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PHOTOCONDUCTIVITY STUDIES IN a-$Se_{75}In_{25-x}Pb_x$ THIN FILMS[**]

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The present paper reports the steady state and transient photoconductivity measurements in vacuum evaporated thin films of amorphous $Se_{75}In_{25-x}Pb_x$ (x = 0, 4, 6 & 10). The behaviour of photoconductivity is found to be same in all the compositions except that the photoconductive parameters show a discontinuity at a Pb concentration of 4 at %.This is explained in terms of mechanically stabilized structure at a particular average coordination number following the theory of Phillips and Thorpe for the topological model in case of chalcogenide glasses. Transient photoconductivity measurements at different temperatures indicate that a persistent photoconductivity occurs in these glasses, which increases at higher temperatures. This is attributed to light induced effects in these materials. Even after subtracting the persistent photoconductivity the decay of the resulting photoconductivity is quite slow which is found to be non - exponential in the present case indicating the presence of continuous distribution of defect states.

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1. Introduction

In disordered materials and, primarily, in amorphous and glassy semiconductors, the individual groups of localized centers are energetically spread as it follows from theoretical studies. The presence of these localized states may act as traps for the charge carriers and hence affect many properties of these materials. Presumably, the parameters of traps (their energy position, the character of energy distribution, trapping concentration and cross-section for the charge carriers) are substantially different in various materials, and these parameters determine the specific features of kinetic processes in each case.

Since the photoconductivity kinetics of amorphous semiconductors are to a great extent determined by the process of trapping of non-equilibrium charge carriers on localized centers of various depths, such studies are therefore important to understand the energy distribution of the traps. From application point of view also photoconductive properties are important.

Chalcogenide glasses are normally p-type semiconductors owing to the fact that the number of electrons excited above the conduction band mobility edge is smaller than the number of holes excited below the valence band mobility edge [1]. These systems also contain positively and negatively charged defect states, known as valence alternation pairs (VAPs) [2 - 3], which essentially pin the Fermi level at the middle of the band gap making them rather insensitive to doping [4]. It is known that certain charged additives could change the ratio of VAPs to such an extent that the Fermi level can get unpinned [5].

In spite of the above problem, p to n transition has been observed in chalcogenide glasses. Bi [6 - 9] and Pb [10 - 12] are amongst the metal impurities, which have been used to bring such a transition in Ge - rich chalcogenide glasses. Se-In-Pb are the recently discovered non-Ge chalcogenides, which exhibit p-n transition at Pb ≥ 5 at % [10 -13]. Therefore, in the present work, we have chosen a non- Ge system (a-$Se_{75}In_{25-x}Pb_x$).

The present paper reports the steady state and transient photoconductivity measurements in amorphous thin films of $Se_{75}In_{25-x}Pb_x$ (x = 0, 4, 6 and 10) prepared by vacuum evaporation

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technique. Temperature dependence of steady state photoconductivity is studied at different light intensities. Intensity dependence of photoconductivity, rise and decay of photoconductivity is studied at different fixed temperatures. Section 2 describes the experimental details. The results have been presented and discussed in section 3. The conclusions have been presented in the last section.

2. Experimental

Glassy alloys of $Se_{75}In_{25-x}Pb_x$ are prepared by quenching technique. High purity (99.999 %) materials are weighed according to their atomic percentages and are sealed in quartz ampoules (length ~ 5 cm and internal dia ~ 8 mm) with a vacuum ~ 10^{-5} Torr. The ampoules containing the constituent materials are heated to 1000 °C and held at that temperature for 10 - 12 hours. The temperature of the furnace is raised slowly at a rate of 3 - 4 °C/min. During heating, all the ampoules are constantly rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This is done to obtain homogeneous glassy alloys.

After rocking for about 10 hours, the obtained melts are cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples of $Se_{75}In_{25-x}Pb_x$ are taken out by breaking the quartz ampoules.

Thin films of these glasses are prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom are used for the electrical contact. The thickness of the films is ~ 500 nm. The co-planar structure (length ~ 1.4 cm and electrode separation ~ 0.5 mm) are used for the present measurements. A vacuum ~ 10^{-2} Torr is maintained in the entire temperature range (306 K to 336 K).

Before measuring the photoconductivity, the films are first annealed at 340 K for one hour in a vacuum ~ 10^{-2} Torr. I-V characteristics are found to be linear and symmetric up to 30 V. The present measurements are, however, made by applying only 2 V across the films. The resulting current is measured by a digital Pico-Ammeter. The heating rate is kept quite small (0.5 K/min) for these measurements.

3. Results and discussions

3.1 DC Conductivity

The dc conductivity was measured as a function of temperature (306 K to 336 K) for amorphous thin films of $Se_{75}In_{25-x}Pb_x$ (x = 0, 4, 6 and 10). The results of these measurements are plotted in Fig. 1. This figure shows that ln σ_{dc} vs 1000/T curves are straight lines for all the samples. The dc conductivity can, therefore, be expressed as

$$\sigma_{dc} = \sigma_0 \exp [- \Delta E / k T] \quad (1)$$

where ΔE is the activation energy and k is the Boltzmann's constant.

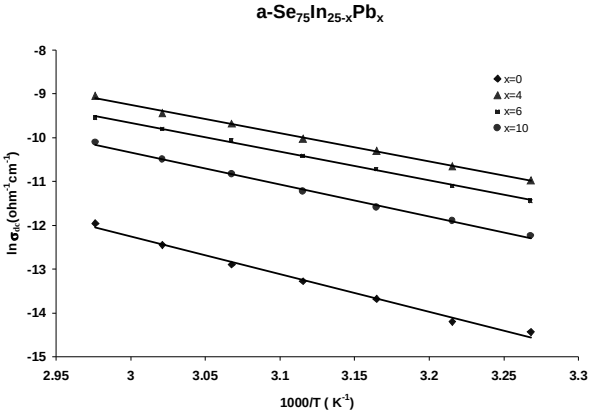

Fig. 1. Temperature dependence of dc conductivity for various samples in amorphous thin films of $Se_{75}In_{25-x}Pb_x$.

The values of σ_{dc} for different samples, at a particular temperature (306 K), are given in Table 1 and plotted in Fig. 2 as a function of Pb concentration. The values of ΔE and σ_0 are also calculated for all the samples. These values are also given in Table 1 and plotted as a function of Pb concentration in Figs. 3 and Fig. 4 respectively. It is clear from these Figs. (2 - 4) that σ_{dc}, ΔE and σ_0 are highly composition dependent and show a discontinuity at x = 4. The origin of this discontinuity is given later in this paper.

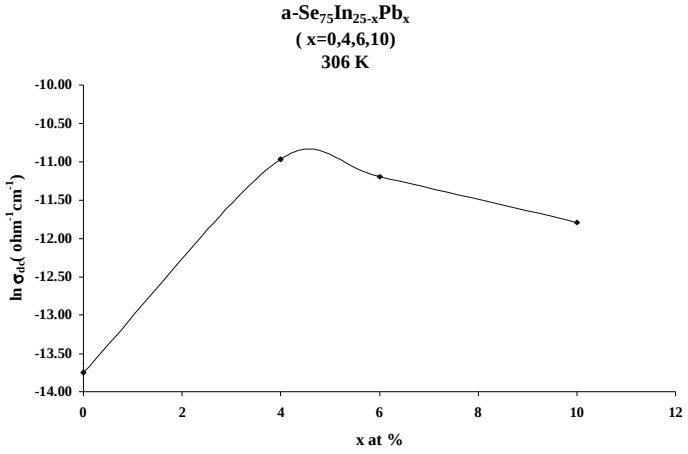

Fig. 2. ln σ_{dc} vs x in amorphous thin films of $Se_{75}In_{25-x}Pb_{x..}$

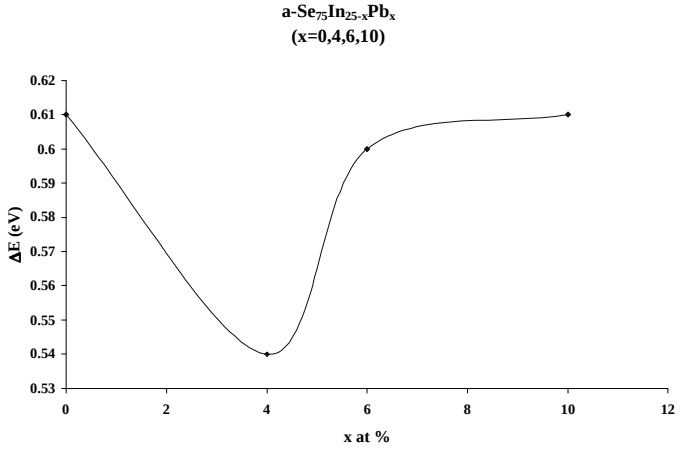

Fig. 3. ΔE vs x in amorphous thin films of $Se_{75}In_{25-x}Pb_{x..}$

Table 1. DC conduction parameters in a- Se_{75} In_{25-x} Pb_x thin films.

Glassy Alloy	σ_{dc} (Ω^{-1} cm^{-1}) 306 K	ΔE (eV)	σ_0 (Ω^{-1} cm^{-1})
$Se_{75}In_{25}$	1.07×10^{-6}	0.61	3.52×10^{4}
Se_{75} $In_{21}Pb_4$	1.72×10^{-5}	0.54	2.67×10^{4}
Se_{75} $In_{19}Pb_6$	1.37×10^{-5}	0.60	2.75×10^{5}
Se_{75} $In_{15}Pb_{10}$	7.57×10^{-6}	0.61	2.27×10^{5}

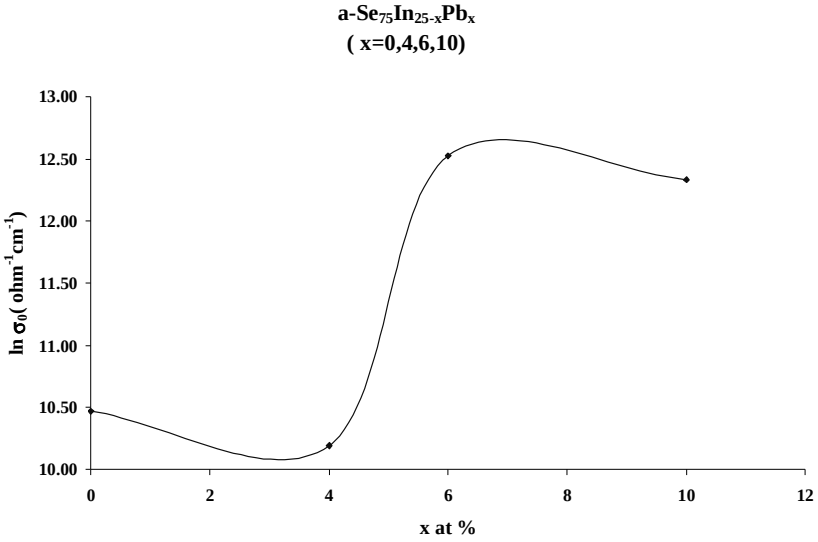

Fig. 4. ln σ_0 vs x in amorphous thin films of $Se_{75}In_{25-x}Pb_{x..}$

3.2 Steady state photoconductivity

Photoconductivity measurements have been made on vacuum evaporated thin films of a-$Se_{75}In_{25-x}Pb_x$. The films are mounted in a specially designed sample holder, which has a transparent window to shine light for photoconductivity measurements. A vacuum ~10^{-2} Torr is maintained throughout the measurements. The temperature of the films is controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the films. Photoconductivity (σ_{ph}) is obtained by subtracting measured conductivity in dark from the measured conductivity in presence of light.

The source of light is a 200 W tungsten lamp. Interference filters are used to get a desired wavelength. The present measurements have been made at a wavelength of 620 nm. The intensity of light is varied, by changing the voltage across the lamp and measured by a digital lux – meter.

3.2.1 Temperature dependence of photoconductivity

The temperature dependence of photoconductivity (σ_{ph}) is studied at different intensities. Fig. 5 shows such results for amorphous thin films of a- $Se_{75}In_{25}$ between 306 K to 336 K. The conductivity (σ_d) in dark is also plotted in the same figure. This figure shows that photoconductivity increases exponentially with temperature as ln σ_{ph} vs 1000/T curves are straight lines similar to dark conductivity. The activation energy of photoconduction is however much smaller as compared to activation energy of conductivity in dark. Similar results were obtained in other glass compositions also (results not shown here). The well - defined activation energies involved in the temperature dependence of photoconductivity suggests that the recombination centers are located at relatively discrete levels of localized states.

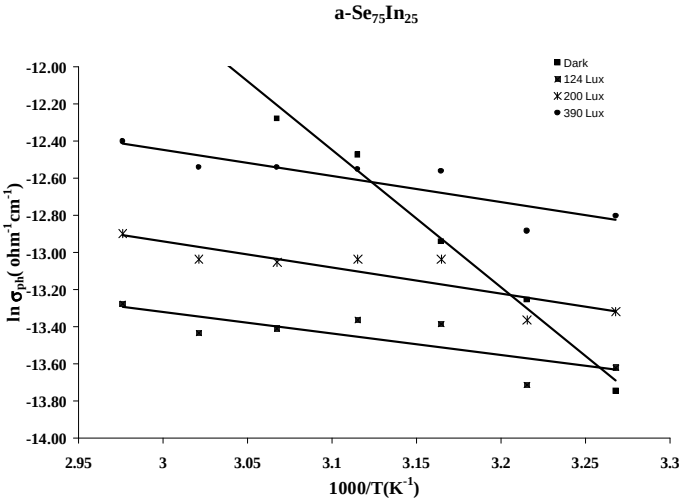

Fig. 5. Temperature dependence of photoconductivity in amorphous thin films of $Se_{75}In_{25}$ at different intensities.

3.2.2 Intensity dependence of photoconductivity

The intensity (F) dependence of photoconductivity (σ_{ph}) is studied at different temperatures in all the glassy alloys used in the present study. The results for a- $Se_{75}In_{25}$ films are shown in Fig. 6. Similar results were found in case of other glass compositions also. It is clear from this figure that, at all temperatures, ln σ_{ph} vs. ln F curves are nearly straight lines which indicates that photoconductivity follows a power law with intensity ($\sigma_{ph} \propto F^{\gamma}$). The power γ is found to vary between 0.5 and 1.0 for all the glassy alloys studied here. Rose [14] has pointed out that the power γ between 0.5 and 1.0 can not be understood by assuming a set of discrete trap levels but demands the existence of continuous distribution of traps. In the present case also γ is between 0.5 and 1.0 which indicates that a continuous distribution of localized states exists in the mobility gap of the present glassy system.

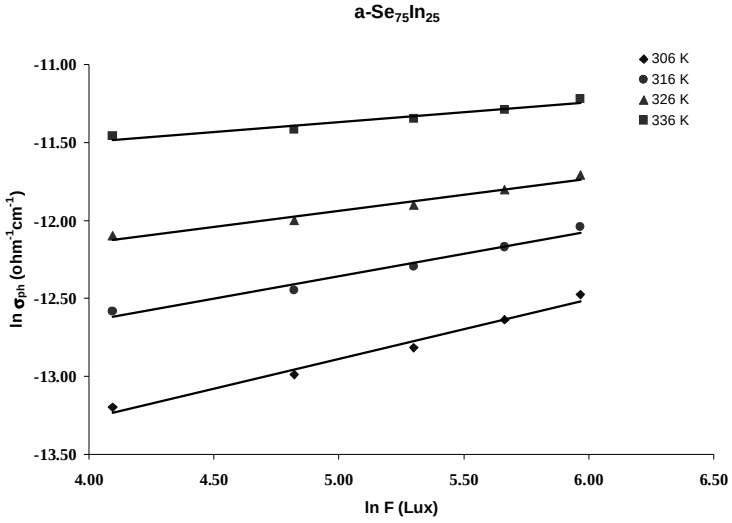

Fig. 6. Intensity dependence of photoconductivity in amorphous thin films of $Se_{75}In_{25}$ at different temperatures.

3.2.3 Composition dependence of photoconductivity

The values of photoconductivity at a particular temperature (306 K) and intensity 390 Lux are given in Table 2 and plotted as a function of x in in amorphous thin films of $Se_{75}In_{25-x}Pb_x$ in Fig. 7. This figure shows that a discontinuity in σ_{ph} vs x curves occurs at x = 4.

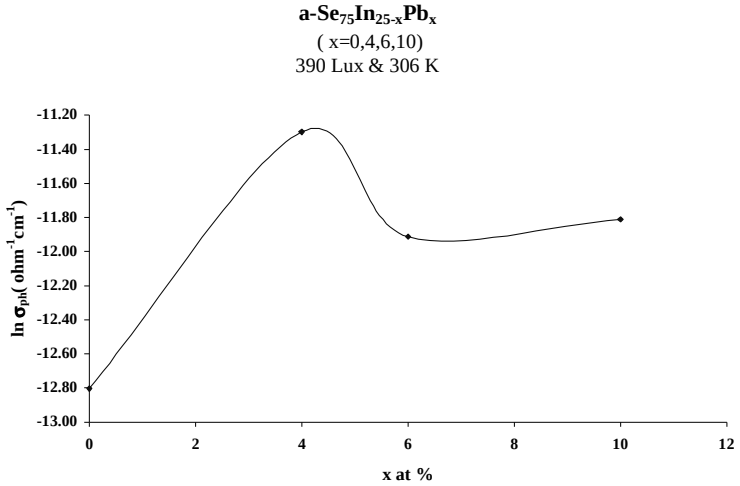

Fig. 7. ln σ_{ph} vs x in amorphous thin films of $Se_{75}In_{25-x}Pb_x$.

The important parameter in photoconductivity measurements is photosensitivity σ_{ph}/σ_d at a particular temperature and intensity. The value of this parameter for a particular material decides the use of the material in the photoconductivity devices. We have, therefore, calculated the value of σ_{ph}/σ_d at a particular temperature 306 K and intensity 390 Lux. These values are given in Table 2 and plotted in Fig. 8 as a function of x in amorphous thin films of $Se_{75}In_{25-x}Pb_x$. It is interesting to note that a discontinuity in σ_{ph}/σ_d also occurs around x = 4. It may be mentioned here that such type of discontinuity at x = 4 was observed in dc conduction parameters (σ_d, ΔE and σ_0) also as reported in earlier section (see Figs. 2 - 4).

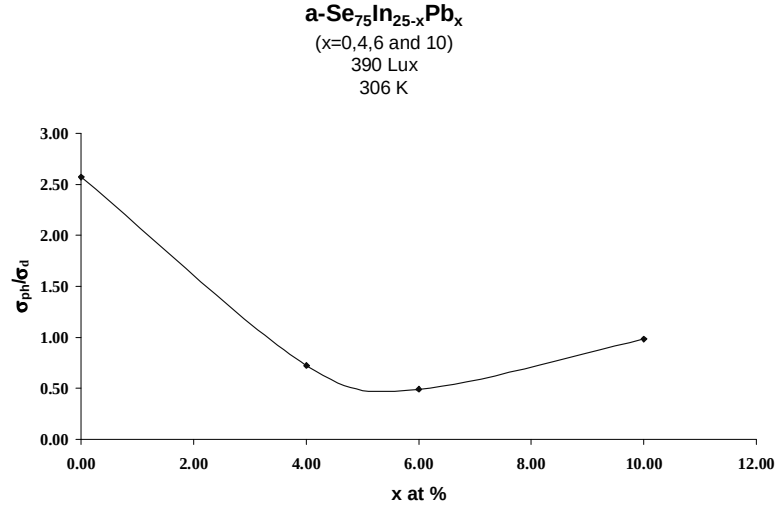

Fig. 8. σ_{ph}/σ_d vs x in amorphous thin films of $Se_{75}In_{25-x}Pb_x$.

Such type of discontinuities in the composition dependence of various physical parameters, have been observed in chalcogenide glasses by various workers and are related to a mechanical threshold at a critical composition where the network changes from an elastically floppy (polymeric glass) type to a rigid (amorphous solid) type [15]. This threshold occurs when the average coordination number <Z> becomes 2.4 at that particular composition. In the present case, a discontinuity in various electrical parameters occurs at a glass composition $Se_{75}In_{21}Pb_4$. The average coordination number for this composition comes out to be 2.3, which is very close to the value <Z>=2.4 expected for the above mechanical threshold. The maxima observed in the present case may therefore be related to the above mentioned structural transition.

Table 2. Photoconduction parameters in a- Se_{75} In_{25-x} Pb_x thin films at 306 K and 390 Lux.

Glassy Alloy	σ_{ph} (Ω^{-1} cm^{-1})	σ_d (Ω^{-1} cm^{-1})	σ_{ph}/σ_d
$Se_{75}In_{25}$	2.75×10^{-6}	1.07×10^{-6}	2.57
Se_{75} $In_{21}Pb_4$	1.24×10^{-5}	1.72×10^{-5}	0.72
Se_{75} $In_{19}Pb_6$	6.70×10^{-6}	1.37×10^{-5}	0.49
Se_{75} $In_{15}Pb_{10}$	7.43×10^{-6}	7.57×10^{-6}	0.98

3.3 Transient photoconductivity

To measure the rise and decay of photoconductivity with time, thin film samples were mounted in the same metallic sample holder and light of desired wavelength was shown through a transparent window. After a certain time of exposure, the light was turned off and the decay of current was measured as a function of time. The initial dark value of current was subtracted to obtain photoconductivity during decay.

Fig. 9 shows the results of the rise of photoconductivity with time in a-$Se_{75}In_{21}Pb_4$ thin films at different temperatures. The ratio σ_{ph}/σ_d has been plotted in Fig. 9, which shows that initially the photocurrent rises very fast and then rises slowly before saturating at a particular value. This figure also indicates that the values of σ_{ph}/σ_d are smaller at higher temperatures at all the times during the rise process. Similar results were found in other glassy alloys also (results not shown here).

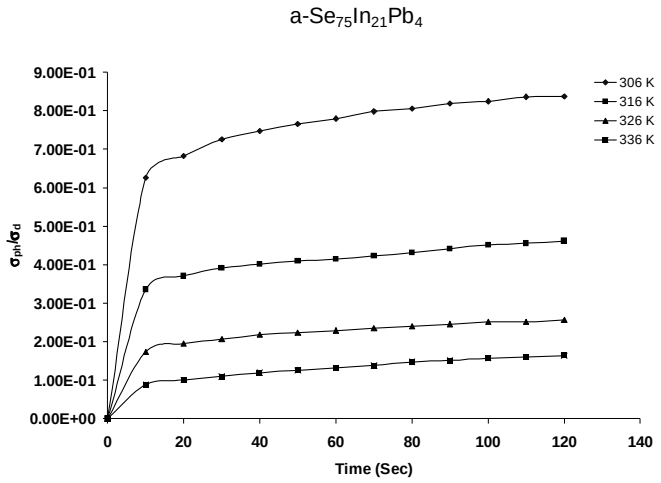

Fig. 9. Rise of photoconductivity with time at different temperatures in a- Se_{75} $In_{21}Pb_4$.

The decay of photoconductivity in a-$Se_{75}In_{21}Pb_4$ is shown in Fig. 10. It is clear from this figure that the decay curve has two components. The first component decays very fast and the second one is very slow and takes about 8 minutes time to saturate at a particular value. A persistent photoconductivity is also observed at each temperature. Similar results are also found in other glassy alloys.

Fig. 10 shows that the behavior of the decay curves is similar at different temperatures except that the persistent photoconductivity increases as temperature of measurement increases. This is observed in all the glassy samples studied here.

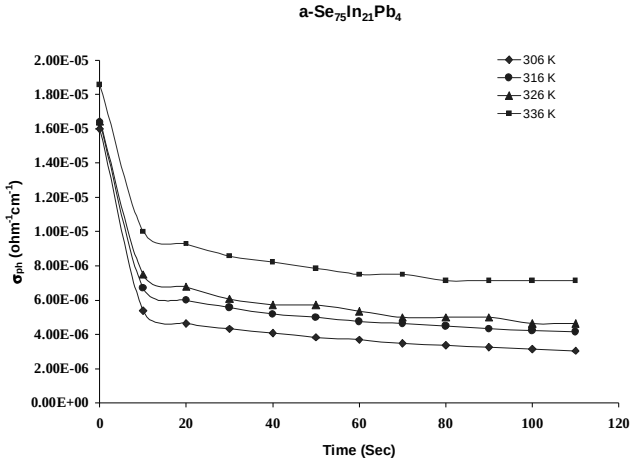

Fig. 10. Decay of photoconductivity with time at different temperatures in a- Se_{75} $In_{21}Pb_4$.

The persistent photoconductivity is observed in other chalcogenide glasses by many workers [16-18] and is attributed to some kind of photo- induced structural changes and may not be due to trapping of charge carriers in the traps because of the large time constants involved.

To understand the trapping effects, the persistent photoconductivity is subtracted from the measured photoconductivity, and then the natural log of corrected photoconductivity is plotted against time at different temperatures in Fig. 11. These curves must be straight lines in case of single trap level. However, in the present case, these curves are not having same slope but the slope goes on decreasing continuously as the time of decay increases (see Fig. 11). This indicates that the traps exist at all the energies in the band gap which have different time constant and hence giving the non-exponential decay of photoconductivity. This indicates the presence of a continuous distribution of localized states in the mobility gap of the present glassy alloys. The similar conclusion was drawn from the intensity dependence of the steady state photoconductivity measurements.

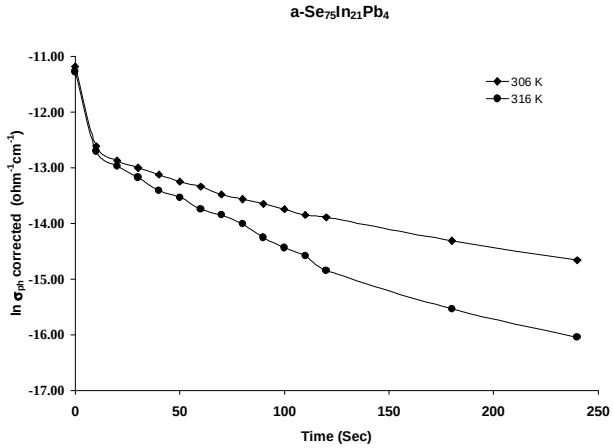

Fig. 11. Logarithmic photoconductivity as a function of time in a- $Se_{75}In_{21}Pb_4$ after subtracting persistent photoconductivity.

To analyze the decay curves in case of non-exponential decay, we prefer to use the concept of differential lifetime suggested by Fuhs and Stuke [19] which is given as:

$$\tau_d = [\ (d \ln \sigma_{ph} / dt)\ ]^{-1} \quad (2)$$

In the case of exponential decay, the differential lifetime will be equal to the carrier lifetime. However, in case of a non-exponential decay τ_d will increase with time and only the value at t = 0 will correspond to the carrier lifetime.

From the slope of ln σ_{ph} vs time curves, we have calculated the values of τ_d using equation (2) at various times of the decay curves of Fig. 11. The results have been plotted in Fig. 12 in case of a- $Se_{75}In_{21}Pb_4$ at two different temperatures 306 K and 316 K. The results for other samples were of the same nature.

It is clear from Fig. 12 that τ_d increases with the increase of time. This confirms the non-exponential decay in the present case as, for an exponential decay τ_d should be constant with time. A decrease of τ_d with increasing temperature (see Fig. 12) is consistent with the decay of photoconductivity in presence of traps [14].

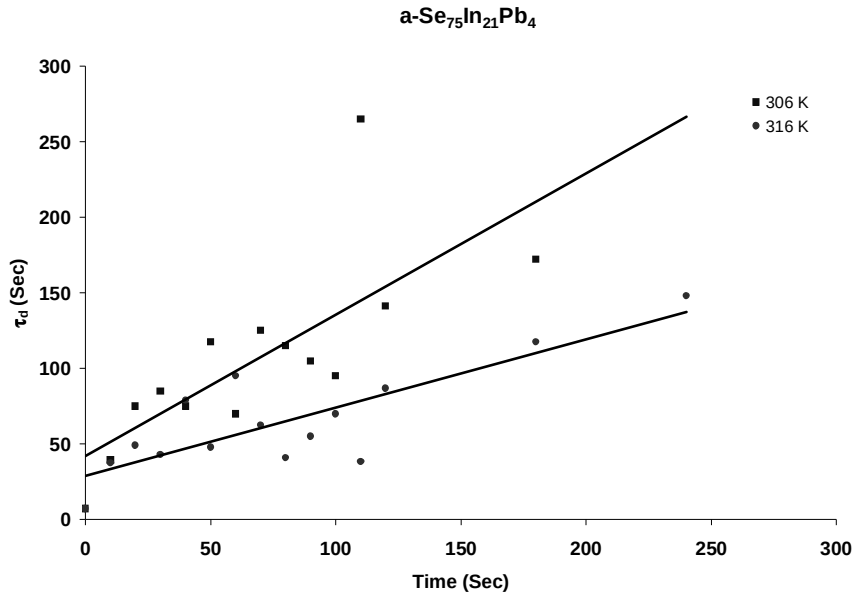

Fig. 12. Differential life time as a function of time at different temperatures in a- $Se_{75}In_{21}Pb_4$.

4. Conclusions

Temperature dependence of dark and steady state photoconductivity is studied in amorphous thin films of $Se_{75}In_{25-x}Pb_x$ (x = 0, 4, 6 and 10), prepared by vacuum evaporation technique, in the temperature range 306 K to 336 K.

Temperature dependence of photoconductivity measurements at different intensities indicate that photoconductivity is also thermally activated in the above temperature range in all the samples studied as in case of dark conductivity. The activation energy of photoconduction is found to be much smaller as compared to activation energy in dark. The well defined activation energies involved in the temperature dependence of photoconductivity suggests that the recombination centers are located at relatively discrete levels of localized states.

The behavior of photoconductivity is found to be same in all the compositions except that the photoconductive parameters show a discontinuity at a Pb concentration of 4 at %. This is explained in terms of mechanically stabilized structure at a particular average coordination number

following the theory of Phillips and Thorpe for the topological model in case of chalcogenide glasses.

Transient photoconductivity measurements at different temperatures indicate that decay of photoconductivity has two components. Initially it is very fast and then become quite slow. This component is found to be non- exponential in the present case indicating the presence of continuous distribution of defect states. A persistent photocurrent is also observed which increases at higher temperatures. This is attributed to light induced effects in these materials. An analysis of non-exponential decay of photoconductivity is done by the differential life time concept which is consistent with the kinetics of photoconduction in presence of traps.

References

[1] N. F. Mott, E. A. Davis. Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, (1979).
[2] M. Kastner, D. Adler, H. Fritzsche, Phys Rev Lett. **37**, 1504 (1976).
[3] M. Katner, J. Non-Cryst. Sol. **31**, 223 (1978).
[4] D. Adler, E. J. Yoffa, J. Phys. Rev. Lett. **36**, 1197 (1976).
[5] N. F. Mott, Philos. Mag. **34,** 1101 (1976); **36,** 413 (1977).
[6] N. Thoge, Y. Yamamoto, T. Minami, M. Tanaka, Appl. Phys. Lett. **34,** 640 (1979).
[7] N. Thoge, T. Yonesaka, T. Minami, J. Appl. Phys. **58**, 4225 (1985).
[8] K. L. Bhatia, G. Parthasarthy, A. Sharma, E. S. R. Gopal, Phys. Rev. **B 38,** 6342 (1988).
[9] K. L. Bhatia, J Non-Cryst Sol. **58,** 151 (1983).
[10] N. Thoge, H. Matsuo, T. Minami. J. Non-Cryst. Sol. **95/96,** 809 (1987).
[11] K. L. Bhatia, S. K. Malik, N. Kishore, S. P. Singh, Phil. Mag. **B 66,** 587 (1992).
[12] S. Kohli, V. K. Sachdev, R. M. Mehra, P. C. Mathur. Phys. Stat. Sol.(b) **209,** 389 (1998).
[13] R. M. Mehra, S. Kohli, A. Pundir, V. K. Sachdev, P. C. Mathur, J. Appl. Phys. **81,** 7842 (1997).
[14] A. Rose, Concept in Photoconductivity (Interscience, New York) 1963.
[15] J. C. Phillips, J. Non-Cryst. Sol. **34**, 153 (1979).
[16] I. Watanabe, T. Sekiya, Jap. J. Appl. Phys. **28,** 638 (1989).
[17] S. K. Srivastava, P. K. Dwivedi, A. Kumar, Physica B. **183,** 409 (1993).
[18] M. Dixit, A. Kumar, Physica B. **252,** 286 (1998).
[19] W. Fuhs, J. Stuke, Phys. Stat. Solidi. **27,** 171 (1968).