# Optical properties of thin films from new chalcogenide $GeSe_2$-$Sb_2Se_3$-PbTe glasses

K. PETKOV*, J. TASSEVA, V. VASSILEV[a], L. ALJIHMANI[a]
*Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 109, 1113 Sofia, Bulgaria.*
[a]*Department of Semiconductors, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky Blvd, 1756 Sofia, Bulgaria*

Thin $GeSe_2$–$Sb_2Se_3$–PbTe films with controllable composition were deposited by thermal evaporation. Their optical properties are studied as a function of the PbTe content and at different $GeSe_2/Sb_2Se_3$ ratio. The optical constants (refractive index, $n$ and absorption coefficient, $\alpha$) and thickness, $d$ as well as the optical band gap, $E_g$, depending on the PbTe content are derived from the transmission and reflection spectra measured in the region 500-2500 nm applying the Swanepoel's envelop method and Tauc's procedure. With the increase of PbTe content in the layers, the absorption edge is shifted to the longer wavelengths, i.e. lower energies - from 1.52 eV for $(GeSe_2)_{80}(Sb_2Se_3)_{20}$ to1.14 eV for $(GeSe_2)_{48}(Sb_2Se_3)_{12}(PbTe)_{40}$, the refractive index increases while the optical band gap decreases. Similar dependence was observed with the increase of $Sb_2Se_3$ content in the layers with 10 at. % PbTe. A correlation between the optical band gap and the composition of the thin films from the studied system could be seen. These results indicate an increase of the bond's stronger metal character and probable formation of a complicated band gap structure.

(Received June 14, 2011; accepted November 23, 2011)

*Keywords*: Thin films, Chalcogenide glasses, Optical properties, IR spectroscopy

## 1. Introduction

Amorphous thin films of chalcogenide glasses are very promising photo- and radiation-sensitive materials for nanotechnology with very high optical resolution and quality. They are usable in optical switching, optical interconnects and optical sensing. Most of these applications are based on the wide variety of light induced effects exhibited by these materials [1-5].

The glasses from the Ge-Se system and those based on the $GeSe_2$ glass-former have been intensively studied as glassy matrixes for different additives because of their high glass-forming ability and aging resistance [6]. It is well known that $Sb_2Se_3$ added to $GeSe_2$ improves the $GeSe_2$ glass-forming ability and extends the glass forming limits [7, 8]. During the last decade many papers were published on the study of physicochemical and optical properties of multi-component chalcogenide glasses from the $GeSe_2$-$Sb_2Se_3$-ZnSe (PbSe, PbTe, AgI) systems [9-12]. The accurate determination of the optical constants of thin films prepared by evaporation of bulk samples from these materials is important from a view point to find possibilities for their application.

In this work some results from the investigation of the photo- and thermo-induced changes in the optical properties of new chalcogenide glasses from the $GeSe_2$-$Sb_2Se_3$-PbTe system are presented with the aim to determine the influence of the constituents $GeSe_2$, $Sb_2Se_3$ and PbTe on the optical properties of the thin films.

## 2. Experimental

Bulk glasses with 7 different compositions, disposed in the glass forming region (Fig.1) were prepared by conventional melt quenching technique of $GeSe_2$, $Sb_2Se_3$, and PbTe (preliminary synthesized from elements Ge, Se and Te with purity of 5N and Sb and Pb – 4N) [11]. The compositions of the bulk glasses and of the thin films were determined by scanning electron microscopy with an X-ray microanalyser (Jeol Superprobe 733, Japan). Thin films were deposited onto non-absorbing optical glass BK7, graphite and two-side polished Si wafers by thermal evaporation from a Mo crucible under vacuum of $6\text{-}8.10^{-6}$ Torr. The thin films (~ 900 nm thick) were deposited at temperature 350 - 500 °C, depending on the composition, with a rate of evaporation 15–25 $Å.s^{-1}$. [12]. The substrates temperature during evaporation was 25-30 °C and the films were not annealed after deposition. Thin films were prepared under the same conditions on glass substrates covered with Au or Al for electrical measurements (results from this investigation will be published elsewhere).

Optical transmission and reflection measurements in the spectral range 500 - 2500 nm were carried out using an UV–VIS–NIR spectrophotometer (Cary 05E, USA). The films were exposed to light by a halogen lamp (60 $mW/cm^2$). The exposure time to saturation (i.e. the time beyond which the absorption edge did not change) was experimentally established for each sample. The optical constants of the films (refractive index, $n$, and absorption coefficient, $k$) and the film thickness ($d$) were calculated using Swanepoel's method [13] and a computer program developed by Konstantinov [14]. The refractive indices and the thicknesses of the films were determined with an accuracy of 1 %.

In the case of semiconductors, the optical absorption coefficient, $\alpha$, increases rapidly for photon energies higher than the energy of the optical bang gap, $E_g$ At high values of the absorption coefficient, $\alpha$, such as the condition $\alpha d > 1$ is realized, α can be calculated from the equation :

$$T = (1 - R)^2 e^{-\alpha d} \quad (1)$$

where $T$ is the transmittance, $R$ is the reflectance and $d$ is the film thickness. In the same spectral region the absorption coefficient can be described by the relation, suggested by Tauc [15]

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

where $B$ is a substance parameter, $h$ is Planck's constant and $\nu$ is the frequency, $E_g$ is the optical band gap.

## 3. Results and discussion

### 3.1 X-ray microanalysis

The influence of the composition, light exposure and annealing of vacuum deposited thin $GeSe_2$-$Sb_2Se_3$-PbTe films on their optical properties in a wide compositional interval was studied. Two series of chalcogenide layers were prepared by thermal evaporation of bulk samples: the first one with different ratio between $GeSe_2$ and $Sb_2Se_3$ at a constant content of PbTe (10 mol %) and the second one – with different content of PbTe. Using X-ray microanalysis, we have found that the element content of bulk is very close (within ±1 at.%) to the expected composition while for thin layers some differences were obtained, due to the different rate of evaporation of fragments presented in the bulk samples (Table 1).

### 3.2 Optical properties of $GeSe_2$-$Sb_2Se_3$-PbTe thin films

The optical constants of thin $GeSe_2$-$Sb_2Se_3$-PbTe films and their changes under exposure to light and annealing, as well as their variation with the film composition, were calculated from transmission measurements of layers (~ 900 nm thick). In Fig. 2a the plots of the optical transmission of as-deposited thin $GeSe_2$-$Sb_2Se_3$-PbTe films (at 10 mol. % PbTe) vs. wavelength are presented.

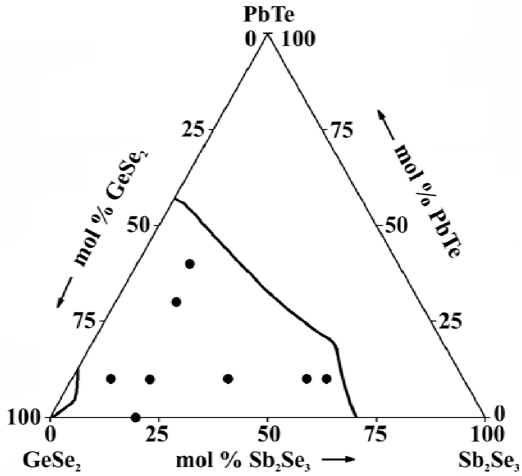


*Fig.1. Bulk samples from the glass forming region (indicated by dots) used in this study [11].*

*Table 1. Data for the element content of the bulk and thin film chalcogenide samples*

| Bulk glasses (at. %) | Thin films (at. %) |
|---|---|
| $Ge_{23.5}Sb_{11.8}Se_{64.7}$ | $Ge_{14}Sb_{26}Se_{60}$ |
| $Ge_{26.8}Sb_{5.2}Se_{61.4}Pb_{3.3}Te_{3.3}$ | $Ge_{27}Sb_6Se_{59}Pb_1Te_7$ |
| $Ge_{22.1}Sb_{11.0}Se_{60.7}Pb_{3.1}Te_{3.1}$ | $Ge_{16}Sb_{18}Se_{59}Pb_7$ |
| $Ge_{14.9}Sb_{19.8}Se_{59.7}Pb_{2.8}Te_{2.8}$ | $Ge_8Sb_{32}Se_{54}Pb_2Te_4$ |
| $Ge_{9.1}Sb_{27.1}Se_{58.8}Pb_{2.5}Te_{2.5}$ | $Ge_4Sb_{39}Se_{53}Pb_1Te_3$ |
| $Ge_{18.8}Sb_{9.4}Se_{51.7}Pb_{10.0}Te_{10.0}$ | $Ge_{15}Sb_{15}Se_{48}Pb_{12}Te_{10}$ |
| $Ge_{16.9}Sb_{8.5}Se_{46.5}Pb_{14.0}Te_{14.0}$ | $Ge_{17}Sb_9Se_{45}Pb_{17}Te_{12}$ |
| $Pb_{50}Te_{50}$ | $Pb_{46}Te_{54}$ |

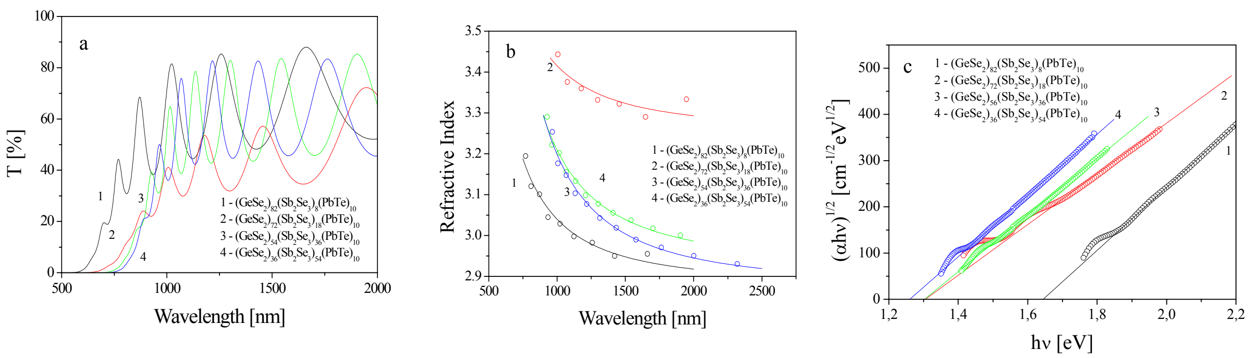


*Fig.2. Spectral dependence of the transmission (a), refractive index dispersion (b) and Tauc's plot $(\alpha h\nu)^{1/2}$ vs. energy of photon ($h\nu$) (c) of as-deposited thin films from the system $GeSe_2$-$Sb_2Se_3$-PbTe system (for 10 mol. % PbTe).*

It is seen that the absorption edge is shifted to the higher wavelengths increasing the $Sb_2Se_3$ content in the layers. The dispersion of the refractive index, *n* at different wavelengths for as-deposited thin $GeSe_2$-$Sb_2Se_3$-PbTe films is shown in Fig. 2b and 3b. The refractive index increases when $GeSe_2$ content in the layers decreases showing maximal values for the composition $(GeSe_2)_{72}(Sb_2Se_3)_{18}(PbTe)_{10}$ (Fig. 2b). The optical bad gap decreases from 1.64 eV for $(GeSe_2)_{82}(Sb_2Se_3)_8(PbTe)_{10}$ to 1.26 eV for composition $(GeSe_2)_{36}(Sb_2Se_3)_{54}(PbTe)_{10}$ (Fig. 2c).

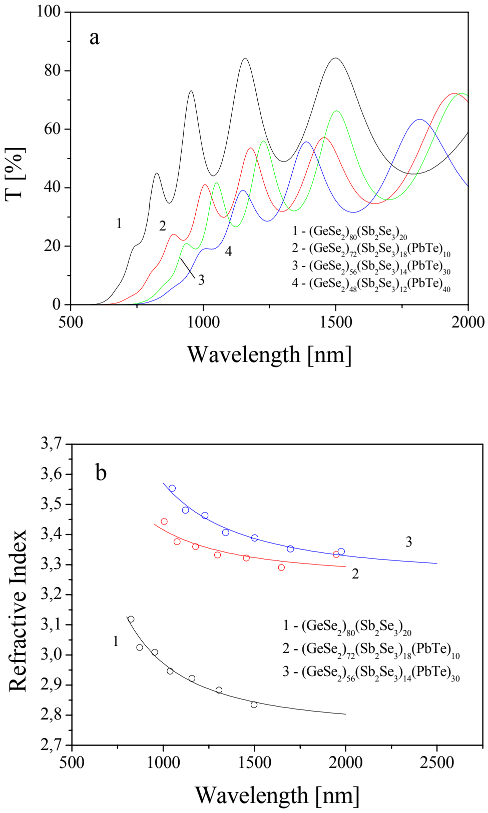


*Fig. 3. Spectral dependence of the transmission (a), and refractive index dispersion (b) of unexposed thin films from the $GeSe_2$-$Sb_2Se_3$-PbTe system depending on the PbTe content.*

The increasing of the PbTe content in the films leads to a similar dependence for the optical parameters of the system studied. The absorption edge is shifted to higher wavelengths (Fig. 3a), the refractive index increases (Fig. 3b) and the optical band gap decreases from 1.52 eV for the composition $(GeSe_2)_{80}(Sb_2Se_3)_{20}$ to 1.14 eV for $(GeSe_2)_{48}(Sb_2Se_3)_{12}(PbTe)_{40}$ (Fig. 4).

We have studied the influence of the light exposure (exposure time 4 hours to a halogen lamp – 60 mW.cm$^{-2}$), as well as the annealing at a temperature 20°C below $T_g$. In Fig. 5 transmission spectra of some thin $GeSe_2$-$Sb_2Se_3$-PbTe films are shown.

For all compositions the shift of the absorption edge after illumination was negligible. Only for the composition $(GeSe_2)_{80}(Sb_2Se_3)_{20}$ a shift of 63 nm to the higher wavelengths was found after annealing. For the composition $(GeSe_2)_{82}(Sb_2Se_3)_8(PbTe)_{10}$ the shift was to the shorter wavelengths (36 nm) due to a possible effect of homogenisation of the films after heating.

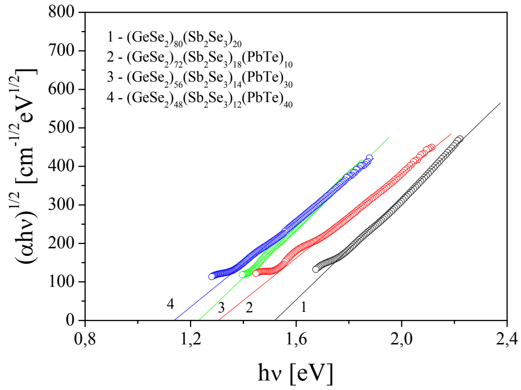


*Fig.4. Optical absorption edge $(\alpha h\nu)^{1/2}$ vs. energy of photon ($h\nu$) of unexposed thin films from the system $GeSe_2$-$Sb_2Se_3$-PbTe system depending on the PbTe content.*

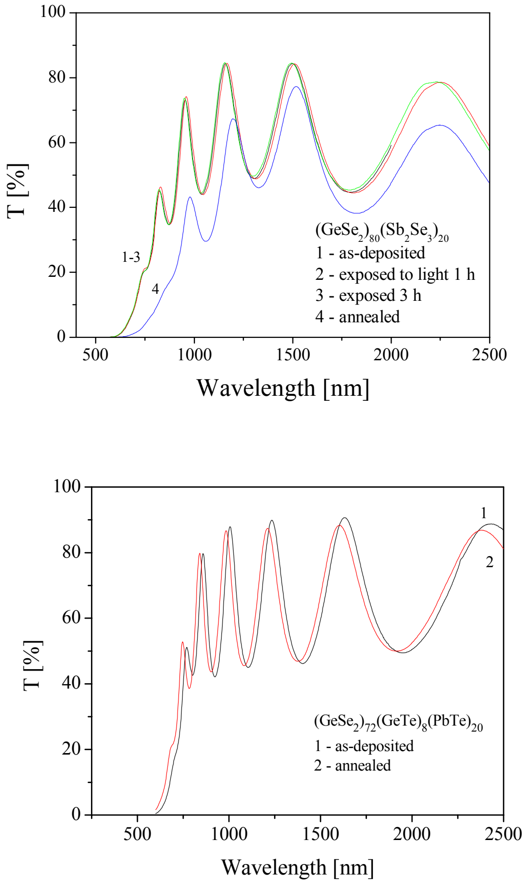


*Fig. 5. Spectral dependence of the transmission of as-deposited, exposed and annealed thin films from the system $GeSe_2$-$Sb_2Se_3$-PbTe system.*

Data for the photo- and thermo-induced changes in the refractive index of thin $GeSe_2$-$Sb_2Se_3$-PbTe films are presented in Table 2. It is seen that $n$ decreases after exposure to light for all compositions as a result of increasing in the film thickness. The values of $E_g$ and the slope of Tauc's edge, B are presented in Table 3. It is found that for unexposed layers, the optical band gap changes in wade limits (between 1.52 -1.14 eV) increasing the PbTe-content in the films which could mean that the width of the localized states increases. However, the system is very complicated and for explicit conclusions about the effect of illumination of thin films further investigations should be conducted.

*Table 2. Data for refractive index variation depending on the composition, exposure and annealing of thin $GeSe_2$-$Sb_2Se_3$-PbTe films*

| Composition | $n$ at 1550 nm | | |
|---|---|---|---|
| | unexp | exp | ann |
| $Ge_{14}Sb_{26}Se_{60}$ | 2.84 | 2.82 | 3.00 |
| $Ge_{27}Sb_6Se_{59}Pb_1Te_7$ | 2.94 | 2.93 | 2.94 |
| $Ge_{16}Sb_{18}Se_{59}Pb_7$ | 3.32 | 3.25 | 3.24 |
| $Ge_8Sb_{32}Se_{54}Pb_2Te_4$ | 3.03 | 3.00 | 3.00 |
| $Ge_4Sb_{39}Se_{53}Pb_1Te_3$ | 3.00 | 2.92 | 2.91 |
| $Ge_{15}Sb_{15}Se_{48}Pb_{12}Te_{10}$ | 3.38 | 3.29 | 3.21 |
| $Ge_{17}Sb_9Se_{45}Pb_{17}Te_{12}$ | 3.52 | 3.52 | 3.52 |

*Table 3. Data for optical band-gap, $E_g^{opt}$ and the slope of Tauc's plot,B for thin $GeSe_2$-$Sb_2Se_3$-PbTe films.*

| Composition | Unexposed | | Exposed | |
|---|---|---|---|---|
| | $E_g^{opt}$ [eV] | B [$cm^{-1/2}$ $eV^{-1/2}$] | $E_g^{opt}$ [eV] | B [$cm^{-1/2}$ $eV^{-1/2}$] |
| $Ge_{14}Sb_{26}Se_{60}$ | 1.52 | 661 | 1.25 | 538 |
| $Ge_{27}Sb_6Se_{59}Pb_1Te_7$ | 1.64 | 680 | 1.68 | 692 |
| $Ge_{16}Sb_{18}Se_{59}Pb_7$ | 1.30 | 548 | 1.31 | 555 |
| $Ge_8Sb_{32}Se_{54}Pb_2Te_4$ | 1.30 | 614 | 1.30 | 607 |
| $Ge_4Sb_{39}Se_{53}Pb_1Te_3$ | 1.26 | 662 | 1.26 | 649 |
| $Ge_{15}Sb_{15}Se_{48}Pb_{12}Te_{10}$ | 1.23 | 650 | 1.24 | 624 |
| $Ge_{17}Sb_9Se_{45}Pb_{17}Te_{12}$ | 1.14 | 556 | 1.15 | 556 |

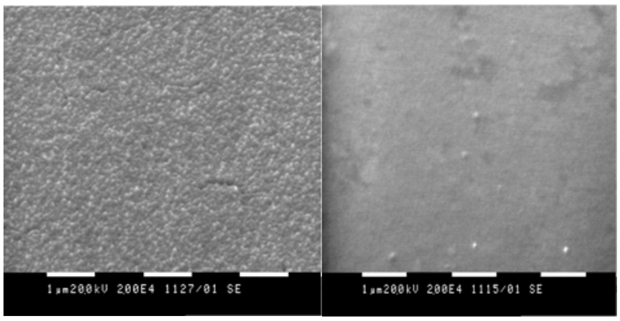

*Fig. 6. SEM micraphs of PbTe (a) and $(GeSe_2)_{54}(Sb_2Se_3)_{36}(PbTe)_{10}$ (b) thin films.*

Fig. 6 shows the SEM micrographs of PbTe and $(GeSe_2)_{54}(Sb_2Se_3)_{36}(PbTe)_{10}$ thin films surface. As seen, the PbTe film surface contains only grains less than 100 nm in size. The surface of the multicomponent chalcogenide layer is quite smooth with grains with the same size. We could conclude that thin layers containing PbTe are nanoicrystalline than amorphous.

As it was mentioned above new chalcogenide glasses from the system $GeSe_2$-$Sb_2Se_3$-PbTe were sintesized for the first time and thin films were deposited from them by thermal evaporation. By X-ray microanalysis, we found that the element content of thin films differs from those of bulk glasses due to the different rate of evaporation of fragments of bulk samples. Using spectropotometric measurements we have calculated the refractive index, $n$ and thickness, $d$ and the optical band gap of thin chalcogenide films from the above system.

The illumination and annealing of the films (with small exceptions) don't lead to a shift of the absorption edge and to significant changes in the refractive index and the optical band gap. It might be concluded that the layers are not photo-sensible, and but they respond to the annealing. These experiments will be continued with structural investigations by IR spectroscopy.

## 4. Conclusions

Thin films from the system $GeSe_2$-$Sb_2Se_3$-PbTe were deposited by thermal evaporation from and their optical properties were studied for the first time. From spectrophotometric measurements, the optical constants and thicknesses of the layers, and their optical band gap were determined. It was found that the refractive index, $n$ (at 1550 nm) increases from 2.84 for $(GeSe_2)_{80}(Sb_2Se_3)_{20}$ to 3.52 for $GeSe_2)_{48}(Sb_2Se_3)_{12}(PbTe)_{40}$. For the composition richest in PbTe the optical band-gap, $E_g$, shows a minimum value.

The transmittance measurements of the studied chalcogenide films showed that after exposure to light and annealing no shift of the absorption was obtained.

**Acknowledgement**

The authors would like to acknowledge the financial support of the national Scientific Found (Contract DO02-123/2008).

## References

[1] S.R. Elliott, *Physics of Amorphous Materials*, 2nd Edition, Longman, Essex, 1990.
[2] Ke. Tanaka, Rev. Solid State Sci. **4**, 641 (1990).
[3] P.J.S. Ewen and A.E. Owen, in Hig- Performance Glasses, (Cable M. and J.M. Parker, Editors), Blsckie, London, 1992, pp. 287-308.
[4] M. Frumar, M. Vlcek, Z. Cernosek, Z. Polak, B. Frumarova, in Physics and Application of Non-Crystalline Semiconductors in Optoelectronics, Proc. NATO Workshop, Kishinev, Kluwer Acad. Publ., (Andries A. and M.Bertolotti, Editors), London, 1997, pp. 123-139.
[5] A.V. Kolobov. Ed., Photo-induced Metastability in Amorphous Semiconductors, Wiley-CH, Weinheim, 2003.
[6] P. Boolchand, D.G. Georgiev, M. Micolaut, J. Optoelectron. Adv. Mater. **4**, 823 (2002).
[7] S. Boycheva, V. Vassilev, P. Petkov, J. Optoelectron. Adv. Nater. **3**, 503 (2001).
[8] V. Vassilev, S. Boycheva, Z.G. Ivanova, J. Mater. Sci. Letters **17**, 2007 (1998).
[9] S.V. Boycheva, V.S. Vassilev, P. Petkov, Y. Nedeva, Matter. Letters **59**, 1521 (2005).
[10] V. Vassilev, K. Tomova, V. Parvanova, S. Parvanov, Mater. Chem. Physics **103**, 312 (2007).
[11] V. Vassilev, M. Radonova, S. Boycheva, E. Fidancevska, J. Optoelectron. Adv. Mater. (2011) in press.
[12] K. Petkov, G. Vassilev, R. Todorov, J. Tasseva, V. Vassilev, J. Non-Cryst. Solids **357**, 2669 (2011).
[13] R. Swanepoel, Phys. E **16**, 1214 (1983).
[14] I. Konstantinov, private communication.
[15] J. Tauc, Amorphous and Liquid Semiconductors, Chapter 4, New York, Plenum (1974).

*Corresponding author: kpetkov@clf.bas.bg