# Composition Dependence of Optical Constants of $Ge_{1-x}Se_2Pb_x$ Thin Films

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*Optical constants of vacuum evaporated thin films in the $Ge_{1-x}Se_2Pb_x$ (x = 0, 0.2, 0.4, 0.6) system were calculated from reflectance and transmittance spectra. It is found that the films exhibit non-direct gap which decrease with increasing Pb content. The variation in the refractive index and the imaginary parts of the dielectric constant with photon energy have been also reported. The relationship between the optical gap and chemical composition in chalcogenide glasses is discussed in terms of the average heat of atomization.*

## 1. Introduction:

Chalcogenide glasses have been recognized as promising materials for IR optical elements and transfer of information. The nature of glass structure and the glass forming tendency of these compounds is one of the most challenging problems of glass science and condensed matter of physics. The doping of chalcogenide glassy semiconductors with metal is an effective step of controlling the electrical and optical properties of glasses in a desired direction [1-3].

Investigation of narrow band gap IV-VI semiconductors (mainly PbTe and PbSe) doped with impurities like Ge attracts much attention due to impurity induced ferroelectricity in these compounds. The changes in the physical properties of these S.C. due to the ferroelectric phase transition may be used in the IR optoelectronics (tunable IR lasers, photoelectric devices)[4-6].

The interest in the optical properties of chalcogenide compounds containing metal atoms has been established by their potential applications as switching and memory devices and optical transmission media, as well as by their use as passivating materials for integrated circuits. It is well known that the optical gap strongly depends on the structure of the compounds [7].

The present paper is concerned with the effect of Pb substitution on the optical parameters of thin films $Ge_{1-x}Se_2Pb_x$ (x=0, 0.2, 0.4 and 0.6), deposited by thermal evaporation technique from the as-quenched ingots.

## 2. Experimental:

The bulk glassy material was prepared by means of widely known quench method [8]. Films were prepared by thermal evaporator technique using standard unit Edward 360. The films preparaion method was considered elsewhere [9]. The thickness of the films was determined by a thickness monitor. The chemical composition were determined by the Joel SEM-5400 scanning electron microscope with an electron dispersion X-ray (EDX) detector. The X-ray diffraction (Philips type 1710 with Cu as a target) was used to characterize the thin films structure. Figure (1) shows the X-ray diffraction pattern for the investigated thin films.
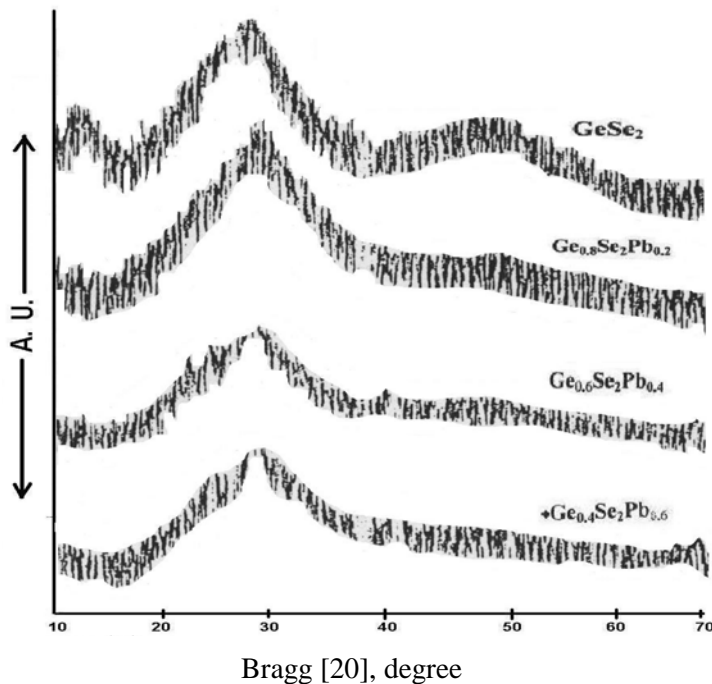


Bragg [2θ], degree

**Fig .(1): X**-ray diffraction pattern for the as-prepared films.

X-ray diffraction patterns reveal the amorphous nature of the prepared thin films. The transmittance (T) and the reflectance (R) were measured for the films using Uvikon 860 Kourton spectrometer.

## 3. Results and Discussion:

The absorption coefficient $\alpha(\nu)$ is calculated according to the relation [10]:

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

Where T is the transmittance, R the reflectance and d the film thickness (4000A°). Figure (2a&b) shows the dependence of the optical transmission and reflection, respectively, of the investigated thin film with the wavelength.
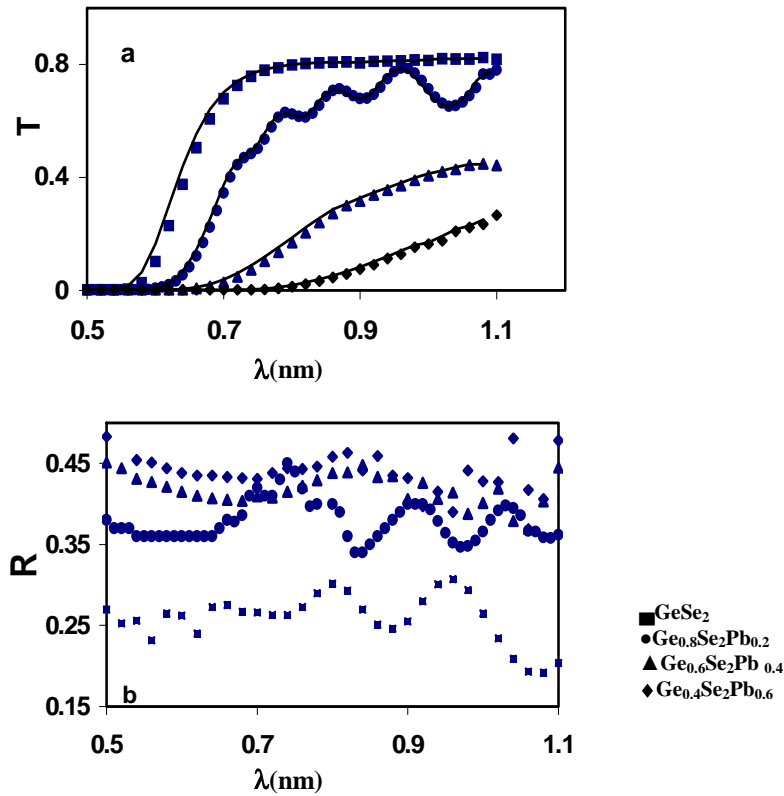


**Fig.(2)** a. transmission and b. reflection of the investigated films.

It is observed that the transmission decreases with increasing Pb content. Figure (3) shows the plot of $\alpha(\nu)$ versus photon energy (h$\nu$) for the studied films. It is clear that Pb substitution for Ge shifts the absorption to lower energies. The figure shows two well defined transition regions: (i) the absorption region related to transition between band tails (ii) the saturation region of $\alpha$ (h$\nu$) which correspond to the fundamental optical transition between the valence and the conduction bands (see references 12,13)
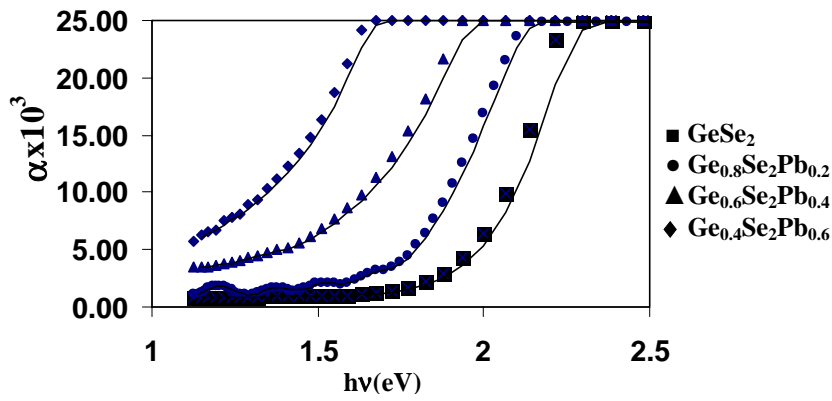
**Fig. (3):** The absorption coefficient vs. photon energy.

A spectral change in the optical absorption near the band edge is characterized by $\alpha(\nu)$ which increase exponentially with $h\nu$ obeying the exponential relation:

$$\alpha(\nu) = \alpha_o \exp (h\nu/ E_s) \qquad (2)$$

where $\alpha_o$ is constants and $E_s$ is interpreted as the width of tails of the localized states in the gap, it represents the degree of disorder [11]. Plotting $\log \alpha$ as a function of $h\nu$ (Fig.(4)) one can calculate $E_s$(see Table1). It is observed that adding Pb to $GeSe_2$ increases $E_s$. It is interesting to note that adding Pb at low concentration (x=0.2) leads to the appearance of structured absorption tails at $h\nu < 1.6$ eV. This structure of $\alpha$ ($h\nu$) reflects the distribution of states induced by the incorporation of Pb at this concentration.
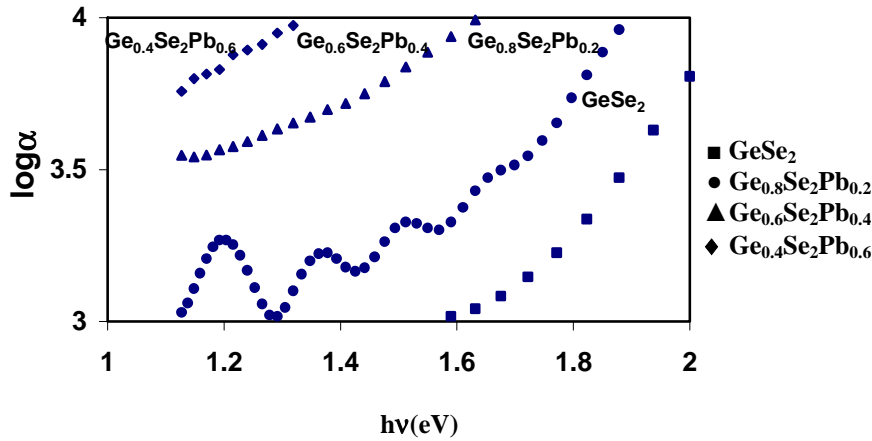


**Fig.(4):** The dependence of $\log \alpha$ on photon energy for the investigated films.

To determine the optical gap of the investigated films the following relation is used [12]:

$$\alpha \, h\nu = \beta \, (h\nu - E_o)^a \qquad (3)$$

where $E_o$ is the optical gap, $\beta^{-1}$ the edge width parameter and a is an integer usually equals to 1, 2, 3 for amorphous materials [13]. The present results were found to obey equation (3) with a=2 (refers to allowed non-direct transition).The plots in Fig. (5) fit the linear relation of $(\alpha h\nu)^{0.5}$ versus $h\nu$ for the investigated films.
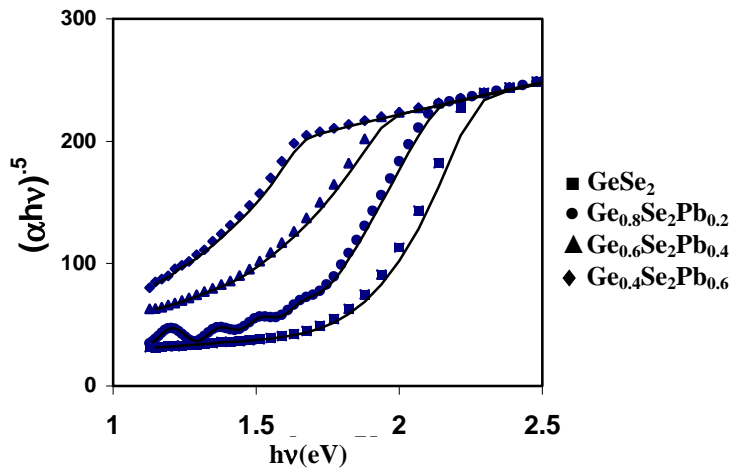


**Fig.(5):** The plots of $(\alpha h\nu)^{0.5}$ vs. photon energy for the investigated films.

**Table (1):** The optical gap ($E_o$) and the width of localized states ($E_s$).

| Composition | $H_s$, (kj/mol) | $E_s$, eV | $E_o$ ,(eV) |
|---|---|---|---|
| $GeSe_2$ | 242.2 | 0.39 | 1.78 |
| $Ge_{0.8}Se_2Pb_{0.2}$ | 237 | 0.43 | 1.55 |
| $Ge_{0.6}Se_2Pb_{0.4}$ | 231.9 | 0.81 | 1.21 |
| $Ge_{0.4}Se_2Pb_{0.6}$ | 226.59 | 0.86 | 0.97 |

Table (1) lists the values of $E_o$ determined from the intersections of the straight lines with the abscissa. From the results in table (1), it is obvious that $E_s$ increased while $E_o$ decreased by increasing Pb content. Therefore increasing Pb content increases the the width of the tails of localized states ($E_s$) in the energy gap. Since $E_s$ represents the degree of disorder hence increasing Pb content in $GeSe_2$ increases the disorder in the films. The increase of disorder is responsible for the decreasing of the optical gap.

In chalcogenide glasses containing a high concentration of group VI element the lone-pair form the top of the valence band and the antibonding band forms the bottom conduction band [14]. The optical gap corresponds closely to the energy difference between the top of the valence band and the bottom of the conduction band. Metal atoms can form a dative bonds with group VI atoms (lone pair with empty orbital) without any cost in energy, due to the presence of high-energy lone pair on the latter. Dative bonds have corresponding (empty) antibonding levels which could give localized acceptors states in the gap [15].

It is interesting to relate the optical gap with the chemical bond energy. For this purpose we calculate the average heat of atomization ($H_s$) [16]. Heat of atomization is the quantity of heat energy required to change one mole of an element in its standard state at 298 K to gaseous atoms. The average heat of atomization is defined, for a compound $A_\alpha B_\beta C_\gamma$ as a direct measure of the cohesive energy and thus of the average bond strength, as

$$H_s = (\alpha H_s^A + \beta H_s^B + \gamma H_s^C)/(\alpha + \beta + \gamma) \tag{4}$$

The calculated values of $H_s$ for the investigated materials are listed in table (1). The obtained data declares that $H_s$ decreases with increasing Pb content i.e. the average bond of the compound decreased.

The bond energy values of Ge-Ge, Pb-Pb, Se-Se, Ge-Se and Pb-Se are 205.2, 85.7, 206.1, 234.9 and 231.2 Kjmol$^{-1}$, respectively [17,18]. Since Se remains constant, so substitution of Ge with Pb atom results in the reduction of Ge-Se bonds and increase in Pb-Se bonds which have the lower energy bond. Therfore, addition of Pb leads to decrease the average bond energy. This reduction in the average bond energy of the films is reflected in the reduction of the optical gap ($E_o$) of these films.

There has been an increasing need for an accurate knowledge of the optical constants n and k of thin absorbing films over a wide wavelength range, for example in the field of photothermal conversion of solar cell, many new materials have been proposed as constituents of selectively absorbing films. The refractive index (n) was calculated according to the relation:

$$R = [(n-1)^2 + K^2]/[(n+1)^2 + K^2] \tag{4}$$

where K is the extinction coefficient ($K = \alpha\lambda/4\pi$). Variation of refractive index with photon energy for the investigated films are shown in Fig.(6).

There was no significant difference between the forms of the curves for these films. However, the refractive index reflects the average mass of the atoms making up the films [19]. Therefore, the refractive index at a given energy increases with Pb content of  which is the heaviest atom among the compound.
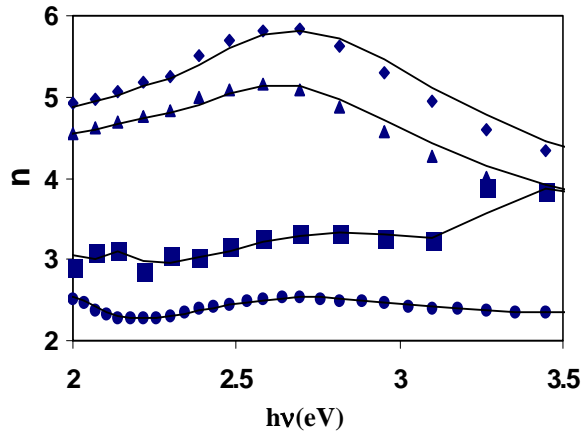


**Fig. (6):** The variation of the refractive index vs. photon energy for the investigated films.

The imaginary part of the dielectric constant $\varepsilon_2$ ($\varepsilon_2 = 2nK$) as it is directly related to the density of states within the forbidden gap of the amorphous semiconductor [20]. Fig.(7) compares the variation of $\varepsilon_2$ with photon energy for the investigated films. As it is seen $\varepsilon_2$ is increasing as Pb content is increasing.



■ $GeSe_2$
● $Ge_{0.8}Se_2Pb_{0.2}$
▲ $Ge_{0.6}Se_2Pb_{0.4}$
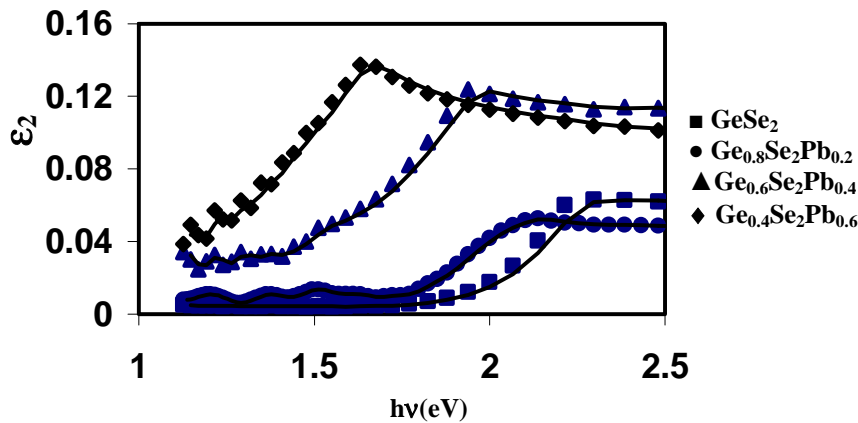♦ $Ge_{0.4}Se_2Pb_{0.6}$

**Fig.(7):** The variation of the imaginary part of the dielectric constant as a function of photon energy.

## 4. Conclusion:

Thin films have been deposited using the synthesized ingots as a source material. Optical measurements indicate that the electronic non-direct transition is the mechanism responsible for the photon absorption inside the investigated films. Increasing Pb content leads to decrease the optical gap and increase the width of localized states, this indicates that Pb substitution introduces a narrow band of disorder states at band edges.

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