

Sn Addition on $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ Glass Alloys, Theoretically Prediction and Experimental Optical Properties of Thin Films

M. Rashad^{1,2}, R. Amin³, M. M. Hafiz¹

¹Physics Department, Faculty of Science, Assiut University, Assiut, Egypt

²Physics Department, Faculty of Science, Tabuk University, P.O. Box 741, Tabuk, 71491, KSA

³Physics Department, Faculty of Science, New Valley, Assiut University, Egypt

Abstract: The present article is divided to two parts, the theoretical part study the effect on the physical properties such as average coordination number and fraction of floppy modes with the variation in tin content for $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12,$ and 15 at.%) glassy alloys. We show that, by taking more Sn content in $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12,$ and 15 at.%) glassy alloys, it reduces the fraction of floppy modes. The experimental part study the optical properties of ternary glassy of $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12,$ and 15 at.%) thin films. These thin films of $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12,$ and 15 at.%) were prepared by the conventional thermal evaporation technique on glass substrate. Optical reflection and transmission spectra of $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12,$ and 15 at.%) chalcogenide thin films have been obtained in the range $200\text{--}2500$ nm at room temperature. The absorption coefficient (α) has been determined as a function of Sn content. It was found that the optical band gap decrease with increasing the Sn content. The results are interpreted in terms of the change in concentration of localized states due to the shift in Fermi level as a result of varying of Sn content.

Keywords: SeTeSn, thin films, Optical energy gap, coordination number, Chalcogenides.

1. Introduction

Chalcogenide glasses have been widely studied for their various and unique optical properties which make them very promising materials for use in optical and micro-optical elements such as gratings [1], optical recording media [2], fibre optics and waveguided devices in integrated optics since they exhibit a good transparency in the infrared region, especially at the telecommunication wavelengths at 1.30 and $1.55\mu\text{m}$ [3]. Characterization of linear optical properties of a material requires not only the values of both the refractive index and absorption coefficient at a specific wavelength but also the knowledge of their evolution as a function of the optical wavelength [4]. Various device applications like rectifiers, photocells, xerography, switching and memory, etc. have made selenium attractive. Pure Se element has disadvantages like short lifetime and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms (As, Te, Bi, Ge, Ga, Sb etc), which gives higher sensitivity, higher crystallization temperature and smaller ageing effects [5-7].

The present paper is concerned with the theoretical prediction of the physical parameters related to composition, viz. coordination number, and fraction of floppy modes for $\text{Se}_{20}\text{Te}_{80-x}\text{Sn}_x$ alloys. The optical transmittance and reflectance data were analyzed to determine optical constants and band gap for $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12,$ and 15 at.%) thin films.

2. Experimental Details

The bulk $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12$ and 15 at.%) chalcogenide glasses were prepared by the melt-quench technique. Materials (99.999% pure) were weighted according to their atomic percentages and were sealed in an evacuated silica tubes, which were heated at 1100°C for 15 h. The ampoules were frequently rocked at maximum temperature to make the melt homogeneous. The quenching was performed in ice water. Thin films were prepared by thermal evaporation at vacuum of 10^5 Torr using an Edwards E-306 coating system. The evaporation rates as well as the film thickness were controlled by using a quartz crystal monitor FTM5. In order to determine the absorption coefficient α and the optical constants of the films as a function of the incident light wavelength, the transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were recorded at room temperature using a double-beam spectrophotometer (Shimadzu UV-2101 combined with PC).

3. Results and discussion

3.1 Theoretical prediction of the physical parameters

3.1.1 Deviation from the stoichiometry of composition

The parameter R that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms.

For $Se_{80}Te_{20-x}Sn_x$ system, the parameter R is given by [8, 9]:

$$R = \frac{aCN(Se)+bCN(Te)}{cCN(Sn)} \quad (5)$$

where a, b, c are the atomic frictions of Se, Te and Sn respectively. The values of R are listed in table 1.

Depending on R values, the chalcogenide systems can be organized into three different categories:

- For $R = 1$, the system reaches the stoichiometric composition since only hetero polar bonds are present.
- For $R > 1$, the system is chalcogen-rich. There are hetero-polar bonds and chalcogen–chalcogen bonds pre-sent.
- For $R < 1$, the system is chalcogen-poor. There are only hetero-polar bonds and metal–metal bonds present. It is clear from the values of R that the present system is chalcogen rich.

3.1.2 Coordination number (r) and fraction of floppy modes

The average coordination number $\langle r \rangle$ is calculated by using the standard method [1, 2].

The composition of glasses is varying with coordination number. For the composition $Se_{80}Te_{20-x}Sn_x$ ($x = 6, 9, 12, 15$) average coordination number $\langle r \rangle$ is given by:

$$\langle r \rangle = \frac{\alpha N_{Se} + \beta N_{Te} + \gamma N_{Sn}}{\alpha + \beta + \gamma} \quad (3)$$

where α, β, γ are concentrations (at %) of Se, Te, Sn respectively and $N_{Se} = 2, N_{Te} = 2, N_{Sn} = 4$ are their respective coordination number.

The calculated coordination numbers (r) lie in the range $2.12 \leq r \leq 2.3$ and are given in Table 1. From table 1, one can find that coordination numbers increases with increase of Sn content for the glassy system.

The fraction of floppy modes available in a network is given by:

$$f = 2 - \frac{5 \langle r \rangle}{6} \quad (4)$$

The values of f are listed in Table 1. It has been observed from the table that the value of f decreasing from 0.233 to 0.083 with increase in Sn content from 6 to 15 at. %.

Table 1. Values of average coordination number and fraction of floppy modes for $Se_{80}Te_{20-x}Sn_x$ ($x = 6, 9, 12, 15$) glassy system.

$Se_{80}Te_{20-x}Sn_x$	$\langle r \rangle$	R	f
x=6	2.12	7.83	0.233
x=9	2.18	5.06	0.183
x=12	2.24	3.67	0.133
x=15	2.30	2.83	0.083

3.2 Optical properties

The optical transmittance and reflectance of the films with different film thicknesses were studied. The spectral distribution of transmittance and reflectance for $Se_{80}Te_{20-x}Sn_x$ ($x=6, 9, 12$ and 15 at.%) films at film thickness of 400 nm are shown in figure (1a) and (1b), respectively.

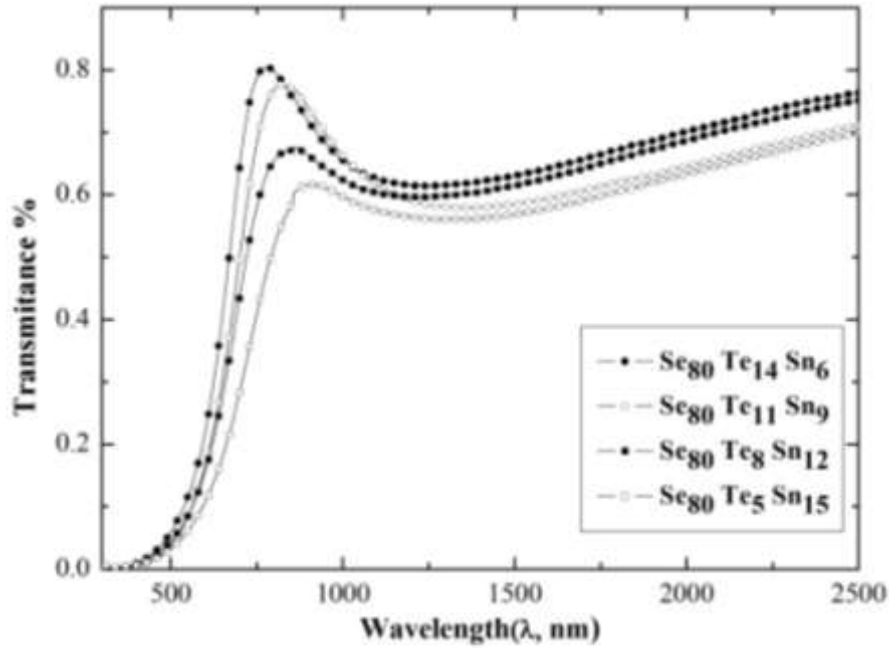


Figure (1a): Spectral distribution of transmittance for $Se_{80}Te_{20-x}Sn_x$ films.

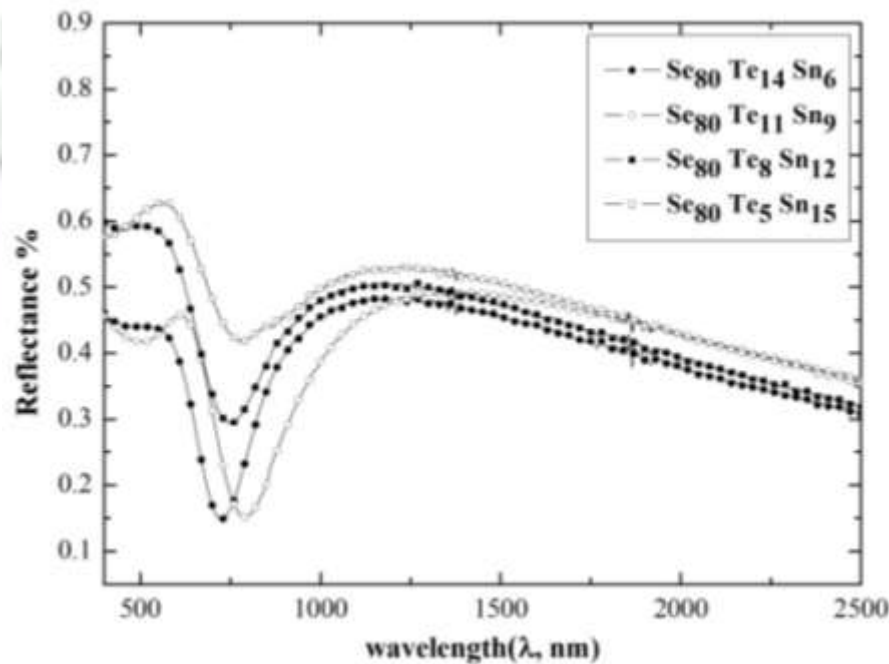


Figure (1b): Spectral distribution of reflectance for $Se_{80}Te_{20-x}Sn_x$ films

The absorption coefficient (α) is one of the most significant parameter in semiconducting thin films. This parameter can be calculated from the experimentally measured values of the transmittance (T) and the reflectance (R) according to the following equation [10]:

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

where A is the absorbance and d is the thickness of the film.

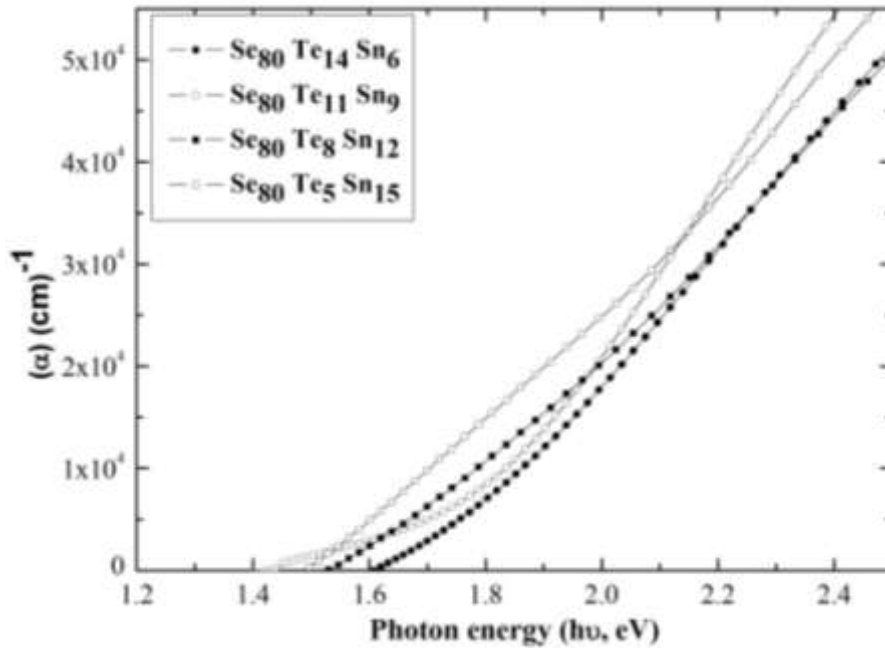


Figure (2): α vs. photon energy ($h\nu$) for $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ films.

It is observed that the value of α increases with increasing the photon energy. On the other hand, it increases with increasing Sn content. For absorption coefficient (α) of less than 10^4cm^{-1} there is usually an Urbach tail, where (α) depends exponentially on the photon energy $h\nu$ according to Urbach's empirical relation [11]:

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

where ν is the frequency of the radiation, α_0 is a constant and E_c is interpreted as the width of the tails of localized states in the gap region and in general represents the degree of disorder in an amorphous semiconductor. Figure 3 shows the dependence of the natural logarithm of absorption coefficient on the photon energy for $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12$ and 15 at.%) thin films. The reciprocal of the slope yields the magnitude of the width of the tail (E_c) while the interception at lower energy gives α_0 according to Eq. (2). These values of the width of the tail (E_c) are strongly dependent on the film thickness which shown in Figure 5.

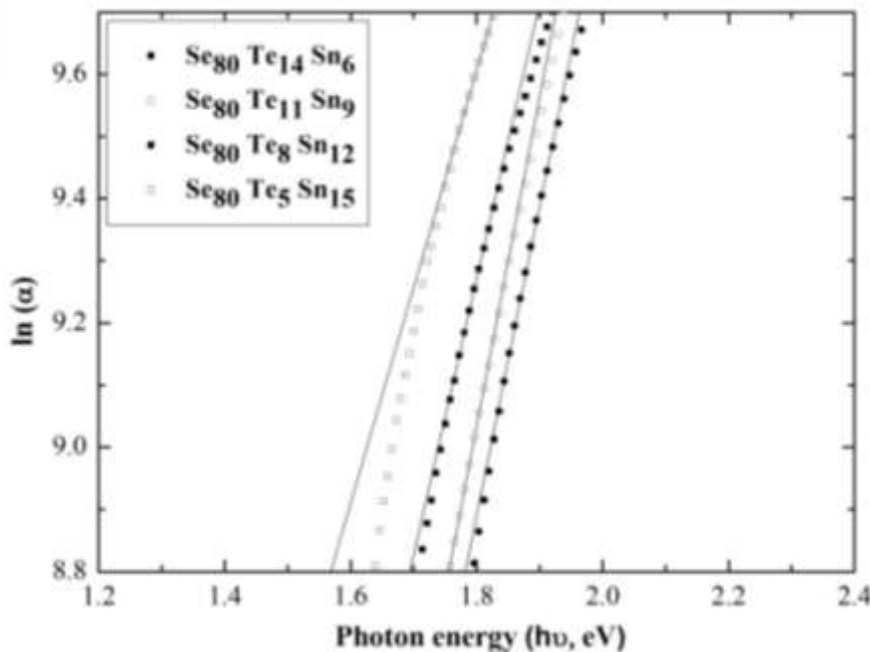


Figure (3): $\ln\alpha$ vs. photon energy ($h\nu$) for $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ films.

The optical band gap E_g of the films can be determined from the dependence of absorption coefficient on the photon energy. The direct or indirect nature of optical transition between parabolic bands can be studied using the relation [12]

$$\alpha = \frac{C}{h\nu} (h\nu - E_g)^r \quad (2)$$

where C is a constant and r assumes values of 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. For the polycrystalline $Se_{80}Te_{20-x}Sn_x$ thin film, value of $r = 1/2$ validates Eq. (2). These values of r characterize indirect allowed optical transitions.

The energy bandgap values of the investigated thin films are determined by extrapolation of the linear regions on the energy axis ($h\nu$) given in Figure 4. These values of optical band gap are illustrated in Figure 5. It was found that the optical band gap decrease with increasing the Sn content. The results are interpreted in terms of the change in concentration of localized states due to the shift in Fermi level as a result of varying of Sn content. These optical results confirm that, the increasing of Sn content, increase scattering effect on free carriers from ionized impurities.

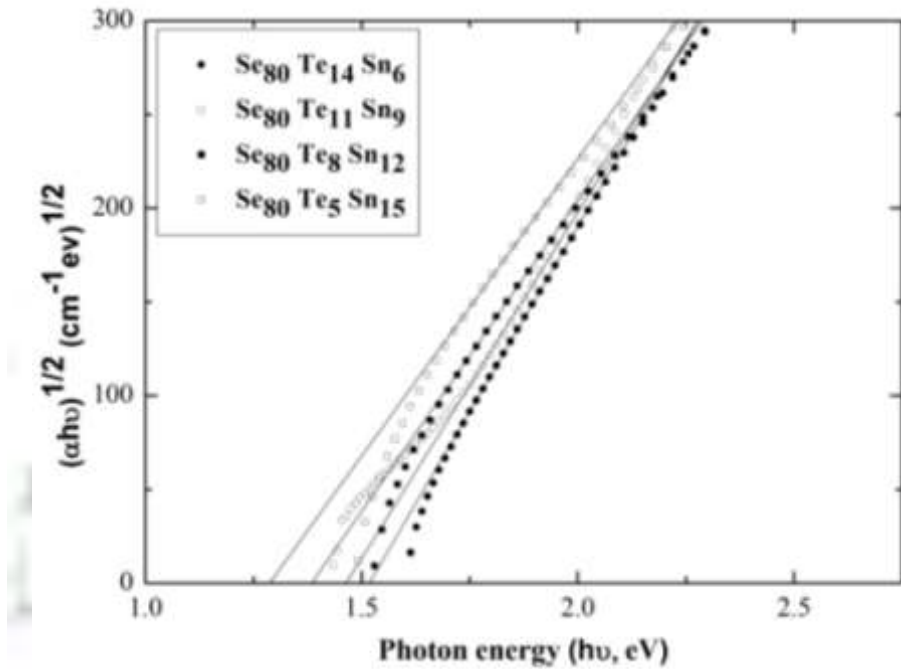


Figure (4): $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$) for $Se_{80}Te_{20-x}Sn_x$ films.

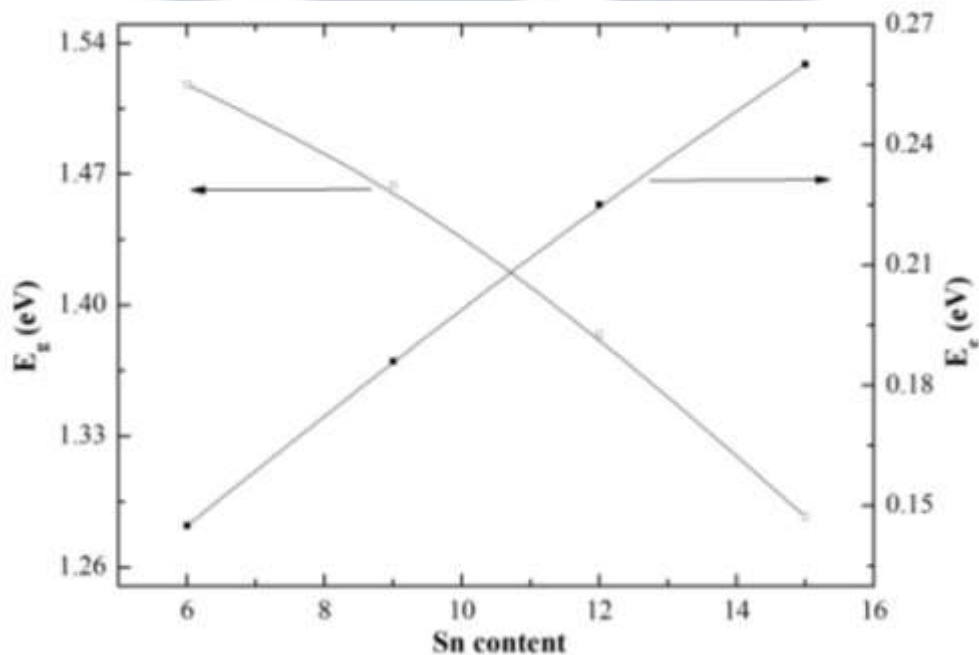


Figure (5): band gap and width of localized state vs. Sn content for $Se_{80}Te_{20-x}Sn_x$ films

Conclusion

It is concluded from the theoretical part, that the variation in Se content in Se-Te-Sn glassy alloys leads to change in the physical properties. The present study shows that $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12, \text{ and } 15 \text{ at.}\%$) is a good glasses former. Our predictions for the physical properties are consistent with the earlier predictions for chalcogenide glasses. Alternatively, from the experimental part, optical properties of $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=6, 9, 12, \text{ and } 15 \text{ at.}\%$) chalcogenide thin films have been obtained in the range 200–2500 nm at room temperature. The optical absorption measurements for the as deposited $\text{Se}_{80}\text{Te}_{17}\text{Sn}_3$ and $\text{Se}_{80}\text{Te}_{11}\text{Sn}_9$ films indicate the indirect transition of the absorption mechanism. It was found that the optical band gap decrease with increasing the Sn content. The results are interpreted in terms of the change in concentration of localized states due to the shift in Fermi level.

References

- [1]. J.C. Phillips, *J.Non-Cryst.Solids*.34, 153 (1979).
- [2]. R. Ganesan, A. Srinivasan, K. N. Madhusoodanan, K. S. Sangunni, E. S. R. Gopal, *Phys Status (b)* 190, 23 (2006).
- [3]. J.H. Dessaur, H. E. Clarke, xerography and related processed, Local London (1965).
- [4]. A. Sharma, P.B. Barman, *J.Therm.Anal.Cal.*96, 413 (2009).
- [5]. L. Zhenhua, *J.Non-Cryst.Solids* 127, 298 (1991).
- [6]. S. S. Fouad, S. A. Fayek, M. H. Ali, *Vacuum* 49, 25 (1998).
- [7]. Mainkaa, P. Sharma, N. Thakur *Phil. Mag.* 89, 3027 (2009).
- [8]. L. Tichy, H. Ticha, *Mater. Lett.*, 21, 313 (1994).
- [9]. L. Tichy, H. Ticha, *J Non-crystalline Solids*, 189, 141 (1995).
- [10]. M. Fox, *Optical Properties of Solids*, Oxford University Press, 2001. pp. 3.
- [11]. F. Urbach, *Phys. Rev.* 92 1324 (1953).
- [12]. J. Tauc, in: J. Tauc (Ed.), *Amorphous and Liquid Semiconductors*, Plenum, New York, 1974, p. 159.

