

OPTICAL BAND GAP OF GALLIUM CONTAINING TELLURIDE THIN FILMS

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Optical properties of chalcogenide amorphous thin films from $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ ($x=0, 5, 10, 15, 20$ at.%) systems have been determined and analyzed. The investigation of the optical absorption has shown that the introduction of gallium leads to a shift in the absorption edge towards higher energies in comparison with binary glass. Optical band gap has been determined from absorption coefficient data by Tauc procedure and from the energetic distribution of the absorption coefficient. The introduction of third element increases the disorder in the system reflected in the increase of optical band gap values.

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1. Introduction

Chalcogenide glasses are attractive and widely investigated materials. Scientific and industrial interest exists since long time due to their unique properties. These glasses are used as optoelectronic device materials [1], promising material in the IR optics, microelectronics etc. [2, 3] because of their excellent transmittance, reaching the far-infrared spectral region. Therefore, a lot of work has been done on both bulk and thin films of glassy chalcogenides regarding their optical properties [4, 5]. Tellurium rich Ge-Te amorphous alloys are used as recording materials in the phase change optical discs [6]. Besides, the Ge-Te system often serves as a model for the alloys used in the industry. It is well known that alloys of the group III elements (Ga, In, Tl) with the chalcogen elements (S, Se, Te) form a large range of semiconducting crystals in the solid state with compositions $\text{A}^{\text{III}}\text{B}^{\text{VI}}$ and $\text{A}_2^{\text{III}}\text{Te}_3^{\text{VI}}$. For example amorphous alloys can be obtained by local overheating of thallium in sulfur vapors in evacuated ampoules only [7]. Previous experiments of some of the authors show that the addition of Ga and Tl to chalcogenide glasses is generally accompanied by a marked change in their structural and optical properties [8-10] similar to the results reported by Abdel-Aziz et al. in [11].

The present investigation is a continuation of our previous studies on the possibilities to obtain amorphous thin films by evaporation and condensation in three component systems based on Ge and Se(Te) with participation of Tl, B or Ga as a third component. The aim is to trace the influence of the third component on the thin film structure and optical absorption.

2. Experimental procedure

Bulk samples from the systems $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ ($x=0, 5, 10, 15, 20$ at.%) were prepared by melt-quenched technique, using 5N purity elements of Te, Ge and Ga. Evacuated ampoules with the initial substances were heated in a rotated furnace with a constant heating ratio of

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3 K/min up to a final temperature 1200 K. Glasses were obtained after a quenching in a mixture of water and ice.

Vacuum installation Leybold LB 370, with a residual gas pressure of 1.33×10^{-4} Pa was used for the preparation of the thin films. The conditions of film preparation were: distance source-substrate 0.12 m, temperature of the evaporation source 800-900 K. Thin films were evaporated on glass substrates using the respective bulk composition as a source material. The typical thickness was about 0.5 μm .

The film composition was investigated by Auger electron spectroscopy. The thin film structure was studied with a transmission electron microscopy (TEM) and selected area electron diffraction (AED) using EM-400 Philips electron microscope.

Transmission spectra and reflection spectra of the thin films were measured using a double-beam UV/ VIS/ NIR computer controlled spectrophotometer (Perkin Elmer, model Lambda 19) in the spectral range 400 – 2500 nm.

All experiments were carried out at room temperature.

3. Results

The investigated films are amorphous as proved by microscope investigations. Transmission electron microscope study evidences the homogeneous surface of the films, while the electron diffraction investigation evidences the amorphous state of the binary films (small picture inside) - Fig. 1a. It is obvious that the addition of gallium do not change the homogeneous and amorphous structure of the films. The lack of crystallites in the ternary films is verified by absence of narrow rings in electron diffractogram as it is shown in Fig. 1b (small picture).

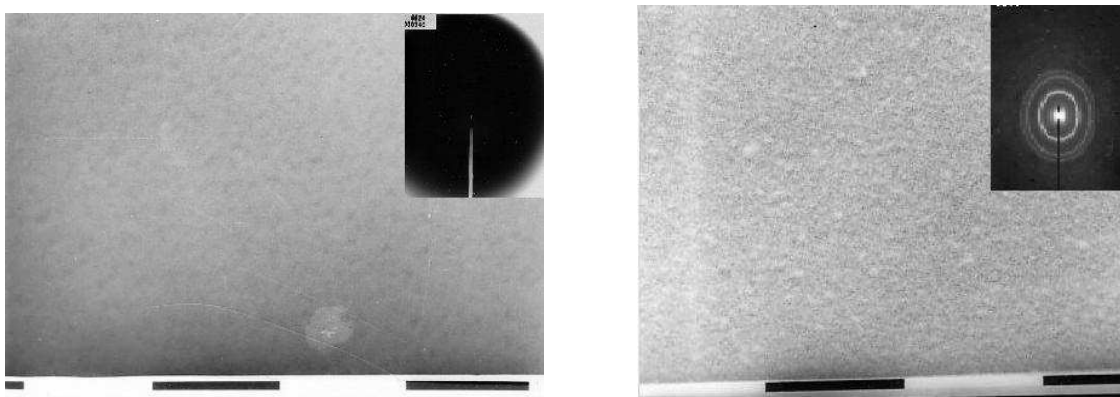


Fig. 1. Electron microscope pattern of (a) $\text{Ge}_{20}\text{Te}_{80}$ film and (b) $\text{Ge}_{13}\text{Te}_{67}\text{Ga}_{20}$ film.

The optical absorption coefficient, α , is calculated using the relation

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

where, d is the thickness of the film and R the reflectivity. The absorption spectra of the thin films are determined by measuring the transmission through the thin films. In Fig. 2a are plotted the spectral dependence of the absorption coefficient, α , for thin films of $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ and in Fig. 2b for $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ films.

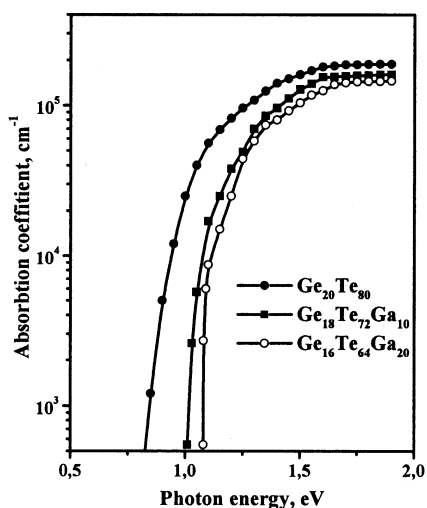


Fig. 2a. Spectral distribution of absorption coefficient in $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ films.

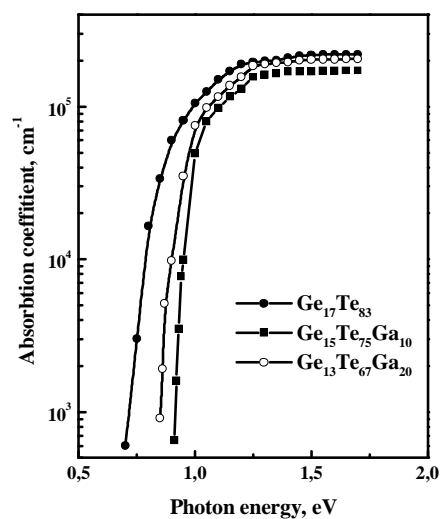


Fig. 2b. Spectral distribution of absorption coefficient in $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ films.

In general the introduction of gallium in the glass increases the absorption coefficient values.

The optical band gap is calculated by two methods: from the spectral distribution of absorption coefficient and by Tauc procedure. The optical band gap, E_g^{04} , of amorphous materials [12] is usually defined as the energy at which α takes the value of 10^4 cm^{-1} . The values of the optical gap, E_g^{04} , obtained from the graphical relation are given in Table 1. The photon energy at $\alpha=10^4 \text{ cm}^{-1}$ is larger than the optical band gap, E_g , determined by Tauc procedure.

Table 1.

No	Composition	E_g^{04} , eV	$E_{gopt.}$, eV	Z	ϵ	A
1	$\text{Ge}_{20}\text{Te}_{80}$	0.93	0.86	2.40	0.22	23.72
2	$\text{Ge}_{19}\text{Te}_{76}\text{Ga}_5$	1.27	1.09	2.43	0.24	35.34
3	$\text{Ge}_{18}\text{Te}_{72}\text{Ga}_{10}$	1.07	1.00	2.46	0.25	31.01
4	$\text{Ge}_{17}\text{Te}_{68}\text{Ga}_{15}$	1.04	0.98	2.49	0.27	32.87
5	$\text{Ge}_{16}\text{Te}_{64}\text{Ga}_{20}$	1.13	1.03	2.52	0.29	37.99
6	$\text{Ge}_{17}\text{Te}_{83}$	0.78	0.73	2.33	0.18	16.28
7	$\text{Ge}_{16}\text{Te}_{79}\text{Ga}_5$	0.86	0.80	2.36	0.20	19.94
8	$\text{Ge}_{15}\text{Te}_{75}\text{Ga}_{10}$	0.96	0.87	2.40	0.22	24.23
9	$\text{Ge}_{14}\text{Te}_{71}\text{Ga}_{15}$	1.01	0.95	2.43	0.24	28.10
10	$\text{Ge}_{13}\text{Te}_{67}\text{Ga}_{20}$	0.91	0.83	2.46	0.26	28.03

The absorption that is associated with inter band transitions can be described by the following relation

$$\alpha = B(h\nu - E_g)^n \quad (2)$$

The exponent n equals to $1/2$ for allowed direct optical transitions and 2 – for indirect transitions. For direct transition one can expect a straight line for the dependence $\log(\alpha h\nu)$ vs. \log

(hv). Fig. 3 shows the plot which yields a line different from straight. The non-linear relation proves the indirect transitions in the films.

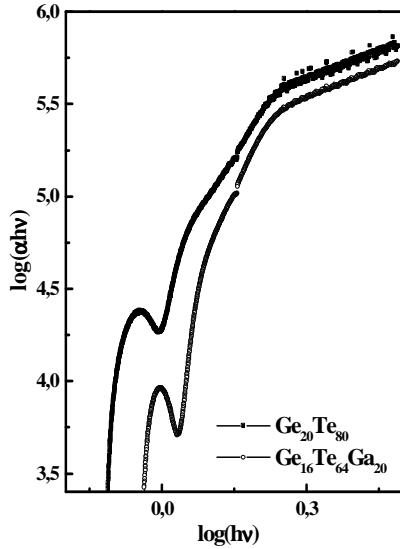


Fig. 3. Dependence of $\log(\alpha hv)$ vs. $\log(hv)$.

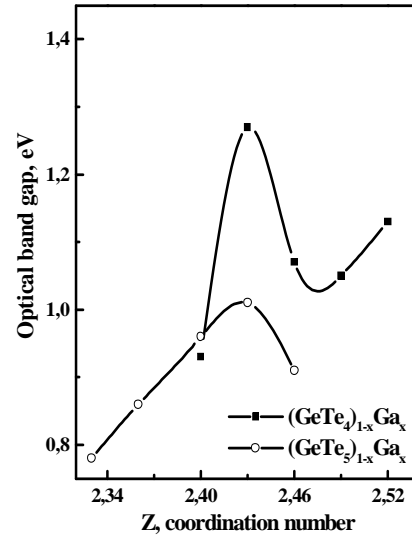


Fig. 4. Plots of E_g against coordination number.

The average coordination number of the samples is calculated and the values are listed in Table 1. In Fig. 4 is plotted the variation of E_g^{04} , as a function of Z . The values of $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ films are larger but show a similar trend like that observed in $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ films.

In order to correlate the optical parameters (E_g) with the film composition we used the energetic parameter A introduced by Angell [13]:

$$A = \varepsilon E_o^{04} / K \quad (3)$$

Where $\varepsilon = \delta(N_c - 2) = \delta X$, K is Boltzman constant, E_o^{04} is the optical band gap and δ is an independent constant which value is assumed to be 0.55. The calculated values of ε and A are given in Table 1. The plot A vs. Ga content, presented in Fig. 5, shows a tendency of increasing the energetic parameter with the increase of gallium content.

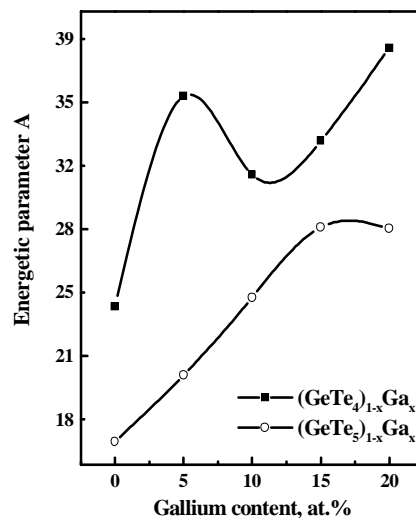


Fig. 5. Energetic parameter A vs. gallium content.

4. Discussion

The observed compositional variation of the band gap can be explained in terms of structural arguments. The structure of the Ge-Te-Ga glasses can be assumed as made up from tetrahedral GeTe_2 and pyramidal Ga_2Te_3 units. According to the chemically ordered covalent network model [14] the GeTe_2 and the Ga_2Te_3 units are connected with extra Te atoms interacting with weak intermolecular bonds.

There is a similarity in the structure of chalcogen elements Se and Te. Each selenium and tellurium atom has six valence electrons, two s and four p electrons. Two of the p electrons contribute to bonding and construct a chain structure. The remaining two p electrons become lone-pair electrons. Tellurium is much heavier than selenium, and the strength of the Te-Ge bond is lower than Se-Ge bond so that the optical absorption edge shifts to a higher value compared with Ge-Se-Ga films reported earlier [8]. As a result of this isoelectronic replacement of selenium by tellurium the structure of film is transformed from a chain-like to trigonal one depending on Te concentration [15] and the optical band gap decreases with increasing Te content. The decrease of E_g is related to the increase of Te content that may also be caused by the tendency of Te atoms to form chemical disordering and to create localized states in the band gap [16]. According to the model of density of states proposed by Mott and Davis [12] the width of the localized states near the mobility edges depends on the degree of the disorder and defects present in the amorphous structure. In particular, it is known that the unsaturated bonds are responsible for the formation of some defects in amorphous solids. Such defects produce localized states in the band gap. The presence of high concentration of localized states in thin films is responsible for low values of optical band gap.

It is known that Ge bonds in chalcogenide glasses are responsible for electron conduction. The small variations in Ge content for the all investigated films may be attributed to the presence of approximately equivalent concentration of covalent bonds in the samples with the same Ge content.

In general, the optical parameters investigated in this work show a tendency of increasing with increase of the gallium content as it is shown from the energetic parameter values. Linear increase in E_{gopt} with increasing gallium content has been found. Small anomalies of this relation are observed around $Z = 2.4$ for both investigated systems.

Gallium additives must bring about a compositional change of the host material. The formation of stronger bonds could be the cause of the increase of the optical band gap. The observed increase in E_g is the same as that observed in Ge-Se-Ga glasses.

5. Conclusions

The results from the optical properties investigation of $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ films can be summarized as follows:

- Thin $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ films prepared by vacuum evaporation are amorphous irrespective of gallium concentration;
- The spectral dependence of the absorption coefficient indicates an indirect allowed transition. The result is verified by energetic parameter relation vs. composition;
- The optical band gaps of $(\text{GeTe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeTe}_5)_{1-x}\text{Ga}_x$ films depends on the composition. Their values increase from 0.93 eV to 1.13 eV on increasing composition x from 0 to 20 at.% with small variations around $Z = 2.4$, where structural transformations take place. The increasing of optical band gap with gallium content may be due to the formation of stronger bonds in the films;
- The absorption edge undergoes a shift to the inside of the forbidden gap as tellurium content increases. The valence band intensity depends on the composition, and increases with tellurium content.

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