

SOME OPTICAL CHARACTERISTICS OF Cu-As-S-Se BULK CHALCOGENIDE GLASSES

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Optical transmittance spectra were measured on amorphous $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ bulk glasses. The range of optical investigation were situated in near infrared and visible spectrum. The dispersion of the absorption coefficient for the sample with 0; 0.5; 1 and 3 at.% Cu, absorption edge and optical gap E_g were determined. Finally, the analytical expression for the dependence of E_g on the copper concentration was modeled.

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1. Introduction

Due to their specific electrical and optical properties, chalcogenide glasses have conquered an important place in the field of applications of the non-crystalline materials. The first researches of physical and chemical characteristics have already shown that chalcogenides possess semiconducting properties, quite large thermoelectromotive force can be obtained on their basis and exhibit a large photoconductivity [1-3].

The chalcogenides are characterized by wide range of transmittance in infrared and visible part of the spectra, high stability against to water, air, water-stem, acids and other chemical properties. By varying the ratio of their starting structural components or changing the conditions of its preparation, it is possible to get materials with controlled physical and chemical characteristics [4-6].

In recent years, the chalcogenides proved to be promising elements in manufacturing of optical lens, prisms, plan-parallel plates and other parts of optical system which operates, in the visible and infrared part of the spectra. This is due, first of all, to high values of refraction index [7,8] compared with classical optical glasses, and to wide range of transmittance. Because of the possibility of changing their optical characteristics under illumination for a given wavelength, the chalcogenide glasses are applicable in devices for optical holographic recording i.e. for storing optical information [9].

In this paper the optical properties of the disordered material $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ are presented as a part of our complex investigations of Cu-containing chalcogenide glasses.

2. Experimental

The investigated samples of $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ system were synthesized by fast cooling from the melt. Synthesis was carried out in quartz, vacuum sealed ampoules, previously filled with elementary components of high purity. The ampoules were heated in steps up to the maximum temperatures of synthesis which was 900 °C for the samples with 0.5; 1 and 3 at.% Cu, and 720 °C for the sample of composition $\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3$.

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

Transmittance spectra in range 400 - 1000 nm were recorded by using a system based on monochromatic SPM-2 (Zeiss-Jena) with quartz optics and adaptable cell. The mechanical processing of the samples in a form of plan-parallel plate, were done by carborundum powder of various granulation (from 260 μm to 28 μm), while final polishing was taken by granular Al_2O_3 powder (0.3 μm).

The transmission spectra in infrared range from 2500 nm to 10 000 nm were recorded with a PERKIN-ELMER Infracord spectrometer, on powdered samples embedded in KBr.

3. Results and discussion

Fig. 1 illustrates the results of the diffraction on the investigated samples. The absence of diffraction maximums which characterizes the crystalline phase, confirms the amorphous nature of all the investigated samples.

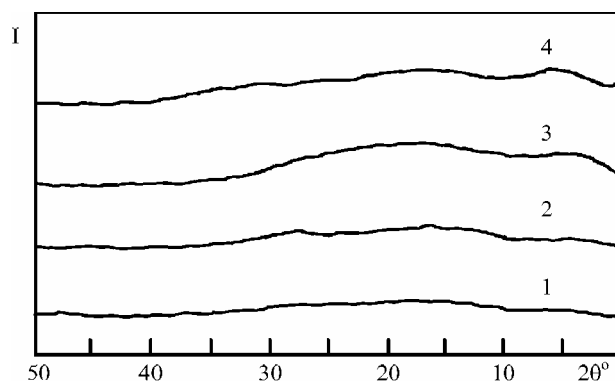


Fig. 1. Diffractograms of $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ curve 1: $x=0$, curve 2: $x=0.5$, curve 3: $x=1$ and curve 4: $x=3$.

Fig. 2 shows the transmission spectra in the infrared range for the samples $\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3$ and $\text{Cu}_3[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{97}$. Absorption peak at 3450 cm^{-1} is not due to specific vibration of internal structural units. The peak is related to the absorbed water and corresponds to the absorption due to H-O-H bond in KBr. The peak at 1600 cm^{-1} is a result of OH group vibration.

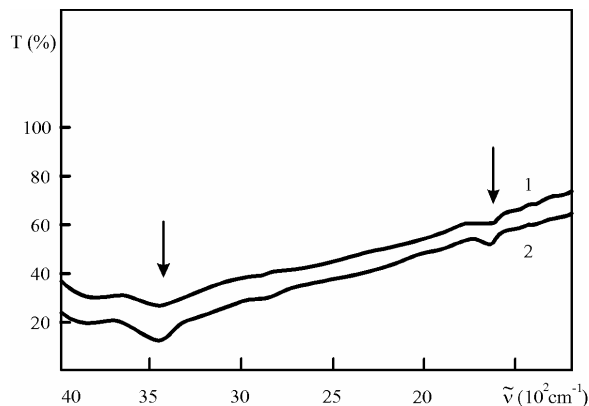


Fig. 2. Transmission spectra in IR range for $\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3$ (curve 1) and $\text{Cu}_3[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{97}$ (curve 2).

Taking into consideration that vibrational energies, which correspond to possible bonds of the structural components are situated in far infrared range, these transmittance spectra are completely excepted.

The transmission spectra in visible range is shown in Fig. 3. The presented results are obtained on the samples of thickness $d \sim 0.1$ mm. It must be noticed that the increasing content of copper in the material, leads to the decrease of the range and level of transmittance. Very small copper concentration in the structure of the sample significantly influence the transmittance properties. The results show that the amount of 0.5 at.% Cu in material decreases the transmittance level down to ~ 20 %.

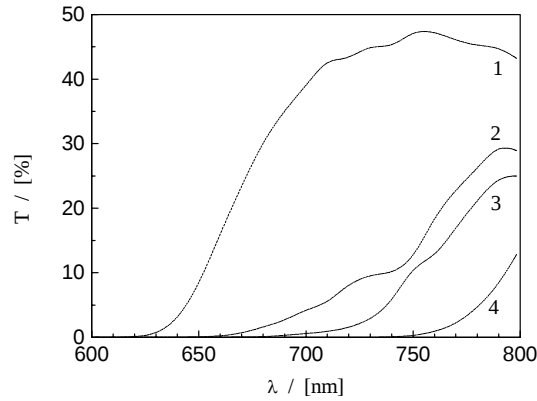


Fig. 3. Transmittance spectra of $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ in visible range.

The limit of the transmittance interval comes from the absorption, caused by electron crossing from localized states from the top valence zone to the spread states at the bottom of the conducting zone. This short wave boundary represent the absorption edge region and correspond to the optical energy gap. The analyzed spectra of transmittance were used in the calculation of the absorption coefficients. Since the thickness, d , of the samples is determined by an independent method and the refraction is eliminated, the coefficient will be calculated by the following relation

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

Fig. 4 illustrates the dispersion of the absorption coefficient in the range 500 to 800 nm. The short-wave boundary is determined by extrapolation of the linear part of the dispersion curves in the Urbach region. The intersection point of the extrapolated curve with abscissa determines the shortwave boundary λ_g , so using the simple relation (1) it is possible to calculate the optical energy gap E_g .

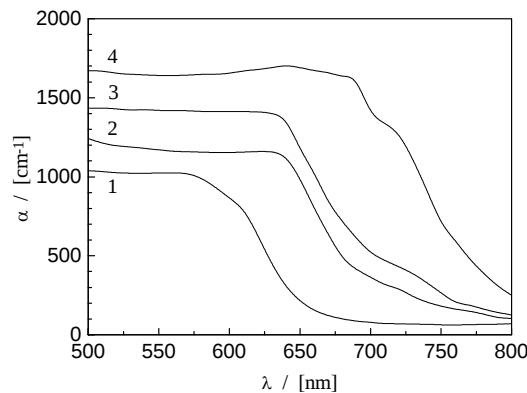


Fig. 4. Dispersion curves of absorption coefficient curve 1: $x=0$, $d = 0.12$ mm; curve 2: $x=0.5$, $d = 0.1$ mm; curve 3: $x=1$, $d = 0.11$ mm; curve 4: $x=3$, $d = 0.1$ mm.

The shortwave boundary λ_g , was obtained by extrapolation of the linear part of the dependence $\alpha = f(\lambda)$ are 661.7 nm, 687 nm, 707.7 nm and 776.8 nm for the samples with $x=0$; 0.5; 1 and 3, respectively. The corresponding values of the optical energy gap are 1.874(28) eV, 1.804(24) eV, 1.752(22) eV and 1.596(20) eV.

The plot of the correlation between optical energy gap E_g and copper content is shown on Fig. 5. It is noticed that as the content of the copper in the structure increases, the values of

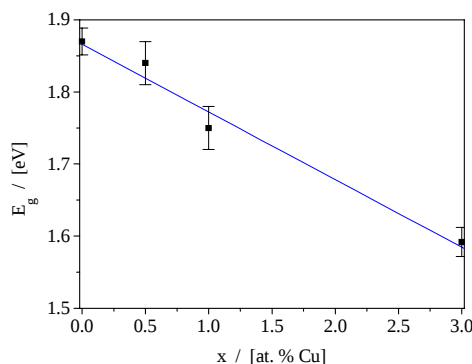


Fig. 5. Dependence of the energy gap on the concentration of copper.

E_g becomes lower. The observed dependence of the energy gap on the concentration of elementary component is linear. The corresponding analytical expression is:

$$E_g = 1.874 - 0.089 \cdot x \quad (2)$$

where x is the copper content in the material.

4. Conclusions

The method of cascade heating and cooling in air makes possible to get bulk glasses of $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ with up to 3 at % Cu. The amorphous state of the investigated material is confirmed by X-ray diffraction. It is noticed that even a small concentration of copper significantly influences the transmission properties of these glasses. The values of the optical energy gap (1.69-1.87 eV) prove the semiconducting properties of the material.

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