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Carrier type reversal in Pb modified $Se_{80}In_{20}$ semiconducting glassy alloys

Indra Sen Ram[a], Jagjiwan Ram[a] & Kedar Singh[b,c]*

[a]Department of Physics, Dyal Singh College, University of Delhi, New Delhi 110 003, India
[b]Department of Physics, Ban aras Hindu University, Varanasi 221 005, India
[c]School of Physical Science, Jawaharlal Nehru University, New Delhi 110 067, India

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The effective thermal conductivity (λ_e), effective thermal diffusivity (χ_e) and specific heat per unit volume (ρC_p) of twin pellets of $Se_{80}In_{20-x}Pb_x$ (x = 0, 5, 10 and 15) glasses have been measured at room temperature by using transient plane source (TPS) technique. All three parameters have been varied with Pb content and show reversal trend for 5 at. wt.% of Pb. This reversal trend can be explained on the basis of carrier type reversal as a consequence of unpinning of the Fermi level due to incorporation of Pb in Se-In glassy system.

Keywords: Thermal conductivity, Thermal diffusivity, Fermi level, Carrier type reversal

1 Introduction

Chalcogenide glasses are vitreous material consist of one or more chalcogen elements of group VI of the period table. Their physical properties are varying with chemical compositions[1]. These glasses have many useful properties and have recently drawn a great attention due to their use in solid state and optoelectronics devices[2,3].

The thermal transport properties of a material in bulk form provide useful consequence from structural point of view[4]. Thermal transport properties such as thermal conductivity, thermal diffusivity and specific heat of materials depend on the scattering behavior of phonons with lattice defects, impurities and dislocations present in them[5]. Thermal transport properties of materials in the crystalline and liquid state have been well investigated and known for long time, whereas these investigations in amorphous materials are not so well studied yet. These properties are significant to understand the dissipation of heat in the opto-electronic and solid state devices, as well as they can provide information about the thermal degradation of chalcogenide materials.

In general, chalcogenide glasses are known to be amorphous *p*-type semiconductors[6,7] owing to the number of holes excited below the valence band mobility edge and their lifetime are larger than the number of electrons excited above the conduction band mobility edge and their lifetime. The earlier studies show that the addition of certain heavy elemental metallic impurities[8,9] like Bi and Pb in certain chalcogenide glassy systems, at a particular concentration of impurity, the conduction mechanism begins to change from *p* to *n*-type. This phenomenon is called carrier type reversal (CTR), this occurs due to unpinning of the Fermi level and consequent enhancement in electron density in the system. This property may be helpful in designing *p*-*n* junctions with higher rectification proportion.

Nowadays, our laboratory is involved in study of thermal transport properties along with other physical properties of various chalcogenide glassy systems. Some works on these properties already have reported by our group[5,10-14]. In our recent studies, we have reported the crystallization kinetics[15], glass transition kinetics[16] and dielectric relaxation[17] in $Se_{80}In_{20-x}Pb_x$ glassy systems.

In the present work an attempt has been made to study the variation of thermal transport properties like thermal conductivity, thermal diffusivity and specific heat per unit volume of $Se_{80}In_{20-x}Pb_x$ glassy systems at room temperature. The purpose of present investigation is to determine the effect of Pb content on the thermal transport properties of Se-In glassy system. The thermal conductivity, thermal diffusivity, specific heat per unit volume is measured simultaneously by using transient plane source technique (TPS), as discussed by Gustafsson[18].

*Corresponding author (E-mail: kedarbhp@rediffmail.com)

2 Experimental Details

The bulk $Se_{80}In_{20-x}Pb_x$ (x = 0, 5, 10 and 15) chalcogenide glasses were prepared from high purity (99.999%) Se, In and Pb elements by the melt quenched technique as described in our earlier work[15]. The amorphous nature of prepared samples is confirmed from XRD patterns in our earlier work[15]. The modification of chemical bonds due to incorporation of Pb in $Se_{80}In_{20}$ glassy system is confirmed from Raman spectra in our previous work[17]. Thermal transport properties of as prepared samples were measured with transient plane source (TPS) (Model: TPS 2500 S). For this, samples were pressed into cylindrical pellet forms having diameter 10 mm and thickness around 1.0 mm under uniform load of 5 tons using hydraulic press. The TPS sensor is sandwiched between two pellets of same material in sample holder and surfaces of these pellets were made smooth in order to ensure good thermal contact between sample and sensor. The power output to the sample is adjusted according to the nature of materials and it is kept in range 0.01-0.02 W/cm^2 for chalcogenide glasses. The TPS sensor is made up of a 10 μm thick nickel foil (resistance~ 5.286 Ω at room temperature and a temperature coefficient of resistance (TCR) ~ 4.6×10^{-3} K^{-1}) with an insulating layer of 50 μm thick kapton, on each side of metal pattern.

3 Results and Discussion

The effective thermal transport properties (thermal conductivity, thermal diffusivity and specific heat per unit volume) of $Se_{80}In_{20-x}Pb_x$ (x = 0, 5, 10 and 15) glasses were measured at room temperature by using TPS technique. The variations of thermal conductivity and thermal diffusivity with Pb concentration are shown in Figs 1 and 2, respectively. Both thermal conductivity and thermal diffusivity show a reversal trend at 5 at. wt.% of Pb and each has a minimum value for that composition. This reversal trend can be explained on the basis of carrier type reversal due to incorporation of Pb in $Se_{80}In_{20}$ glassy system.

The carrier type reversal in $Se_{80}In_{20-x}Pb_x$ glassy systems can be explained as follows; The total density of valence alternation pairs (N) is calculated by the following relation[19]:

$$N = [Se_3^+] + [Se_1^-] \quad \ldots (1)$$

Where, Se is the chalcogen atom used in present study. The superscript denotes the formal charge on the Se and subscript represents the number of covalent bonds by which Se is linked to other atoms. Without a metallic additive, the positively and negatively charged native defects are equal in number, i.e., ($[Se_3^+] = [Se_1^-]$) and $N = 2N_0$, where N_0 is the concentration of individual native charged defects.

Also, the density of native VAPs equilibrating at the quenching or glass transition temperature (T_g) is estimated as follows:

$$N_0^2 = [Se_3^+]\,[Se_1^-] = N_A^2 \exp(-E_{VAP}/kT_g) \quad \ldots (2)$$

Where, N_A is the density of Se and E_{VAP} is the amount of energy needed to create a valence alternation defect pair from a normally bonded Se. If n and n_0, are electron density in the presence and absence of Pb additives, respectively, two are related by following relation[20]:

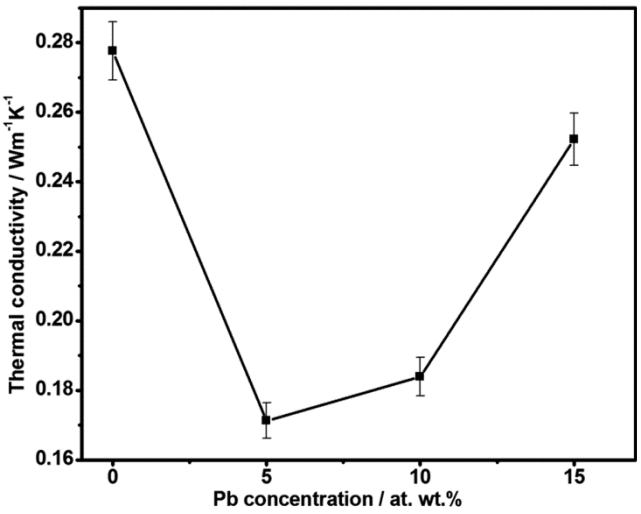

Fig. 1 — Effective thermal conductivity versus Pb concentration.

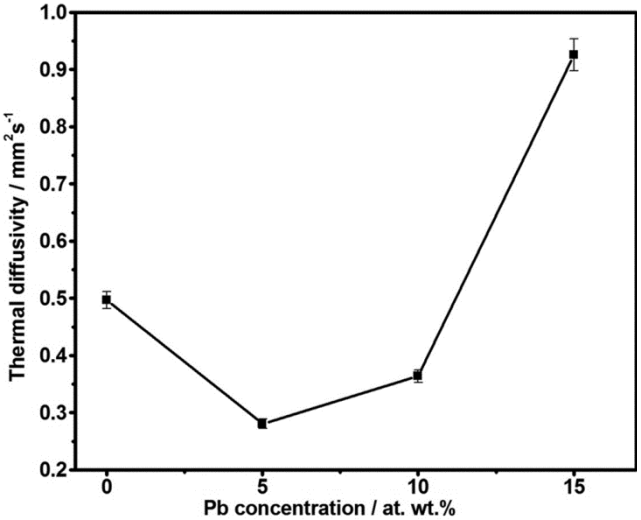

Fig. 2 — Effective thermal diffusivity versus Pb concentration.

$$n^2[Se_3^+] / [Se_1^-] = N_c^2 \exp(-2\varepsilon_n / kT) = n_0^2 \quad \ldots (3)$$

Where N_c is the effective density of conduction band states and ε_n is the electron activation energy. This is related with the mobility gap (E_g) as $\varepsilon_n \approx E_g/2$. It is considered that metallic additives like Pb equilibrate at T_g and create positive centers of concentration $[Pb^+]$. In order to estimate the thermal activation energy for various concentrations of $[Pb^+]$, the total density of valence alternation centers (N_0) that equilibrate with $[Pb^+]$ throughout the glass transition, which remains unaltered in the range of interest ($T < T_g$), should be determined.

Further assuming that $n_0 << N_0$, the defects density after the addition of Pb atoms into the chalcogenide glass can be estimated as follows[20]:

$$[Se_3^+]^* = -1/2\,[Pb^+] + (N_0^2 + 1/4\,[Pb^+]^2)^{1/2} \quad \ldots (4)$$

$$[Se_1^-]^* = 1/2\,[Pb^+] + (N_0^2 + 1/4\,[Pb^+]^2)^{1/2} \quad \ldots (5)$$

Total density of VAPs after addition of Pb atoms, N_m is given by:

$$N_m = [Se_3^+]^* + [Se_1^-]^* = 2\,(N_0^2 + 1/4\,[Pb^+]^2)^{1/2} \quad \ldots (6)$$

It is clear from Eq. (6) that the density of Pb additives has to approach or exceed N_0 to facilitate any appreciable effect. The value of n, after incorporation of the additive Pb can be estimated as follows:

$$n^2\,(2\,N_0^2/[Pb^+] + n) = 2\,[Pb^+]\,n_0^2 \quad \ldots (7)$$

For low Pb concentrations, Eq. (7) can take the form:

$$n = [Pb^+]\,n_0 / N_0 \quad \ldots (8)$$

Whereas, for high Pb concentrations, Eq. (7) can take the form:

$$n = (2[Pb^+])^{1/3}\,n_0^{2/3} \quad \ldots (9)$$

These expressions clearly, indicate that electron density increases due to incorporation of Pb in present chalcogenide glassy system.

In the $Se_{80}In_{20-x}Pb_x$ glassy systems, the addition of Pb in Se-In glassy system converts some of Se_3^+ centers into Se_1^- centers. Consequently, the number (concentration) of Se_3^+ centers that can undergo thermal excitation as per model of Kolobov *et al.*[21] decreases. Thereby a decrease in the number of free holes formed by the conversion of Se_3^+ centers into Se_1^- centers. Also, the number of traps that can capture electrons excited into the conduction band decreases with the decrease in the number of Se_3^+ centers. This causes an overall increase in the electron density in the system. Besides, the number of shallow acceptors that capture holes from the valence band enhances due to increase in the number of Se_1^- charged defect states. These two effects collectively shift the Fermi level towards the conduction band resulting in *p* to *n* transition at a particular concentration of Pb.

The carrier type reversal (CTR) in the $Se_{80}In_{20-x}Pb_x$ glassy systems could also be explained on the basis of charged dangling bond model, when Pb is added to the Se-In network, the equilibrium between positively and negatively charged dangling bonds which pin the Fermi level near the middle of the gap gets affected[22]. As a result, the Fermi level gets unpinned and moves towards the conduction bands which results p to n transition at a particular concentration of Pb.

Further, the carrier type reversal (CTR) could be explained on the basis of formation of ionic Pb-Se bonds instead of covalent bonds at higher concentration[23] of Pb. The formation of ionic bonds disturbs the equilibrium between charge defects states, owing to shift in the Fermi level towards the conduction band, consequently *p* to *n*-type transition occur at a particular concentration of Pb.

Generally, thermal conductivity and thermal diffusivity show a decrease as system undergoes carrier type reversal[19]. Effective thermal conductivity and thermal diffusivity in chalcogenide glasses are subjugated by transport of heat by vibrational (phonon) modes of the glassy matrix (network). The mean free paths of the propagating phonon are limited by molecular vibrations and density of localized states in structure. On the other hand, electronic contribution to thermal resistance is rather small due to the low concentration of electrons in medium. Further, addition of Pb (> 5 at. wt. %) in the Se–In system causes increase in density of localized states in system, which is responsible for increase in values of thermal conductivity and thermal diffusivity for higher concentration of Pb. This type of reversal trends in electrical conductivity and dielectric parameters at 5 at. wt.% of Pb is already reported in our previous work[17].

Figure 3 shows the variation of specific heat per unit volume with Pb concentration. It is observed that the variation in specific heat per unit volume also

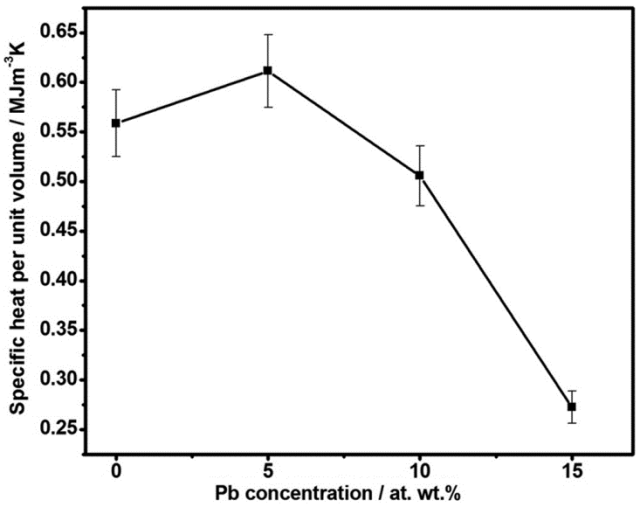

Fig. 3 — Specific heat per unit volume versus Pb concentration.

shows a reversal trend at 5 at. wt. % of Pb and has a maximum value for that composition. It suggests that glass containing 5 at. wt. % of Pb has availability of the large number of degrees of freedom. The decrease in value of specific heat per unit volume for higher concentration of Pb may be due to the non availability of the large number of degrees of freedom in these alloys, which could absorb heat energy[13].

4 Conclusions

Effective thermal conductivity and thermal diffusivity show reversal trend at 5 at. wt. % of Pb, this reversal trend could be explained on the basis of carrier type reversal due incorporation of Pb in $Se_{80}In_{20}$ glassy system. The occurrence of carrier type reversal in present systems has been explained on basis of electron density and unpinning of Fermi level. This type of reversal trend for electrical conductivity and dielectric parameters is also confirmed by dielectric relaxation study. The variation of specific heat per unit volume can be explained on the basis of availability of the large number of degrees of freedom in the systems.

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