

OPTICAL GAP AND dc CONDUCTIVITY OF DISORDERED MATERIALS OF (As₂Se₃)_{100-x}(SbSI)_x TYPE

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The paper presents the results of a study of some electrical and optical properties of the five-component chalcogenide glasses in the quasi-binary (As₂Se₃)_{100-x}(SbSI)_x system. It is a system with the variable ratio of classical amorphous compound As₂Se₃ and the molecule of antimony sulfoiodide, SbSI, which in the monocrystal form is characterized as a ferroelectric. The investigated glasses, with various concentration of SbSI, were synthesized from high-purity elemental components by fast cooling from the melt. The amorphous character of the samples was proved using standard optical and X-ray techniques. The temperature dependence of dc conductivity of bulk samples has been investigated in the range from room temperature to the temperature below the glass transition temperature T_g . On the basis of the obtained results, the conductivity activation energy was determined. By studying transparency spectra in a wide range of optical and IR part of the electromagnetic radiation, it was found that the position of the absorption edge depends on the Sb content. Optical band gap and tail-state region were determined.

(Received May 19, 2005; accepted July 21, 2005)

Keywords: Chalcogenide glasses, dc electrical conductivity, Optical band gap

1. Introduction

Chalcogenide glasses are transparent in a wide range of wavelengths in the IR spectral region [1,2], which makes them suitable for manufacturing infrared optoelectronic elements [3], infrared optical fibers [4] and information transfer devices [5]. They possess high values of refraction index and, in view of electric properties they belong to semiconductors. Besides, they are characterized by a high chemical stability and radiation resistance, but also exhibit poor thermal and mechanical characteristics [6].

The fact that the energy of electromagnetic radiation in the visible region (340÷780 nm) covers the range from 1.55 eV to 3.65 eV, offers the possibility of estimating the energy bandgap, as an extremely important characteristic of semiconducting materials, on the basis of measurements related to the optical part of the spectrum, and thus determine the width of the optically forbidden band. As a rule, these experiments are based on recording transparency of the investigated sample in dependence of the energy of incident photons, so that the behavior of absorption coefficient is defined by the function $\alpha = \alpha(h\nu)$.

In the interpretation of measurement results it is necessary to bear in mind the different approaches in dependence of whether one deals with ordered crystalline structure or disordered, amorphous systems. The problems that arise are primarily a consequence of the complexity of the dependence of dispersion of the absorption coefficient in the range of short-wave transparency edge.

In the approach according to Stuke, one starts from the fact observed with many amorphous semiconductors that the photon energy corresponding to the mobility gap is characterized by a coefficient of optical absorption of the order of 10^4 cm^{-1} [7]. After introducing the correction for the change of the band gap with temperature, the position of mobility threshold with many materials

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corresponds to the absorption coefficient of the order of 10^3 cm^{-1} . In the other approach, the width of the optically forbidden band (optical gap) is determined by extrapolating the linear part of the curve $\sqrt{\alpha(h\nu)}$. It should be pointed out that this is considered as a rough approach, and the values thus determined are, as a rule, smaller than the mobility gap by 0.1 to 0.2 eV [8].

Absorption coefficient can be determined from the measured values of transparency provided it is ensured that $\alpha d \sim 1$, where d is the sample thickness [9]. Then, it is possible to assume that, due to strong absorption of electromagnetic radiation by the material, the fraction related to manifold reflection is eliminated. Because of that, as a rule, it is necessary to prepare the glass sample in the form of slides about 0.1 mm in thickness. Curves of the absorption coefficient dispersion are constructed for various thicknesses, ending with the smallest one that still allows mechanical preservation of the sample to perform the measurement. After that, using one of the above approaches, optical gap of the material is estimated.

In practice, there may appear the cases in which is very difficult to ensure the experimental conditions for the application of any of the mentioned two methods. First of all, the mechanical characteristics and degree of transparency in the actual part of the spectrum do not sometimes allow achieving sufficiently small thickness of the real sample to apply Stuke's method. On the other hand, the same characteristics of a concrete material prevent or, in some cases, severely hinder preparation of a large number of transparent samples with the appropriate difference in thickness, to identify intrinsically common parts of the curves of absorption coefficient dispersion, and thus make possible the application of the extrapolation method.

The investigated materials are pseudo-binary five-component systems of the type $(\text{As}_2\text{Se}_3)_{100-x}(\text{SbSI})_x$ in which varies the ratio of typical glass-forming material As_2Se_3 and molecules of SbSI, which in monocrystalline state possesses significant ferroelectric properties [10]. As antimony sulfoiodide cannot be obtained in amorphous state, an attempt was made to introduce it into the material that is relatively easily prepared in a disordered state, with the aim of investigating the properties of such a system. Additional heating of the material to the temperatures above the softening temperature caused partial crystallization of structural units present in the glass matrix, and thus of SbSI molecules too. Also, successive change of the composition, i.e. of the ratio of the starting components, results in the materials in which dominate various structural units, and thus, in some cases, it is possible to change to a significant extent their general characteristics. Of course, it is necessary to carry out various investigations and determine the compositions and synthesis conditions that would yield optimal results. In order to establish potential advantages of such a complex system this work considers dc electric conductivity and optical transparency characteristics of bulk samples with the aim of determining mobility gap, that is the width of the optically forbidden band in relation to the material composition.

2. Experimental

Chalcogenide glasses of the type $(\text{As}_2\text{Se}_3)_{100-x}(\text{SbSI})_x$ ($x=20, 30, 50, 70$ and 80 at. %) were prepared by a direct synthesis starting from elemental high-purity substances (99.999 %). The substances were sealed in evacuated (10^{-2} Pa) quartz ampoules and subjected to the regime of cascade heating [11,12]. At the maximum temperature of the synthesis of 923 K, the ampoules were held for not less than 24 h, and then they were abruptly cooled to room temperature in Al_2O_3 powder. Amorphous character of the structure of obtained materials was confirmed by X-ray diffraction and polarization microscopy.

Electrical conductivity was measured using slides of a thickness ≤ 1 mm, on both sides of which were deposited graphite electrodes. Measurements were carried out on a specially constructed apparatus with a thermostated chamber, using a bridge R 4060 MP to measure ohmic resistance with an accuracy of 1 %. The applied voltages were 20 and 40 V, whereas temperature was varied from room temperature to somewhat below T_g , determined previously by dilatation measurements [13]. Specific conductivity was calculated on the basis of data of resistance measurements and dimensions of the glass sample using the relation $\sigma=d/(RS)$, where d is the slide thickness and S the surface area of the graphite electrode.

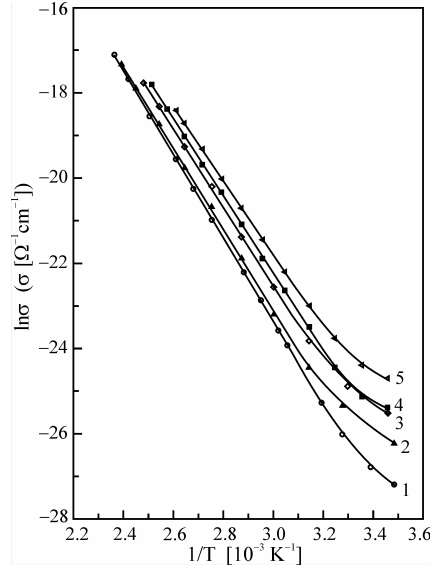


Fig. 1. Temperature dependence of the dc conductivity σ in glassy samples $(As_2Se_3)_{100-x}(SbSI)_x$ 1 – $x=20$; 2 – $x=30$; 3 – $x=50$; 4 – $x=70$; 5 – $x=80$.

Transparency spectra were also taken for slide samples of variable thickness with both sides polished to an optical quality. The spectra were recorded in the range of wavelengths from 400 to 1000 nm on a spectrophotometer SPM-2 with quartz optics. Absorption coefficients were calculated on the basis of the transparency data (T) and the thickness d of bulk samples, using the approximate relation:

$$\alpha = \frac{1}{d} \ln \frac{1}{T}. \quad (1)$$

3. Results and discussion

3.1. dc electrical conductivity

In Fig. 1 are presented the results of measurements of specific electrical conductivity in unidirectional temperature regime, in the interval from room temperature to below the glass transition temperature. The curves represent the dependence of the type $\ln \sigma = f(1/T)$ for each of the investigated material in the system $(As_2Se_3)_{100-x}(SbSI)_x$.

Table 1. Electrical parameters of glassy samples $(As_2Se_3)_{100-x}(SbSI)_x$ ΔE – activation energy, σ_0 – pre-exponential factor, σ_{300K} – conductivity at 300 K.

x [at. % SbSI]	ΔE [eV]	σ_0 [$\Omega^{-1} \text{cm}^{-1}$]	σ_{300K} [$\Omega^{-1} \text{cm}^{-1}$]
20	0.84	386	3.4×10^{-12}
30	0.82	225	7.9×10^{-12}
50	0.79	149	1.4×10^{-11}
70	0.78	130	1.4×10^{-11}
80	0.73	43	2.9×10^{-11}

It was found that the conductivity of all samples increases with increase in temperature, which indicates the semiconducting character of the material. These results suggest the conclusion that conductivity is a consequence of thermally activated processes, which can be described by the conventional Arrhenius relation:

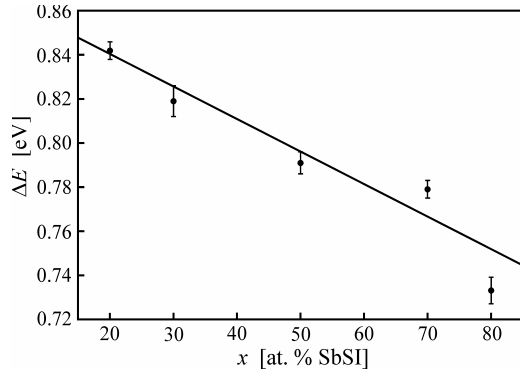


Fig. 2. Plot of activation energy ΔE vs SbSI concentration (x) in glassy samples $(As_2Se_3)_{100-x}(SbSI)_x$.

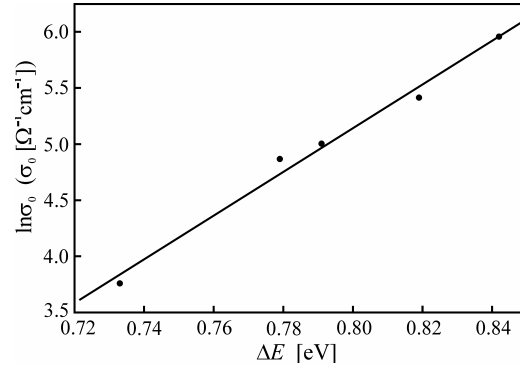


Fig. 3. Plot of pre-exponential factor σ_0 vs activation energy ΔE in glassy samples $(As_2Se_3)_{100-x}(SbSI)_x$.

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right) \quad (2)$$

where σ_0 is the pre-exponential factor, ΔE is the conductivity activation energy, and k is the Boltzmann constant. The parameter σ_0 was determined from the intersection of linear part of the function with the ordinate axis (when $T \rightarrow \infty$), and the activation energy ΔE on the basis of its slope. Calculated values of these parameters are given in Table 1. It can be noticed that the activation energy changes only a little with the change in the glass composition, i.e. it decreases very slowly with increase in content of antimony and its structural units. (Fig. 2). This is probably a consequence of the shift of the Fermi level to the band of delocalized energy states because of the increased concentration of defect states, appearing as a consequence of the more complex structure due to the involvement of new structural units. However, it is known that there are four types of mechanisms of dc conductivity that may be operating in glassy materials. According to Mott and Davis, the activation energy itself does not indicate the predominant mechanism of conductivity [8]. There may be present thermally activated transitions of charge carriers to delocalized states of the conduction, that is, valence band (extended states). Also, hopping mechanism may be involved in localized states of the mobility gap, which are a consequence of the disordered matrix structure band (band tailing at the edge of the mobility gap), or they may be due to the effect of impurities or defects. Finally, what is most probable, there may operate simultaneously both mechanisms, whereby at lower temperature predominates the conductivity in localized states. In the first case, the activation energy represents the difference between the edge of mobility gap and Fermi level ($E_C - E_F$ or $E_F - E_V$), whereas in the second case it is the energy difference between the localized states in the forbidden band between which hopping is taking place.

With the aim of making distinction between the conductivity mechanisms, Mott and Davis [14] proposed that the pre-exponential factor in the case of conduction involving extended states one should take the value $10^3 - 10^4 \Omega^{-1} \text{cm}^{-1}$, whereas for the case of conduction in localized states in the mobility gap, σ_0 should be by 2 to 3 orders of magnitude lower. In the case the hopping takes place in the localized energy states adjacent to the Fermi level, and this happens at temperatures that are significantly below room temperature, the factor σ_0 has a still lower value. According to this classification, the value of pre-exponential factor for the investigated materials are such that it is possible to state that the conduction takes place predominantly in localized states of band tailing, and that the value ΔE represents the energy difference between the Fermi level and mobility gap edge. The decrease of σ_0 at a higher content of antimony suggests the increasing role of conduction in localized states in the mobility gap. The curvature observed on the curves $\ln \sigma = f(1/T)$ suggests the conclusion that, with a decrease in temperature, this conductivity starts to contribute predominantly already at room temperature.

In Table 1 are also given the values of specific conductivity of the glasses at room temperature $\sigma_{300\text{ K}}$. The higher value of this quantity measured for the compositions with higher content of SbSI structural units is a logical consequence of the decrease in the activation energy ΔE and increased density of localized states in the mobility gap because of the higher concentration of defect states in the structurally more complex materials.

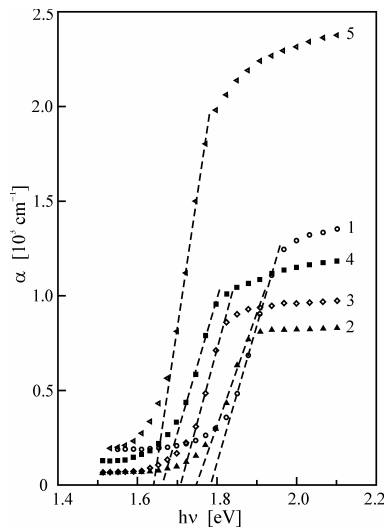


Fig. 4. Absorption spectra of the glassy samples $(As_2Se_3)_{100-x}(SbSI)_x$ 1 - $x=20$; 2 - $x=30$; 3 - $x=50$; 4 - $x=70$; 5 - $x=80$.

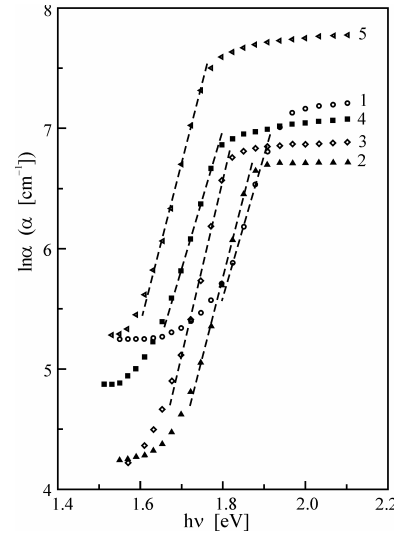


Fig. 5. Optical absorption of the glassy samples $(As_2Se_3)_{100-x}(SbSI)_x$ in accordance with Urbach rule 1 - $x=20$; 2 - $x=30$; 3 - $x=50$; 4 - $x=70$; 5 - $x=80$.

Finally, the data of dc conductivity measurements were analyzed from the viewpoint of applying the Meyer-Neldel Rule (MNR). This rule, also termed 'compensation law', was established still in 1937 [15], and it can be applied onto various thermally activated phenomena, such as kinetics (hopping) and thermodynamics (number of charge carriers in the band state), in crystalline, amorphous, and liquid semiconductors [16,17]. In the case when electrical conductivity is thermally activated and satisfies equation (2), the MNR gives the relationship between the pre-exponential factor σ_0 and the activation energy ΔE :

$$\sigma_0 = \sigma_{00} \exp\left(\frac{\Delta E}{E_{MN}}\right) \quad (3)$$

where σ_{00} and $E_{MN}=kT_o$ are the constants characteristic of the given class of materials. E_{MN} is also called the Meyer-Neldel characteristic energy. In Figure 3 is presented the dependence $\ln\sigma_0=f(\Delta E)$ for the investigated glasses, and it can be seen that the linearity predicted by the MNR is satisfied. This confirms that the dc conductivity in these materials is thermally activated. The intercept and slope of the graph of this function allow the determination of the above parameters. The determined value for σ_{00} is $2.9 \times 10^{-5} \Omega^{-1}cm^{-1}$, and for E_{MN} 51 meV. These values are comparable with those observed for other chalcogenide systems [16].

3.2. Absorption edge

In order to determine the optical band gap E_g^{opt} on the basis of the recorded transparency spectra for bulk samples of the glasses from the system $(As_2Se_3)_{100-x}(SbSI)_x$ an analysis was carried out of the absorption coefficient α as a function of the energy of incident photons $h\nu$ (Fig. 4). In

the region of high absorption (the absorption coefficient $\alpha \geq 10^4 \text{ cm}^{-1}$) optical transitions take place between the valence and conduction band, and the coefficient α is given by the relation [14,18]:

$$\alpha = \frac{B(h\nu - E_g^{opt})^r}{h\nu} \quad (4)$$

where B is a constant dependent on the transition probability, which is related to the magnitude of band tailing, and r is a number determined by the nature of transition, taking the values 1/2 and 2 for all allowed direct and indirect transitions, respectively, or 3/2 and 3 for forbidden direct and indirect transitions. In the spectral region of the Urbach exponential tail ($\alpha = 10^2 \div 10^4 \text{ cm}^{-1}$) optical transitions take place between the localized states in the tails and extended band states. In this region, the absorption coefficient is of the form [19,8,20]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_e}\right) \quad (5)$$

where α_0 is a constant and E_e is interpreted as the width of localized state tails in the gap region, and also as a measure of disorder in the amorphous semiconductor. For the investigated glasses of the pseudo-binary system $(\text{As}_2\text{Se}_3)_{100-x}(\text{SbSI})_x$ the coefficient α did not exceed the value of 10^4 cm^{-1} , so that the values of optical gap were calculated from the intersection of the extrapolated straight part of the dependence $\alpha = f(h\nu)$ with the abscissa.

In Figure 5 are presented the functions $\ln \alpha = f(h\nu)$ (in accordance with the absorption in the Urbach region) on the basis of which were determined the parameters of the tail width of localized states at the edges of the bands, E_e (Table 2). The values for E_e are in the range usually observed for chalcogenide glasses [21] and do not depend on glass composition. Since the band width of localized states near the optical gap edge depends on the degree of topological disorder, it is evident that all the investigated materials, irrespective of the complexity of their composition and potential presence of more structural units, were prepared with an approximately identical degree of amorphism. The observed decrease in the mobility gap ΔE and increase in the electrical conductivity σ with more complex compositions, that is with a higher concentration of antimony sulfide, is then a consequence of an increased density of localized states in the gap itself due to the appearance of new defect states and antimony-containing structural elements. Namely, the presence of an increased density of localized states in the band structure is responsible for the reduction in both the optical gap and mobility gap [14].

If one compares the values of the optical band gap E_g^{opt} with the values of activation energy of dc electrical conductivity, it is evident that $E_g^{opt} > 2\Delta E$. This observation is in agreement with the Mott viewpoint that the position of the Fermi level in amorphous materials is not exactly in the middle of the forbidden band because of the differences in the smearing of the valence and conduction bands [22], also indicating active participation of localized defect states in electron transfer processes.

Table 2. Optical parameters of glassy samples $(\text{As}_2\text{Se}_3)_{100-x}(\text{SbSI})_x$

E_g^{opt} – optical bandgap, E_e – width of the tails.

x [at. % SbSI]	E_g^{opt} [eV]	E_e [meV]
20	1.78	84.8
30	1.75	74.0
50	1.71	68.6
70	1.66	87.9
80	1.64	75.0

4. Conclusions

On the basis of the recorded transparency spectra and dc electrical conductivity of bulk samples of glasses of the pseudo-binary system $(As_2Se_3)_{100-x}(SbSI)_x$ ($x=20, 30, 50, 70$, and 80 at. %) it can be concluded that they are semiconducting materials in which the gap of mobility of charge carriers changes only a little with increase in their structural complexity, i.e. by introducing antimony into their composition. In the interval from room temperature to below the softening temperature the dominant conduction mechanism is in localized states in the band tails. The change in concentrations of particular components in the glass composition increases the concentration of localized states in the bandgap, causing a shift in the Fermi level. The relationship between the conduction activation energy ΔE and the pre-exponential factor σ_0 satisfies the Meyer-Neldel empirical rule related to thermally activated processes. The width of optical gap also obeys a mildly decreasing trend observed as a consequence of introducing antimony (as well as of S and I) into the arsenic-selenide basic material, whereas the magnitude of localized states tailing in the forbidden band does not undergo significant changes.

Acknowledgement

This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia, Project "Amorphous and Nanostructural Chalcogenides and Ceramics", No. 1812.

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