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THE INFLUENCE OF IRON ON THE OPTICAL ENERGY GAP IN GLASSES OF Sb-S-I TYPE

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The paper investigates the optical transmittance of amorphous chalcogenide semiconductors in the composition series $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ in visible and near-infrared spectrum of electromagnetic radiation. Extrapolation of functional dependence of short-wavelength edge and sample thickness to the zero-th thickness, allowed for the determination of the optical energy gap (E_g^{opt}). The energy gap decreases linearly with the increase of Fe concentration up to 1 at % (1.84-1.56 eV), while for higher concentration of Fe (1-3 at %) the gap increases slowly (1.56-1.62 eV).

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1. Introduction

Many of chalcogenide glasses are very interesting materials for infrared optics, because of their large range and high values of transparency (in visible and infrared part of the spectrum). High value of the refraction indexes (>2.5), good mechanical and chemical properties, such as hardness, adhesion, low internal stress and water resistance, give possibility to their application in visible-infrared optical equipments.

The thermal activation energy of the conductivity in amorphous chalcogenide semiconductors is usually about half of the optical energy gap. This is due to carriers whose concentration is governed by the Fermi energy, which is pinned near the gap center, and gives rise to intrinsic conduction at the mobility edge. Small changes in glass composition and the presence of impurities have a little effect on the properties except for small changes in optical gap energy and thermal activation energy with composition.

Incorporation of transition metal atom in the matrix of chalcogenide glasses, produced materials with continuously shifted the values of physical parameters as a function of metal concentration [1]. However, obtaining of homogeneous glasses with transition metal is limited to relatively small concentration range. This range varies in dependence of glass matrix and metal atoms. In case of Fe atoms in the selenide glasses appear crystalline centers yet at 0.2 at % of Fe [2, 3], while the maximum concentration in Ge-Sb-S systems is 2.2 at % Fe [4]. Above these concentrations of metal atoms, the thermal and mechanical properties of glasses do not change, until electroconductivity passes from semiconducting to metallic conductivity type [5].

The glasses of quasi-binary section Sb_2S_3-SbI_3 can be synthesized in broad area of mutual mixing, between 60 and 85 % of Sb_2S_3 [6, 7]. The composition $(Sb_2S_3)_{0.75}(SbI_3)_{0.25}$ is the eutectic composition with the best suitable property of synthesis and low degree of crystallinity (high activation energy of crystallization). Glasses of type Sb-S-I have a semiconducting character with high values of refractive index and dielectric permeability (20-28 at 10^7 Hz) and optical gap between 1.30 and 1.75 eV [8].

In this paper the optical transmission of chalcogenide semiconductor glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ was presented. The aim of the investigation was to determine the variation of the optical energy gap as a function of Fe atom concentration and to study the degree of Fe incorporation in the glass matrix.

2. Experimental

a) Measurements

The investigated samples of $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ type, with 0; 0.01; 0.1; 0.5; 0.8; 1; 1.5; 2 and 3 at %Fe, were synthesized by fast cooling from the melt. Synthesis was carried out in quartz, vacuum-sealed ampoules (~6.67 × 10^{-3}Pa) previously filled with elementary components of high purity (99.999 %). The ampoules were heated in steps up to the maximum temperatures of synthesis which was 800 °C [6, 7]. The heating rate in the furnace was 100 °C/h (Fig. 1). In order to carry out homogenization, solutes were kept at the maximal temperature for 20 h. Samples were then taken out of the furnace and fast cooled to room temperature.

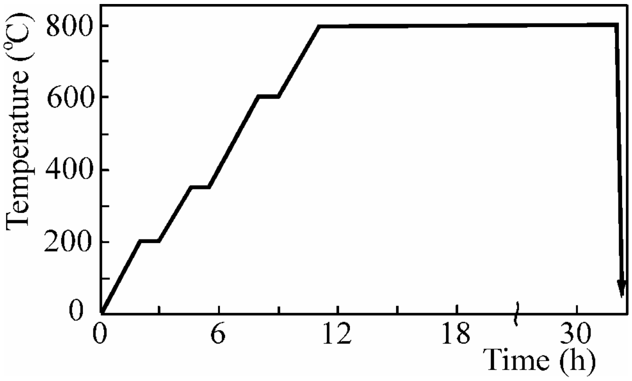


Fig. 1. Diagram of process for obtaining $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ glasses.

The amorphous character of synthesized samples was controlled by X-ray diffraction on powders. Measurements were performed on a conventional X-ray diffractometer PHILIPS PW 1373-PW 1965/50 with a θ-2θ geometry and proportional counter as detector, using a high-voltage generator SEIFERT ID 3000 with copper anticathode whose radiation is monochromatized by nickel filter.

The transmission spectra in infrared range from 2500 nm to 10000 nm were recorded with a PERKIN-ELMER Infracord spectrometer, on powdered samples embedded in KBr.

Transmittance spectra in range 400-1600 nm were recorded by using a system based on monochromatic SPM-2 (Zeiss-Jena) with quartz optics and adaptable cell. The mechanical preparation of the samples in form of parallel-plan plate was carried out using carborundum powder of various granularity (from 260 μm to 28 μm), while final polishing was made with granular Al_2O_3 (0.3 μm).

b) Results

Fig. 2 illustrates the results of the X-ray diffraction measurements on some of the investigated samples. The absence of diffraction maxima, which characterize the crystalline phase, confirms the amorphous nature of the investigated samples.

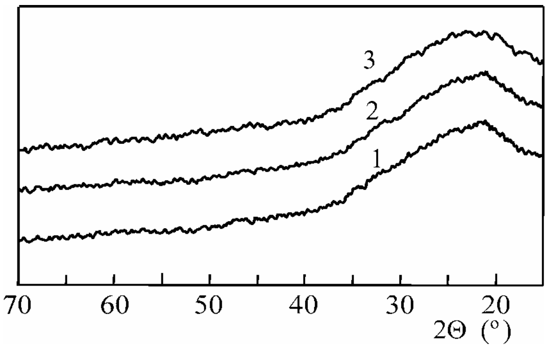


Fig. 2. Diffractograms of $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ glasses at room temperature:
1- x=0; 2- x=1 and 3- x=3 at % Fe.

Fig. 3 shows the transmission spectra in the infrared range for the samples with 0 and 1 at % Fe. There is no peak related to specific vibration of internal structural units. Namely, detected peaks at 1600 and 3450 cm^{-1} are result of the OH group and H-O-H bond vibration, respectively. They exist because of the presence of water in KBr.

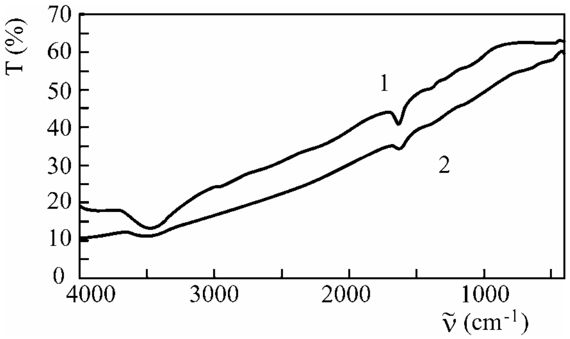


Fig. 3. Transmission spectra in IR range for $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ glasses:
1- x=0; 2- x=1 at %.

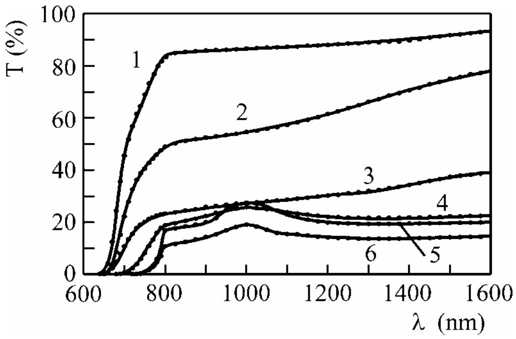


Fig. 4. Transmission spectra of $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ glasses in visible and part of near infrared region: 1- x=0, d=0.10mm; 2- x = 0.01, d = 0.15 mm; 3- x=0.1, d = 0.13 mm; 4- x = 0.5, d = 0.11 mm; 5- x = 0.8, d = 0.13 mm; 6- x=1, d=0.11 mm.

Transmission spectra of the investigated glasses are presented in Fig. 4. They were recorded for the preparations of lowest thickness and for all the glasses from the system containing up to 1.0 at % Fe. The spectra exhibit a distinct short-wavelength edge, which shifts towards higher wavelengths with increase in Fe content, while sample transmittivity shows a decrease.

3. Data processing and discussion

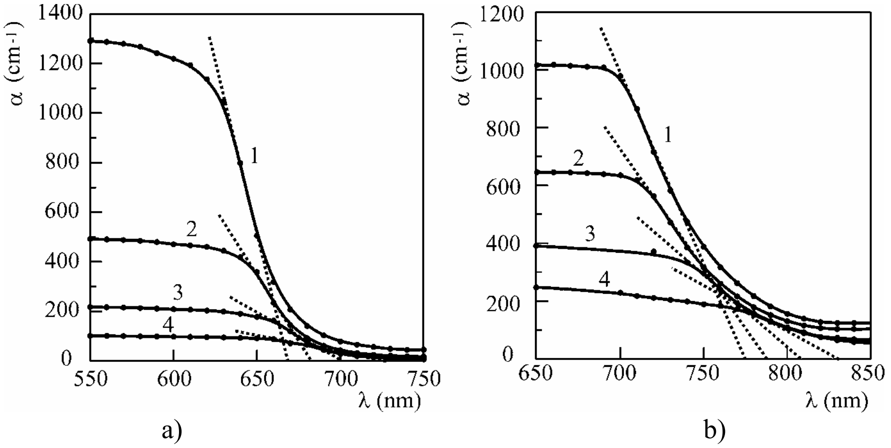
The obtained results were processed by using a relatively rough procedure for calculating the absorption coefficients from the recorded transmission spectra. Namely, numerous experimental investigations of chalcogenide glasses have shown that in the analysis of the behavior of this coefficient one can neglect the effect of reflection on a parallel-plane plate [9-11].

Starting from the assumption that the above affirmation is also valid for the glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$, the absorption coefficients α for samples of different thickness (d) were calculated from the transmittance (T) using the formula

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

Graphical presentation of the values of absorption coefficients obtained for the samples of different thickness allows for the determination of the optical band gap (E_g^{opt}) by extrapolating the linear part of the dispersion curves. As an illustration can serve the dispersion curves without Fe and with 0.8 at % Fe, shown in Fig. 5. It can be noticed that the values of α coefficient are relatively small, which represents a limiting factor in selecting the method for estimation of E_g^{opt}. Namely, the value of an order of magnitude of 10^2-10^3 cm^{-1}, obtained for the samples of smallest thickness, is not sufficient for applying the Stuke method [12] or the method of graphical extrapolation of the dependence $\sqrt{\alpha h\nu} = f(h\nu)$ [13].

This pointed out the need for finding another approach to solve the problem of correct estimation of the energy gap. Hence, correlation was sought between the energies obtained as extrapolation values of the tail end and sample thickness. These values E_g were obtained as the crossing of the broken lines with the wavelength axis on the dispersion curves shown in Fig. 5. It appeared that this correlation could be characterized by a linear function (Fig. 6). Extrapolation of this functional dependence to the zero-th thickness yielded the value of the optical band gap E_g^{opt} of the glass.



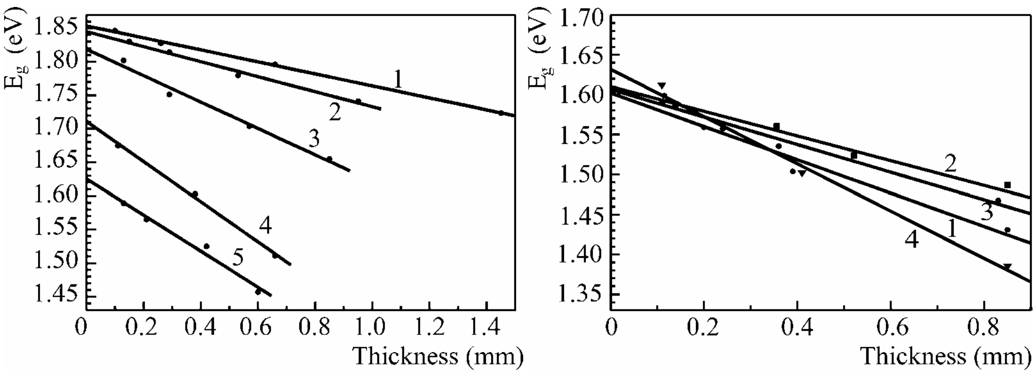
a) b)

Fig. 5. Dispersion curves of absorption coefficient:
(a) sample $(Sb_2S_3)_{0.75}(SbI_3)_{0.25}$ (thickness of the sample: 1- 0.10; 2- 0.26; 3- 0.66; 4- 1.45 mm) and (b) $Fe_{0.8}[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{99.2}$ (thickness of the sample 1- 0.13; 2- 0.21; 3- 0.42; 4- 0.60 mm).

The dependence of this energy on the Fe concentration in the glasses is presented in Fig. 7. It is evident that the behavior of the optical gap changes significantly with increase of Fe content in the glass. The decreasing trend that E_g^{opt} shows up to the sample with 1 at. % Fe, completely changes with the further increase in iron content. Hence, the optical gap can be described by the two analytical functions:

$$E_g^{opt}\,(eV) = 1.850\,(2) - 0.280\,(4)\cdot x \qquad 0 < x < 1 \text{ at \% Fe} \tag{2}$$

$$E_g^{opt}\ (\mathrm{eV}) = 1.587\ (5) + 0.014\ (2) \cdot x \qquad 1 < x \leq 3 \text{ at \% Fe} \tag{3}$$



a) b)

Fig. 6. Correlation between the values of energies obtained by extrapolation of short-wavelength edge and thickness of the sample $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ (concentration of Fe in at % are: (a) 1- 0; 2- 0.01; 3- 0.1; 4- 0.5; 5- 0.8; (b) 1- 1; 2- 1.5; 3- 2 and 4- 3).

The linear change of the optical band gap of the glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ for the concentrations below 1 at % Fe shows that Fe atoms in these glasses enter the glass structure and thus influence its energy characteristics. The same could be concluded from some preliminary measurements of the electrical conductivity of the samples [14, 15]. Up to this concentration of iron, the glasses behave as semiconductors and the Fe atoms are in their high-spin Fe^{2+} state, situated in an octahedral surroundings, the chalcogenide atom being in the first coordination sphere [16].

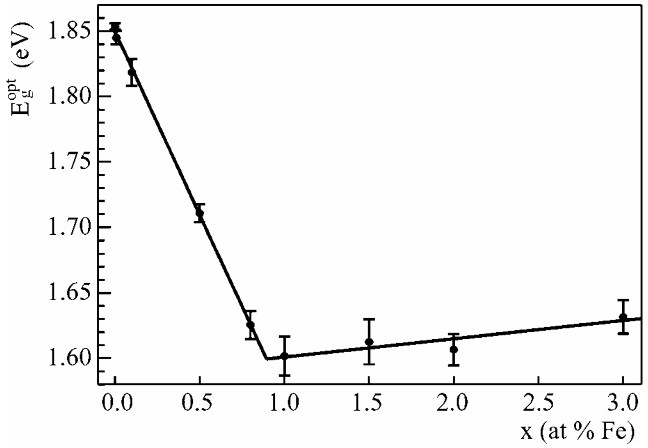


Fig. 7. Dependence of the energy gap on the concentration of iron.

At the concentrations exceeding 1 at. % Fe, optical gap shows a weak dependence on the iron content. Such a finding points to some specific changes in the structure of the material with increase in iron content that have no effect on the energy pattern. Similar conclusions were also derived on the basis of the findings by other experimental methods. Thus, for example, NMR studies of iron-doped chalcogenide glasses [2] showed that at high concentrations iron is present in its Fe^{3+} state, forming finely dispersed centers separated from the global glass structure.

Because of that it can be concluded that the measurements of optical transparency of the investigated glasses showed that at the content exceeding 1 at. % Fe, iron is present in the form of separate centers which weakly interact with the glass matrix.

4. Conclusions

X-ray diffraction on the powdered samples of chalcogenide glasses of the type $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ (for 0<x<3 at % Fe), synthesized by the method of cascade heating and annealing gave evidence of their amorphous character. The values of optical band gap obtained for the glasses with different contents of iron ranging from 1.56 to 1.83 eV indicate that these glasses are semiconducting materials. A linear decrease of the optical gap as a function of iron concentration was observed up to 1 at. % Fe. The dependence of the energy gap on iron content indicates that all dopant atoms enter the glass matrix. However, at higher concentrations Fe atoms appear as finely dispersed (defect) centers, exhibiting no significant interaction with the matrix. The optical gap is further weakly influenced by the Fe content in the material.

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