OPTICAL PROPERTIES OF THIN $GeSe_2$-CdI_2(Sb_2Se_3)-CdSe FILMS

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Abstract

Optical properties of thin films in the complicated chalcogenide $GeSe_2$-CdI_2(Sb_2Se_3)-CdSe systems are studied as a function of the cadmium (antimony) content. The optical spectra of these thin films with different thickness are investigated using spectrophotometer for visible and NIR region in the spectral range 400-3000 nm. The spectra are analyzed using special computer software "Layers". The optical constants are determined – the real and imaginary part of the dielectric function, the refractive index and the extinction coefficient.

Keywords *: Chalcogenide glasses, Thin films, Optical properties.*

1. INTRODUCTION

Chalcogenide glasses have thermophysical and optical properties that make them suitable for many applications [1, 2]. They also have a high refractive index, low optical losses and a possibility as optical materials application has been discussed recently [3, 4]. An intensive attention has been paid to the preparation and physical properties studies of new chalcogenide glasses. The examination of the composition dependence on the physical properties in order to improve their optical transmission is still of interest.

The phase diagrams of the $GeSe_2$-CdI_2-CdSe (I) and $GeSe_2$-Sb_2Se_3-CdSe (II) systems have been investigated. Stable glass-forming compositions cover regions in the Gibbs diagram, situated on the side $GeSe_2$-70 mol.% Sb_2Se_3 for system (I) and $GeSe_2$-45 mol.% CdI_2 for system (II), respectively. It has been found that the maximal CdSe concentration is 30 mol.% for the first system and 15 mol.% for the second one. The phases obtained have been characterized by the basic thermal and physicochemical parameters (the temperatures of glass transition, crystallization and melting temperatures, density and microhardness).

In this work we present the results of an investigation on optical properties of $GeSe_2$- -CdSe (I) and $GeSe_2$- -CdSe (II) systems containing CdI_2, Sb_2Se_3, respectively and the additives' influence on the physical properties of the systems.

2. EXPERIMENTAL

Bulk samples from the investigated systems $GeSe_2$-CdI_2-CdSe (I) and $GeSe_2$-Sb_2Se_3-CdSe (II) are prepared by a direct monotemperature synthesis. Thin films of the presented compositions were evaporated on the glass substrates in a standard vacuum installation. The conditions of the process were –1.33 10^{-5} Torr the residual pressure, 0.12 m – the distance source-substrate, 800-900 K – evaporation temperature. The amorphous natures of the prepared materials either in bulk or thin films form were proved by X-ray diffraction analysis.

The thin film morphology and structures were studied with a transmission electron microscope TEM Philips 3003. The film composition has been investigated by Auger electron spectroscopy.

The transmission and the reflection of the thin films were measured using a double channel spectrophotometer in VIS and NIR regions. From the spectral data the refractive index and absorption coefficient was obtained using a special computer program.

3. RESULTS AND DISCUSSION

In Figure 1 are plotted the transmission spectra of the thin films from the $GeSe_2$-CdI_2-CdSe (I) system. It can be seen that the increase of CdI_2 content leads to an increase in the transmission when the CdSe concentration is constant. The absorption edge shifts towards shorter wavelength with CdI_2 concentration.

The spectral dependence of the transmission in the films from $GeSe_2$-Sb_2Se_3-CdSe (II) system is shown in Figure 2. It is observed a tendency of shifting the absorption edge towards the shorter wavelength with Sb_2Se_3 content. Higher Sb_2Se_3 content are responsible for a lower transmission of the films. The decrease of the $GeSe_2$ content leads to an increase of the transmission and shifts the absorption edge to the longer wavelength.

The movement of the absorption edges in both systems is probably connected to the structural changes in the thin film systems. In the system (I) the increase of CdI_2 content changes the type of the bonding in the films. The increased metallic character of the bond makes them shorter and decreases the free volume in the films. In the system II the replacement of tetrahedral $GeSe_2$ units with pyramidal Sb_2Se_3 increases the optical density of the films.

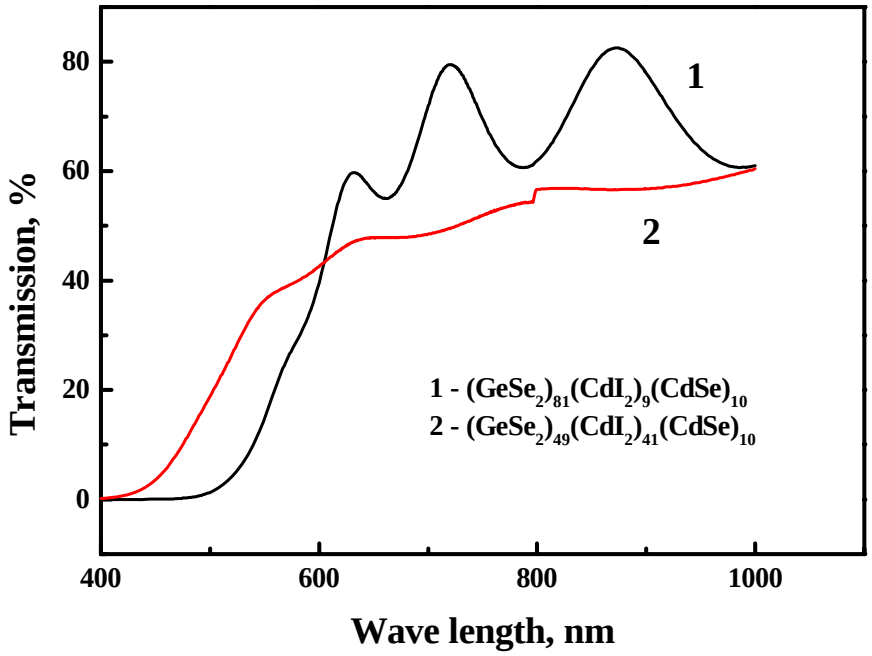

Figure 1. Spectral dependence of the optical transmission in the system I.

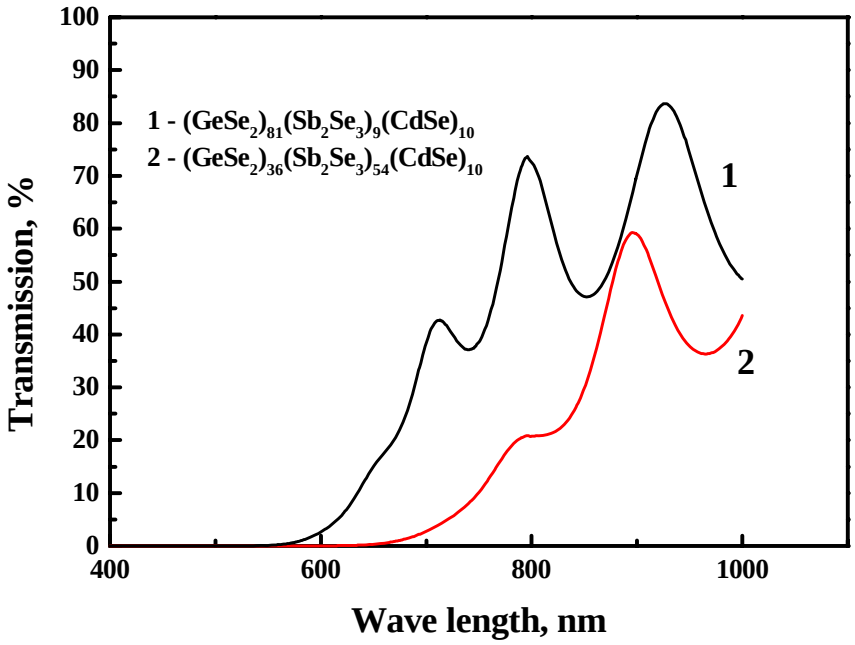

Figure 2. Spectral dependence of the optical transmission in the system II.

The absorption coefficient is obtained from the non-oscillatory part of the transmission. The spectral distribution of the absorption coefficient is determined after

fitting of the experimental data of R and T with simulated spectra using Lorentz-theory and Brend equations. In the amorphous materials, the optical gap, E_g, is defined as the energy where the absorption coefficient has a value $>10^4$ cm^{-1}.The absorption of the thin films gives information about for the density of states at the Urbach tail. The slope of this exponential variation gives an indication of the structural disorder of the material.

The values of the absorption coefficient α are obtained by a computer programme "Layers". The optical band-gap is determined by means of Tauc's procedure [5]. The relationship between the absorption coefficient a and the optical band-gap E_{go} is:

$$\alpha = \frac{B}{h\nu}\left(h\nu - E_{go}\right)^k \qquad (1)$$

where B - parameter of the investigated substance, h - Plank's constant, ν - frequency. The value of the power factor k is governed by the mechanism of the electron transition. In chalcogenides indirect intrasonal transitions are observed, i.e. the photon energy is used for a indirect vertical transition; in this case k = 2 [6]. The calculated values of Eg are given in Table 1. The increase of CdI_2 in system (I) leads to a slow increase of the optical band gap. In the system (II) the decrease of Sb_2Se_3 content at a constant CdSe concentration provokes changes in optical gap values going to higher values.

Samples composition	**E_{gopt}, eV**	**Samples composition**	**E_{gopt} , eV**
$(GeSe_2)_{81}(CdI_2)_9(CdSe)_{10}$	2.61	$(GeSe_2)_{81}(Sb_2Se_3)_9(CdSe)_{10}$	1.78
$(GeSe_2)_{49}(CdI_2)_{41}(CdSe)_{10}$	2.95	$(GeSe_2)_{36}(Sb_2Se_3)_{54}(CdSe)_{10}$	2.22

Table 1

The calculation of the optical constants are made by means of the transmitance values only using a method described by Swanepoel [7]. The technique is based on the extrapolation of the interference fringes, which are used to evaluate both the refractive index and the thickness of the film. The transmission maximum and the transmission minimum are considered as continuos function of λ through $n(\lambda)$ and $\alpha(\lambda)$. These functions are the envelopes of the maxima and minima. The spectral dependences of the refractive index for the systems (I) and (II) are presented in Figs.3 and 4.

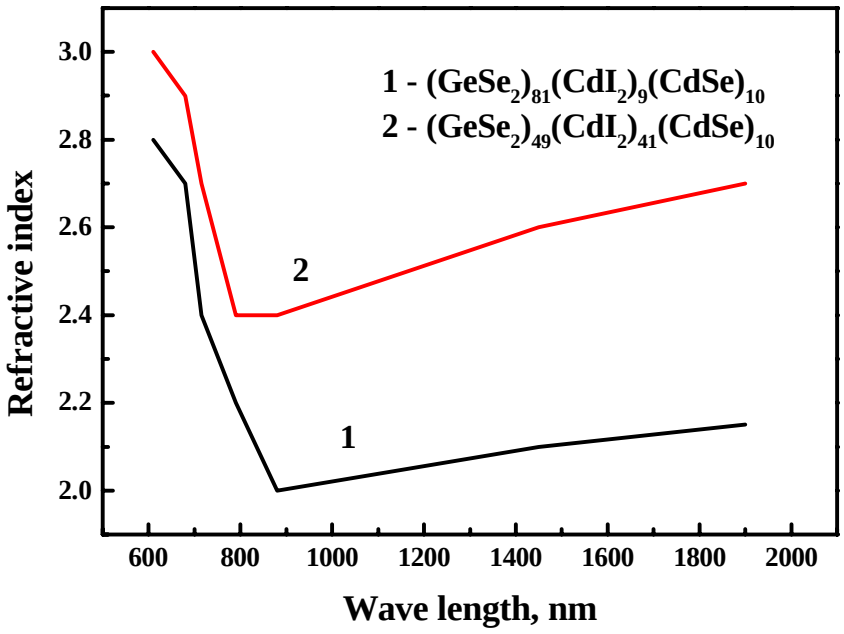

Figure 3. Spectral dependence of the refractive index in the system (I)

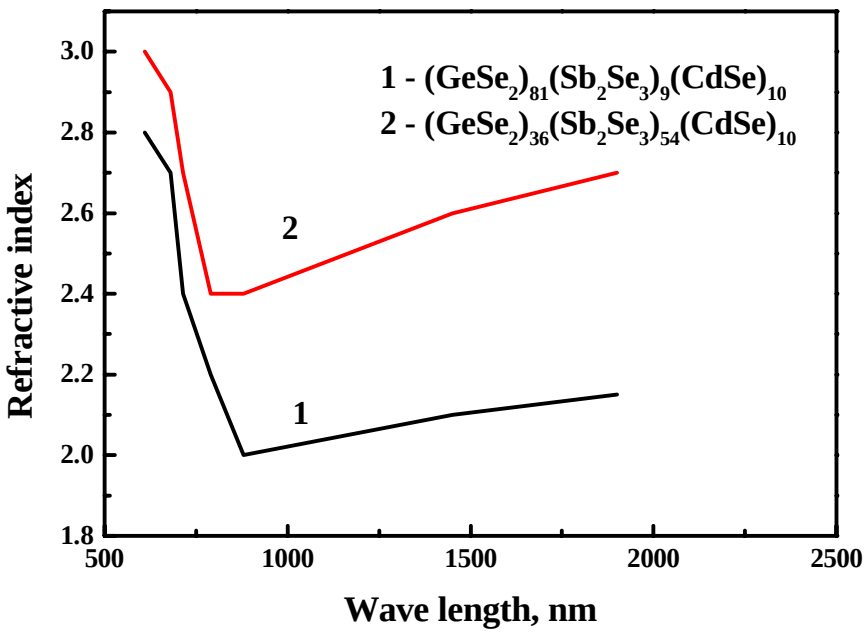

Figure 4. Spectral dependence of the refractive index in the system (II)

4. CONCLUSIONS

Optical properties of new chalcogenide glasses - $GeSe_2$-CdI_2-CdSe (system I) and $GeSe_2$-Sb_2Se_3-CdSe (system II) are investigated. The results of the influence of different quantities of CdI_2 or Sb_2Se_3 on the properties of $GeSe_2$-CdSe system show:

(i) thin films from the both system are transparent in a wide spectral range from VIS to NIR;

(ii) the absorption edge in the system I changes with CdI_2 content in direction to the shorter wavelength, in the system II - the increase of Sb_2Se_3 content moves the absorption edge to the longer wavelength ;

(iii) the refraction in the system I decrease linearly with CdI_2 concentration, in the system II – the relation of R vrs. Sb_2Se_3 content is opposite;

(iv) the optical band gap in the system I changes with CdI_2 concentration from 2.61 eV to 2.95 eV, in the system II –the values are – 1.78 – 2.22 eV.

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