

***n*-type conduction in Pb doped Se–In chalcogenide glasses**

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This paper reports on the *p* to *n* transition in Pb doped Se–In chalcogenide glasses. Measurements of thermoelectric power in the temperature range $300\text{ K} \leq T \leq 315\text{ K}$, dc conductivity in the temperature range $100 \leq T \leq 300\text{ K}$, and optical band gap (E_g^{opt}) have been carried out for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ ($x=0,5,10,15$) samples. The *p*-*n* transition occurs with very low addition of Pb impurity (5 at. %). The conductivity and pre-exponential factor also change by five to six orders of magnitude with Pb doping. Results are explained on the basis of the formation of ionic Pb–Se bonds, instead of covalent bonds. Formation of ionic bonds disturbs the equilibrium between the charged defect states of Se–In glass and unpins the Fermi level and thus leads to *n*-type conduction in these glasses. © 1997 American Institute of Physics. [S0021-8979(97)06011-8]

I. INTRODUCTION

Bulk chalcogenide glasses, obtained by quenching from melt, had long been considered to be undopable, characterized by *p*-type conduction. The Fermi level in these materials is essentially pinned since the added impurities do not alter the large charged defect concentration present in the forbidden gap and impurities enter the material in an alloying sense. However, in the recent past it has been observed that the addition of certain heavy metallic elemental impurities like Bi¹⁻⁶ and Pb⁷ to the bulk Ge based chalcogenide glasses can cause the *p*- to *n*-type transition.

Electrical, thermal, and optical properties of Se–In–Pb glasses are presently being investigated in this laboratory for their suitability as phase change material for the reverse phase change optical recording (RPCOR) memories. The composition was selected on the basis of certain calculations to have an alloy with higher thermal stability and minimum erase time. More details regarding the calculations and other properties pertinent to the RPCOR memories will be discussed in succeeding publications which are under preparation. The present article is the first in a series of such publications.

II. EXPERIMENT

Bulk samples of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ ($x=0,5,10,15$) glasses were prepared by quenching the melt in ice water using the procedure described elsewhere.⁸ Elements of 5N purity (Aldrich, USA) were used for the preparation of samples. The amorphous nature of the samples was confirmed by the absence of any sharp peak in the x-ray diffraction pattern. Compositional analysis was performed using electron probe microanalysis (EPMA). Thermopower studies have been performed on the bulk samples in the sandwich geometry using a conventional setup. The sample was placed between two copper electrodes. The temperature gradient, measured using a differential thermocouple, was established using two small heater wires electrically insulated but thermally connected to

the sample. DC conductivity measurements were performed on bulk samples in the sandwich geometry in the temperature range 100–300 K. A running vacuum of the order of 10^{-3} Torr was maintained in the cell during measurements. Optical band gap has also been estimated for these samples by measuring absorption coefficient as function of wavelength of light in the range 300–900 nm using a Shimadzu UV-VIS spectrophotometer. Optical band gap has been estimated by plotting $(\alpha h\nu)^{1/2}$ vs $h\nu$ and taking the intercept of the line on abscissa.

III. RESULTS

Compositional dependence of Seebeck coefficient, S (mV/K), for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ ($x=0,5,10,15$) samples is shown in the inset in Fig. 1. As seen in figure the thermopower reverses its sign from positive value to negative value at $x=5$ at. % and thereafter the magnitude of S increases with the increase in x values. Variation of S with the temperature is shown in Fig. 1. As seen in the figure, the Seebeck coefficient varies inversely as a function of temperature and can be expressed for extended state conduction as

$$S = \pm \frac{k}{e} \left(\frac{\Delta E_s}{kT} + A \right), \quad (1)$$

where “ e ” is the electronic charge, “ k ” the Boltzmann constant, “ T ” the absolute temperature, “ ΔE_s ” the activation energy for thermoelectric power (TEP), and “ A ” a constant dependent on the mechanism of the electrical transport; positive and negative signs represent the *p*- and *n*-type conduction mechanism, respectively. Composition dependence of ΔE_s is shown in Fig. 3(a). ΔE_s decreases with increased percentage of Pb impurity. ΔE_s values for $x=0,5,10,15$ are 0.72, 0.5, 0.39, and 0.32 eV, respectively.

DC conductivity measurements have been performed on the bulk samples in the temperature range 100–300 K. Variation of conductivity (σ) with Pb content at 273 K is shown in the inset in Fig. 2. It is observed that conductivity of Pb doped samples is several orders of magnitude larger than the undoped Se–In sample. Figure 2 shows the variation of conductivity with temperature. Curves representing the temperature variation of σ show two slopes. The change in

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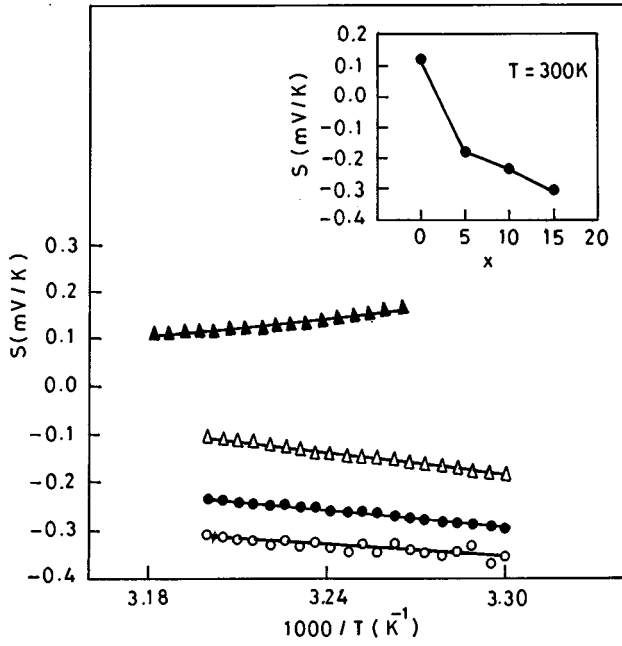


FIG. 1. Variation of Seebeck coefficient, $S(\text{mV/K})$ as a function of $1000/T$ (K^{-1}); (∇) $x=0$, (∇) $x=5$, (\bullet) $x=10$, (\circ) $x=15$ for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$. Inset shows the compositional dependence of S .

slope occurs at a temperature represented as T_s . Conductivity is thermally activated in the high temperature range $300\text{ K} > T > T_s$. However, below the temperature T_s , i.e., $T_s > T > 100\text{ K}$ the conductivity is dominated by localized state hopping conduction near the Fermi level E_F . Conductivity in the temperature range $300\text{ K} > T > T_s$ follows the Arrhenius equation

$$\sigma = \sigma_0 e^{-\Delta E_a / KT} \quad (2)$$

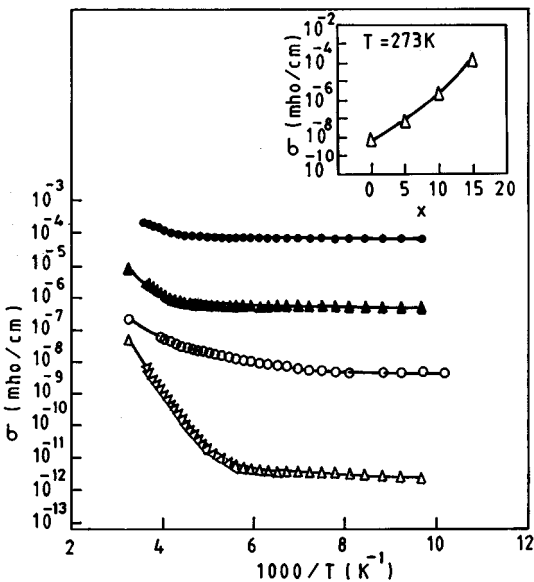


FIG. 2. Variation of dc conductivity (σ) as a function of $1000/T$ (K^{-1}) (∇) $x=0$, (\bullet) $x=5$, (∇) $x=10$, (\square) $x=15$ for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$. Inset shows the composition dependence of dc conductivity (σ) at 273 K .

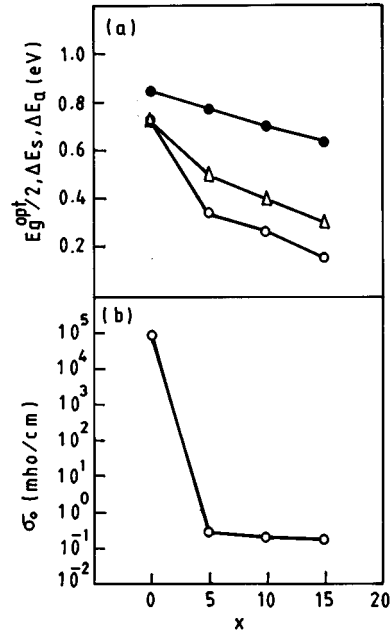


FIG. 3. (a) Composition dependence of (\bullet) optical band gap [$E_g^{\text{opt}}/2$]; (∇) activation energy for thermoelectric power [ΔE_s]; (\circ) dc activation energy for extended state [ΔE_a]. (b) Composition dependence of pre-exponential factor (σ_0).

The dc activation energy ΔE_a is calculated from the slope of $\ln \sigma$ vs $1/T$. Compositional dependence of ΔE_a is shown in Fig. 3(a). ΔE_a is found to decrease with an increase in Pb content. In the present case the $\Delta E_a \cong \Delta E_s$ for $x=0$, however for $x \geq 5$ at. % $\Delta E_a < \Delta E_s$. The value of the pre-exponential factor σ_0 for the samples is shown in Fig. 3(b). As seen in the figure the values of the pre-exponential factor decrease by five to six orders of magnitude with the addition of Pb 5 at. %.

The low temperature data, i.e., $T_s > T > 100\text{ K}$ was replotted as $\ln(\sigma\sqrt{T})$ vs $T^{1/4}$ in accordance with Mott's variable range hopping (VRH) relation

$$\sigma = \frac{\sigma_0}{\sqrt{T}} e^{-AT^{-1/4}}, \quad (3)$$

where $A^4 = T_0 = \lambda \alpha^3 / kN(E_F)$.

$N(E_F)$ is the density of localized states at E_F , λ the dimensional constant (≈ 18), α the decay constant of the wave function of localized states near E_F ($\approx 10^7\text{ cm}^{-1}$), and k the Boltzmann constant. The plot of $\ln(\sigma\sqrt{T})$ vs $T^{-1/4}$ shows a linear relationship.

We define hopping distance "R" as

$$R = \left(\frac{9}{8\pi\alpha kTN(E_F)} \right)^{1/4} \quad (4)$$

The variable range hopping distance has been calculated and is $\approx 10\text{ \AA}$ for these samples.

Figure 3(a) also shows the composition dependence of optical band gap (E_g^{opt}) estimated for these samples by measuring absorption coefficient as function of wavelength of light in the range 300–900 nm. As indicated in the figure, the optical band gap also decreases with the addition of Pb to the

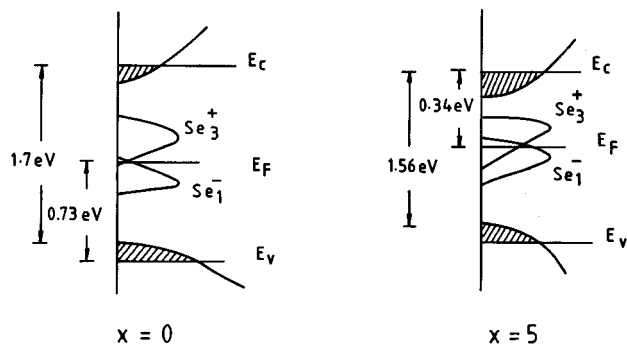


FIG. 4. Band gap picture for p -type ($x=0$) and n -type ($x=5$).

host Se–In matrix. It is observed that $2\Delta E_a$ is much less than E_g^{opt} for $x \geq 5$ at. % indicating that the Fermi level does not lie at around the center of the band gap.

IV. DISCUSSION

It is assumed that the dominant conduction in the $\text{Se}_{75}\text{In}_{25}$ sample is through the extended states because of the high value of $\sigma_0 \cong 9.7 \times 10^4 \Omega^{-1} \text{cm}^{-1}$. The Fermi level (E_F) is pinned and placed towards the valence band at an energy of 0.73 eV. The band picture with symmetric band tailing is shown in Fig. 4. However, the band picture changes drastically as the Pb impurities are added. The localized state conduction now becomes dominant since the value of σ_0 ($\cong 0.34 \Omega^{-1} \text{cm}^{-1}$) decreases by five to six orders. The fact that for $x \geq 5$ at. % $\Delta E_a < \Delta E_s$ suggests that the band tailing becomes more asymmetric with possible more tailing in conduction band as compared to valence band.⁹ The n -type conduction for $x \geq 5$ at. % can be considered to be a result of the unpinning of E_F which now moves towards the conduction band as seen in Fig. 4. The unpinning of Fermi level is assumed to be a consequence of the formation of ionic PbSe bonds, instead of covalent bond.⁷ As seen in other chalcogenide glasses with Pb impurities,¹⁰ it is assumed that the Pb atoms are present in the Pb^{2+} ionized state. The formation of negatively charged Se centers, which occurs as a result of the addition of Pb, disturbs the equilibrium between the Se_1^- and Se_3^+ centers, by the law of mass action,¹¹ thereby unpinning the Fermi level which moves towards the conduction band and hence the n -type conduction is observed in the present case. This also leads to the decrease of the observed dc ac-

tivation energy. The decrease in E_g^{opt} with increasing Pb could be the effect of compositional disorder.¹² Pb is more electropositive than Se and indium. The lone pair (LP) electrons adjacent to Pb atoms will, therefore, have higher energies than those remote from Pb atoms, causing a broadening and tailing of the LP valence band. This leads to the observed decrease in the E_g^{opt} values with the addition of Pb.

In the earlier studies on Pb doping in the Ge–Se system,⁷ the p to n transition occurs at $\text{Pb} > 9$ at. % while in the present case it occurs at $\text{Pb} \geq 5$ at. % with higher values of room temperature conductivity (two to three orders). This property may be useful in forming p - n junctions with higher rectification ratio.

V. CONCLUSION

Pb impurities are incorporated into the host Se–In matrix in charged state thereby disturbing the equilibrium between the charged defect states present in the band gap. This disturbance unpins the Fermi level and it moves towards the conduction band, and thus causes the p to n transition in the Se–In–Pb glasses. Addition of Pb also causes asymmetric tailing in the band gap.

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