

Pre-exponential factor in $a\text{-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films

D KUMAR and S KUMAR*

Department of Physics, Christ Church College, Kanpur 208 001, India

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Abstract. Temperature dependence of d.c. conductivity is studied in $a\text{-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films where x is varied from 0–10. From these measurements, the values of the pre-exponential factor (S_0) and activation energy (ΔE) are calculated for each glassy alloy. An approximate linear dependence of $\ln S_0$ on ΔE is observed in this glassy system with good agreement between the expected and calculated S_0 values using Meyer–Neldel rule. Linear dependence of $\ln S_0$ on ΔE in case of amorphous materials indicates that the conduction band tails a finite energy distance towards the valence band and Fermi level is controlled by fixed dominant hole levels deeper in the gap.

Keywords. Chalcogenide glasses; Meyer–Neldel rule; conductivity pre-exponential factor.

1. Introduction

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 (Mott and Davis 1979). These systems also contain positively and negatively charged defect states, known as valence alternation pairs (VAPs) (Kastner *et al* 1976) which essentially pin the Fermi level at the middle of the band gap making them rather insensitive to doping. It is known that certain charged additives could change the ratio of VAPs to such an extent that the Fermi level can get unpinned (Mott 1977).

In spite of the above problem, p to n transition has been reported in these glasses. Bi (Thoge *et al* 1979) and Pb (Thoge *et al* 1987; Mehra *et al* 1997) 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 chalcogenide glasses which exhibit p – n transition at $\text{Pb} \geq 5$ at % (Thoge *et al* 1987; Bhatia *et al* 1992; Mehra *et al* 1997; Kohli *et al* 1998). Therefore, in the present work, we have chosen a non-Ge system ($a\text{-Se}_{75}\text{In}_{25-x}\text{Pb}_x$), which exhibits p – n transition, for the study of pre-exponential factor variation as a function of activation energy. Temperature dependence of d.c. conductivity is studied in various amorphous alloys in the above glassy system.

2. Experimental

Glassy alloys of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ were prepared by quenching technique. High purity (99.999%) materials were

weighed according to their atomic percentages and sealed in quartz ampoules (length, ~ 5 cm and internal dia, ~ 8 mm) with a vacuum $\sim 10^{-5}$ Torr. The ampoules containing the constituent materials were heated to 1000°C and held at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate of $3\text{--}4^\circ\text{C}/\text{min}$. During heating, all the ampoules were constantly rocked by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogenous glassy alloys.

After rocking for about 10 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ were taken out by breaking the quartz ampoules. The amorphous nature of the prepared alloys and their thin films was ascertained by X-ray diffraction patterns, which do not show any sharp Bragg diffraction peaks.

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

Before measuring d.c. conductivity, the films were first annealed at 340 K for 1 h in a vacuum, $\sim 10^{-2}$ Torr. I – V characteristics were found to be linear and symmetric up to 30 V. The present measurements were, however, made by applying only 2 V across the films. The resulting current was measured by a digital Pico-Ammeter. The heating rate was kept quite small (0.5 K/min) for these measurements.

For d.c. conductivity measurements, vacuum evaporated thin films of $a\text{-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ were mounted in a specially designed sample holder. The temperature of the films is controlled by mounting a heater inside the sample

*Author for correspondence

holder and measured by a calibrated copper-constantan thermocouple mounted very near to the films.

3. Results and discussion

Semiconductors exhibit an exponential dependence of conductivity (S) on temperature following the relation

$$S = S_0 \exp(-\Delta E/kT). \quad (1)$$

For many classes of materials, experimental evidence suggested that a correlation exists between ΔE and S_0 which is given by

$$S_0 = S_{00} \exp(\Delta E/kT_0), \quad (2)$$

where S_{00} and T_0 are constants. Equation (2) is often referred to as Meyer–Neldel (MN) rule. This rule, in which all S curves cross at the same temperature T_0 , was first observed for a variety of organic substances e.g. polynuclear hydrocarbons and phthalocyanines (Gutman and Lynos 1967) and also in a wide variety of single-crystal and polycrystalline semiconductors (Meyer and Neldel 1937). In the class of amorphous semiconductors, the Meyer–Neldel rule has been reported for a -Si:H films in which ΔE is varied by doping, by surface absorption, or by light soaking (Staebler and Wronski 1977; Carlson and Wronski 1979; Spear *et al* 1980). Such type of effect has also been observed in chalcogenide glasses (Arora and Kumar 1991; Yelon and Movaghar 1997; Dwivedi *et al* 1998).

To see the above type of correlation, we have made electrical conductivity measurements as a function of temperature in various compositions in $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ glassy system, where x is taken as 0, 4, 6 and 10. Results of these measurements are shown in table 1. It is clear from this table that, at all the temperatures of measurements, the value of S_0 first increases with the addition of Pb, becomes maximum at 4 at % and then starts decreasing with further addition of Pb up to 10 at %. 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 (Phillips 1979). This threshold occurs when the average coordination number $\langle Z \rangle$ becomes 2.4 at that particular composition. In the present case, a maximum in conductivity occurs at a glass composition $\text{Se}_{75}\text{In}_{21}\text{Pb}_4$. The average coordination number for this composition comes out to be 2.3, which is very close to the value of $\langle Z \rangle = 2.4$ expected for the above mechanical threshold. The maximum observed in the present case may, therefore, be related to the above mentioned structural transition.

Figure 1 plots the results of conductivity measurements. It is clear from the figure that $\ln S$ vs $1000/T$ curves are straight lines showing the validity of (1) in the present case. This indicates that conduction is through an activated process having single activation energy for all the glassy alloys in the operating range of temperatures (306–336 K).

From the slope of $\ln S$ vs $1000/T$ curves, the values of ΔE and S_0 were calculated for each glassy alloy. The values of these parameters are given in table 2. Mott and Davis (1979) pointed out that the value of S_0 may distinguish the conduction whether it is in the extended states or in localized states. For the extended state conduction, the value of S_0 lie in the range 10^3 – $10^4 \Omega^{-1} \text{cm}^{-1}$, whereas for hopping conduction in localized states the value of S_0 is much smaller than this range. In the present case, the values of S_0 are more than $10^4 \Omega^{-1} \text{cm}^{-1}$, which indicates that conduction in the present samples is in extended states in the measured temperature range.

Figure 2 shows a plot of $\ln S_0$ vs ΔE which is found to be a straight line showing the validity of (2). The slope of this line yields the values of $(kT_0)^{-1} = 19.7 (\text{eV})^{-1}$ and $S_{00} = 5.85 \times 10^{-1} (\Omega^{-1} \text{cm}^{-1})$ for the present glassy system. Using these values, the expected S_0 values have been calculated and compared with the reported values (see table 2). An overall good agreement between the last two columns confirms the validity of (2).

Table 1. Temperature dependence of d.c. conductivity in a - $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films.

Temperature (K)	S ($\Omega^{-1} \text{cm}^{-1}$)			
	$\text{Se}_{75}\text{In}_{25}$	$\text{Se}_{75}\text{In}_{21}\text{Pb}_4$	$\text{Se}_{75}\text{In}_{19}\text{Pb}_6$	$\text{Se}_{75}\text{In}_{15}\text{Pb}_{10}$
306	5.36×10^{-7}	1.72×10^{-5}	1.07×10^{-5}	4.82×10^{-6}
311	6.79×10^{-7}	2.36×10^{-5}	1.51×10^{-5}	6.79×10^{-6}
316	1.14×10^{-6}	3.35×10^{-5}	2.21×10^{-5}	9.29×10^{-6}
321	1.71×10^{-6}	4.43×10^{-5}	3.01×10^{-5}	1.33×10^{-5}
326	2.5×10^{-6}	6.25×10^{-5}	4.26×10^{-5}	1.99×10^{-5}
331	3.93×10^{-6}	7.93×10^{-5}	5.57×10^{-5}	2.77×10^{-5}
336	6.43×10^{-6}	1.18×10^{-4}	7.14×10^{-5}	4.07×10^{-5}

A model of thermally excited electron tunneling leading to an activated mobility was suggested by Many *et al* (1955) to explain the MN rule. Eley (1967) and Kemeny

and Rosenberg (1970) also considered the mechanism of tunneling of carriers with high effective mass through intermolecular barriers. However, no quantitative agreement

Table 2. Electrical parameters in $a\text{-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films.

Glassy alloy	ΔE (eV)	$(kT_0)^{-1}$ (eV) ⁻¹	S_{00} ($\Omega^{-1}\text{cm}^{-1}$)	S_0 ($\Omega^{-1}\text{cm}^{-1}$)	$S_0 = S_{00} \exp$ $[\Delta E/kT_0]$
$\text{Se}_{75}\text{In}_{25}$	0.72	19.7	5.85×10^{-1}	8.05×10^5	8.46×10^5
$\text{Se}_{75}\text{In}_{21}\text{Pb}_4$	0.54	19.7	5.85×10^{-1}	2.67×10^4	2.44×10^4
$\text{Se}_{75}\text{In}_{19}\text{Pb}_6$	0.55	19.7	5.85×10^{-1}	2.44×10^4	2.97×10^4
$\text{Se}_{75}\text{In}_{15}\text{Pb}_{10}$	0.61	19.7	5.85×10^{-1}	1.12×10^5	9.70×10^4

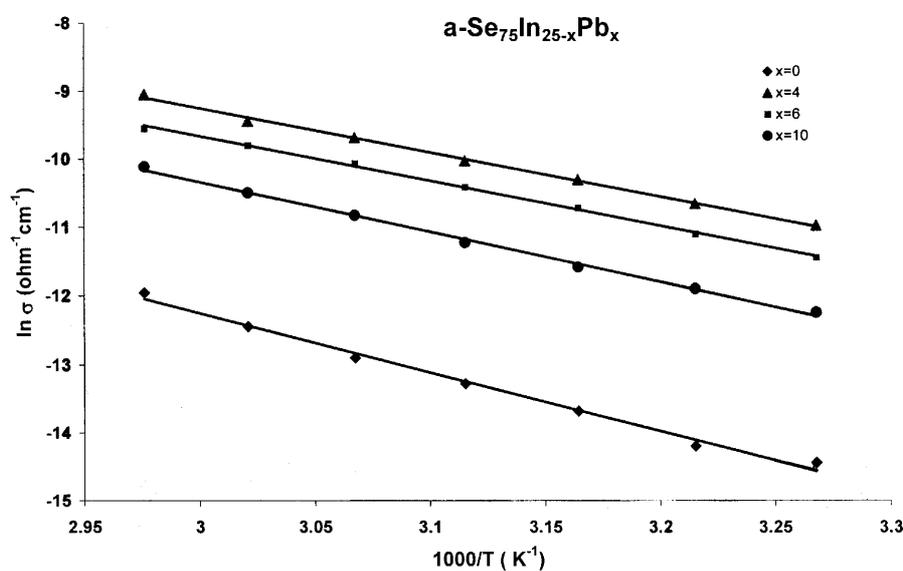


Figure 1. Temperature dependence of d.c. conductivity for $a\text{-Se}_{75}\text{In}_{25-x}\text{Pb}_x$ ($0 \leq x \leq 10$).

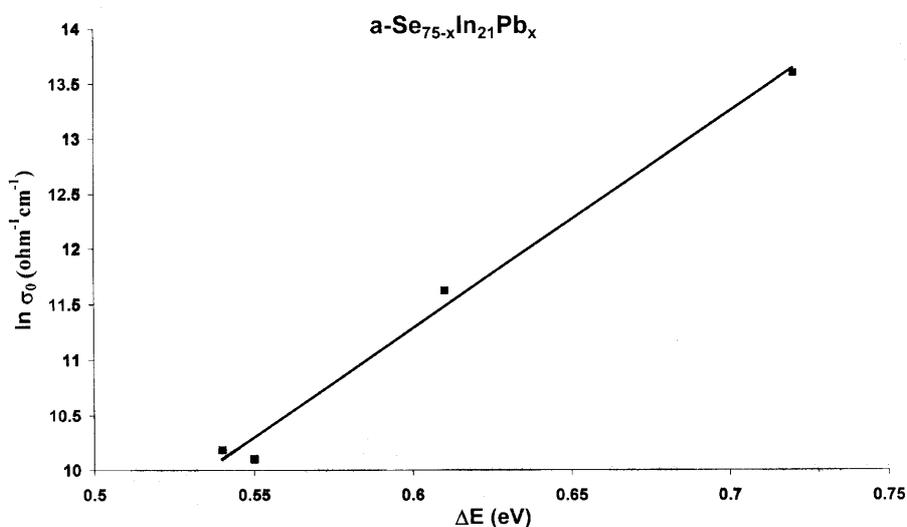


Figure 2. Plot of $\ln S_0$ vs ΔE for $a\text{-Se}_{75-x}\text{In}_{21}\text{Pb}_x$ ($0 \leq x \leq 10$).

was obtained with experimental data. Roberts (1971) gave a model to explain the MN rule as a consequence of some basic features in the band structure of a solid. According to this model, if the conduction band tails off exponentially a finite energy distance towards the valence band and the Fermi level is also controlled by a fixed dominant hole level deeper in the gap, the MN rule follows in the expression for the density of free carriers.

Evidence for the validity of the MN rule in the present glasses is quite likely as the Fermi level is controlled by localized states in certain energy ranges.

4. Conclusions

From the present results one can conclude that in a $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ system the MN rule is obeyed which indicates that their valence and conduction bands tails off exponentially with energy. The second inference that can be drawn from the observation of the MN rule on the basis of Roberts (1971), is that these glasses are wide band gap materials where some localized states within the band gap tend to become dominant by controlling the carrier statistics and leading to non-extrinsic conduction. That the position of Fermi level is controlled by the mid gap localized states in these materials is also supported by a.c. conductivity measurements on these glasses (Guintini *et al* 1981; Goyal *et al* 1982; Arora and Kumar 1989; Arora *et al* 1990).

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