

OPTICAL PROPERTIES OF GLASSES IN THE $\text{As}_2\text{S}_3\text{-AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ SYSTEM

S. J. Skuban, S. R. Lukić, I. O. Gúth, D. M. Petrović

Institute of Physics, Faculty of Sciences, University of Novi Sad
Trg Dositeja Obradovića 4, 21000 Novi Sad, Yugoslavia

The paper describes the results obtained by studying transparency spectra and index of refraction of glassy chalcogenide semiconductors of the type $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$, for $x=0, 5, 10, 15, 20, 25, 30$ and 35 mol % $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$. It was found that the glasses are transparent in a wide range of the electromagnetic spectrum and the position of the absorption edge depends on the arsenic disulphide content. Optical bandgap was determined and correlated to the glass composition. The dispersion of the refraction index was recorded in the range between the absorption edge and 1150 nm. It was found that the glasses exhibit a normal dispersion with a high value of the refraction index, which shows a linear increase with increase in the $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ content in the glass. Taking into account the approximation that the dispersion properties can be described by algebraic equation, an analytical expression was given for the oscillator force. It was found that the wavelength of the eigenvalue of electron oscillation in this system is situated in the near UV range.

(Received July 2, 2002; accepted July 22, 2002)

Keywords: Chalcogenide, $\text{As}_2\text{S}_3\text{-AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ glass, Optical spectrum, Index of refraction

1. Introduction

The classical approach to the model of energy bands in crystalline semiconductors is primarily based on dispersion of the Bloch waves on a periodic grid. The problems related to the materials with relatively low mobility of charge carriers culminate with the class of semiconducting materials, so that somewhat different approaches had to be sought.

Intrinsic semiconductor characteristics of amorphous materials fit into the scheme of energy levels, whose bands extend as tails of the localized states. In view of the low mobility of charge carriers this results in the energy gap even in the cases of the real systems with the overlapping tails.

In the case of some chalcogenide glasses, the energy gap thus defined, whose existence is due to the lack of mobility of charge carriers have been better characterized by the approach derived from the Kastner-Adler-Fritzsche model [1], and in the frame of two-centres molecular orbitals. Equally important results related to forming the models of these materials have been obtained on the basis of the approach by Street and Mott, based on the existence of defect centres [2].

In the vicinity of the middle of the forbidden gap, (i.e. the mobility gap), a real glass possesses a narrow band of localized states with a sufficiently high density to fix the Fermi level to this region. These energy states are strongly influenced by the components involved and structure defects, whose number depends on the nature of components introduced and the method of sample preparation and annealing.

The range of glass formation in the system As-S-Se is extremely wide [3], somewhat narrower in the system As-Se-Te [4], whereas in the concentration triangle As-S-Te there are two separated regions in which an amorphous phase can be obtained [5]. When a chalcogen element is introduced in the amorphous matrix, it was observed that the highest tendency to glass formation have the chalcogenides involving iodine ($\text{As-B}^{\text{VI}}\text{-I}$, where $\text{B}^{\text{VI}} = \text{S, Se, Te}$). It should be pointed out that the regions of forming stable radicals are relatively small, taking into account that the melts exhibit tendency to liquefy below the solidus line [6].

The primary aim of this work was to study the changes of some optical properties as a consequence of variable ratio of arsenic sulphide and As-Se-Te-I in the material. The introduction of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ into the basic matrix of amorphous arsenic disulphide additionally disturbs both the first coordinations and long-range ordering. This has a direct influence on the characteristics of the energy gap and on the very important optical properties.

A closer characterization of this effect was achieved on the basis of the results of the study of dispersion characteristics of the refraction index and absorption properties of the material in the region of the absorption edge.

It is known that the considerations regarding the behaviour of refraction index are based on the assumption that electrons in condensed media oscillate at a frequency in the visible and UV range and that the electronic polarizability of structural units is a function of the field frequency. The dependence of the refraction index on the wavelength of the incident light is usually described by the Ketteler-Helmholtz relation [7]:

$$n^2 - 1 = \sum_i A_i \frac{\lambda^2}{\lambda^2 - \lambda_i^2} \quad (1)$$

where the summation is carried out over the eigenvalue of the oscillator states of the condensed system. The value λ is the wavelength of the external electromagnetic field and the coefficient A_i is an empiric coefficient of proportionality, known as "oscillator force". The system parameters λ_i and A_i are strongly influenced by the structure of the material, synthesis conditions, as well as by external effects (primarily temperature).

2. Experimental

Glasses of the type $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$, for $x=0, 5, 10, 15, 20, 25, 30$ and 35 were synthesized according to the previously published procedure [8, 9].

Glass transparency in the range of the absorption edge was recorded using a system based on an SPM-2 Zeiss monochromator with quartz optics. A bulb with tungsten filament served as a light source, an EMI 9684 B photomultiplier was used as detector, and current signal was measured using a universal instrument of the DC microvoltmeter, PM-2436/06 (Philips). Samples for measurement were prepared by mechanical treatment to get plates of different thickness and highly parallel planes, whereby the minimal thickness was 0.15 mm. Reflection IR spectra (KBr pellet) in the range of 2.5-10 μm were recorded on an Infracord Perkin Elmer spectrometer.

Dispersion of the refraction index was studied on the basis of the refraction of light beam on the prisms specially prepared of glasses of the corresponding composition. The angle between the polished prism surfaces was determined by reflection method using a two-circle optical goniometer Enraf Nonius Y-881 with an accuracy of $\pm 1'$. Measurements were carried out at room temperature in the wavelength interval from the absorption edge to 1150 nm. The source of electromagnetic radiation was an Osram XBO 450 W lamp and monochromatic light was obtained using an SPM-2 monochromator, while detection was performed with the aid of an Si photodiode.

3. Results and discussion

The measured dependence of the refraction index of the glasses on the wavelength of electromagnetic radiation is presented in Fig. 1. It is evident that all the compositions show a normal dispersion of the refraction index.

The value of the refraction index increases with increase in content of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$. Its change at a fixed wavelength as a function of the $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ content in the glasses is presented in Fig. 2. It is evident that the presented dependence can be (in the limits of error) approximated by a first-order exponential function. The fact that it is possible to establish a correlation of this physical parameter and composition via monotonous function indicates that these glasses along the chosen cut behave as solid solutions [10].

In order to model optical behaviour of the investigated glasses on the basis of the theory of electronic oscillator, whereby for an ideal glass one can consider that the bound and localized electrons are excluded from the process, it was supposed that the predominant valence electrons oscillate at close, practically identical, frequencies. In that case equation (1) reduces to an ordinary algebraic expression [7], so that the coefficient A represents the total oscillator force of the electronic system. As it is accustomed in these procedures, in order to determine A and λ_0 , the mentioned algebraic equation has to be linearized to the form:

$$\frac{\lambda^2}{n^2 - 1} = \frac{1}{A} \lambda^2 - \frac{1}{A} \lambda_0^2 \quad (2)$$

The results of this procedure are presented in Fig. 3.

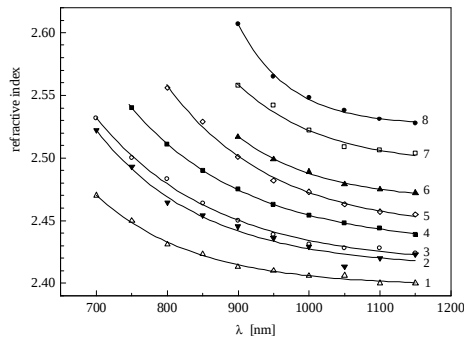


Fig. 1. Dispersion of the refractive index of the glasses of the type $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$ at room temperature: 1) $x = 0$; 2) $x = 5$; 3) $x = 10$; 4) $x = 15$; 5) $x = 20$; 6) $x = 25$; 7) $x = 30$; 8) $x = 35$.

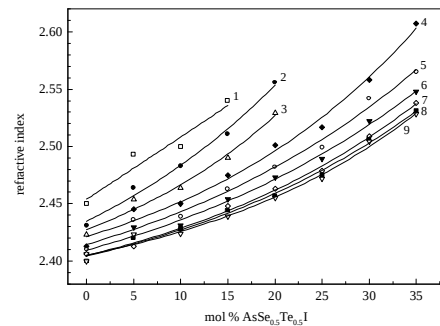


Fig. 2. Changes of the refractive index at a given wavelength as a function of the content of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ in the glasses $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$ at: 1) 750 nm; 2) 800 nm; 3) 850 nm; 4) 900 nm; 5) 950 nm; 6) 1000 nm; 7) 1050 nm; 8) 1100 nm; 9) 1150 nm.

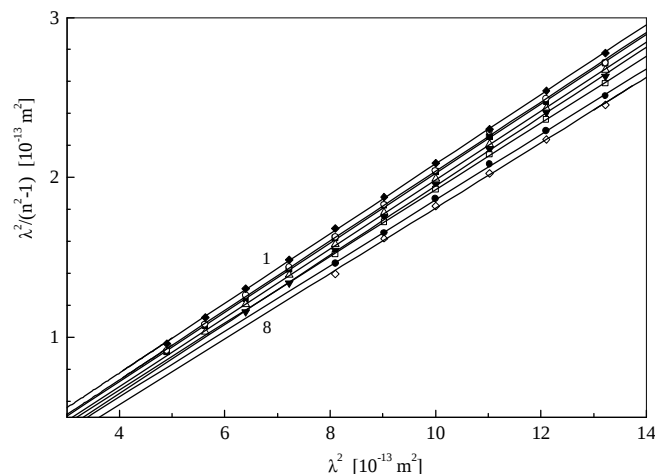


Fig. 3. Linearization of dispersion of the refractive index of the glasses of the type $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$: 1) $x = 0$; 2) $x = 5$; 3) $x = 10$; 4) $x = 15$; 5) $x = 20$; 6) $x = 25$; 7) $x = 30$; 8) $x = 35$.

On the basis of the straight-line parameters it was possible to determine the wavelengths of eigenvalues of the oscillator frequency (λ_0) and oscillator force of the system (A) for each of the investigated glasses. In Table 1, along with the values of these two quantities, we also present the oscillation energy values (E_{osc}) and eigenvalues of oscillator frequencies (ν_{osc}).

It was found that all the values of the frequencies of electron oscillation correspond to wavelengths in the near-ultraviolet range of the electromagnetic spectrum, and that they depend on the material composition. In Fig. 4.a is presented the corresponding correlation describing this dependence.

Table 1. Values of the oscillator force, wavelength of eigenvalue of oscillator frequency, energy and frequency of the oscillator for the glasses of the type $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ at room temperature.

x [mol %]	c [at. % Te]	A	λ_o [nm]	E_{osc} [eV]	ν_{osc} [10^{15} Hz]
0	0	4.59	209.84	5.91	1.43
5	0.83	4.60	251.16	4.93	1.19
10	1.66	4.61	260.22	4.76	1.15
15	2.49	4.64	281.11	4.41	1.06
20	3.32	4.72	317.02	3.91	0.95
25	4.15	4.80	280.07	4.43	1.07
30	4.99	4.87	309.12	4.01	0.97
35	5.83	4.89	341.14	3.95	0.88

Fig. 4.b shows the dependence of the oscillator force on tellurium content in the glass. It is obvious that increase in Te content, through the structural element $AsSe_{0.5}Te_{0.5}I$, yields a linear increase in this parameter.

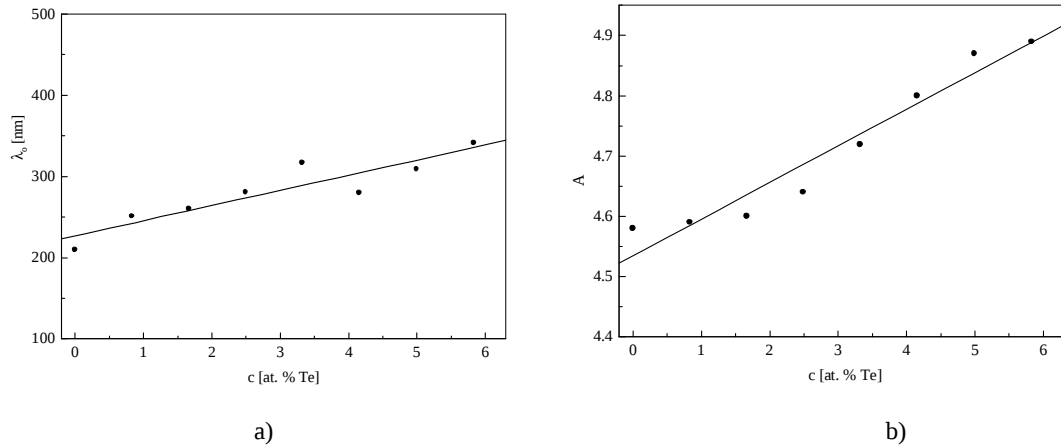


Fig. 4. Concentration dependence of the wavelength of the oscillator eigenvalue frequency (a) and oscillator force of the material (b) for the glasses $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ at room temperature.

On the basis of experimental data and all these considerations, the changes of refractive index as a function of material composition and wavelength of the electromagnetic spectrum for the investigated glasses from the series $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ (starting from the absorption edge to 1150 nm) can be described by the following equation:

$$n(x, \lambda) = 1 + A(x) \cdot \frac{\lambda^2}{\lambda^2 - \lambda_o^2} \quad (3)$$

where A is given by the expression:

$$A(x) = 4.53 - 0.061 \cdot c \quad (4)$$

where c is the Te content in at %.

Spectral studies of the glasses of this series showed a wide range of their transparency. In Fig. 5 are presented the IR spectra for certain chosen compositions. The observed peaks at about 3450 and 1600 cm^{-1} are due to the experimental technique and not to the glass structure itself. Namely, both maxima are caused by the presence of water in KBr (the first is a consequence of the absorption of the H-O-H bond and the second one indicates the presence of the OH-group). Such spectrum, without other maxima, is quite expectable for the given energy interval, bearing in mind that the oscillation energies corresponding to the possible bonds of the material components are in the far-IR region [11].

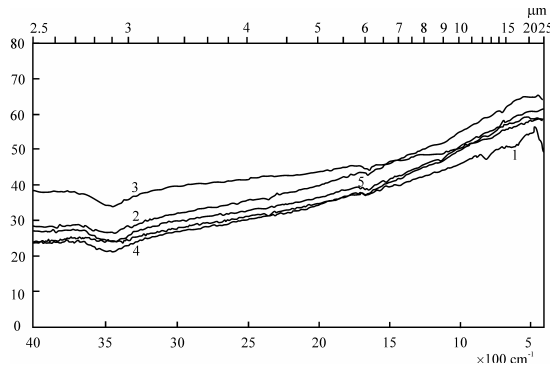


Fig. 5. IR spectra (KBr pellet) of the glasses of the type $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$: 1) $x=100$; 2) $x=5$; 3) $x=15$; 4) $x=25$; 5) $x=35$.

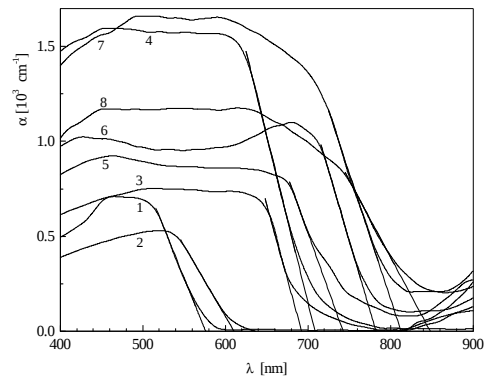


Fig. 6. Absorption coefficients in the range of the absorption edge for the glasses of the type $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$: 1) $x=0$; 2) $x=5$; 3) $x=10$; 4) $x=15$; 5) $x=20$; 6) $x=25$; 7) $x=30$; 8) $x=35$.

The optical bandgap of amorphous chalcogenides is most often determined on the basis of transparency spectra in the region of the absorption edge. This quantity has been assessed in our previous works [8].

The experimental data related to the refraction index dispersion corrected for reflection, made possible to establish a full analytical dependence of the absorption coefficient of wavelength. The values thus obtained are presented in Fig. 6.

The values of the optical bandgap obtained by extrapolation of the linear parts of the corresponding curves are in the range from 1.46 to 2.15 eV . The correlation of this quantity and the $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ content in the material is presented in Fig. 7.

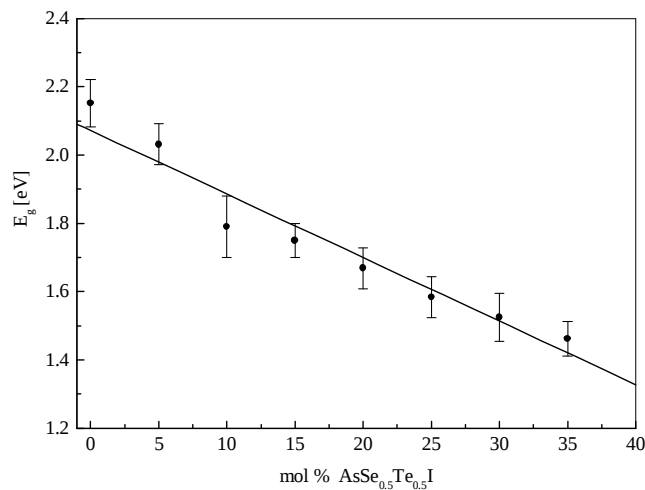


Fig. 7. Dependence of the optical bandgap of the glass on the content of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$.

It can be seen that the value of the optical bandgap decreases linearly with increase in the part of the structural element involving tellurium in the composition of the investigated glass. The modelled analytical form of this dependence is:

$$E_g^{opt} = 2.07 - 0.019 \cdot x \quad (5)$$

where x is the content of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ (in mol %).

The introduction of the structural units $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ into the As_2S_3 glass changes the structure of the basic matrix. The observed monotonicity of relevant changes suggests that one deals with solid solutions and it is a characteristic of the investigated system to 35 mol % of the doping component. This is accompanied by a shift of the delocalized and localized energy states, which produced the narrowing of the energy bandgap and the corresponding effects on the optical characteristics in the range of the absorption edge.

4. Conclusions

The presence of the structural units of the type $\text{A}^{\text{V}}\text{B}^{\text{VI}}\text{C}^{\text{VII}}$ in the basic matrix of the amorphous semiconductor of the type $\text{A}^{\text{V}}\text{B}^{\text{VI}}$ results in significant changes of a number of physical parameters as well as in the changes of energy states distribution.

The introduction of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ into the basic matrix of the glass As_2S_3 causes a shift of its absorption edge, i.e. reduction of the optical bandgap. The values of the energy bandgap are characteristic of semiconducting materials.

All the glasses from the series $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$ possess at room temperature a normal dispersion of the refraction index close to the glass absorption edge up to the value of 2.61.

The increase in Te concentration, i.e. the content of $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$, in the glass, produces an increase in the value of the refraction index measured at a fixed wavelength of the incident light. It was found that the electrons of this system oscillate at different frequencies, depending on the glass composition. All the values of wavelengths corresponding to electron oscillation frequencies are in the near UV range of the electromagnetic spectrum. The overall dispersion behaviour of the system was described by an analytical expression involving the calculated parameters of the system.

Acknowledgement

This work was supported by the Serbian Ministry of Science, Technology and Development, Project "Amorphous and Nanostructural chalcogenides and ceramics", No. 1812.

References

- [1] M. Kastner, D. Adler, H. Fritzsche, *Phys.Rev.Lett.* **37**, 22, 1504 (1976).
- [2] R. A. Street, N. F. Mott, *Phys. Rev. Lett.* **35**, 22, 1293 (1975).
- [3] S. S. Flaschen, A. D. Pearson, W. R. Northower, *J. Amer. Ceram. Soc.* **43**, 274 (1960).
- [4] Z. U. Borisova, V. R. Panus, A. A. Obrazcov, *Vest. Lening. Univ.* **22**, 121 (1970).
- [5] A. A. Obrazcov, V. R. Panus, Z. U. Borisova, *Neorg. materialy* **13**, 9, 1581 (1977).
- [6] G. Rouson, *Neorganicheskie stekloobrazuyuschie sistemy*, Mir, Moskva (1970).
- [7] M. E. Borisova, S. N. Kaykov, *Fizika dielektrikov*, Lening.Gost.Univ., Leningrad (1979).
- [8] S. J. Skuban, S. R. Lukić, I. O. Gut, A. F. Petrović, *Proc. XLIII Conf. ETRAN*, Ed. Dušan Spasojević, Yugoslavia, Vol. IV, p. 244, 1999.
- [9] S. R. Lukić, D. M. Petrović, "Complex Amorphous Chalcogenides", *Grafo Atelje*, Novi Sad (2002).
- [10] H. Schumann, "Metallographie", VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig (1975)
- [11] A. Feltz, *Amorphe und Glassartige Anorganische Festkörper*, Akademie – Verlag, Berlin (1983).