

## Study of electrical properties of glassy $\text{Se}_{100-x}\text{Te}_x$ alloys

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**Abstract.** Temperature and frequency dependence of a.c. conductivity have been studied in glassy  $\text{Se}_{100-x}\text{Te}_x$  ( $x = 10, 20$  and  $30$ ) over different range of temperatures and frequencies. An agreement between experimental and theoretical results suggests that the a.c. conductivity behaviour of selenium–tellurium system ( $\text{Se}_{100-x}\text{Te}_x$ ) can be successfully explained by correlated barrier hopping (CBH) model. The density of defect states has been determined using this model for all the glassy alloys.

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 density of charged defect states increase with increase in Te concentration. This is in agreement with our previous results obtained from SCLC measurements.

**Keywords.** Chalcogenide glasses; hopping conduction; density of defect states.

### 1. Introduction

There has been an increased interest in the properties of amorphous Se (*a*-Se) rich semiconducting glassy alloys due to their current use as photoreceptors in TV videocon pick-up tubes (Maruyama 1982), and particularly in digital X-ray imaging (Hunt *et al* 2002). Recently, it has been pointed out that Se–Te 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. Therefore, glassy Se–Te alloys are used to extend the utility of *a*-Se.

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 centres in disordered systems since it is assumed that they are responsible for this type of conduction. The general frequency behaviour 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  $\leq 1$ . Various models have been formulated to explain this behaviour and classical approach has been to consider a.c. and d.c. conduction separately.

The correlated barrier-hopping (CBH) model (Elliott 1977) has been extensively applied to the chalcogenide glassy semiconductors. According to this model, the conduction occurs via a bipolaron hopping process wherein two electrons simultaneously hop over the potential bar-

rier between two charged defect states ( $D^+$  and  $D^-$ ) and the barrier height is correlated with the intersite separation via a Coulombic interaction. Shimakawa (1982) suggested further that, at higher temperatures,  $D^\circ$  states are produced by thermal excitation of  $D^+$  and  $D^-$  states and single polaron hopping (i.e. one electron hopping between  $D^\circ$  and  $D^+$  and a hole between  $D^\circ$  and  $D^-$ ) becomes a dominant process.

In this paper we present the results of a.c. measurements performed on glassy  $\text{Se}_{100-x}\text{Te}_x$  ( $x = 10, 20$  and  $30$ ) 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 (Maan *et al* 1989; Singh *et al* 1995) that a.c. conductivity varies with frequency according to following relation

$$S_{\text{a.c.}} \propto \mu \omega^s, \text{ with } s \leq 1. \quad (1)$$

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

$$W = W_m - (ne^2/p \epsilon \epsilon_0 r), \quad (2)$$

where  $W_m$  is the maximum barrier height,  $\epsilon$  the bulk dielectric constant,  $\epsilon_0$  the permittivity of free space,  $r$  the distance between hopping sites and  $n$  the number of electrons involved in a hop ( $n = 1$  and  $n = 2$  for the single polaron and bipolaron processes, respectively).

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

$$t = t_0 \exp(W/kT), \quad (3)$$

where  $t_0$  is a characteristic relaxation time which is of the order of an atomic vibrational period and  $k$  the Boltzmann constant. The a.c. conductivity,  $\mathbf{s}_{\text{a.c.}}(\omega)$ , for bipolaron hopping originating from intimate  $D^+$  and  $D^-$  pairs having a non-random distribution can be written as

$$\mathbf{s}_{\text{a.c.}}(\omega) = (1/6) n \mathbf{p}^3 \epsilon \epsilon_0 N N_p \omega(R_w)^6 \exp(e^2/4 p \epsilon \epsilon_0 k T_g R_w), \quad (4)$$

where the hopping distance,  $R_w$ , is given by

$$R_w = (n e^2/p \epsilon \epsilon_0 W_m) [1 + k T/W_m \ln(t_0 \omega)]^{-1}. \quad (5)$$

Here  $N$  is the density of localized states at which carriers exist,  $N_p$  the density of localized states to which the carriers hop,  $T_g$  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 (Elliott 1977).

The a.c. conductivity,  $\mathbf{s}_{\text{a.c.}}(\omega)$ , for single polaron hopping originating from randomly distributed defect centres can be expressed (Elliott 1977, 1987) as

$$\mathbf{s}_{\text{a.c.}}(\omega) = \mathbf{p}^3 \epsilon \epsilon_0 N N_p \omega(R_w)^6/6, \quad (6)$$

where

$$R_w = (e^2/p \epsilon \epsilon_0 W_m) [1 + k T/W_m \ln(t_0 \omega)]^{-1}. \quad (7)$$

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

$$\mathbf{s}_{\text{a.c.}}(\omega) = [\mathbf{s}_{\text{a.c.}}(\omega)]_s + [\mathbf{s}_{\text{a.c.}}(\omega)]_b, \quad (8)$$

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

### 3. Material preparation

Glassy alloys of  $\text{Se}_{100-x}\text{Te}_x$  were prepared by quenching technique. The exact proportions of high purity (99.999%)

Se and Te elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of  $10^{-4}$  g. The materials were then sealed in evacuated ( $\sim 10^{-5}$  Torr) quartz ampoules (length,  $\sim 5$  cm and internal diameter,  $\sim 8$  mm). The ampoules containing material were heated to  $1000^\circ\text{C}$  and were held at that temperature for 12 h. The temperature of the furnace was raised slowly at a rate of  $3\text{--}4^\circ\text{C}/\text{min}$ . 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 h, 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,  $\sim 6$  mm and thickness,  $\sim 1$  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 electrodes. The pellets were mounted in between two steel electrodes of a metallic sample holder for d.c. conductivity measurements using a digital electrometer (Keithley, model 614). The temperature measurement was facilitated by a copper-constantan thermocouple mounted very near to the sample. A vacuum of  $\sim 10^{-2}$  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 stray capacitances.

## 4. Results and discussion

### 4.1 D.c. conductivity behaviour of glassy

#### $\text{Se}_{100-x}\text{Te}_x$ 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

$$\mathbf{s}_{\text{d.c.}} = \mathbf{s}_0 \exp(-\Delta E/kT), \quad (9)$$

where  $\Delta E$  is the activation energy and  $\mathbf{s}_0$  is called the pre-exponential factor. These parameters are of significance to differentiate various conduction mechanisms.

Figure 1 shows the temperature dependence of d.c. conductivity in glassy  $\text{Se}_{100-x}\text{Te}_x$  alloys. From this figure, it is clear that the d.c. conductivity ( $\mathbf{s}_{\text{d.c.}}$ ) varies exponentially with temperature as  $\ln \mathbf{s}_{\text{d.c.}}$  vs  $1000/T$  curves are

straight lines. Such behaviour is consistent with (9). The values of electrical parameters ( $\Delta E$  and  $S_0$ ) are given in table 1.

Mott (1970) suggested that the pre-exponential factor ( $S_0$ ) for conduction in localized states should be two or three orders smaller than that for conduction in the extended states. For conduction in the extended states, the values of  $S_0$  reported for  $a$ -Se and other Se alloys (Street

1982) are of the order of  $10^4$  (ohm-cm) $^{-1}$ . In the present case, the values of  $S_0$  are of the order of  $10^3$  to  $10^4$  (ohm-cm) $^{-1}$  for two compositions (see table 1), which suggests that the conduction is in extended states for these two glassy alloys. However, in case of one composition ( $Se_{70}Te_{30}$ ), the value of  $S_0$  is of the order of  $10^{-3}$ , which suggests that the conduction is in the localized states near band edges in this glassy alloy. This may be due to increase in the density of defect states on increase in Te concentration (Kumar *et al* 1992).

#### 4.2 A.c. conductivity behaviour of glassy $Se_{100-x}Te_x$ alloys

The frequency dependence of a.c. conductivity for glassy  $Se_{100-x}Te_x$  alloys at different temperatures is shown in figure 2. From these figures, it is clear that  $S_{a.c.} \propto \omega^\delta$ ,

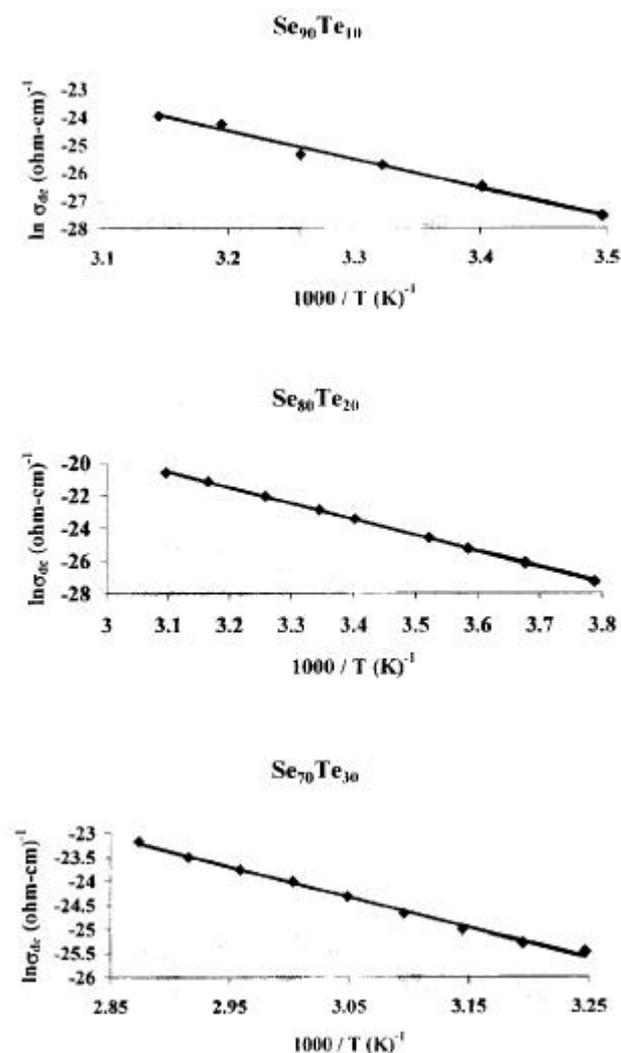


Figure 1. Plots of  $\ln S_{d.c.}$  vs  $1000/T$  for glassy  $Se_{100-x}Te_x$  alloys.

Table 1. Semiconduction parameters of  $a$ - $Se_{100-x}Te_x$  glassy alloys.

Sample	$\Delta E$ (eV)	$S_0$ (ohm-cm) $^{-1}$
Se <sub>90</sub> Te <sub>10</sub>	0.88	$4.1 \times 10^3$
Se <sub>80</sub> Te <sub>20</sub>	0.85	$1.5 \times 10^4$
Se <sub>70</sub> Te <sub>30</sub>	0.55	$6.1 \times 10^{-3}$

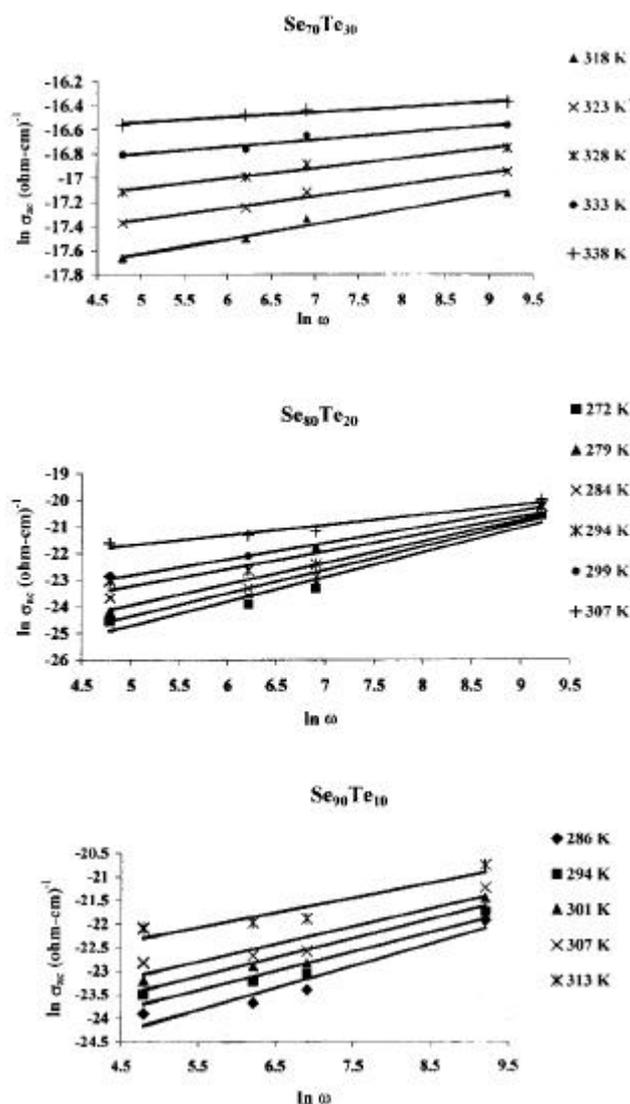


Figure 2. Plots of  $\ln S_{a.c.}$  vs  $\ln \omega$  for glassy  $Se_{100-x}Te_x$  alloys.

**Table 2.** Parameters used in curve fitting of  $a$ - $\text{Se}_{100-x}\text{Te}_x$  glassy alloys using single polaron theory ( $n = 1$ ) and bipolaron theory ( $n = 2$ ).

Sample	$W_m$ (eV)		$NN_p$ (cm) <sup>-6</sup>		$T_g$ (K)	$\epsilon$
	( $n = 1$ )	( $n = 2$ )	( $n = 1$ )	( $n = 2$ )		
$\text{Se}_{90}\text{Te}_{10}$	0.95	1.9	$5.60 \times 10^{35}$	$4.55 \times 10^{37}$	331	3.5
$\text{Se}_{80}\text{Te}_{20}$	0.85	1.7	$1.11 \times 10^{36}$	$2.01 \times 10^{38}$	337	3.5
$\text{Se}_{70}\text{Te}_{30}$	0.75	1.5	$2.06 \times 10^{36}$	$8.30 \times 10^{38}$	354.2	3.5

where  $s$  is the frequency exponent and  $A$  a constant. The decrease in slope with increasing temperature clearly indicates that the values of  $s$  decrease with increasing temperature for all samples.

As mentioned earlier, the a.c. 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  $\ln s_{a.c.}(w)$  vs  $1/T$  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,  $\epsilon$ , was estimated from the measured capacitive component of the samples. The various parameters used in the fitting procedure are summarized in table 2.

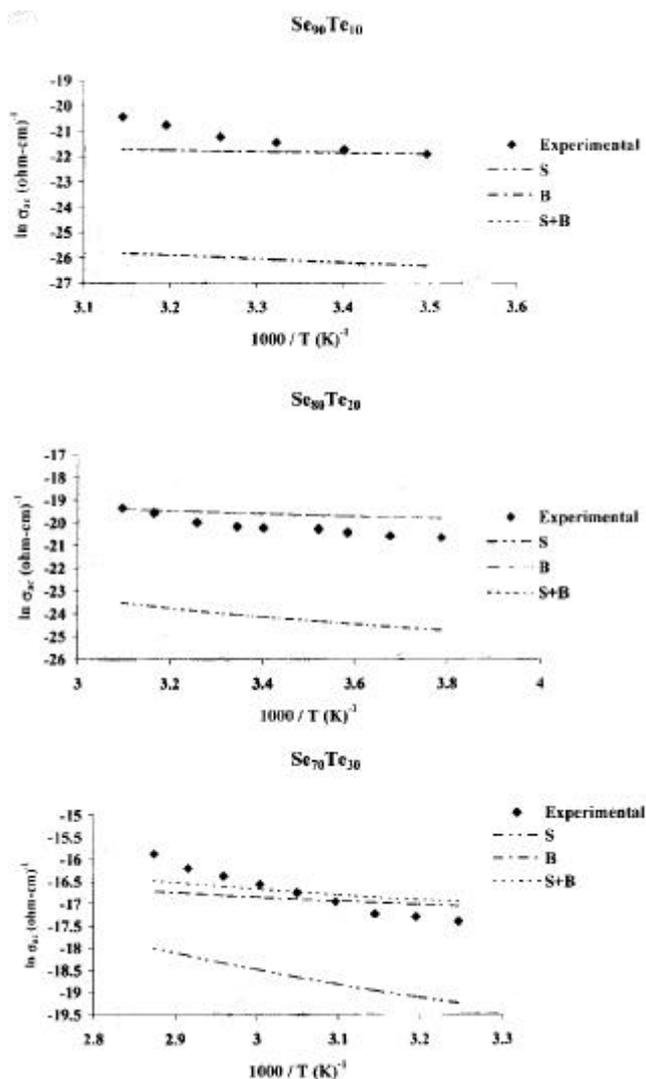
Figure 3 shows the contributions for single-polaron and bipolaron hopping processes and their sum for glassy  $\text{Se}_{100-x}\text{Te}_x$  alloys at a frequency of 10 kHz. As seen from this figure, calculated curves are in fair agreement with the experimental results. It is also clear from this figure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

It is observed that the condition ( $w_{max}$ )  $\gg 1$  does not hold at high temperatures for small values of  $W_m$  for  $n = 1$ . In such a case, the curve cannot be extended to the high temperature region because there will be a dielectric loss peak at the frequency,  $w_m$  (Elliott 1977, 1979) where

$$w_m = t_0^{-1} \exp(-W_m/kT). \quad (10)$$

Since  $[s_{a.c.}(w)]_s \propto w^2$ , the single-polaron contribution to a.c. conductivity may, therefore, be smaller than bipolaron contribution to a.c. conductivity due to dielectric loss 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. From this table, it is clear that the value of  $N$  increases with increase of Te concentration in glassy  $\text{Se}_{100-x}\text{Te}_x$  alloys (see figure 4). This is in agreement with our previous results (Kumar et al 1992) of space charge limited conduction (SCLC) measurements on glassy Se-Te alloys, which show that the density of defect states (DOS) increases with the increase in Te concentration in glassy  $\text{Se}_{100-x}\text{Te}_x$  system.

**Figure 3.** Plots of  $\ln s_{a.c.}$  vs  $1000/T$  for glassy  $\text{Se}_{100-x}\text{Te}_x$  alloys at 10 kHz.**Table 3.** The density of charged defect states of glassy  $\text{Se}_{100-x}\text{Te}_x$  alloys.

Sample	$N$ (cm) <sup>-3</sup>
$\text{Se}_{90}\text{Te}_{10}$	$9.54 \times 10^{18}$
$\text{Se}_{80}\text{Te}_{20}$	$2.00 \times 10^{19}$
$\text{Se}_{70}\text{Te}_{30}$	$4.10 \times 10^{19}$

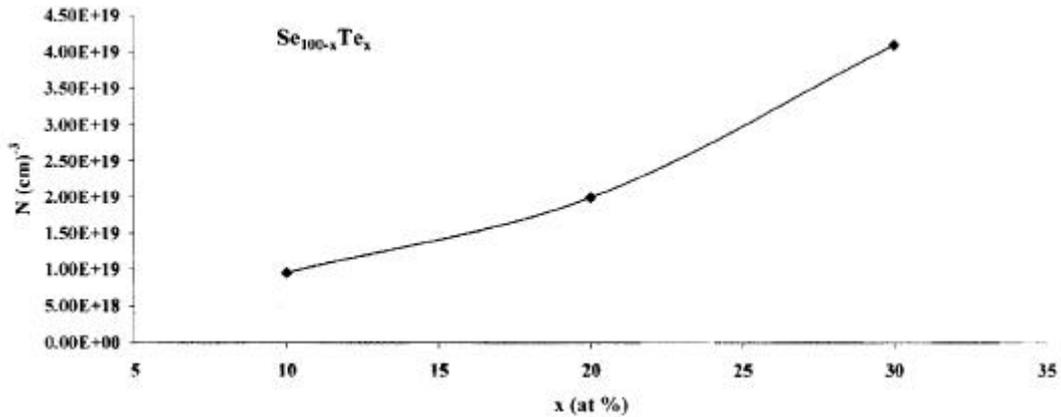


Figure 4. Composition dependence of  $N$  for glassy  $\text{Se}_{100-x}\text{Te}_x$  alloys.

## 5. Conclusions

The electrical properties of glassy  $\text{Se}_{100-x}\text{Te}_x$  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  $\text{Se}_{100-x}\text{Te}_x$  alloys, the bipolaron hopping dominates over single-polaron hopping. This is explained in terms of lower values of  $W_m$  for single-polaron hopping. The values of the density of charged defect states,  $N$ , increases with increase in

Te concentration, which is in agreement with our previous results obtained from SCLC measurements.

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