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Photo- and thermo-induced changes in optical constants and structure of thin films from GeSe₂-GeTe-ZnTe system

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Abstract

We examined the condition of preparation of thin films from GeSe₂-GeTe-ZnTe system by thermal evaporation and changes in their optical properties after exposure to light and thermal annealing. The results for composition analysis of thin films showed absence of Zn independently of the composition of the bulk glass. By X-ray diffraction (XRD) analysis it was found that a reduction of ZnTe in ZnSe in bulk materials takes place during the film deposition. A residual from ZnSe was observed in the boat after thin film deposition. Optical constants (refractive index, n and absorption coefficient, α) and thickness, d as well as the optical band gap, E_g , depending of the content of Te in ternary Ge-Se-Te system are determined from spectrophotometric measurements in the spectral range 400-2500 nm applying the Swanepoel's envelope method and Tauc's procedure. With the increase of Te content in the layers the absorption edge is shifted to the longer wavelengths, refractive index increases while the optical band gap decreases from 2.02 eV for GeSe₂ to 1.26 eV for Ge₃₄Se₄₂Te₂₄. The values of the refractive index decrease after annealing of all composition and E_g increase, respectively. Thin films with composition of Ge₂₇Se₄₇Te₉Zn₁₇ and Ge₂₈Se₄₉Te₁₀Zn₁₃ were prepared by co-evaporation of (GeSe₂)₇₈(GeTe)₂₂ and Zn from a boat and a crucible and their optical properties, surface morphology and structure were investigated. The existence of a correlation between the optical band gap and the composition of thin films from the system studied was demonstrated.

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1. Introduction

Amorphous chalcogenide glasses have been extensively studied for several decades because of their interesting fundamental properties and because of their potential applications in optical imaging, optical

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recording, infrared and integrated optics, microelectronics and optical communications [1-5]. The properties of glass forming systems, such as As-S, As-Se, Ge-S and Ge-Se were widely studied while the information on more complex multicomponent systems is still exiguous. In our previous reports we have demonstrated that the composition of the chalcogenide thin films the refractive index and the optical band gap of these materials could be varied in wide limits [6-8]. The values of the optical constants and the absorption edge of these materials change after light irradiation and annealing of thin films.

Investigations are carried out on bulk samples and thin films Ge-containing chalcogenide semiconductors [9-12] and possibilities are sought for application in spite of their considerably lower sensitivity compared to As-containing glasses. Some papers were published on the study of photochemical and optical properties of multicomponent chalcogenide glasses from the system $\text{GeSe}_2\text{-Sb}_2\text{Se}_3\text{-PbSe}$ (PbTe) [13-15].

2. Experimental

Bulk glasses with 6 different compositions, disposed in the glass forming region (Fig.1) were synthesized by conventional melt quenching technique of GeSe_2 , GeTe , and ZnTe (preliminary prepared from elements Ge, Se, Te and Zn with high purity) [16]. It is seen that the glass forming region is very narrow (the possible adding of ZnTe in the glasses is around 17 mol. % or 6 at. % of Zn). Thin films were deposited by thermal evaporation from a Ta boat ("Knudsen type) onto optical glass substrates BK-7, graphite and two-side polished Si wafers under vacuum $6\text{-}8 \cdot 10^{-6}$ Torr with a rate of deposition $0.8 \text{ nm} \cdot \text{s}^{-1}$. Their composition was determined by scanning electron microscopy (SEM) with an X-ray microanalyser (Jeol Superprobe 733, Japan).

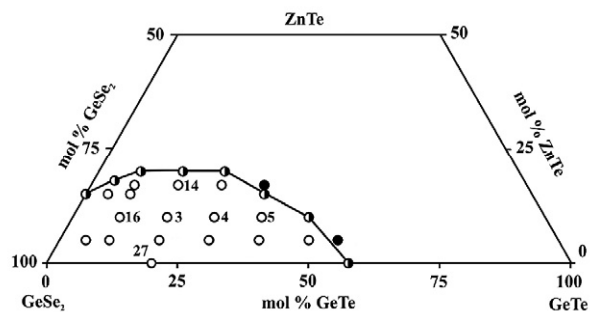


Fig. 1. Bulk samples from the glass forming region (indicated by circles with numbers) used in the study [15]

The X-ray diffraction in the range of $5.3\text{-}80^\circ 2\theta$ (Bruker D8 Advanced Diffractometer with $\text{Cu K}\alpha$ radiation and LynEye detector) was used to examine the amorphous or crystalline nature of $\text{GeSe}_2\text{-GeTe-ZnTe}$ films.

The transmittance and reflectance spectra in spectral range $450\text{-}2500 \text{ nm}$ of as-deposited, illuminated and annealed films were performed in an UV-VIS-NIR spectrophotometer (Cary 05E, Australia). The as-deposited thin films were illuminated or annealed in vacuum at 10^{-3} Pa . The exposure time to saturation with a halogen lamp ($60 \text{ mW} \cdot \text{cm}^{-2}$) (i.e. the time beyond which the absorption edge did not changed) was experimentally established for each sample. Samples from all compositions were annealed for two hours in vacuum at temperature 25°C below T_g for each one. The surface morphology of thin films was investigated in Philips SEM 515 under an angle of 40° between the sample and the scanning electron flux.

The structure of the films was probe high resolution transmission electron microscope (TEM) JEM 2100. The IR absorption spectra of thin films on Si wafer substrates were measured in the range of $150\text{-}500\text{ cm}^{-1}$ by the Bruker IFS 113v spectrometer.

3. Results and discussion

The results from the compositional analysis of the bulk glasses and thin films samples from $\text{GeSe}_2\text{-GeTe-ZnTe}$ system are presented in Table 1. It is seen the lack of zinc in the thin films evaporated from bulk materials. The analysis of the elements of thin films showed only Ge, Se and Te in the layers. We found by X-ray diffraction that the composition of the residue in the boat is crystalline ZnSe after evaporation of the thin films from bulk glasses. The thin films deposited by co-evaporation of $(\text{GeSe}_2)_{80}(\text{GeTe})_{20}$ and Zn yields composition of the layers that is close to the expected one. In the text below we discussed the thin films according their composition determined by X-ray microanalysis.

Table 1. Composition of bulk glasses and thin films from $\text{GeSe}_2\text{-GeTe-ZnTe}$ system

Bulk glasses (mol. %)	Bulk glasses (at. %)	Thin films (at. %)
$(\text{GeSe}_2)_{80}(\text{GeTe})_{20}$	$\text{Ge}_{36}\text{Se}_{57}\text{Te}_7$	$\text{Ge}_{32}\text{Se}_{61}\text{Te}_7$
$(\text{GeSe}_2)_{81}(\text{GeTe})_9(\text{ZnTe})_{10}$	$\text{Ge}_{32}\text{Se}_{58}\text{Te}_9\text{Zn}_3$	$\text{Ge}_{30}\text{Se}_{62}\text{Te}_8$
$(\text{GeSe}_2)_{72}(\text{GeTe})_{18}(\text{ZnTe})_{10}$	$\text{Ge}_{33}\text{Se}_{53}\text{Te}_{10}\text{Zn}_4$	$\text{Ge}_{32}\text{Se}_{56}\text{Te}_{12}$
$(\text{GeSe}_2)_{63}(\text{GeTe})_{27}(\text{ZnTe})_{10}$	$\text{Ge}_{34}\text{Se}_{48}\text{Te}_{14}\text{Zn}_4$	$\text{Ge}_{34}\text{Se}_{49}\text{Te}_{17}$
$(\text{GeSe}_2)_{54}(\text{GeTe})_{36}(\text{ZnTe})_{10}$	$\text{Ge}_{35}\text{Se}_{43}\text{Te}_{18}\text{Zn}_4$	$\text{Ge}_{34}\text{Se}_{42}\text{Te}_{24}$
$(\text{GeSe}_2)_{66}(\text{GeTe})_{17}(\text{ZnTe})_{17}$	$\text{Ge}_{31}\text{Se}_{50}\text{Te}_{13}\text{Zn}_6$	$\text{Ge}_{32}\text{Se}_{53}\text{Te}_{15}$
$(\text{GeSe}_2)_{78}(\text{GeTe})_{22}/\text{Zn}$	Co-evaporation	$\text{Ge}_{28}\text{Se}_{49}\text{Te}_{10}\text{Zn}_{13}$
$(\text{GeSe}_2)_{78}(\text{GeTe})_{22}/\text{Zn}$	Co-evaporation	$\text{Ge}_{27}\text{Se}_{47}\text{Te}_9\text{Zn}_{17}$
$(\text{GeSe}_2)_{78}(\text{GeTe})_{22}/\text{Zn}$	Co-evaporation	$\text{Ge}_{23}\text{Se}_{43}\text{Te}_9\text{Zn}_{25}$

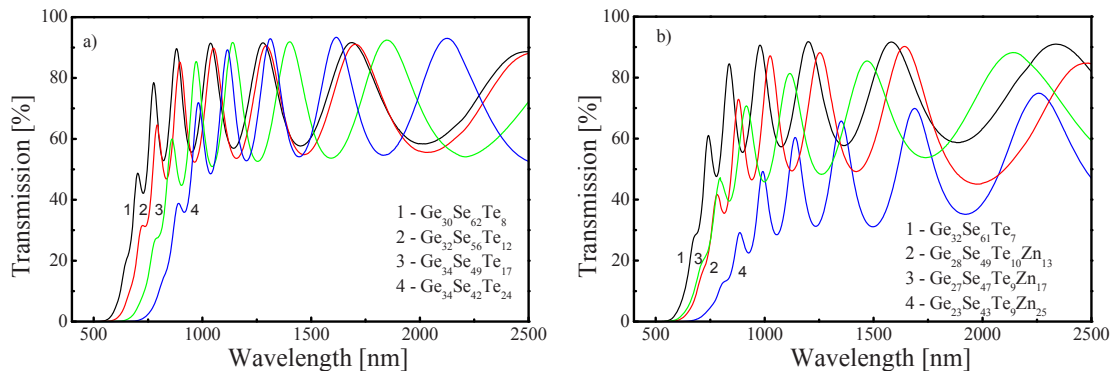


Fig. 2. Spectral dependence of the transmission of thin Ge-Se-Te (a) and $(\text{GeSe}_2)_{80}(\text{GeTe})_{20}/\text{Zn}$ (b) films.

The transmittance spectra of thin films with typical interference pattern are shown in Fig. 2. The refractive index, n and thickness, d of thin $\text{GeSe}_2\text{-GeTe-ZnTe}$ films were calculated from the interference extrema in the transmission spectra using Swanepoel's method [16, 17]. The program used to calculate n will determine it to maximal accuracy of $\pm 0.5\%$ for an error in the transmittance of $\pm 0.1\%$ [17]. The experimental error for the refractive index is in the range of $\delta n = 0.013\text{-}0.016$. The spectral dependencies of the refractive index, $n(\lambda)$ of the as-deposited thin films are plotted in Fig. 3. The thin film with composition $\text{Ge}_{30}\text{Se}_{62}\text{Te}_8$ deposited from bulk $(\text{GeSe}_2)_{81}(\text{GeTe})_9(\text{ZnTe})_{10}$ glass demonstrated the same values for refractive index as a thin film which was thermal evaporated from bulk $(\text{GeSe}_2)_{80}(\text{GeTe})_{20}$ glass. In previous work [15] we found the values for $n = 2.38$ at $\lambda = 1550$ nm for thin film from GeSe_2 . Hence the addition of 8 at % tellurium leads to 0.19 of the refractive index in comparison with GeSe_2 . Further increase of tellurium content from 8 to 24 at % in thin films increase the value of n from 2.57 to 2.73 (at $\lambda = 1550$ nm). The addition of zinc in thin films leads to increasing of n from 2.80 for 13 at % Zn to 3.25 for 25 at % Zn, respectively (Table 2).

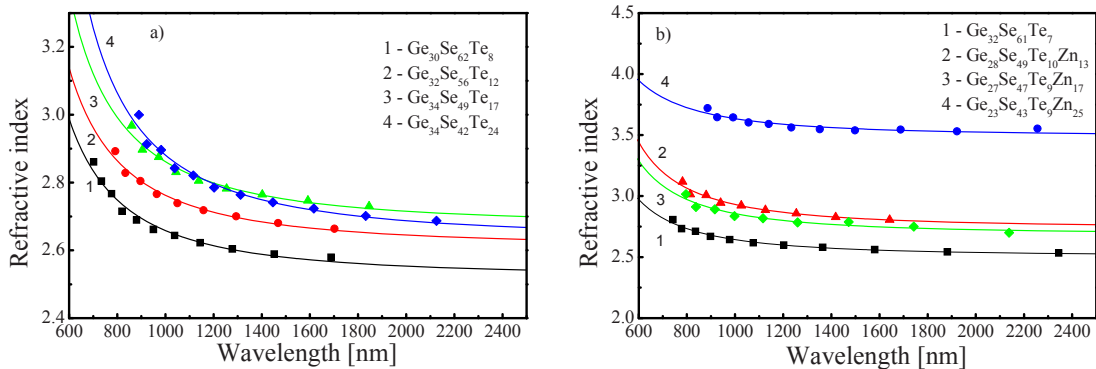


Fig. 3. Dispersion of the refractive index, $n(\lambda)$ for thin Ge-Se-Te (a) and $(\text{GeSe}_2)_{80}(\text{GeTe})_{20}/\text{Zn}$ (b) films.

Table 2. Optical parameters of virgin, exposed and annealed $\text{GeSe}_2\text{-GeTe-ZnTe}$ films.

Composition	Refractive index at $\lambda = 1550$ nm			Optical band gap [eV]			Film thickness [nm]			$\Delta\lambda$ [nm] annealed films
	Virgin	Exp.	Annealed	Virgin	Exp.	Annealed	Virgin	Exp.	Annealed	
$(\text{GeSe}_2)_{80}(\text{GeTe})_{20}$	2.56	2.53	2.50	1.65	1.67	1.75	925	928	949	-65
$\text{Ge}_{30}\text{Se}_{62}\text{Te}_8$	2.57	2.56	2.50	1.66	1.67	1.86	975	983	988	-55
$\text{Ge}_{32}\text{Se}_{56}\text{Te}_{12}$	2.67	-	2.58	1.55	-	1.64	970	965	957	-60
$\text{Ge}_{32}\text{Se}_{53}\text{Te}_{15}$	2.66	2.66	2.62	1.44	1.45	1.57	1000	980	990	-82
$\text{Ge}_{34}\text{Se}_{49}\text{Te}_{17}$	2.75	2.76	2.70	1.38	1.41	1.53	1014	990	1000	-60
$\text{Ge}_{34}\text{Se}_{42}\text{Te}_{24}$	2.73	2.74	2.64	1.26	1.28	1.44	1187	1184	1190	-32
$\text{Ge}_{28}\text{Se}_{49}\text{Te}_{10}\text{Zn}_{13}$	2.80	2.90	2.90	1.45	1.47	1.49	880	860	870	-12
$\text{Ge}_{27}\text{Se}_{47}\text{Te}_9\text{Zn}_{17}$	2.76	2.76	2.75	1.47	1.49	1.53	790	795	760	-46
$\text{Ge}_{23}\text{Se}_{43}\text{Te}_9\text{Zn}_{25}$	3.25	2.95	2.55	1.30	1.34	1.44	950	1140	1170	-74

At high values of the absorption coefficient α , where the condition $\alpha d \geq 1$ is observed, the absorption

coefficient α should be calculated from the equation:

$$T = (1 - R)^2 \exp(-\alpha d) \quad (1)$$

where T is transmittance, R is reflectance and d is thin film's thickness. Analysis of the strong absorption region ($10^4 \leq \alpha \leq 10^5 \text{ cm}^{-1}$) has been carried out using the following well-known quadratic equation, often called *Tauc's law* [18]:

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g^{\text{opt}}) \quad (2)$$

where B is a substance parameter, which depends on the electronic transition probability, $(h\nu)$ is the photon energy and E_g^{opt} is the so-called *Tauc's gap*. The spectral variation for absorption coefficient plotted as $(\alpha h\nu)^{1/2}$ versus the photon energy ($h\nu$) is shown in Fig. 3. The optical gap decrease when tellurium or zinc content in thin films increase. We found that the values of E_g decrease from 1.65 to 1.26 eV when tellurium in thin films increase from 8 to 24 at%, while for Zn contains films E_g is in the range of 1.45 to 1.30 eV.

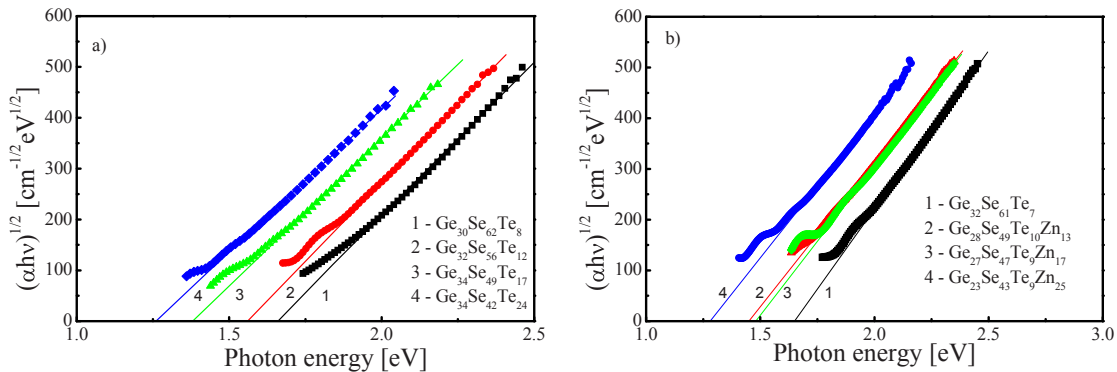


Fig.4. Optical absorption edge $(\alpha h\nu)^{1/2}$ vs. photon energy of thin Ge-Se-Te (a) and $(\text{GeSe}_2)_{80}(\text{GeTe})_{20}/\text{Zn}$ (b) films.

The results for the changes of the refractive index, optical gap and thickness after exposure to light or annealing are given in Table 2. It seen that illumination or heat treatment leads to decreasing of the refractive index and increasing of the values for E_g^{opt} . The calculated values for n and E_g^{opt} demonstrated that thermoinduced changes are more pronounced than photoinduced effects in $\text{GeSe}_2\text{-GeTe-ZnTe}$ films. The photoinduced changes of the refractive index of thin Ge-Se-Te films are in the range of $\Delta n = 0.01\text{-}0.03$, while the thermoinduced changes are higher $\Delta n = 0.06\text{-}0.09$. The obtained photo-induced changes for Ge-Se-Te films are very close to the limit of the experimental error. The increase of the value of n with 0.01 observed for $\text{Ge}_{34}\text{Se}_{49}\text{Te}_{17}$ and $\text{Ge}_{34}\text{Se}_{42}\text{Te}_{24}$ layers can be due only of the error of the calculations. Thin films containing zinc demonstrated higher photo- and thermo-induced changes. The maximal decrease of the value of n were obtained for thin $\text{Ge}_{23}\text{Se}_{43}\text{Te}_9\text{Zn}_{25}$ layer, where the Δn was 0.3 and 0.7 after exposure to light and annealing, respectively.

The effect of decreasing of the values of n was contributed with increasing of the optical band gap of thin films. The maximal changes was found for thin $\text{Ge}_{30}\text{Se}_{62}\text{Te}_8$ film from Ge-Se-Te system,

$E_g = + 0.2$ eV. The changes of the optical band gap of the thin layers from $(\text{GeSe}_2)_{28}(\text{GeTe})_{22}/\text{Zn}$ was smaller. The maximal changes for $\Delta E_g = + 0.14$ eV was obtained for composition $\text{Ge}_{23}\text{Se}_{43}\text{Te}_9\text{Zn}_{25}$.

There are two reasons for explanation of presence of thermoinduced changes in chalcogenide glassy materials. The first one is the conception of network rigidity. It suggests that increasing of rigidity leads to insensitivity to illumination, meanwhile assuming existence of significant thermally induced changes in the bonding arrangement [19]. The second reason is the presence of phase separation in thin films [20]. To analyze structure of thin films and presence of different phase we used transmission and scanning electron microscopy and infrared spectroscopy.

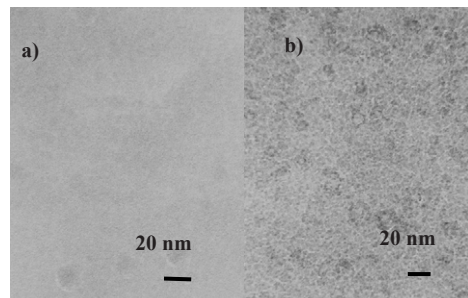


Fig.5. TEM pictures of thin $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7$ film (magnification is 300 000 times) (a) and $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7/\text{Zn}$ film (magnification is 200 000 times)(b)

The TEM images of thin films with composition $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7$ and $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7/\text{Zn}$ are shown in figs. 5a and 5b, respectively. We have not observed any grains for thin film with composition $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7$ even the magnification was 300 000 times, while the picture of zinc coating $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7/\text{Zn}$ demonstrated presence of particles with size about 5-20 nm. The SEM picture (fig. 6) of thin $\text{Ge}_{28}\text{Se}_{49}\text{Te}_{10}\text{Zn}_{13}$ film shows presence of spherical particles on the layer's surface. Observed increase of the refractive index for thin $\text{Ge}_{28}\text{Se}_{49}\text{Te}_{10}\text{Zn}_{13}$ films after exposure or annealing can be due to presence of phase separation.

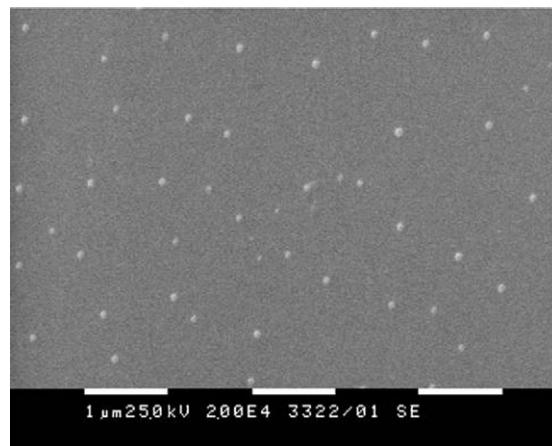


Fig. 6. SEM images of thin film with composition $\text{Ge}_{28}\text{Se}_{49}\text{Te}_{10}\text{Zn}_{13}$

The infrared absorption spectra of thin $(\text{GeSe}_2)_{28}(\text{GeTe})_{22}/\text{Zn}$ films are shown in Fig. 7. The infrared spectrum of GeSe_2 film is characterized with strong asymmetric band in spectral range $200\text{--}340\text{ cm}^{-1}$ with maxima at 254 cm^{-1} and two shoulders at 222 and 304 cm^{-1} . The low intensity band with maxima at 179 cm^{-1} is observed in spectral range $155\text{--}190\text{ cm}^{-1}$. According to [21] the glassy network of thin GeSe_2 films consists from tetrahedral $\text{GeSe}_{4/2}$ structural units, Se-Se chains and Ge-Ge bonds. Follow vibration modes are contributed in infrared absorption in spectral range $200\text{--}340\text{ cm}^{-1}$: the vibration of Se atoms in four-member rings composed of two edge-sharing tetrahedral is active at 215 cm^{-1} ; the stretching vibration of Se atoms in helical chain-like and ring-like arrangements at 250 cm^{-1} , and Se-Se bonds at 260 cm^{-1} . The stretching mode of corner-sharing $\text{GeSe}_{4/2}$ tetrahedral units at 200 cm^{-1} which is Raman active gives small contribution in infrared spectrum of GeSe_2 film. The band at 179 cm^{-1} is attributed with presence of Ge-Ge bonds in ethane-like structural $\text{Se}_3\text{Ge-GeSe}_3$ units [21].

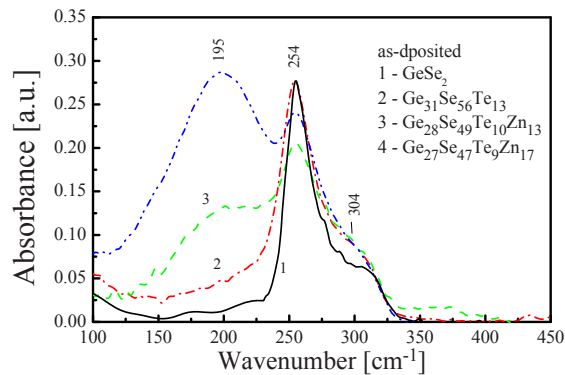


Fig. 7. Infrared absorption spectra of as-deposited thin $\text{GeSe}_2\text{-GeTe-ZnTe}$ films.

It is observed increase of the width of the band at $200\text{--}340\text{ cm}^{-1}$ for thin $\text{Ge}_{31}\text{Se}_{56}\text{Te}_{13}$ film. The addition of tellurium in thin film increases the absorption in frequencies range $150\text{--}250\text{ cm}^{-1}$ and intensity of the shoulder at 302 cm^{-1} . Phillips [22] has reported an absorption band at 230 cm^{-1} in Ge-Te glass and attributed it to $\nu_3(\text{F}_2)$ vibrational mode for GeTe_4 tetrahedra. In [23] has reported the frequency of infrared band in Se-Te alloy at 205 cm^{-1} . In [24] it was observed the absorption peaks at 150 cm^{-1} due to Te-Te bonds in $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ glasses. Therefore the increase of band width of absorption band centered at 254 cm^{-1} could be attributed to bridging of GeSe_4 units with different Te contain structural units.

The new band between $100\text{--}225\text{ cm}^{-1}$ with maximum at 195 cm^{-1} is arise with increasing of zinc content. According to [25] in infrared spectrum of ZnSe is observed follow absorption band $139, 269, 291, 365\text{ cm}^{-1}$ in frequencies range $100\text{--}400\text{ cm}^{-1}$. The authors of [26] found in Raman spectrum of ZnTe that the fundamental frequencies of longitudinal optical mode is $\nu_{\text{LO}} = 208\text{ cm}^{-1}$ and transverse optical modes $\nu_{\text{TO}} = 177\text{ cm}^{-1}$. The infrared spectra of thin $\text{GeSe}_2\text{-GeTe-ZnTe}$ layers suggest that zinc is present in the glassy network mainly in form of structural units of ZnTe.

4. Conclusion

The optical and structural properties of the thin films from $\text{GeSe}_2\text{-GeTe-ZnTe}$ system have been investigated by transmission spectrophotometry, TEM, SEM and IR spectroscopy. The results for composition analysis of thin films showed absence of Zn independently of the composition of the bulk

glass while the deposition of thin films by co-evaporation yields composition of the layers that is close to the expected one. It was found that the refractive index increases with increasing of tellurium and zinc content. The calculated values for n and E_g^{opt} demonstrated that thermoinduced changes are more pronounced than photoinduced effects in $\text{GeSe}_2\text{-GeTe-ZnTe}$ films which is due of presence of phase separation. TEM and SEM images indicated presence of nanoparticles in thin layers with composition $\text{Ge}_{32}\text{Se}_{61}\text{Te}_7/\text{Zn}$ and $\text{Ge}_{28}\text{Se}_{49}\text{Te}_{10}\text{Zn}_{13}$. The far infrared spectra demonstrate that the glassy network of thin $\text{GeSe}_2\text{-GeTe-ZnTe}$ films deposited by co-evaporation is formed from tetrahedral structural units GeSe_4 , Se-Se and Te-Te chains and structural units of ZnTe .

Acknowledgments

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