Chalcogenide Letters Vol. 15, No. 11, November 2018, p. 545 - 553

# EFFECT OF Sn ADDITION ON PHYSICAL AND OPTICAL PROPERTIES OF Ge-Se-Sb-Sn THIN FILMS

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The present work aims to study theoretically the effect of Sn content on many physical parameters, such as coordination number (CN), constraints number (CON), overall mean bond energy (<E>) and cohesive energy (CE) for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) glasses. Likewise, optical constants of the thin films were evaluated via the use of the Swanepoel technique. It is found that, CN, CON, <E>, and CE increase by increasing the Sn content. This behavior is obvious evidence for increasing the rigidity of the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses by increasing the Sn content. The chemical bonds occurred within the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses have been estimated. It was found that, the heteropolar bonds occurred in the examined glasses are Sn-Se, Ge-Se and Sb-Se which have energies 58.818, 49.441 and 43.981 kcal/mol., respectively. The obtained values of the refractive index (n) of the films were fitted to the two-term Cauchy dispersion equation to get the single oscillator ($E_o$) and dispersion ($E_d$) energies. In addition, values of the absorption coefficient ($\alpha$) are obtained using the conditions suggested by Connell and Lewis. An increase of the Sn content from 0 to 10 at. % prompts a decrease of the energy gap ($E_g$) from 1.79 to 1.40 eV.

(Received September 9, 2018; Accepted November 7, 2018)

*Keywords:* Coordination number, Cohesive energy, Refractive index, Swanepoel method

## 1. Introduction

Metal-doped chalcogenide glasses have turned into an essential class of non-crystalline semiconductors. Addition of metals to chalcogenides increases the average coordination number (CN) that changes the structure from flexible to rigid and in addition adjustments in the physical properties due to changing the chemical compositions. Alloying of Se with Ge enhances glass forming region, thermal stability and decrease aging effects. The addition of Sb to Se-Ge enhances thermal stability and improves the IR transmission. The forth element, Sn, acts as chemical modifier which may extend the glass forming area and makes compositional and configurational disorder [1]. Increment the Sn content in Se-based glasses increases the electrical conductivity while it decreases the activation energy of conduction. This kind of glasses likewise has extraordinary properties which affected by the presence of Sn. So these glasses are appropriate for creation the electronic gadgets [2].

Optical constants of chalcogenide films may be obtained through the use of the transmission spectra (Swanepoel technique) [3] as well as reflection spectra (Minkov technique) [4]. Swanepoel and/or Minkov methods don't need any earlier knowledge about film thickness, as well they are truly correct with the optical parameters being perceptible to inside around 1% [5].

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Optical parameters of some chalcogenides were gotten and mentioned by means of numerous authors [6-10].

The present work aims to study theoretically the effect of Sn content on many physical parameters such as CN, CON, <E> and CE for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) glasses. Likewise, optical constants of the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ thin films were evaluated with the aid of the use of the Swanepoel technique.

## 2. Experimental details

Bulk glasses of several compositions of $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) system have been synthesized using the well-known melt quenching method starting with high purity (5N) elements. The used elements had been heated up together in vacuum within an exceedingly spotless silica tube to around 1225 K, then subsequently the temperature maintained stable for around twenty four hour. Over the traverse of warming, the ingots were as often as possible shaken to retain the consistency of the liquefy. Lastly, the ingots were extinguished in super cold water to obtain amorphous specimens.

Thin films for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ family were prepared by way of the thermal evaporation method. The evaporation procedure was done utilizing a coating (Denton Vacuum DV 502 A) equipment. The used substrates have been revolved for the duration of the deposition procedure to get consistent thickness. Energy dispersive x-ray spectroscopy (EDX) analysis confirms the chemical structures for the considered specimens. It had been proved that, the elemental compositions of the prepared films are very close to the nominal compositions. The amorphous nature of the considered films has been affirmed by using x-ray (Philips type 1710) diffractometer, it was assured. Jasco V-630 spectrophotometer has been used to acquire the transmission spectra of the examined films in the extent of wavelength vary from 400 to 2500 nm.

## 3. Results and discussions

### 3.1 Characterization of $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses theoretically

Many properties of non-crystalline chalcogenides are dictated by using the bonding manner in the nearest-neighbor district [11] referred to mean coordination number (CN). Utilizing values of CN for the constituting elements recorded in Table 1, values of CN of $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) glasses may calculated using the following equation:

*Table 1. Coordination number, heat of atomization, bond energy and electronegativity of Ge, Se, Sb and Sn used for calculations.*

| | Ge | Se | Sb | Sn |
|---|---|---|---|---|
| Coordination number | 4 | 2 | 3 | 4 |
| $H_A$ (kcal/g atom) | 90.0 | 49.4 | 62.0 | 72.0 |
| Bond energy (kcal $mol^{-1}$) | 37.60 | 44.04 | 30.22 | 46.70 |
| Electronegativity | 2.01 | 2.55 | 2.05 | 1.88 |

$$CN = 4\,MF_{Ge} + 2\,MF_{Se} + 3\,MF_{Sb} + 4\,MF_{Sn} \quad (1)$$

where $MF_{Ge}$, $MF_{Se}$, $MF_{Sb}$ and $MF_{Sn}$ are the mole fractions for Ge, Se, Sb and Sn respectively. Knowing CN lets in obtaining the constraints number (CON) which is related to the rigidity of the glasses. CON of the non-crystalline substances is defined as [12]:

$$CON = CN/2 + (2\,CN - 3) \quad (2)$$

CN and CON were estimated, utilizing the above equations, for the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ system and listed in Table 2. We can notice from Table 2 that, both of CN and CON increase with the expansion of Sn content. That behavior may be ascribed to an increase of the cross-linking whereas Sn gets into the system in 4-fold coordination [13]. Increasing the cross-linking means an increase of the rigidity of the structure.

*Table 2. Some physical parameters and distribution of chemical bonds for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) glassy system.*

| Sn at. % | CN | CON | $H_A$ (kcal/g atom) | LP | CE | <E> | DS | Distribution of chemical bonds | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | eV | | | Ge-Se | Ge-Ge | Sb-Sb | Sn-Se | Sb-Se |
| 0.0 | 2.600 | 3.500 | 54.71 | 2.80 | 2.71 | 2.71 | 1.000 | 0.769 | 0.000 | 0.000 | 0.000 | 0.231 |
| 2.5 | 2.625 | 3.563 | 56.49 | 2.75 | 2.79 | 2.78 | 0.981 | 0.763 | 0.000 | 0.008 | 0.076 | 0.153 |
| 5.0 | 2.650 | 3.625 | 58.26 | 2.70 | 2.96 | 2.86 | 0.963 | 0.730 | 0.000 | 0.015 | 0.146 | 0.109 |
| 7.5 | 2.675 | 3.688 | 60.04 | 2.65 | 2.94 | 2.93 | 0.945 | 0.752 | 0.000 | 0.023 | 0.226 | 0.000 |
| 10.0 | 2.700 | 3.750 | 61.81 | 2.60 | 3.03 | 3.00 | 0.929 | 0.667 | 0.037 | 0.000 | 0.296 | 0.000 |

The lone-pair electrons (LP), that form the top of the valence band, of $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses equals the valence electrons (VE) minus CN, was computed using the widely recognized relation:

$$LP = VE - CN \quad (3)$$

The computed values of LP have been listed in Table 2. It can be seen that, LP decreases from 2.8 to 2.6 with increasing Sn content from 0 to 10 at. %. This may be due to the interaction between Sn ion and lone pair electrons of bridging Se atom [14].

The heat of atomization ($H_A$) for the $Ge_\alpha Se_\beta Sb_\gamma Sn_\lambda$ may be written as [15]:

$$H_A = \frac{\alpha H_A(Ge) + \beta H_A(Se) + \gamma H_A(Sb) + \lambda H_A(Sn)}{\alpha + \beta + \gamma + \lambda} \quad (4)$$

Using $H_A$ for the constituent components recorded in Table 1, values of $H_A$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) system are computed and appeared in Table 2. As appeared in the table, $H_A$ increases with increasing the Sn content. Expanding of $H_A$ with increasing the Sn content might be because of the higher value of $H_A$ of Sn than that of antimony.

For obtaining the overall mean bond energy (<E>) of the examined glasses, we should obtain the deviation of stoichiometry (*DS)* as well as the distribution of chemical bonds expected within the glasses. Estimations of *DS* for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) system were obtained using the equation [16]:

$$DS = \frac{65\,CN_{Se}}{25\,CN_{Ge} + (10-x)\,CN_{Sb} + x\,CN_{Sn}} \quad (5)$$

Values of *DS* are computed and listed in Table 2. According to values of DS (see table 2), the first composition $Ge_{25}Se_{65}Sb_{10}$ can be called stoichiometric glass (where *DS*=1) while the other compositions are called Se-poor glasses (where *DS*<1).

By utilizing the homo-polar bond energies $BE(A-A)$ and $BE(B-B)$ and the electronegativities $\chi_A$ and $\chi_B$ of the included atoms listed in Table 1, the heter-polar bond energy $BE(A-B)$ may be obtained using the relation [17, 18]:

$$BE(A-B) = [BE(A-A).BE(B-B)]^{1/2} + 30(\chi_A - \chi_B)^2 \quad (6)$$

The chemical bonds anticipated within the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses have been estimated with the aid of the use the chemical bond approach [19] and the distribution of chemical bonds is recorded in Table 2. It was found that, the heteropolar bonds occurred in the examined glasses are Sn-Se, Ge-Se and Sb-Se which have energies 58.818, 49.441 and 43.981 kcal/mol., respectively.

The energy of cohesive (*CE*) for glasses can be estimated by adding the bond energies according to the relation [20]:

$$CE = \sum(C_i.BE_i/100) \quad (7)$$

in which $BE_i$ is the bond energy and $C_i$ is the number of that bond. Values of CE for the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) glasses are obtained and listed in Table 2. As appeared in this table CE improves with increasing the Sn content.

Utilizing the bond energies and their distribution within the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses, <*E*> has been evaluated using the Tichy's relation [16]. The detailed procedure for the calculation of <*E*> may be seen in our previous paper [15]. Values of <E> were evaluated and listed in Table 2. As appeared in table 2, <E> increases with the increment of Sn content. Increasing of <E> by increasing the Sn content is attributed to substitution of the lower Sb-Se by the more robust Sn-Se bonds.

The increment of CN, CON, <E>, $H_A$ and CE are obvious evidences for increasing the rigidity of the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses by increase the Sn content. This behavior may be because of the increase of cross-linking with the addition of the 4-fold coordinated Sn in place of the 3-fold coordinated Sb atoms.

### 3.2 Estimation of the refractive index

To estimate the optical parameters a film has thickness t and complex refractive index n+ik was evaporated on clean glass substrate. Swanepoel's approach, based on the idea of Manifacier et al. [21], has been utilized to obtain the optical parameters of the examined films. Complete details of calculations had been shown in our preceding papers [22, 23].

Fig. 1 demonstrates the transmission spectra of $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ thin films. As shown in the inset, the absorption edge shifts to longer wavelengths due to increasing the Sn content.

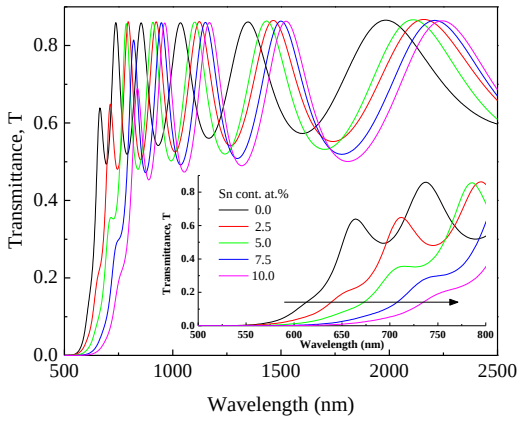


*Fig. 1. Transmission spectra for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) thin films.*

Values of n of the films were fitted to the two-term Cauchy dispersion equation [24]:

$$n(\lambda) = a + \frac{b}{\lambda^2} \tag{8}$$

Utilizing the previous equation the whole spectral distribution of n was obtained as appeared in Fig. 2. As shown, n(λ) demonstrates a typical dispersion as well n increases by an increase of Sn content.

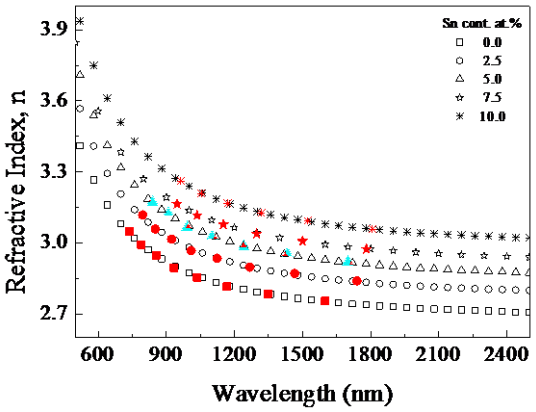


*Fig. 2. Spectral dependence of the refractive index for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) thin films.*

Refractive index was Fitted to the Wemple–DiDomenico (WDD) equation [25] prompts obtaining the single-oscillator energy ($E_o$) and the dispersion energy ($E_d$) for the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) films. WDD equation is given by:

$$n^2(h\nu) = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2} \tag{9}$$

The static refractive index $n_0$ can be obtained by substituting $h\nu = 0$ in the above equation. $E_o$ and $E_d$ have been gotten from the plots of $(n^2-1)^{-1}$ versus $(h\nu)^2$ as shown in Fig. 3. $E_o$, $E_d$ and $n_0$ are listed in Table 3. $E_o$ is identified with the energy gap, $E_o=2E_g$, as suggested by Tanaka [26]. As appeared in Table 3, $E_d$ increases whereas $E_o$ decreases with increasing the Sn content. The increment of $E_d$ may be attributed to modifying the ionicities because of increasing Sn content.

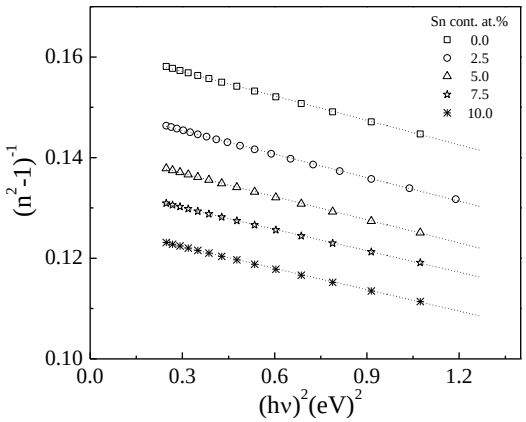


*Fig. 3. Plots of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) thin films.*

*Table 3. Compositional dependence of some optical constants for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) thin films.*

| Sn at.% | $E_d$ | $E_o$ | $E_g$ | $E_e$ | $n_0$ | $\varepsilon_L$ | N/m* |
|---|---|---|---|---|---|---|---|
| | eV | | | | | | $10^{52}g^{-1}cm^{-1}$ |
| 0.0 | 21.00 | 3.40 | 1.79 | 0.026 | 2.68 | 7.17 | 4.35 |
| 2.5 | 22.04 | 3.31 | 1.64 | 0.029 | 2.77 | 7.67 | 16.08 |
| 5.0 | 22.85 | 3.22 | 1.56 | 0.032 | 2.85 | 8.09 | 19.16 |
| 7.5 | 23.56 | 3.18 | 1.47 | 0.038 | 2.90 | 8.41 | 20.48 |
| 10.0 | 24.52 | 3.11 | 1.40 | 0.041 | 2.98 | 8.87 | 23.14 |

Variation of n with the lattice dielectric constant ($\varepsilon_L$) is obtained by use of the relation [27]

$$n^2 = \varepsilon_L - (e^2/\pi c^2)(N/m^*)\lambda^2 \quad (10)$$

$m^*$ is the effective mass and $N$ is the carrier concentration. Fig. 4 shows the variation of $n^2$ as a function of $\lambda^2$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) films. Values of $N/m^*$ as well as $\varepsilon_L$ have been computed from the plots, and listed in Table 3. $N/m^*$ and $\varepsilon_L$ increase (see Table 3) by the increase of Sn content.

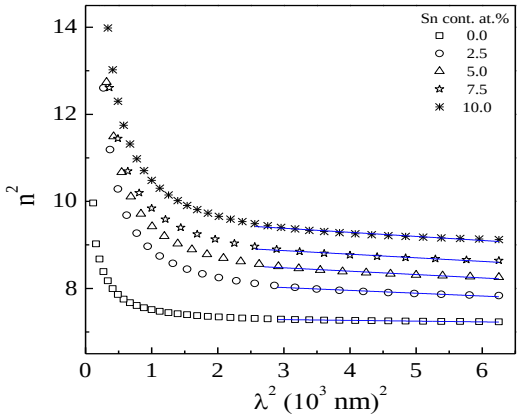


*Fig. 4. Plots of $n^2$ vs. $\lambda^2$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) thin films.*

### 3.3 Calculation of the band gap

Utilizing the values of n, the values of the absorption coefficient (α) are obtained using the conditions suggested by Connell and Lewis [28]. Complete details of estimations were presented in our previous work [22, 23]. The extinction coefficient (k) has been calculated using $\alpha$ and $\lambda$ according to the widely recognized formula:

$$k = \alpha\lambda/4\pi \quad (11)$$

Fig. 5 shows the spectral dependence of $k$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \le x \le 10$ at. %) thin films. As showed by Tauc's equation [29, 30] of the allowed non-direct transitions, the variation of α as a function of hν is obtained by use of the relation:

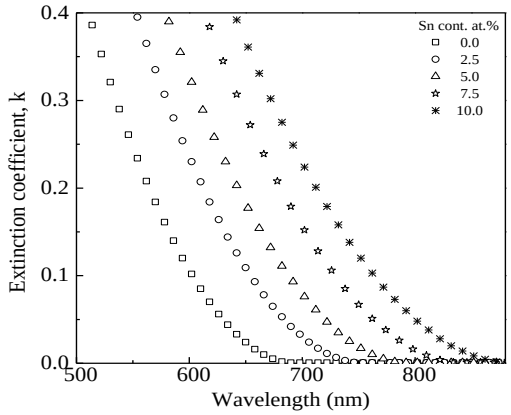


*Fig. 5. The spectral dependence of the extinction coefficient k for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) thin films.*

$$(\alpha h\nu)^{1/2} = B\,(h\nu - E_g) \tag{12}$$

in which $B$ represents a constant and $E_g$ represents the energy gap. Fig. 6 demonstrates the variation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ thin films. $E_g$ may be obtained from intercepts at hν = 0. The dependence of $E_g$ on composition is listed in Table 3. An increase of the Sn content from 0 to 10 at. % prompts a decrease of $E_g$ from 1.79 to 1.40 eV (see Table 3).

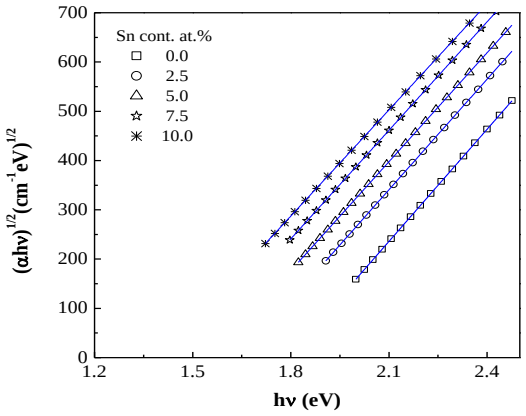


*Fig. 6. Variation of $(\alpha h\nu)^{1/2}$ with photon energy $h\nu$ for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) thin films.*

Urbach energy ($E_e$) may be estimated using the exponential variation of α with photon energy as indicated by the following equation [31]

$$\ln(\alpha) = \ln(\alpha_0) + (h\nu / E_e) \tag{13}$$

$E_e$ is an imperative factor for characterizing the non-crystalline semiconductors. Fig. 7 shows the plots of ln(α) versus hν for the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) films in which $E_e$ is obtained and listed in Table 3. One can see in table 3, increasing the Sn content prompts a decrease in $E_g$ and an increase in $E_e$.

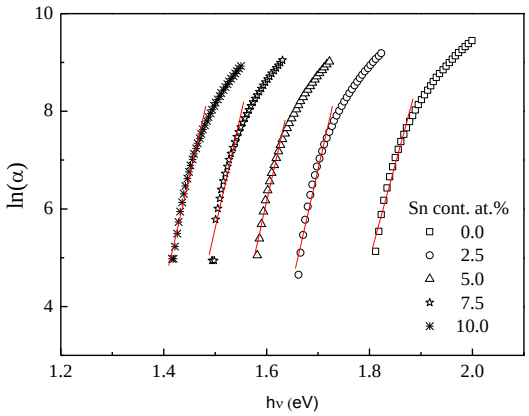


*Fig. 7. Dependence of ln(α) on photon energy h ν for $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ (where $0 \leq x \leq 10$ at. %) thin films.*

## 4. Conclusions

The dependence of CN, CON, <E>, $H_A$ and CE on Sn content of $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses has been explored theoretically. It was found that, CN, CON, <E>, $H_A$ and CE increase with increasing the Sn content. This increment is obvious evidence for increasing the rigidity of the $Ge_{25}Se_{65}Sb_{10-x}Sn_x$ glasses due to an increase of Sn content. This may be because of increasing the cross-linking due to the addition of the 4-fold coordinated Sn in place of the 3-fold coordinated Sb atoms. In addition, increasing the Sn content from 0 to 10 at. % prompts an increase of $E_d$ (from 21.00 to 24.52 eV), $n_0$ (from 2.68 to 2.98) and $E_e$ (from 0.026 to 0.041 eV) whereas a decrease of $E_g$ (from 1.79 to 1.40 eV) and $E_o$ (from 3.40 to 3.11 eV).

### Acknowledgements

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through General Research Project under grant number (G.R.P- 302 -39).

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