

Influence of Composition on Optical Constants and dc Conductivity of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ Thin Films

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Thin films of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at. %) were deposited under vacuum (10^{-5} Torr) on glass substrates by thermal evaporation technique of the bulk compounds. The optical transmission and reflection spectra of these films were measured in the range $1000 - 2200$ nm and the optical constants (absorption coefficient α , refractive index n , extinction coefficient k , real ϵ_r and imaginary part ϵ_i of the dielectric constant) were calculated for $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ compositions films as a function of photon energy ($h\nu$). The absorption data revealed the existence of allowed direct and indirect transitions. It has been found that the optical band gap E_g decreases with increasing Pb content up to $x = 36$ at.% then, increases as Pb content raised up to 40 at.%. The results were interpreted in terms of the change in the average band energy of the films as a function of composition. The increase of the optical energy gap at $x = 40$ at.% which allows to the decrease in density of localized states in the band gap.

The temperature dependence of dc conductivity σ for the as deposited films of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ in the temperature range ($303 - 423$ K) was recorded. For these films, it is suggested that the conduction is due to thermally activated process through the extended states. The effect of composition on the pre-exponential factor S_0 and the activation energy DE were studied. It is found that the values of S_0 and DE decreases with increasing Pb content ($x = 28, 31,$ and 36 at. %) but for higher concentration of Pb ($x = 40$ at. %) S_0 and DE were increased.

1. Introduction

Knowledge of chalcogenide semiconducting is one of the most active fields of research in the physics of non crystalline materials. The great interest in these materials is largely due to its properties and their ever increasing application in technology such as switching and memory devices, reversible phase change optical recordings, optical imaging and photo induced wave guides [1-9].

The investigation of the optical properties of chalcogenide semi-conducting materials is of considerable interest, and affords critical information about the electronic band structure, optical transition and relaxation mechanisms. The optical band gap, refraction index and extinction coefficient are the most significant parameters in semiconducting thin films.

D. Kumar et al. [10] studied the temperature dependence of dc conductivity in a- $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films, ($x = 0, 2, 4, 6, 10$). From their measurements, the values of activation energy (ΔE) were calculated for each glassy alloy. A. K. Pattanaik et al. [11] prepared thin films of composition $\text{Pb}_x\text{In}_{25-x}\text{Se}_{75}$ ($1 \leq x \leq 7$) by thermal evaporation of the appropriate bulk materials on glass substrates. Their results indicate that the size of the nanocrystallites could be varied by controlling the deposition temperature of the films. They showed that the optical band gap decrease with an increase in Pb content.

Since no study has been reported in the literature for $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at. %) thin films and no information about its optical and electrical properties are available, the author in this thesis motivated to prepare $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at. %) films and to investigate their optical and electrical properties.

The present work deals with some experimental observation on the effect of composition and heat treatment on the optical properties of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at.%).

2. Experimental details

In order to prepare the starting material for the deposition, the constituent element Se, In and Pb (99.999% pure) were weighed according to their atomic percentages and were sealed in an evacuated quartz ampoules which were heated in a furnace and heated stepwise up 900°C to allow Se, In and Pb to react completely. The ampoules were frequently rocked for 10 hours at maximum temperature (900°C) to make the melt homogeneous. Subsequently, the ampoules were cooled to room temperature, and then the alloy is taken out and crush into fine powder.

Thin films of different compositions of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ are prepared by thermal evaporation method onto cleaned glass substrates using an Edwards E-306 coating system. The XRD of as deposited films were proved to be in polycrystalline state.

In order to determine the absorption coefficient α and the optical constants of the film as a function of the incident light wavelength, the transmittance T and reflectance R are recorded at room temperature using a double-beam spectrophotometer (Jasco- 570) combined with Pc. The Dc and Ac electrical conductivity measurements were recorded using two probe method.

3. Results and Discussions

3.1. Effect of composition on the optical constants

Figure (1) shows the transmittance (T) and reflectance (R) spectra of the as deposited $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films ($x = 28, 31, 36$ and 40 at.%) of thickness 270 nm. The spectra are recorded at room temperature in the wavelength range 1000 - 2200 nm with normal incidence light on the films. It is evident that both T and R show a change with increasing photon energy and with Pb content. A significant change in the spectra is observed at $x = 40$ at. %.

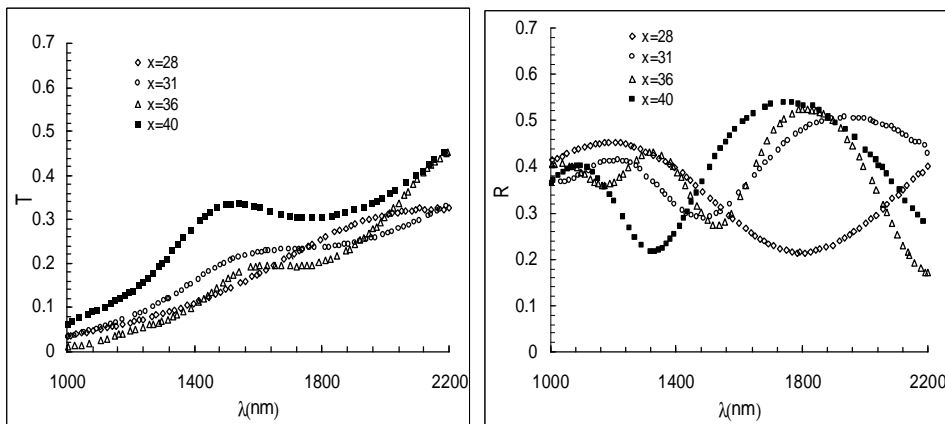


Fig.(1): Spectral distribution of the transmittance T and reflectance R of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ thin films.

The optical absorption coefficient (α) for the compositions were calculated using the relation [12]:

$$a = \frac{1}{d} \ln \left[\frac{(1-R)^2 + [(1-R)^4 + 4R^2T^2]^{\frac{1}{2}}}{2T} \right] \quad (1)$$

Where R is the reflectance, T is the transmittance and d is the film thickness. While $\alpha(h\nu) = B (h\nu - E_g)^r$ was used to calculate the optical energy gap E_g .

Where B is a constant that depends on the transition probability and r is the number which characterizes the transition process. For allowed direct transition $r = 1/2$ and for indirect allowed transition $r = 2$. The experimental results for the prepared samples of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at.%) thin films of different compositions with thickness 270 nm shows a good fit to equation (2) with $r = 2$ and $r = 1/2$. The present system of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ obeys the rule of allowed indirect transition and allowed direct transition. This indicates that, for the different compositions, direct and indirect transitions are existed.

Figure (2) shows the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for as-deposited films with thickness 270 nm, while Fig.(3) shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for prepared films. From the two figures we find that $(h\nu)^{1/2}$ and $(h\nu)^2$ are linear function of $(h\nu)$. This linearity indicates the existence of both allowed indirect and direct transitions. The optical energy gap can be obtained from the intercept of the straight lines with the energy axis at $(h\nu)^{1/2} = 0$ and $(h\nu)^2 = 0$ as shown Fug. (2) and (3).

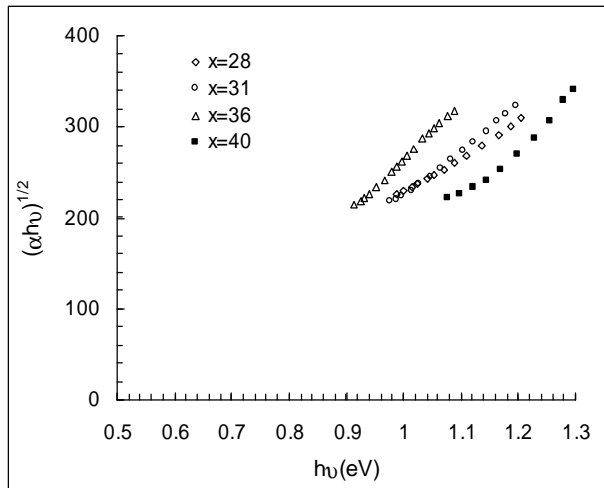


Fig.(2): $(\alpha h\nu)^{1/2}$ against $(h\nu)$ for $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ Films

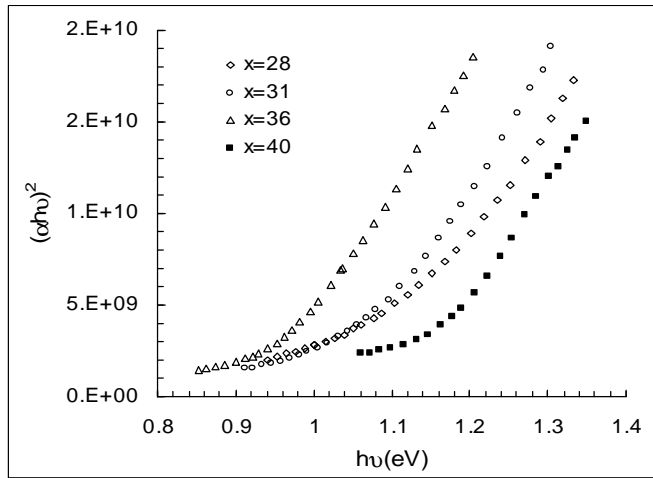


Fig.(3) : $(\alpha h \nu)^2$ against $(h\nu)$ for $Se_{52}In_{48-x}Pb_x$ films.

The calculated values of the indirect and direct optical energy gap for prepared $Se_{52}In_{48-x}Pb_x$ films are listed in Table [1].

Table [1]: The dependence of E_{gi} and E_{gd} on the Pb content for $Se_{52}In_{48-x}Pb_x$ thin films.

| Composition | E_{gi} (eV) | E_{gd} (eV) |
|-------------------------|---------------|---------------|
| $Se_{52}In_{20}Pb_{28}$ | 0.58 | 1.08 |
| $Se_{52}In_{17}Pb_{31}$ | 0.56 | 1.04 |
| $Se_{52}In_{12}Pb_{36}$ | 0.54 | 0.94 |
| $Se_{52}In_8Pb_{40}$ | 0.80 | 1.12 |

The obtained values of E_{gi} and E_{gd} are plotted as a function of Pb content and shown in Fig.(4). From the figure it is shown that, the values of the indirect energy gap decreases from 0.58 eV to 0.54 eV with increasing Pb content but at $x = 40$ at. % the indirect optical energy gap increases to 0.8 eV. The same behavior is obtained in which the values of the direct energy gap decreases from 1.08 to 0.94 eV, then increases to 1.12 eV at $x = 40$ at. %. The variation of indirect and direct energy gaps E_{gi} and E_{gd} with Pb content indicate that:

- The values of E_{gd} are in general higher than those of E_{gi}
- The energy gaps decrease slowly as the Pb content increases from 28 to 36 at. %, but for Pb = 40 at. %, the energy gap increases.

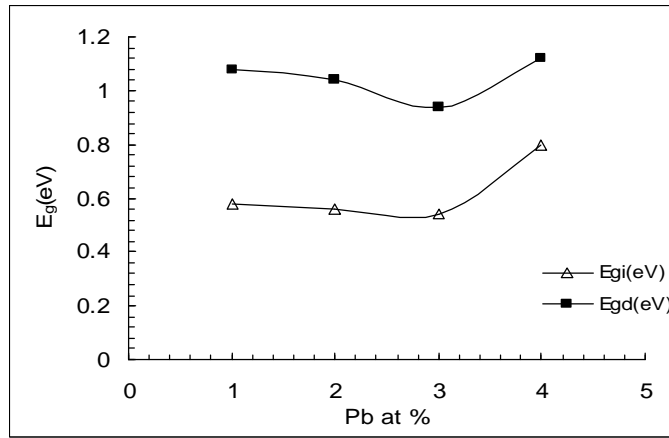


Fig (4) : The dependence of the indirect (E_{gi}) and direct (E_{gd}) optical energy gap on the pb content for $Se_{52} In_{48-x} Pb_x$ films.

The variation in the optical energy gap of thin films with change in Pb concentration could be understood on the basis of the change in the average bond energy of the films as a function of composition. The single band energy values [13] of In-In (84.5 KJ.mol^{-1}), Pb-Pb (85.7 KJ.mol^{-1}) and Se-Se ($206.1 \text{ KJ.mol}^{-1}$) and the single covalent bond energies of In-Se ($257.5 \text{ KJ.mol}^{-1}$) Pb-Se ($231.2 \text{ KJ.mol}^{-1}$). When Pb is added to $In_{52}Se_{48}$ at $x = 28, 31$ and 36 at. % Pb-Se bonds replace In-Se bonds. Since the energy of Pb-Se bond is lower than that of In-Se bond so, the average bond energy of the solid decreases as the Pb concentration is increased in $In_{52}Se_{48-x}Pb_x$. Since the optical band gap is a bond sensitive property, a decrease in the average band energy results in the decrease in the optical band gap energy of the film. Hence the optical band gap decreases with an addition of Pb to $Se_{52} In_{48-x} Pb_x$ ($x = 28, 31$ and 36 at. %) films. Increase of optical energy gap at $x = 40$ at.% may be due to decrease in density of localized states in the band gap [14,15].

No direct and indirect optical band gap were previously reported except that of A.K Pattanaik, et al [11] whose reported that, these films of $Pb_x In_{25-x} Se_{75}$ ($1 \leq x \leq 7$) deposited at 200 K, have indirect optical energy gap which decreases from 1.76 to 1.58 eV as the Pb concentration increases. The values of refractive index n and the extinction coefficient k have been calculated using the following relations [16].

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

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

The spectral dependence of refractive index n on the photon energy $h\nu$ for the prepared $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at. %) films are shown in Fig.(5). In general, the refractive index (n), increase with increasing Pb content except composition $x = 40$ at. %.

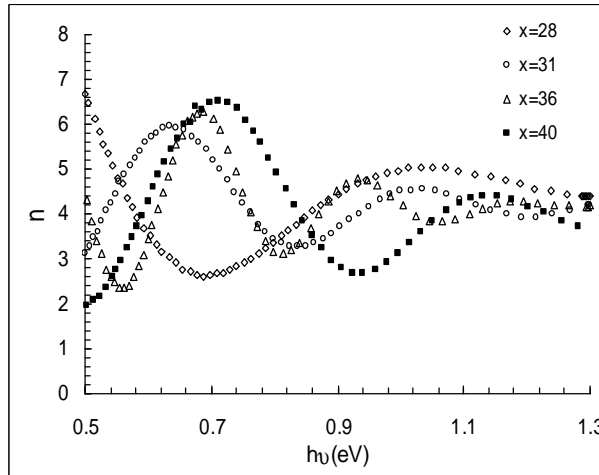


Fig.(5) : Spectral distribution of the refractive index (n) for $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films.

The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films have been calculated using the relations [17]:

$$e_r = n^2 - k^2 \tag{5}$$

$$e_i = 2nk \tag{6}$$

The variation of real part (ϵ_r) of the dielectric constant of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ with photon energy ($h\nu$) are shown in Fig. (6). The change of the optical constants, refractive index n , extinction coefficient, k , real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant associated with the introduction of Pb in the usual manner has a direct relation to the amount and strength of the possible different bonds formed in the network structure of the investigated compositions.

The relation between the refractive index n , and the oscillator strength below the band gap is given by the expression [18,19].

$$n^2 - 1 = (E_s E_o) / (E_o^2 - E^2) \tag{7}$$

where E_o is the energy of the effective dispersion oscillator, E is the photon energy and E_s is the so- called dispersion energy which measures the overage strength of inter band optical transitions.

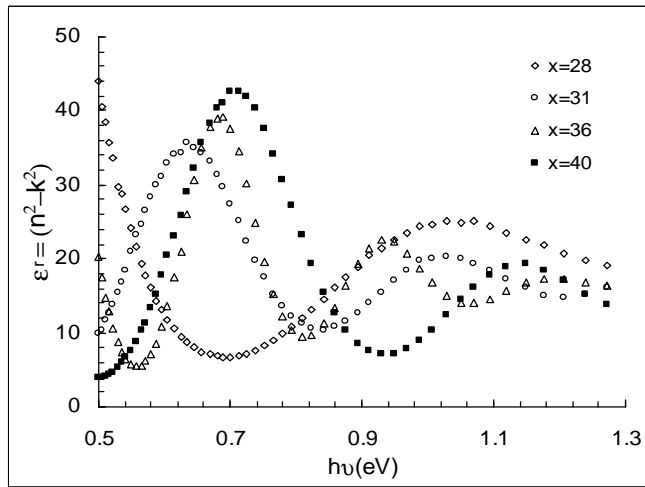


Fig.(6): Spectral distribution of the real part (ϵ_r) of the dielectric constant for $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films .

Figure (7) shows the relation between $1/(n^2-1)$ versus $(h\nu)^2$ for the investigated compositions. The values of E_s and E_o have been determined from the slope ($-1/E_o E_s$) and the intersection of the straight lines with $1/(n^2-1)$ axis. The variation of E_s and E_o with the concentration of Pb in the investigated compositions are shown in Fig. (8). The values of E_o and E_s decreases with increasing Pb content up to 36, then E_o and E_s at $x = 40$ are increases. The decrease of E_o and E_s may be explained by the increase in number of scattering centers due to dissolving Pb atoms in the present matrix [20].

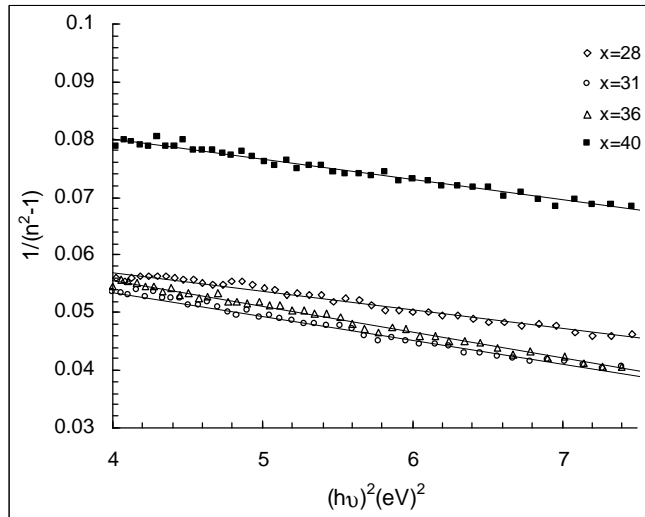


Fig.(7) : Plots of $(n^2-1)^{-1}$ versus $(h\nu)^2$ for as-deposited $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films

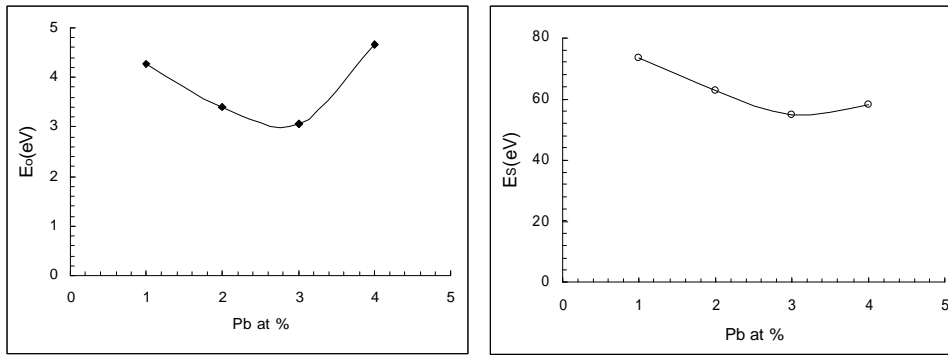


Fig.(8): Plots of E_s and E_o versus Pb content for as-deposited films of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films.

The values of the energy of the effective dispersion oscillator E_o and dispersion energy E_s are listed in Table [3].

Table [3]: values of the effective dispersion oscillator E_o and dispersion energy E_s .

| composition | E_o | E_s |
|--|-------|-------|
| $\text{Se}_{52}\text{In}_{20}\text{Pb}_{28}$ | 4.26 | 73.39 |
| $\text{Se}_{52}\text{In}_{17}\text{Pb}_{31}$ | 3.39 | 62.76 |
| $\text{Se}_{52}\text{In}_{12}\text{Pb}_{36}$ | 3.07 | 54.82 |
| $\text{Se}_{52}\text{In}_8\text{Pb}_{40}$ | 4.65 | 58.13 |

3.2 DC conductivity of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ films:

The temperature dependence of dc conductivity for the as-deposited films of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at. %) of thickness 270 nm is shown in Fig. (9). It is clear that the plot of $\ln s_{dc}$ vs. $1000/T$ is linear in nature in the temperature range 303 - 423 K. It is evident from this figure that the dc conductivity (s_{dc}) increases exponentially with increasing temperature. The dc conductivity can be expressed by the conventional relation [21]:

$$s_{dc} = s_o \exp(-\Delta E / kT) \quad (8)$$

Where s_o and ΔE represent the pre-exponential factor and activation energy respectively, k is Boltzmann constant. On the basis of best fitting of our data with

thermally activated type of conduction, the values of activation energy and pre-exponential factor were calculated, and these values are given in table [4]. For these films, it is suggest that the conduction is due to thermally activated process through the extended states.

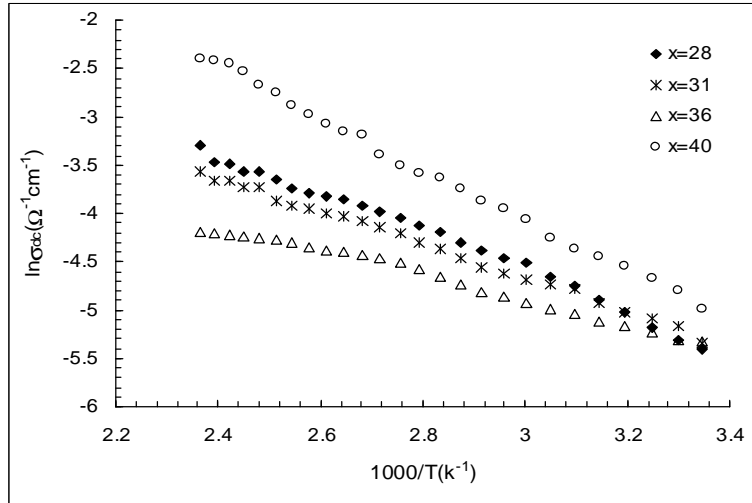


Fig.(9): Plots of $\ln\sigma$ versus $1000/T$ for the $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at.%) films for thickness 270nm .

From the table, it can be noticed that the values of s_o and ΔE decrease with increasing Pb content ($x = 28, 31$ and 36 at. %) but for higher concentration of Pb ($x = 40$ at. %), s_o and ΔE have been increases. Also the values of dc conductivity at room temperature, increase for $x = 28, 31$ and 36 at. %, then it decreases for higher concentration of Pb at $x = 40$ at. %.

The same behavior is observed in the optical energy gap, in which both E_{gi} and E_{gd} decrease with increasing Pb content up to $x = 36$ at.%, then it increases for $x = 40$ at.%. The calculated values of (ΔE) are found to be about half the magnitude of the direct optical energy gap.

The decrease in the values of activation energy DE and pre-exponential factor σ_o with Pb concentration ($x = 28, 31$ and 36 at.%) show that the mobility (conduction) of charge carriers in the trap states decreases with Pb content which can be attributed to increase the width of the localized states region. At higher concentration of Pb ($x = 40$ at.%), the increase in the value of σ_o and DE can be attributed to the decrease in the density of localized states. The variation of activation energy and dc conductivity with the Pb concentration ($x = 28, 31, 36$ and 40 at. %) in the present sample are presented in Fig. (10).

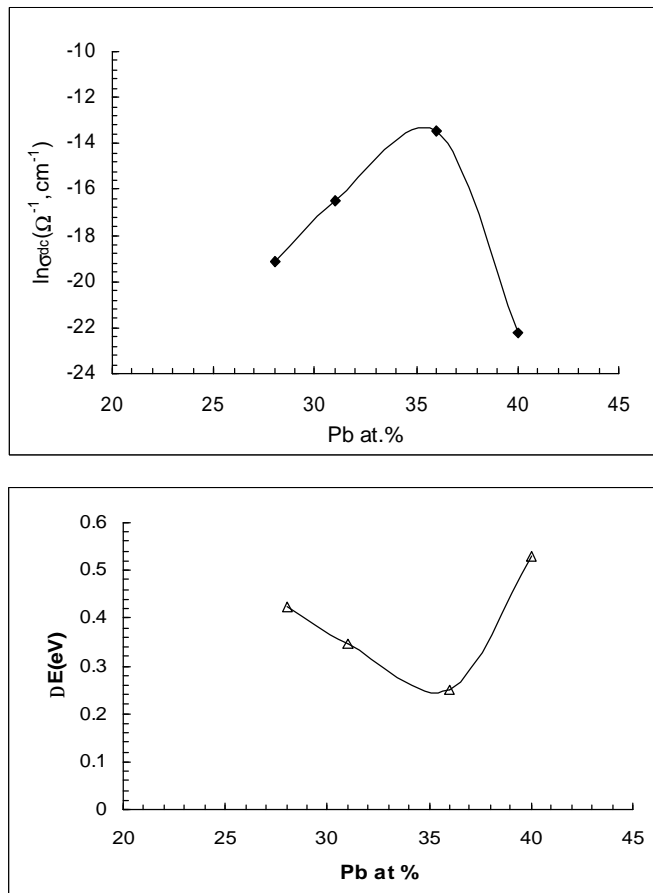


Fig.(10): Variation of dc conductivity and activation energy vs concentration for a $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at.%) thin films.

Table [4]: Electrical parameters of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ ($x = 28, 31, 36$ and 40 at. %) thin films.

| Composition | Activation Energy DE (eV) | Pre-exponential factor σ_0 ($\text{W}^{-1} \text{cm}^{-1}$) | DC conductivity |
|--|-----------------------------|--|------------------------|
| $\text{Se}_{52}\text{In}_{20}\text{Pb}_{28}$ | 0.42 | 0.049 | 4.76×10^{-9} |
| $\text{Se}_{52}\text{In}_{17}\text{Pb}_{31}$ | 0.35 | 0.038 | 7.09×10^{-8} |
| $\text{Se}_{52}\text{In}_{12}\text{Pb}_{36}$ | 0.25 | 0.019 | 1.38×10^{-6} |
| $\text{Se}_{52}\text{In}_8\text{Pb}_{40}$ | 0.53 | 0.142 | 2.17×10^{-10} |

Conclusion:

The present investigations of $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ system ($x = 28, 31, 36$ and 40 at.%) shows the following notable features:

- Films $\text{Se}_{52}\text{In}_{48-x}\text{Pb}_x$ was prepared by a thermal evaporation technique on glass substrates.
- All compositions in the form of powder and thin films are polycrystalline in nature.
- The optical energy gap E_g for the as deposited films decreases with increase Pb content except at $x = 40$ at.%. This is attributed to the decrease of bond energy with increasing Pb content. The increase in E_g with $x = 40$ at.% is due to increase in grain size, the reduction in disorder and decrease in density of localized states in the band gap.
- The dc conductivity results of as deposited films suggest that the conduction is due to thermally activated process through the extended states and the activation energy ΔE decreases with increasing Pb content up to 36 at.% then it increases.
- At $x = 40\%$, the results are too large than $x=28-36$, Therefore, it is preparalele to investigate samples with $x > 40\%$ to ensure the obtained results.

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