ISSN 1313-2539

OPTICAL CHARACTERISTICS OF THE CHALCOGENIDE $Sb_{32}As_5S_{48}I_{15}$ GLASS

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Abstract

The paper describes a study of some optical parameters of the amorphous chalcogenide glass of the composition $Sb_{32}As_5S_{48}I_{15}$. Dispersion of the refraction index was determined by the direct method on the prism made of the investigated glass, and the obtained results served as the basis for determining the value of the wavelength corresponding to the characteristic frequencies of elementary oscillations (λ_0) and total oscillator force of the electronic system (A). The recorded transparency spectra were used to determine spectral distribution of the absorption coefficient (α), with and without taking the reflection into account. It was shown that the reflection can be neglected in the first approximation. The values of the absorption edge (λ_g), optical band gap (E_g), as well as the width of the tails of localized states in the band gap region (Γ_0), were also determined.

Key words: *chalcogenides, refraction index, optical constants*

1. INTRODUCTION

Amorphous chalcogenides represent a group of noncrystalline materials involving sulfides, selenides, or tellurides of the elements of the fourth and fifth groups of the periodic system of elements. The nature of the components of the given system determines the structural units that are formed in the glass matrix. With increase in the number of components increases also the region of glass formation, since this enhances the possibility of formation of the different structural units.

The objective of this work was to study the amorphous semiconducting material from the system Sb(As)-S-I, primarily interesting as ferroelectric sitals. It may be expected that by varying the arsenic to antimony ratio in the glass composition one can tailor the ferroelectric characteristics of the resulting material by influencing the thermal induction of the ferroelectric centers of antimony sulfoiodide (SbSI).

The glasses of the type Sb-S-I have a narrow range of amorphousness of the island character [1], so it could be expected that the addition of arsenic atoms, having in mind the wide range of amorphousness of the glasses from the system As-S-I, would facilitate the preparation of the amorphous material within which it would be possible to thermally induce the important ferroelectric centers SbSI. This might bring about all the advantages of the amorphous structure in respect of their properties, first of all the ferroelectric characteristics.

References

[1] Виноградова Г. З.: *Стаклообразование и фазовы равновесия в халькогенидных системах*, Издательство „Наука”, Москва (1984)

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Measurements of the optical characteristics of the glasses from the same system showed also the significance of their behavior, first of all of the index of refraction [2].

2. EXPERIMENTAL

The $Sb_{32}As_5S_{48}I_{15}$ glass was synthesized from the high-purity elementary components in quartz ampoules, using the method of cascade heating and annealing in the air. To achieve best homogenization, the ampoule was held at the maximal temperature of 923 K for a sufficiently long time, not shorter than 12 hours [3].

Dispersion of the refraction index of the investigated glass was measured by direct method on the prism made of the investigated material (Figure 1). If it is ensured that the incident ray is perpendicular to the prism side, the standard equation of light refraction can be transformed into the following form:

$$n = n(\lambda) = \frac{sin(\delta + \varphi)}{sin(\varphi)} \qquad (1)$$

where δ is the deflection angle of the refracted ray with respect to the direction of the incident ray, and φ is the prism angle.

Samples for the measurement of the refractive index dispersion were prepared by grinding with abrasive powders of different grain size (using a special holder), and then finely polished on silk.

The prism angle between the polished surfaces φ was measured by reflection method using an Enraf Nonius Y-881 bicircular optical goniometer, with an accuracy of ±1', and it was 15^0 10'.

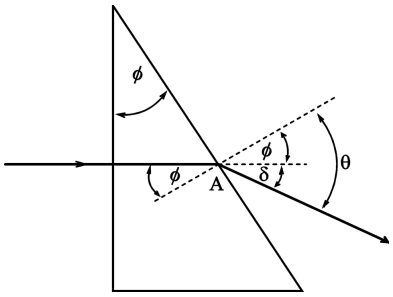


Figure 1. Light refraction on the prism

A high-presure xenon lamp, Osram XBO 450W, was used as the light source and, with the aid of the focusing lenses, the light was directed to the entrance slit of an SPM 2 monochromator. The colimated monochromatatic light was normal to the prism surface. The refracted ray was detected by Si and Ge photodiodes.

The bodies of the photodiodes were firmly fixed to the mobile part of a Philips PM 8120 XY plotter. Such an arrangement allowed the displacement of the detector along the x-axis of the plotter, while the signal from the detector was simultaneously fed to the vertical input of the plotter, ensuring thus the simultaneous recording of the intensity of the photocurrent during the diode displacement along the x-axis.

For measuring the sample transparency in the interval of wavelengths to 1000 nm use was made of a powerful tungsten filament lamp as a light source. Through the broad-band filters, WG5 for 400-600 nm and OG5 for 600-1000 nm, the light enters the SPM 2 monochromator (Carl Zeiss Jena) with an optical grating of 650 lines per mm. After leaving the monochromator the light successively passes through the sample glued to the holder with a fixed aperture and through the same holder but without a sample. In the first case is measured the photocurrent of the transmitted light and in the second case the incidence light. An EMI 9684B photomultiplier was connected to a high-voltage source. The

[2] Lukić S. R., Manić V., Đurić-Stanojević B., Proceedings of the 10th Congress of Physicists of Yugoslavia (2000) 115
[3] Štrbac G. R., Lukić S. R., Avramov M. I., Vinča Bulletin 1-4(8) (2003) 35

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working voltage of 1 kV was selected to ensure an optimum relationship between the sensitivity and the dark current of the photomultiplier. The photomultiplier current was measured using a universal measuring instrument, a Philips PM-2436/06 DC microvoltmeter.

In the sample preparation, the planparallel plates were finely polished to obtain a mirror-like appearance, and transparencies were measured for each plate thickness. The polishing procedure was repeated to the lowest possible thickness achievable, at which the plate broke.

3. RESULTS

In Figure 2 are presented results of the measurement of the refractive index dispersion for the glass $Sb_{32}As_5S_{48}I_{15}$. As can be seen, in the investigated range of wavelengths the sample is characterized by high values of the refraction index, which is in agreement with the previous findings for the glasses from this system [2]. Such values of the refractive index justify the use of the prism method for their measurement.

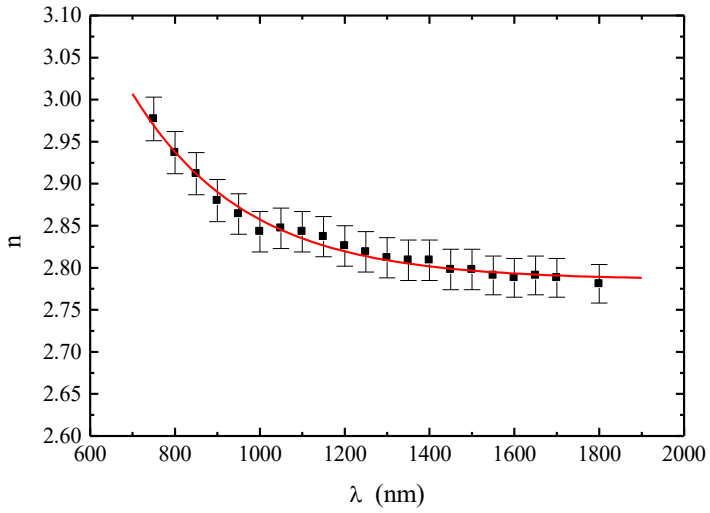


Figure 2. Dispersion of the refractive index for the glass $Sb_{32}As_5S_{48}I_{15}$

In order to model the optical behavior of investigated glasses on the basis of the theory of electronic oscillator it is necessary to consider an ideal glass. In that case the bound and localized electrons are excluded from consideration. Assuming that the dominant valence electrons oscillate at very close, practically identical, frequencies, the following relation holds [4]:

$$n^2 - 1 = \sum_i A_i \cdot \frac{\lambda^2}{\lambda^2 - \lambda_0^2} = A \cdot \frac{\lambda^2}{\lambda^2 - \lambda_0^2} \qquad (2)$$

where A denotes the total force of the oscillator of the electronic system and λ_0 is the wavelength corresponding to the characteristic frequencies of elementary oscillations.

In order to determine the values for A and λ_0 the relation 2 is linearized to the form:

[4] Feltz A.: *Amorphe und glasartige anorganische Festkörper*, Akademie – Verlag, Berlin (1983)

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$$\frac{\lambda^2}{n^2-1}=\frac{1}{A}\lambda^2-\frac{1}{A}\lambda_0^2 \tag{3}$$

and the linear dependence of $\frac{\lambda^2}{n^2-1}$ on λ^2 allows the determination of these parameters.

Graphical presentation of this linearization is shown in Figure 3, and the values of the calculated parameters are given in Table 1.

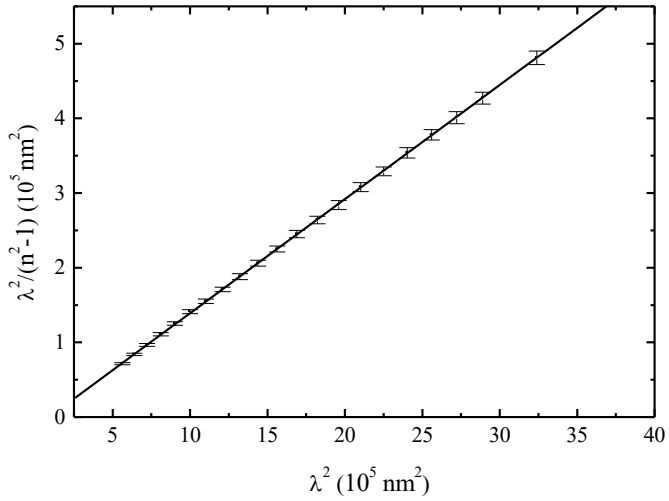


Figure 3. Linearization of the refractive index dispersion for the glass $Sb_{32}As_5S_{48}I_{15}$

Table 1. Values of the wavelengths, energies, and electron oscillation frequencies and oscillator force for the glass $Sb_{32}As_5S_{48}I_{15}$ at room temperature

x *(at %)*	$\lambda_0\ (nm)$	$E_{osc}\,(eV)$	$\nu_{osc}\left(\cdot 10^{14}\,Hz\right)$	A
32	299(4)	4.2	10.0	6.544(17)

ISSN 1313-2539

Calculations showed that the frequencies of electronic oscillator are in the UV range, which is in agreement with the previosly published data for the glasses from this system [2].

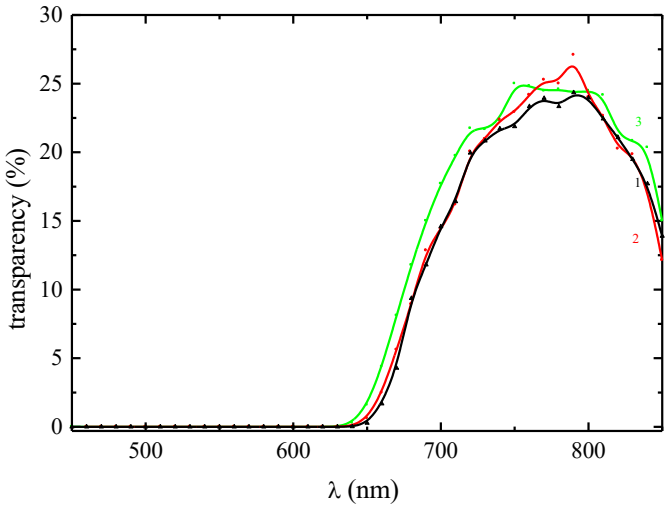


Figure 4. Transparency spectrum of the glass $Sb_{32}As_5S_{48}I_{15}$ for different plate thicknesses: 1 - 0.23 mm, 2 - 0.18 mm, and 3 - 0.12 mm

In Figure 4 are shown the transparancy spectra for the glass $Sb_{32}As_5S_{48}I_{15}$ for the different plate thicknesses. Maximum transparency value was about 25 %. In the region of short wavelengths the limit of the transparency range represents the absorption due to the electron transitions from the valence band to the conduction band. This short-wavelength transparency limit is called absorption edge, and it corresponds to the optical band gap [4].

In Figure 5 are presented the spectral distributions of the absorption coefficient for the different plate thicknesses obtained from the recorded transparency spectra using the relation:

$$\alpha = \frac{1}{d} ln \frac{1}{T} \tag{4}$$

which holds for the materials with small reflection coefficients and high transmissivity (small plate thickness).

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For the determination of the optical band gap by Stuke's method the values of the absorption coefficients even for the thinnest samples were far below $10^4\ cm^{-1}$. Because of that, for the samples for which this was possible, the optical band gap E_g and absorption edge λ_g were determined for the absorption coefficient $\alpha = 10^3\ cm^{-1}$ [5]. The absorption edge thus determined was $\lambda_g = 616.9(17)\ nm$, and the optical band gap $E_g = 2.014(6)\ eV$.

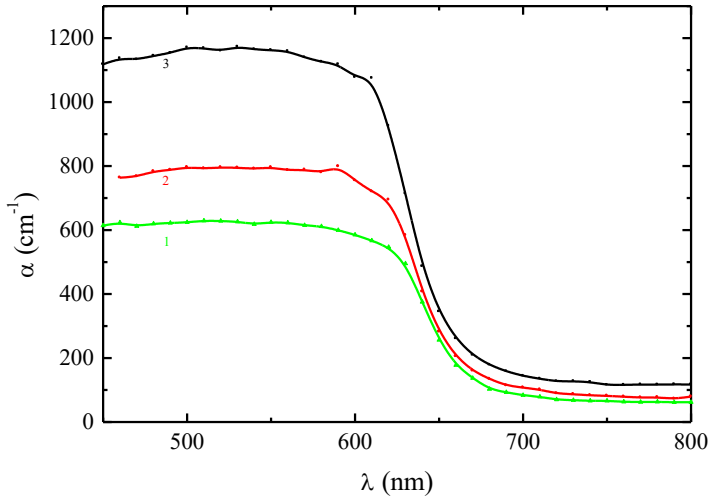


Figure 5. Spectral distribution of the absorption coefficient for the glass $Sb_{32}As_5S_{48}I_{15}$ at the different plate thicknesses:
1 - 0.23 mm, 2 - 0.18 mm, 3 - 0.12 mm

On the other hand, if the reflection is taken into account, the absorption coefficient should be calculated from the relation:

$$\alpha = \frac{1}{d} ln \frac{(1-R)^2 + \sqrt{(1-R)^4 + 4T^2R^2}}{2T} \tag{5}$$

On the basis of the values for λ_0 and A, determined from the dispersion measurements and using relation 3, one can calculate the values of the refraction index at the different wavelengths, and thus obtain the reflection R [4]:

$$R = \frac{(n-1)^2}{n^2+1}; \qquad T = \frac{2n}{n^2+1} \equiv T_o \tag{6}$$

[5] Vahalova R., Tichy L., Vlček M., Ticha H., Phys. Stat. Sol. 181 (2000) 199

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The spectral distribution of the absorption coefficient for the thinnest plate of the investigated glass is shown in Figure 6. The absorption edge obtained for the value $\alpha = 10^3\ cm^{-1}$ was $\lambda_g' = 611.0(17)\ nm$.

The values of absorption edge thus obtained do not deviate much from the values calculated without taking into account reflection, so that the reflection can be neglected in the first approximation.

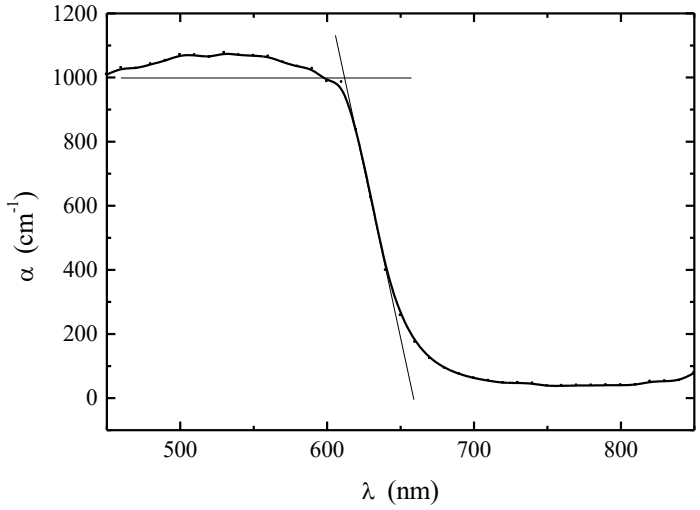


Figure 6. Spectral distribution of the absorption coefficient for the glass $Sb_{32}As_5S_{48}I_{15}$ for the thinnest plate prepared

For the absorption coefficient less than $10^4\ cm^{-1}$, the Urbach tail, holds an exponential dependence between the absorption coefficient and photon energy [6]:

$$\alpha(E,T) = \alpha_o\, e^{\frac{E-E_g}{\Gamma(T,X)}} \tag{7}$$

where *(T,X)* is a constant for each concrete system that determines the slope of the absorption edge, indicating thus the width of the exponential tail; *X* is the parameter of structural disorderliness, and *T* is the temperature. The symbol E_g^o is related to the optical band gap, whereas the constant α_0 is an experimentally determined parameter that corresponds to the absorption coefficient at $h\nu = E_g$.

For the glass-forming structures in which dominates structural disorderliness *(Γ(T,X)=Γ₀)*, it was shown [7] that the relation 7 can be written in the form:

$$\alpha = \alpha_{st}\ exp(h\nu / \Gamma_0) \tag{8}$$

The linearization of this expression allows the determination of the quantity Γ_0, which is interpreted as the width of localized states tails in the region of the band gap.

[6] Urbach F., Phys. Rev., 92 (1953) 1324
[7] Вайштейн И. А., Зацепин А. Ф., Кортов В. С., Физика и химия стекла, 25(1) (1999) 85

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In Figure 7 is presented the quantity $ln\alpha$ as a function of the photon energy $h\nu$ for the thinnest plate in the Urbach region. The slope of the curve gives the quantity Γ_0.

The obtained value for the tails widths of localized states was $\Gamma_0 = 0.09\ eV$.

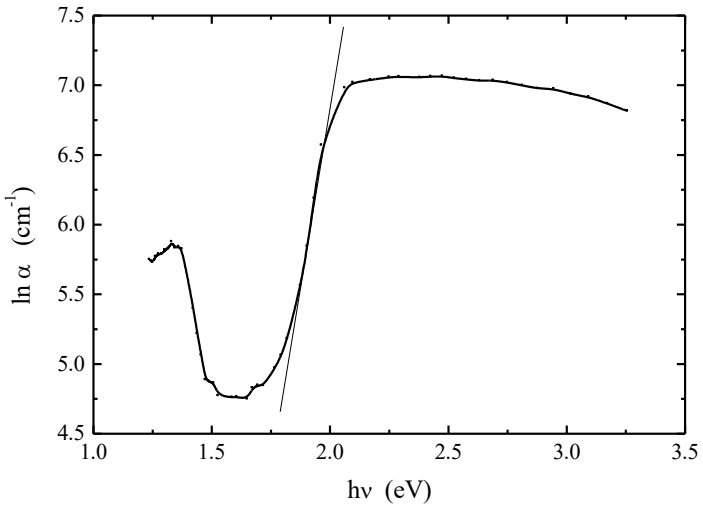


Figure 7. Spectral dependence for the glass $Sb_{32}As_5S_{48}I_{15}$

4. CONCLUSION

The recorded dispersion spectra in the wavelengths of measurement show a normal dispersion and are characterized by high values of the refraction index, which at 750 nm is $n = 2.977(26)$. The frequency of the electronic oscillator is observed in the UV range and its value is $\nu = 10 \cdot 10^{14}\ Hz$, which corresponds to the wavelength of elementary oscillations of $\lambda_0 = 299(4)\ nm$. The optical band gap determined from the transparency spectra is $E_g = 2.014(6)\ eV$. The short-wavelength absorption edge at neglecting reflection is $\lambda_g = 616.9(17)\ nm$, and when the reflection is taken into account $\lambda_g' = 611.0(17)\ nm$, which indicates that the reflection can be neglected in the first approximation. The measurements give for the tails width a value $\Gamma_0 = 0.09\ eV$.

ACKNOWLEDGMENTS

This work was partly financed by the Ministry for Science of the Republic of Serbia, within the project "Amorphous and nanostructural chalcogenides", Project No. 141026 and Provincial Secretariat for Science and Technological Development of AP Vojvodina, within the project "Technology of obtaining and characterization of disordered semiconductors", Project No. 114-451-01397/2006-01.