APPLICABILITY OF CBH MODEL IN THE A.C. CONDUCTION STUDY OF GLASSY $Se_{100-x}In_x$ ALLOYS

N. Mehta[a], D. Kumar[b], S. Kumar[c], A. Kumar[d*]

[a]Department of Physics, Pranveer Singh Institute of Technology, Kanpur, India
[b]Department of Physics, JSS Academy of Technical Education, Noida, India
[c]Department of Physics, Christ Church College, Kanpur, India
[d]Department of Physics, Harcourt Butler Technological Institute, Kanpur, India

Temperature and frequency dependence of a. c. conductivity have been studied in glassy $Se_{100-x}In_x$ for x = 10, 15 and 20. An agreement between experimental and theoretical results suggests that the a. c. conductivity behaviour of selenium-indium system can be successfully explained by correlated barrier hopping (CBH) model. The results show that bipolaron hopping dominates over single-polaron hopping in this glassy system. This is explained in terms of lower values of the maximum barrier height for single-polaron hopping. The values of the density of charged defect states N are also calculated.

1. Introduction

Amorphous Se is very useful material from application point of view due to its current use as photoreceptors in TV vidicon pick-up tubes [1] and particularly in conventional xerographic machines and digital x-ray imaging [2, 3]. Recently, it has been pointed out that Se-In alloys have more advantages than a-Se from the technological point of view due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects. The energy band gap of glassy Se-In alloys is about 1.3 eV at 300 K [4]. This value is close to the theoretical optimum for solar energy conversion and hence several attempts have been made to utilize glassy Se-In alloys in solar cells [5, 6]. Therefore, glassy Se-In alloys are used to extend the utility of a-Se.

From the above point of view, different properties of glassy Se-In alloys have been reported by our group [7-11] and other workers in a series of papers [12-17]. Effect of In addition on crystallization kinetics in a-Se has been studied by Agarwal et al and Imran et al [7, 8, 12, 13]. Steady state and transient photoconductivity measurement on amorphous thin films of Se-In and the effect of photocrystallization on amorphous thin films of Se-In has been studied by Srivastava et al [9, 10]. Stuctural studies on Se-In system have been reported by Kumar et al [11]. Thermoelectric power measurements in glassy Se-In system have been made by Khan et al [14]. Optical band gap of amorphous thin films of Se-In has been determined by Man et al [15]. Enthalpy recovery during relaxation and crystallization kinetics before and after slow neutron radiation has also been reported in glassy $Se_{96}In_4$ alloy by Imran et al [16, 17].

Structural studies of chalcogenide glasses are very important for better understanding of transport mechanisms. A.C. conductivity measurements have been widely used to investigate the nature of defect centers in disordered systems since it is assumed that they are responsible for this type of conduction. The general frequency behavior in this type of materials is of $A\omega^s$ type over a wide frequency range where exponent s is found to be temperature dependent and has a value ≤ 1. Various models have been formulated to explain this behavior and classical approach has been to consider a.c. and d.c. conduction separately.

The correlated barrier-hopping (CBH) model [18] has been extensively applied to the chalcogenide glassy semiconductors. According to this model, the conduction occurs via a bipolaron

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hopping process wherein two electrons simultaneously hop over the potential barrier between two charged defect states (D^+ and D^-) and the barrier height is correlated with the intersite separation via a Coulombic interaction. Shimakawa [19] suggested further that, at higher temperatures, D^o states are produced by thermal excitation of D^+ and D^- states and single polaron hopping (i.e., one electron hopping between D^o and D^+ and a hole between D^o and D^-) becomes a dominant process.

In this paper we present the results of a.c. measurements performed on glassy $Se_{100-x}In_x$ (x = 10, 15 and 20) alloys and discuss these results in terms of the above-mentioned transport models. The concept of the CBH model, incorporating the suggestions of Shimakawa, is applied to the present data.

2. Theoretical basis

The a.c. conductivity in semiconductors has been interpreted in terms of the pair approximation. In this approximation, a pair consists of two localized states between which electronic carriers move back and forth with a particular relaxation time. In amorphous semiconductors, the localized states have been considered to be randomly distributed in the space, and pairs with various relaxation times exist. The a.c. conductivity is the sum of contributions from all the pairs.

It has been reported in many glasses and amorphous materials [20, 21] that a.c. conductivity varies with frequency according to following relation:

$$\sigma_{ac} \propto \omega^s, \text{ with } \quad s \leq 1 \tag{1}$$

In the CBH model, the electrons in charged defect states hop over the Coulombic barrier whose height, W, is given as

$$W = W_m - (ne^2 / \pi \varepsilon \varepsilon_0 r), \tag{2}$$

where W_m is the maximum barrier height, ε is the bulk dielectric constant, ε_0 is the permittivity of free space, r is the distance between hopping sites and n is the number of electrons involved in a hop (n = 1 and n = 2 for the single polaron and bipolaron processes, respectively).

The relaxation time, ι, for the electrons to hop over a barrier of height, W, is given by

$$\iota = \iota_0 \exp (W / kT), \tag{3}$$

where ι_0 is a characteristic relaxation time which is of the order of an atomic vibrational period and k is the Boltzmann constant. The ac conductivity, $\sigma_{ac}(\omega)$, for bipolaron hopping originating from intimate D^+ and D^- pairs having a non-random distribution can be written as

$$\sigma_{ac}(\omega) = (1/6) \, n \, \pi^3 \, \varepsilon \, \varepsilon_0 \, N \, N_p \, \omega \, (R_\omega)^6 \exp (e^2 / 4 \, \pi \, \varepsilon \, \varepsilon_0 \, k \, T_g \, R_\omega) \tag{4}$$

where the hopping distance, R_ω, is given by
$$R_\omega = (n \, e^2 / \, \pi \, \varepsilon \, \varepsilon_0 \, W_m) \, [1 + k \, T / \, W_m \ln (\iota_0 \, \omega)]^{-1} \tag{5}$$

Here N is the density of localized states at which carriers exist, N_p is the density of localized states to which the carriers hop, T_g is the glass transition temperature and n = 2 and n = 1 for bipolaron and single polaron hopping, respectively. The maximum height W_m is regarded as the band gap [18].

The ac conductivity, $\sigma_{ac}(\omega)$, for single polaron hopping originating from randomly distributed defect centers can be expressed [18, 22] as

$$\sigma_{ac}(\omega) = \pi^3 \, \varepsilon \, \varepsilon_0 \, N \, N_p \, \omega \, (R_\omega)^6 / 6 \tag{6}$$

where

$$R_\omega = (e^2 / \pi \, \varepsilon \, \varepsilon_0 \, W_m) \, [1 + k \, T / \, W_m \ln (\iota_0 \, \omega)]^{-1} \tag{7}$$

The maximum barrier height, W_m, for single-polaron hopping is taken as half of the band gap.

Generally, a.c. conductivity of the chalcogenide glasses can be expressed as:

$$\sigma_{ac}(\omega) = [\sigma_{ac}(\omega)]_s + [\sigma_{ac}(\omega)]_b \tag{8}$$

where $[\sigma_{ac}(\omega)]_s$ and $[\sigma_{ac}(\omega)]_b$ are the ac conductivities for single polaron hopping originating from randomly distributed defect states [Eq. (6)] and bipolaron hopping originating from non-random distribution of defect states [Eq. (4)], respectively.

3. Material preparation

Glassy alloys of $Se_{100-x}In_x$ were prepared by quenching technique. The exact proportions of high purity (99.999%) Se and In elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The materials were then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules (length ~ 5cm and internal diameter ~ 8 mm). The ampoules containing material were heated to 1000 ^{o}C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{o}C / minute. During heating, 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 homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melt was cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by X-ray diffraction.

The glassy alloys thus prepared were ground to a very fine powder and pellets (diameter ~ 6 mm and thickness ~ 1 mm) were obtained by compressing the powder in a die at a load of 5 Tons. The pellets were coated with silver paint to ensure good electrical contact between sample and the electrodes. The pellets were mounted in between two steel electrodes of a metallic sample holder for d. c. conductivity measurements using a digital electrometer (Keithly, model 614). The temperature measurement was facilitated by a copper-constantan thermocouple mounted very near to the sample. A vacuum of ~10^{-2} Torr was maintained over the entire temperature range.

For measuring a. c. conductivity, conductance and capacitance were measured using a GR 1620 AP capacitance measuring assembly. The parallel conductance was measured and a.c. conductivity was calculated. Three terminal measurements were performed to avoid the stray capacitances.

4. Results and discussion

4.1. D.C. conductivity behaviour of glassy $Se_{100-x}In_x$ alloys

In general, for a semiconducting material, d.c. conductivity increases exponentially with temperature indicating that the conductivity is a thermally activated process. Mathematically, it can be expressed as:

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E / kT) \tag{9}$$

where ΔE is called the activation energy and σ_0 is called the pre-exponential factor. These parameters are of significance to differentiate various conduction mechanisms.

Fig. 1 shows the temperature dependence of d. c. conductivity in glassy $Se_{100-x}In_x$ alloys. From this figure, it is clear that the d. c. conductivity (σ_{dc}) varies exponentially with temperature as ln σ_{dc} vs 1000/T curves are straight lines. Such behavior is consistent with equation (9). The values of electrical parameters (ΔE and σ_0) are given in Table 1.
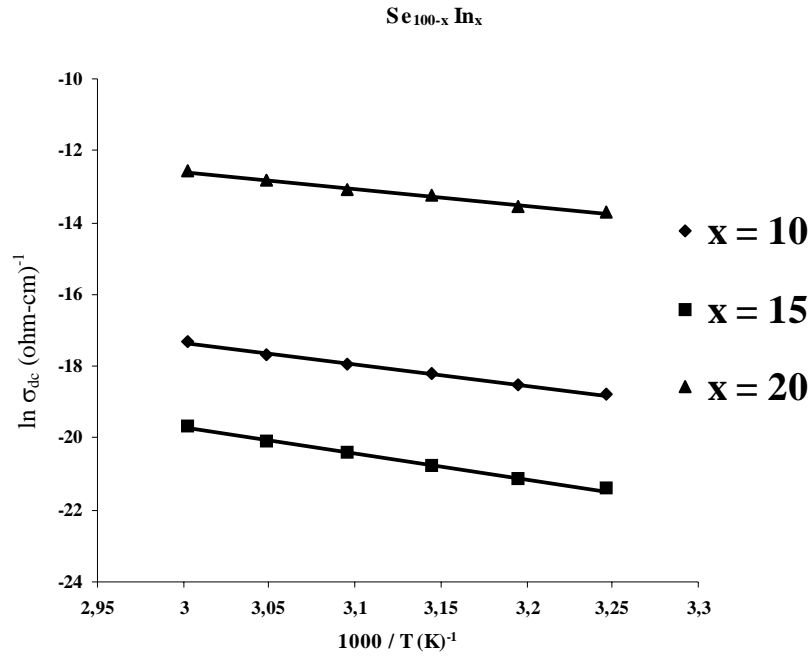
Se$_{100-x}$ In$_x$

Fig. 1. Plots of ln σ$_{dc}$ vs 1000/T for glassy Se$_{100-x}$In$_x$ alloys.

Table 1. Semiconduction parameters of Se$_{100-x}$In$_x$ glassy alloys.

Sample	ΔE (eV)	σ$_0$ (ohm-cm)$^{-1}$
Se$_{90}$In$_{10}$	0.51	0.55
Se$_{85}$In$_{15}$	0.63	2.17
Se$_{80}$In$_{20}$	0.41	1.80

4.2. A.C. conductivity behaviour of glassy Se$_{100-x}$In$_x$ alloys

The frequency dependence of a.c. conductivity for glassy Se$_{90}$In$_{10}$ alloys at different temperatures is shown in Fig. 2. From this figure, it is clear that σ$_{ac}$ ∝ ω^s, where s is the frequency exponent and A is a constant. The decrease in slope with increasing temperature clearly indicates that the values of s decrease with increasing temperature for all samples. Similar graphs are obtained for the other two glassy alloys.
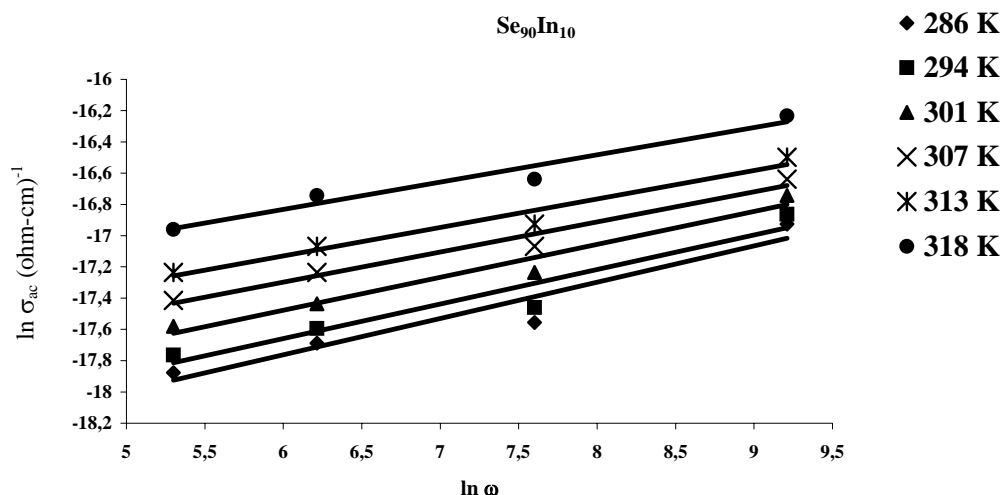
Fig. 2. Plots of ln σ_{ac} vs ln ω for glassy $Se_{100-x}In_x$ alloys.

As mentioned earlier, the ac conduction in chalcogenide glasses can be considered to be sum of two conduction mechanisms (single-polaron and bipolaron hopping). With this point of view, a fit to the experimental data has been made to CBH model. The values of the product of N and N_p are adjusted to fit the calculated curves of ln $\sigma_{ac}(\omega)$ versus 1/T to the experimental curves. The fitting is at one frequency and the same values of parameters are used for other frequencies. The bulk dielectric constant ε was estimated from the measured capacitive component of the samples. The various parameters used in the fitting procedure are summarized in Table 2.

Table 2. Parameters used in curve fitting of $Se_{100-x}In_x$ glassy alloys using single polaron
theory (n = 1) and bipolaron theory (n = 2).

Sample	W_m (e V)		NN_p (cm)$^{-6}$		T_g (K)	ε
	(n = 1)	(n = 2)	(n = 1)	(n = 2)		
$Se_{90}In_{10}$	0.59	1.18	1.9×10^{34}	1.3×10^{37}	335	3.0
$Se_{85}Ine_{15}$	0.49	0.98	8.1×10^{38}	1.1×10^{38}	338	3.0
$Se_{80}In_{20}$	0.47	0.94	1.0×10^{30}	1.8×10^{38}	337	3.0

Fig. 3 shows the contributions for single-polaron and bipolaron hopping processes and their sum for glassy $Se_{100-x}In_x$ alloys at a frequency of 10 kHz. As seen from this figure, calculated curves are in fair agreement with the experimental results. It is also clear from this figure that single polaron contribution is much smaller for present glassy alloys. This may be understood as follows:
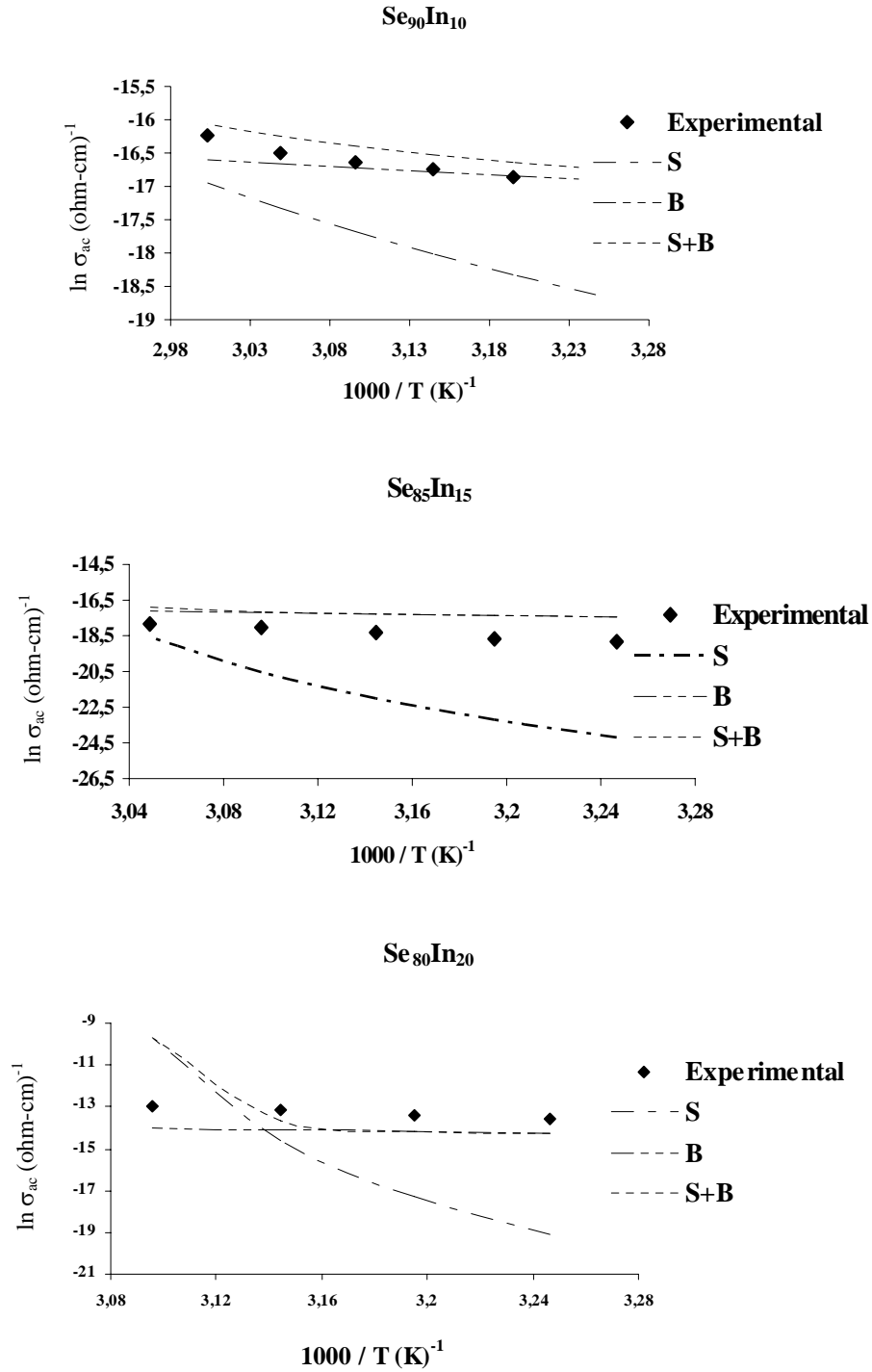
Se$_{90}$In$_{10}$

Se$_{85}$In$_{15}$

Se$_{80}$In$_{20}$

Fig. 3. Plots of ln σ vs 1000/T for glassy Se$_{100-x}$In$_x$ alloys at 10 kHz.

It is observed that the condition $(\omega\iota_{max}) \gg 1$ does not hold at high temperatures for small values of W_m for n = 1. In such a case, the curve can not be extended to the high temperature region because there will be a dielectric loss peak at the frequency ω_m [18, 23] where

$$\omega_m = \iota_0^{-1} \exp(-W_m / kT) \tag{10}$$

Since $[\sigma_{ac}(\omega)]_s \propto \omega^2$, the single-polaron contribution to a. c. conductivity may, therefore, be smaller than bipolaron contribution to a. c. conductivity due to dielectric loss [18] as has been observed in the present case.

The density of charged defect states N is evaluated from the values of NN_p (where $N_p = N/2$). The values of N are given in Table 3.

Table 3. The density of charged defect states of glassy $Se_{100-x}In_x$ alloys.

Sample	N $(cm)^{-3}$
$Se_{90}In_{10}$	5.2×10^{18}
$Se_{85}In_{15}$	1.5×10^{18}
$Se_{80}In_{20}$	5.9×10^{18}

5. Conclusions

The electrical properties of glassy $Se_{100-x}In_x$ alloys are studied using correlated barrier hopping (CBH) model. Application of the CBH model revealed that the electronic conduction takes place by single-polaron and bipolaron hopping processes. It is concluded that the combined mechanism of single-polaron and bipolaron hopping satisfactorily accounts for a. c. conductivity of the present glassy system.

It has also been found that for the glassy $Se_{100-x}In_x$ alloys, the contribution of bipolaron hopping is much more than that of due to single-polaron hopping. This is explained in terms of lower values of W_m for single-polaron hopping.

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