealing with such telluride glasses has increased which reflects the growing interest in these materials [4-11]. Still, there is no comprehensive study of the influence of Te substitution for S on the optical properties of the glasses belonging to the quaternary Ge-Sb-S-Te system. Knowledge of optical constants of these materials is quite essential to examine the material’s potential for opto-electronic applications.

Recently, we have synthesized new quaternary telluride glasses based on Ge-S system with addition of Sb and partial substitution of S by Te and we have started studying the compositional dependences of their physicochemical and optical properties [12, 13]. In this paper we examine the dispersion behavior of the refractive index of these glasses with composition of GeSb40-S50Te10 and GeSb40-S55Te5 (x= 10, 20, and 27), the optical constants being calculated from the spectroscopic ellipsometric (SE) measurements. It should be emphasized, that all considered optical parameters are

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characteristic for an amorphous glassy material as derived from the neutron diffraction measurements performed on these glasses [13].

2. Experimental

The bulk glasses with four compositions, namely Ge$_x$Sb$_{40-x}$S$_{50}$Te$_{10}$ ($x=10$ and 27) and Ge$_x$Sb$_{40-x}$S$_{55}$Te$_{5}$ ($x=20$ and 27), were synthesized from 5N 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 a quartz ampoule which was evacuated down to $10^{-3}$ Pa. The ampoules were loaded in the furnace and were heated up to 950°C. They were kept at this temperature for 24 h rotating the furnace for homogeneous melting and after ending the process the ampoules were pull out and were quenched in ice water. The samples were cut into thick slices and were polished on one side for optical measurements.

The ellipsometric measurements were performed in the spectral region of 400 - 820 nm (1.5 - 3.1 eV) on a manual Rudolf Research ellipsometer with PCSA configuration 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 minimized 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) of the glasses was evaluated.

3. Results and discussion

The refractive index $n$ and extinction coefficient $k$ of the synthesized glasses with composition of Ge$_x$Sb$_{40-x}$S$_{50}$Te$_{10}$ ($x=10$ and 27) and Ge$_x$Sb$_{40-x}$S$_{55}$Te$_{5}$ ($x=20$ and 27) are presented in figure 1(a) and 1(b), respectively. With changing the glass composition by increasing the Ge content or by decreasing the Te content a tendency is observed for these optical parameters to increase.

![Figure 1](image-url)

**Figure 1.** Dispersion curves of the refractive index $n$ and extinction coefficient $k$ of the studied glasses with compositions Ge$_{10}$Sb$_{30}$S$_{50}$Te$_{10}$ (a) and Ge$_{27}$Sb$_{13}$S$_{55}$Te$_{5}$ (b).

From the obtained $n$ and $k$ data (figure 1), the complex dielectric function $\tilde{\epsilon}$ ($\tilde{\epsilon}=\epsilon_1-j\epsilon_2$, where $\epsilon_1=n^2-k^2$ and $\epsilon_2=2nk$) can be determined. In the high frequency range $\epsilon_1$ can be expressed by a simple classical dispersion equation $(n_0^2-1)/(n^2-1)=1-(\lambda_0/\lambda)^2$ [14]. The index $n_0$ is the refractive index of an empty lattice at zero photon energy (at infinite wavelength) and is called static refractive index. It determines the high-frequency component of the relative permittivity $\epsilon_\infty$ in other words the infinite wavelength dielectric constant $\epsilon_\infty=n_0^2$ for a given material. The quantity $\lambda_0$ is the average oscillator wavelength and it is related to the energy at which direct interband electron transitions take place. By plotting $1/(n^2-1)$ versus $1/\lambda^2$ (Figure 2) these quantities were determined, as the intercept of the
approximated line with the vertical axis at zero \(1/\lambda^2\) gave \(n_0\) and the slope of this line gave \(\lambda_0\). Their values are presented in Table 1. There was a clear tendency for the \(n_0\) values, respectively for the \(\varepsilon_\infty\)

values, to decrease with increasing the Ge content or decreasing the Te content in the studied glasses.

Further, the refractive index dependences were analyzed in the spectral region below the interband absorption edge by the single-oscillator theory using the Wempel-DiDomenico’s (WDD) model [15]. The refractive index is connected with the energetic parameters of a single oscillator by the relationship \(n^2-1 = (E_d E_0) / (E_0^2 – E^2)\), where \(E\) is the photon energy; \(E_0\) is the oscillator energy related to an average band gap and it corresponds to the distance between the “centres of gravity” of the valence and the conduction bands; and \(E_d\) is the dispersion energy, a measure of the interband transitions strength. The values of \(E_0\) and \(E_d\) parameters were calculated by plotting \(1/(n^2-1)\) versus \(E^2\) (Figure 3) and by linear approximation of the low-energy part of the curves. The results are also given in Table 1. On the other hand, \(E_0\) is connected with \(\lambda_0\) through the relation \(E_0 = hc/\lambda_0\), where \(h\) and \(c\) are Planck’s constant and velocity of light in vacuum respectively. The \(E_0\) value that was calculated from \(hc/\lambda_0\) and the one deduced from the \(1/(n^2-1)\) versus \(E^2\) plots deviated from each other less than 1 % on average.

![Figure 2](image1.png) ![Figure 3](image2.png)

**Figure 2.** Plots of \(1/(n^2-1)\) versus \(\lambda^2\) for different compositions of the studied glasses.

**Figure 3.** Plots of \(1/(n^2-1)\) versus \(E^2\) for different compositions of the studied glasses.

| Glass composition | \(n_0\) | \(\varepsilon_\infty\) | \(\lambda_0\) (nm) | \(E_0(\lambda_0)\) (eV) | \(E_\theta\) (eV) | \(E_d\) (eV) | \(E_{og}\) eV |
|------------------|--------|----------------|-----------------|----------------|----------------|-------------|------------|
| Ge\(_{10}\)Sb\(_{30}\)S\(_{50}\)Te\(_{10}\) | 2.86   | 8.2           | 279.04          | 4.44           | 4.44           | 31.6        | 1.30       |
| Ge\(_{27}\)Sb\(_{13}\)S\(_{50}\)Te\(_{10}\) | 2.43   | 5.9           | 270.55          | 4.58           | 4.65           | 22.8        | 1.42       |
| Ge\(_{20}\)Sb\(_{30}\)S\(_{55}\)Te\(_{5}\) | 2.50   | 6.3           | 271.96          | 4.56           | 4.56           | 23.9        | 1.47       |
| Ge\(_{27}\)Sb\(_{13}\)S\(_{55}\)Te\(_{5}\) | 2.33   | 5.4           | 247.67          | 5.0            | 4.97           | 22.0        | 1.49       |

The observed compositional dependences of the refractive index can be explained by the different polarizability of the glass constituent elements, as the higher the polarizibility the larger the index \(n_0\) value [16]. It is known that when the covalent atomic radius is larger the electron clouds of atoms are easier to be polarized. Since Ge and S possess smaller covalent radius than Sb and Te atoms [12], the polarizability of Ge and S is lower compared to Sb and Te atoms. This explains why the \(n_0\) and \(\varepsilon_\infty\) values decrease by increasing the Ge content or decreasing the Te content.

The dependences of the extinction coefficient \(k\) (Figure 1) were also considered. The absorption coefficient was determined from the \(k\) data \((\alpha=4\pi k/\lambda)\) and described by the relation \((\alpha E)=B(E-E_{og})^m\) [17,18], where the parameter \(B\) depends on the electron transition probability. The power \(m\) is an
integer number characterizing the transition process and, for chalcogenide glasses with indirect type electron transitions, it is equal to 2. By plotting the \((\alpha E)^{1/2}\) versus \(E\), the energy band gap \(E_{\text{og}}\) was determined, as the interception of the extrapolated linear part of the curve with the photon energy axis provides \(E_{\text{og}}\) with an accuracy of \(\pm 0.05\) eV. The corresponding dependences are presented in Figure 4 and 5, while the optical bandgap values are given in Table 1. As it is seen, the same tendency as the one for \(E_0\) is observed, namely that the \(E_{\text{og}}\) value increases with increasing the Ge content or decreasing the Te content.

The behavior of the optical band gap \(E_{\text{og}}\) with varying the glass composition (Table 1) has been explained by the change of the amount and strength of heteropolar chemical bonds in these materials [13]. For better understanding, we calculated the percent of each possible chemical bond in the glassy composition taking into account the chemical bond ordering, i.e. that the strongest bonds are created first followed by those with decreasing bond strength. The results are presented in Table 2, where from the left column to the right the strongest Ge-S bonds are given followed by the weaker bonds up to the weakest Ge-Ge bonds. According to the chemical bond ordering, the formation of chemical bonds proceeds in strict sequence toward decreasing bond energy until all the valences of the atoms are saturated [19]. The bond energy and covalent character of the possible heteropolar chemical bonds were taken from [12], where the calculation procedure is discussed in detail [12]. As is seen from Table 2, with increasing the Ge or decreasing Te content the number of stronger chemical bonds (such as Ge-S and Te-S) increases making the chemical bonding less covalent.

| Glassy composition | Amount of possible chemical bonds (%) |
|-------------------|----------------------------------------|
|                   | Ge-S        | Te-S        | Sb-S        | Sb-Te       | Sb-Sb       | Ge-Ge       |
| Ge_{10}Sb_{10}S_{50}Te_{10} | 20.0        | 20.0        | 26.8        | -           | 33.2        | -           |
| Ge_{27}Sb_{13}S_{50}Te_{10} | 57.7        | -           | -           | 23.1        | 14.5        | 4.6         |
| Ge_{20}Sb_{20}S_{55}Te_{5}  | 44.4        | 11.1        | 14.9        | -           | 29.6        | -           |
| Ge_{27}Sb_{13}S_{55}Te_{5}  | 65.8        | 2.4         | -           | 6.5         | 25.2        | -           |

In the case of constant S and Te content, the increase of the optical band gap \(E_{\text{og}}\) can be attributed to an increase of the amount of stronger chemical bonds at the expense of the amount of weaker ones. This leads to narrowing of the conduction band tail, while the valence band-tail remains the same, as it is defined mainly by the amount of chalcogenide (S and Te) atoms [1]. When the Te content increases from 5 to 10 at.%, the increase of the number of the much weaker Ge-Te and Sb-Te bonds (Table 2) results in a reduction of the average stabilization energy of chemical bonds [12] and, therefore, in a decrease of the bandgap energy (Table 1).
Since the oscillator energy $E_0$ represents the average band gap energy, its value follows the same compositional dependence as the one for the optical band gap $E_{og}$. Thus, in respect to $E_{og}$, the oscillator energy increases by increasing the number of stronger Ge–S bonds at the expense of the amount of weaker Sb–S bonds, as well as by increasing the number of stronger Ge–S and Sb–S bonds at the expense of weaker Ge–Te and Sb–Te bonds (Tables 1 and 2).

Quite the contrary is observed for the dispersion energy $E_d$, as its value decreases with increasing the Ge content or decreasing the Te content (Table 1). This behavior can be also explained by the change of the number and type of chemical bonds and their bonding energy. In these glasses the formed bonds are predominantly covalent since the constituent elements have close values of electronegativity \[20\]. $E_d$ is connected with bond ionicity, as it can also be expressed by an empirical formula $E_d = \beta N_c Z_a N_e (eV)$ \[15\], where $\beta$ is a parameter which reflects the character of chemical bonding, $N_c$ is the coordination of the cation nearest neighbour to the anion, $Z_a$ is the formal chemical valency of the anion, and $N_e$ is the total number of valence electrons (cores excluded) per anion. For ionic chemical bonds the $\beta$ parameter is equal to $\beta_i = 0.26 \pm 0.03$ eV, while for covalent bonds $\beta_c = 0.37 \pm 0.04$ eV \[15\]. We can conclude that an increase of the number of stronger chemical bonds leads to weakening of the covalent bond character and, as a consequence, to a decrease of $\beta$ value. As the dispersion energy is proportional to the $\beta$ parameter ($E_d = \beta N_c Z_a N_e$), the $E_d$ value decreases accordingly. On the other hand, by increasing the Ge or Te content, the compactness of the glassy structure decreases \[12\], which causes a decrease of the effective cation coordination number $N_c$ which also contributes to the decrease of $E_d$ value.

4. Conclusion
The dispersion behavior of the refractive index of new amorphous quaternary telluride glassy materials with composition of Ge$_x$Sb$_{40-x}$S$_{50}$Te$_{10}$ and Ge$_x$Sb$_{40-x}$S$_{55}$Te$_5$ ($x=$ 10, 20, and 27) has been studied by spectroscopic ellipsometry in the spectral range of 400-820 nm. By applying the single-oscillator theory, from the refractive index dispersion data analysis the values of the oscillator energy $E_0$ and oscillator strength $E_d$ are obtained. The observed changes in these parameters are explained in terms of chemical bonds formation and change of the bonding energy and bond covalency.

References
[1] Tauc J 1974 Amorphous and Liquid Semiconductors (Plenum Press, London/NY) Chap. 4
[2] Savage J A 1985 Infrared Optical Materials and their antireflection coatings (Adam Hilger, Bristol) ISBN 0-85274-790-X
[3] Kosek F, Cimpl Z, Tulka J and Chlebny J 1987 J. Non-Cryst. Solids 90 401
[4] Pamukchieva V and Szekeres A 2008 Opt. Mater. 30 1088
[5] Shiryaev V S, Adam J-L, Zhang X H, Boussard-Plerdel C, Lucas J and Churbanov M F 2004 J. Non-Cryst. Solids 336 113
[6] Michel K, Bureau B, Pouvreau C, Sangleboeuf J C, Boussard-Plédel C, Rouxel T, Adam J-L, Staubmann K, Steinner H, Baumann T, Katzir A, Bayona J and Konz W 2003 J. Non-Cryst. Solids 326&327 434
[7] Keirsse J, Boussard-Plédel C, Loreal O, Sire O, Bureau B, Turlin B, Leroyer P and Lucas J 2003 J. Non-Cryst. Solids 326&327 430
[8] Le Coq D, Boussard-Plédel C, Fonteneau G, Pain T, Bureau B and Adam J L 2003 Mater. Res. Bull. 38 174
[9] Dongol M, Hafiz M M, Abou-Zied M and Elhady A F 2001 Appl. Surf. Sci. 185 1
[10] Pamukchieva V, Szekeres A and Todorova K 2004 Proceeding of SPIE 5581 608
[11] Pamukchieva V and Szekeres A 2005 J. Optoelectron. & Adv. Mater. 7 1277
[12] Pamukchieva V, Szekeres A, Todorova K, Fabian M, Svb E, Revay Zs and Szentmiklosi L 2009 J. Non-Cryst. Solids 355 2485
[13] Pamukchieva V, Szekeres A, Todorova K, Svb E and Fabian M 2009 Opt. Mater. 32 45
[14] Zemel J N, Jensen J D and Schoolar R B 1965 Phys. Rev. 140 A330
[15] Wemple S H and DiDomenico Jr M 1971 Phys. Rev. B 3 1338
[16] Dimitrove V and Sakka S 1996 J. Appl. Phys. 79 1736
[17] Tauc J, Grigorovici R and Vancu A 1966 Phys. Status Solidi 15 627
[18] Mott N F and Davis E A 1970 Philos. Mag. 22 903
[19] Jozef B, Stanford O, Mahadevan S, Gridhar A and Singh A K 1985 J. Non-Cryst. Solids 74 75
[20] http://www.knovel.com/web/portal/periodic_table