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COMPOSITIONAL DEPENDENCE OF THE OPTICAL PROPERTIES OF THE Ge–Se-Ga GLASSES

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Optical properties of the glasses from the systems with a constant ratio of Ge/Se and different concentrations of gallium are investigated. The spectral dependence of the absorption coefficient α, is calculated from transmission spectra. The optical band gap, E_g^4, found to increase with the addition of gallium. This variation is explained by the increase of the average bond energy that occurs with the addition of Ga into the alloys. The optical constants, were also calculated from the transmission spectra, using a method proposed by Swanepoel.

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Keywords: Ge-Se-Ga glasses, Optical properties

1. Introduction

Chalcogenide glasses are promising optical materials due to their transparency in the IR region, relatively good thermal, mechanical and chemical properties and the low optical losses. Germanium chalcogenides with the addition of Sb [1], As [2] and In [3] have already investigated. These studies have mainly focused on the improvement of the optical transmission of the alloys in the IR region [4] and attention has mainly given on the choice of the proper modifier or on the improvements of the preparation conditions.

In the present study we investigate the effect of the addition of Ga in two amorphous systems where the ratio of Ge/Se was kept constant. Mitkova and Boncheva [5] have studied the glass-forming region of the Ge-Se-Ga system. They found that good glasses are prepared having concentrations as high as 35 at.% of Ge and 20 at.% of Ga.

We report the dependence of the optical absorption coefficient, of the refractive index and of the extinction coefficient on the Ga content. On the base of the results we discuss a correlation between the composition and the optical properties in terms of the chemically ordered covalent network model [8].

2. Experimental

We investigated bulk and thin films of $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ systems, with up to 20 at % Ga. Bulk glasses were prepared with the melt-quenched technique, using 4N purity elements of Se, Ge and Ga. Evacuated ampoules with the initial substances were heated in a rotated furnace. The synthesizes were carried out with a constant heating ratio of 3 K/min up to a final temperature 1200 K. Glasses were obtained after a quenching in a mixture of water and ice.

Thin films were evaporated on glass substrates in a standard vacuum installation, using the respective bulk composition as a source material. The residual pressure was 1.33 10^{-5} Torr, the distance source-substrate was 0.12 m, and the temperature of the evaporation source was 800-900 K. The typical thickness was about 0.5μm. The amorphicity of both bulk and thin films was examined by the X-ray diffraction technique.

Optical transmission of the bulk samples was measured in the spectral region 400-900 nm or 1.2-1.8 eV, using a 75 W halogen lamp and a monochromator. The intensities of the incident, I_0 and transmitted light, I, were measured with a silicon detector at the shorter and a germanium detector at

the longer wavelengths. The transmission of the thin films was measured in the energy range of 2.1-3 eV, using two independent techniques: one was similar to that used for the bulk samples and the other was by a double channel spectrophotometer in VIS and NIR regions. The refractive index and the extinction coefficient are obtained using a computer program based on a method described by Swanepoel [6].

3. Results and discussion

The optical absorption coefficient, α, is calculated from the transmission, $T= I_0/I$ and using the relation

$$\alpha=1/d\ [\ln (1-R)^2 / T] \quad (1)$$

where, d is the thickness and R the reflectivity. The energy variation of the absorption coefficient gives an indication of the distribution of the density of states in the energy gap. The low energy region, 1.2-1.8 eV, which is obtained by measuring transmission through the thick bulk samples, gives an estimate of the density of the deep defects states at mid-gap. The absorption spectra of the thin films one are determined at the high-energy region, 2.1-3 eV, obtained by measuring transmission through the thin films. In the region with energies higher than 2.5 eV, the absorption coefficient shows a parabolic variation on the photon energy, while up to 2.5 eV, it depends exponentially on the photon energy [7],

$$\alpha=\alpha_0 \exp (h\nu/E_0) \quad (2)$$

where α_0=const and E_0 is the so-called Urbach slope. Variations in the width of the exponential region, E_0, provide information about the relative changes of the structural disorder induced by an additive. For a good chalcogenide material, a typical value of the slope, E_0, is around 50 meV. Higher values of E_0 indicate that the addition of Ga increases the disorder. In this region the optical band gap of the material is also determined. The optical band gap, E_g, of amorphous materials [7] is usually defied as the energy at which α has a value between 10^4–10^5 cm^{-1}. In our case, where the interference fringes start to dominate the photon energy range below 2.1 eV, we take as an optical gap, E_g^4, the energy where $\alpha=2x10^4$ cm^{-1}.

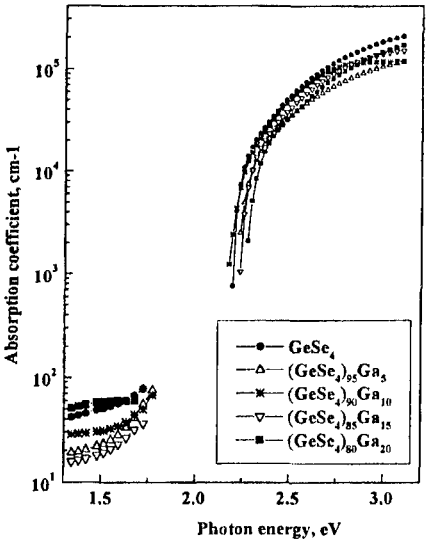

Fig. 1. Spectral dependence of the absorption coefficient for $(GeSe_4)_{1-x}Ga_x$ system.

In Fig.1 are plotted the spectra dependence of the absorption coefficient, α, for bulk (at the low energy range) and for thin films (at the high energy range) of $(GeSe_4)_{1-x}Ga_x$ with x = 0, 5, 10, 15 and 20. As it can seen the optical gap increases slightly with the gallium content.

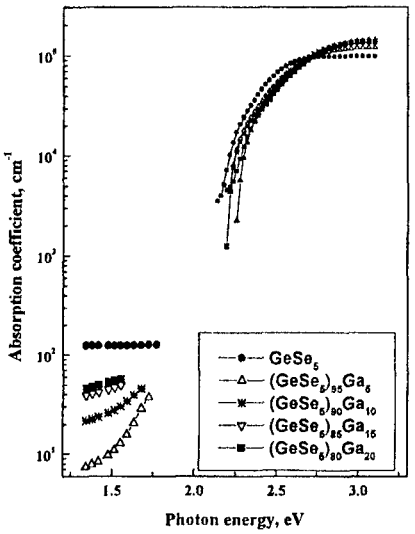

Fig. 2. Spectral dependence of the absorption coefficient for $(GeSe_5)_{1-x}Ga_x$ system.

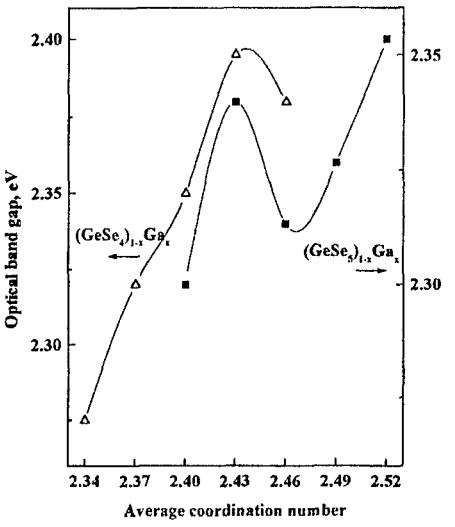

Fig. 3. Optical band gap versus gallium content.

Fig. 2 shows the spectral dependence of the absorption coefficient of bulk and thin films with compositions $(GeSe_5)_{1-x}Ga_x$, where x= 0, 5, 10, 15 and 20. We can see that the addition of up to 5 at.% Ga decreases the midgap absorption, and also the optical gap. The addition of higher concentrations of Ga seems to increase the absorption gap and the midgap absorption. Due to the similar compositions, the variation of the optical band gap with the Ga content for the alloys of the system $(GeSe_5)_{1-x}Ga_x$ is very similar to that of the $(GeSe_4)_{1-x}Ga_x$ alloys. In Fig. 3 is plotted the variation of E_g^4, as a function of the Ga content. The observed increase of the band gap can be explained in terms of structural arguments. It is known that the structure of the Ge-Se-Ga glasses is made up from tetrahedral $GeSe_2$ and pyramidal Ga_2Se_3 units [8]. According to the chemically ordered covalent network model [9] the $GeSe_2$ and the Ga_2Se_3 units are connected with extra Se atoms. The excess Se atoms are connected in chains. Ge-Ge bonds are not expected to form up to 33 at. % Ge. According to ref. 10, the bond energy of Ga-Se bonds (65 kcal/mol) is bigger than Ge-Se bond energy (55.4 kcal/mol), which indicates that the increase of the Ga content, the average bond energy of the system will increase. The formation of stronger bonds could be the cause of the increase of the optical band gap. The optical constants of the thin films were calculated from the transmission spectra, using a method proposed by Swanepoel [6]. The spectral dependence of refractive index, n and extinction coefficient, k for $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ are shown in Fig. 4 and Fig. 5.

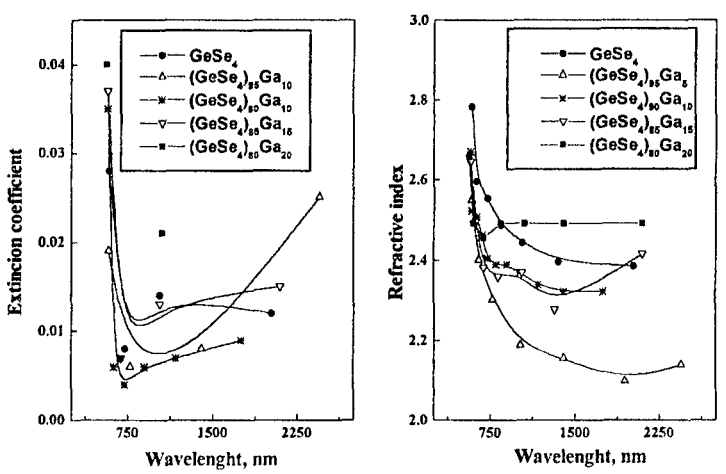

Fig. 4. Extinction coefficient and refractive index for $(GeSe_4)_{1-x}Ga_x$ system.

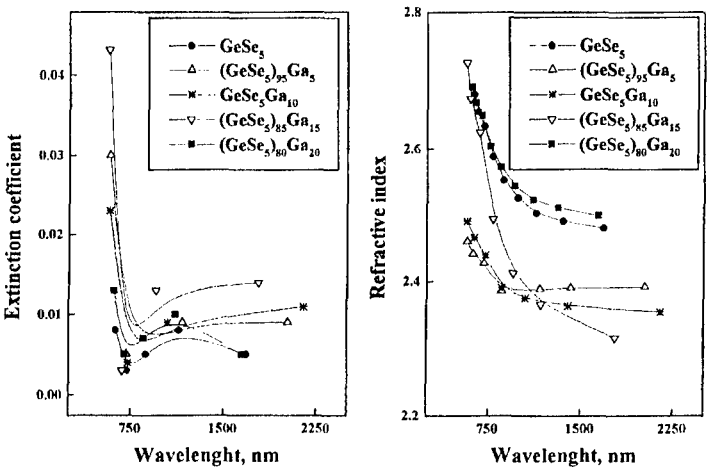

Fig. 5. Extinction coefficient and refractive index for $(GeSe_5)_{1-x}Ga_x$ system.

It is found that, at small wavelengths, both k and n decrease drastically and then remain practically constant. The values of k and n decrease slowly with the increase of the gallium concentration. This trend of lower values with increasing Ga content could assume to be connected with structural transformations. The appearance of new Ga_2Se_3 units changes the density of the material, which is consistent with optical constants' values.

4. Conclusions

Optical properties of the glasses from the systems with a constant ratio of Ge/Se and different quantities of gallium are investigated. The optical gap found to increase with the addition of gallium. This variation could be explained as due to the increase of average bond energy of the alloys that occurs with the addition of Ga.

Acknowledgment

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References

[1] P. Klocek, L. Colombo, Index of refraction, dispersion, bandgap and light scattering in GeSe and Ge-Sb-Se glasses, J. Non-Cryst.Solids, 93, 1 (1987).
[2] M. Fadel, The physical properties and the chemical bond approach for Se-Ge-As amorphous chalcogenide glasses, Vacuum, 48(1), 73 (1996).
[3] S. Saffarin, Compositional trends of the compactness in ternary chalcogenide glasses of the Ge-In-Se system, Physica B, 253, 52 (1998).
[4] B. Kolomiets, Y. Rukhlyadev, V. Shilo, The effect of gallium, indium and thallium on the photoelectric ptoperties of glassy arsenic selenide, J. Non-Cryst. Solids, 5, 402 (1971).
[5] M. Mitkova, Z. Boncheva, Compt. Glassforming region in the Ge-Se-Ga system, Rend. Acad. Bulg. Sci., 28, 189 (1975).
[6] R. Swanepoel, Determination of thr thickness and optical constants of amorphous silicon, J. Phys. E: Sci. Instrum. 16, 1214 (1983).
[7] N. F Mott, E. A Davis, Electronic Processes in Non-Crystalline Materials, Claredon Press (1971).
[8] S. Mahadevan, A. Giridhar, Coexistance of topological and chemical ordering effects, Journal of Non-Crystalline Solids, 152, 42 (1993).
[9] G. Lucovsky, F. Galeener, R. Keezer, R. Geils, H. Six, Phys. Rev B, 10, 5134 (1974).
[10] Gmelin Handbuch anorganischer Chemie, Se, B2, Springer Verlag, (1984).