AC CONDUCTIVITY OF Se$_{85-x}$ Te$_{15}$Ge$_x$ GLASSES

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Frequency and temperature dependent ac conductivity studies of Se$_{85-x}$ Te$_{15}$Ge$_x$ ($x=0, 2, 6, 10, 15$) glasses have been reported. Results indicate that Se$_{83}$ Te$_{15}$ Ge$_2$ obeys well established relation $\sigma_{ac} \propto \omega^s$, frequency exponent $s$ is found to decrease with increase in temperature and results have been explained as the basis of correlated barrier hopping (CBH) model and numerical calculations agree well with experimental results. But a different type of behavior has been observed for Se$_{85-x}$ Te$_{15}$Ge$_x$ ($x=6, 10, 15$). Distinct peaks have been observed in the plots of temperature dependence of ac conductivity for Se$_{85-x}$ Te$_{15}$Ge$_x$ ($x=10, 15$). The results have been interpreted using CHB and “simple pair” model. Ge introduced localized states deep in the band gap and form simple pairs. Theoretical results obtained by using these models have been found to be in agreement with experimental results.

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1. Introduction

The effect of an impurity doping of amorphous semiconductors is of great interest. The effect of impurity depends on the conduction mechanism and the structure of the material [1]. Measurement of frequency and temperature dependence of ac conductivity has been found to be a powerful tool to investigate the gap states in amorphous semiconductors. CBH model is generally used to explain the ac conductivity behavior in chalcogenide glasses [2-11]. We report the temperature and frequency dependent ac conductivity studies of Se$_{85-x}$ Te$_{15}$Ge$_x$ and results have been explained using CBH model [2-4] and simple pair model [12, 13].

2. Experimental detail

For the present work, the glassy materials have been prepared by melt quench method. The constituent elements (5N pure) were weighed in the required atomic weight percentages using electronic balance with accuracy of 0.0001gm. The weighed components were sealed in properly cleaned quartz ampoules under a vacuum of $10^{-5}$ mbar. The sealed ampoules were heated gradually upto $1000^\circ$C in the rocking furnace and later the temperature of the furnace was raised upto $1050^\circ$C and this temperature was maintained for about 24hrs. Rocking has been done to insure proper mixing and homogeneity of samples. Heated ampoules were immediately quenched in ice cold water. The amorphous nature of the samples was confirmed using X-ray diffraction technique. Compressed pellets were prepared by grinding bulk-ingots into fine powder and compressing the powder in a die under a hydraulic press ($10^6$kg/m$^2$). A three terminal sample holder has been fabricated for the measurement of ac and dc conductivity of pellet-shaped

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samples. A thermocouple has been inserted inside the sample holder which has been kept close to the sample for the measurement of correct temperature. A vacuum of the order of $10^{-4}$ to $10^{-5}$ Torr was achieved inside the sample holder using vacuum pump. A general radio bridge (Model 1615-A) was used for the measurements of frequency-dependent ac conductivity and dielectric constant of the materials. This bridge is designed for the precise measurements of capacitance and conductance. Its direct read-out system minimizes the reading errors and permits rapid operation.

3. Results and discussion

The frequency and temperature dependent behaviour of $\text{Se}_{85}\text{Te}_{15}$ had been studied [11] and obeys the well-known relation

$$\sigma_{ac} = A\omega^s$$  \hspace{1cm} (1)

where $s$ is frequency exponent and $A$ is constant.

![Fig. 1. log$\sigma_{ac}$ versus log$f$ for $\text{Se}_{83}\text{Te}_{15}\text{Ge}_2$ glass.](image)

![Fig. 2. Temperature dependence of frequency exponent $s$ for $\text{Se}_{83}\text{Te}_{15}\text{Ge}_2$](image)

Figure(1) shows the frequency dependent behavior of ac conductivity of $\text{Se}_{83}\text{Te}_{15}\text{Ge}_2$ at different temperatures. From figure, it is clear that relation (1) is obeyed for this glass. The
temperature dependence of $s$ for Se$_{83}$Te$_{15}$Ge$_2$ is given in figure 2. The value of $s$ decreases with rise in temperature. So it is clear that the behaviour of Se$_{83}$Te$_{15}$Ge$_2$ is similar to that of Se$_{85}$Te$_{15}$. But the relation (1) has not been followed for Se$_{85}$ Te$_{15}$Ge$_x$ ($x = 6, 10, 15$) and prominent peaks appear in the log $\sigma_{ac}$ versus $1000/T$ graphs for Se$_{75}$ Te$_{15}$ Ge$_{10}$ and Se$_{70}$ Te$_{15}$ Ge$_{15}$ glasses. The peaks are not prominent in case of Se$_{75}$ Te$_{15}$ Ge$_6$. In the following discussion, an attempt has been made to explain this deviation from the general behavior of amorphous semiconductors.

The a.c. conductivity in semiconductors has been interpreted in terms of pair approximation [12,13]. In this approximation, it is assumed that a pair consists of two localized states between which carriers hop back and forth. Each pair has its own relaxation time $\tau$ which is related to the transition probability of the carrier. The contribution of one such pair to a.c. conductivity is given by $C_{\omega} = 2\pi/\omega$ where $C$ is independent of $\omega$ and $\tau$. If the relaxation time is same for all the pairs then the above relation will hold good in the simple pair model [12,13]. But in amorphous semiconductors, the conduction is due to hopping between defect states [2-4].

According to correlated barrier hopping (CBH) model, the a.c. conductivity is given by

$$\sigma_{ac} = n\pi^2 NN_p \kappa \omega R_{\omega}^6/24 \quad (2)$$

Where $n$ is the number of polarons involved in the hopping process, $R_{\omega}$ is the hopping distance for the condition $\omega \tau = 1$ and is given by [4].

$$R_{\omega} = \frac{4n e^2}{k(W + kT \ln(\omega \tau_0))} \quad (3)$$

$NN_p$ is given by

$$NN_p = N_T^2 \quad \text{(for bipolaron hopping)}$$

$$NN_p = N_T^2 \exp(-U_{\text{eff}}/2kT) \quad \text{(for single polaron hopping)}$$

where $N_T$ is the number of density of states and $U_{\text{eff}}$ is the Hubbard intrasite correlation energy.

The value of frequency exponent $s$ is calculated from equation (2) and (3) and is approximately equal to [3]

$$s = \frac{d(\ln \sigma_{ac})}{d(\ln \omega)} = 1 - \frac{6kT}{W - kT \ln(1/wT_0)} \quad (4)$$

$$W = W_M \quad \text{(for bipolaron hopping)}$$

$$W = W_1 \text{ or } W_2 \quad \text{(for single polaron hopping)}$$

$W_1$ is the energy (distortion + electronic) required to take an electron from the valence band and place it on a $D^0$ centre thereby turning it into $D^-$ and $W_2$ is the total energy necessary to take an electron from $D^0$ centre and place it in the conduction band. $W_M$ can also be understood as simply twice the energy difference between Fermi level and conduction band [3].

In general, the experimentally obtained ac conductivity is given by

$$\sigma_{ac} = \sigma_b + \sigma_s \quad (5)$$

Where $\sigma_b$ is contribution from bipolaron hopping and $\sigma_s$ is contribution from single polaron hopping. Single polaron hopping is dominant at higher temperature and bipolaron hopping is dominant at lower temperature.

CBH model explains the frequency and temperature dependent behavior in Se$_{85}$ Te$_{15}$ and is predominantly due to bipolaron hopping in the studied temperature range (213K to 283 K)[11].
Fig. (3) shows the experimental data and calculated curves (from CHB model fitting) for Se$_{83}$Te$_{15}$Ge$_2$. The two curves are in good agreement with each other. Parameters used in the calculations are shown in Table 1. CBH model shows that conductivity in Se$_{83}$Te$_{15}$Ge$_2$ is predominantly due to single polaron hopping in the studied temperature range (263 K to 333K). But the temperature and frequency dependent behavior of ac conductivity for S$_{85-x}$Te$_{15}$Ge$_x$ (x = 6, 10, 15) in the temperature range 263K - 333K and frequency range 5kHz - 20kHz cannot be explained solely on the basis of CBH model of randomly distributed centers.

To explain the ac conductivity in S$_{85-x}$Te$_{15}$Ge$_x$ (x = 6, 10, 15), we assume that Germanium doping gives rise to some neutral defect states called simple pairs in the band gap and ac conductivity due to these defect pairs ($\sigma_{SP}$) is given by [12].

$$\sigma_{SP} = \frac{\epsilon^2 N_S r_0^2}{12kT} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (6)

where $N_S$ is concentration of pairs and $r_0$ is hopping distance.

$\sigma_{SP}$ in (6) is considered to be function of $\tau$ with constant $\omega$, then $\sigma_{SP}$ has a peak at $\omega \tau = 1$. Therefore the pronounced peaks observed in figures 5&6 are justified by equation (6)

The relaxation time $\tau$ for hopping of electrons over a barrier height $W$ is given by

$$\tau = \tau_0 \exp \frac{W}{kT}$$  \hspace{1cm} (7)

Where $\tau_0$ is characteristic relaxation time and $k$ is Boltzmann constant.

Recently it has been reported [14] that for thermally activated ac conduction in chalcogenide glasses,

$$\tau = \tau_0 \exp \frac{W}{kT} \exp \frac{-W}{kT_0}$$  \hspace{1cm} (7)

where $T_0 = E_{MN}$ is Mayer-Neldel energy.
Considering that the contribution to ac conductivity due to simple pairs is thermally activated, relation (7) has been used to calculate $\tau$ by using $E_{MN} = 40.67$ meV. $E_{MN}$ has been calculated from dc conductivity measurements of the glasses under consideration [15].

So, the ac conductivity for Ge doped Se$_{85}$ Te$_{15}$ is expected to be

$$\sigma_{ac} = \sigma_b + \sigma_s + \sigma_{SP}$$  \hspace{1cm} (8)

Where $\sigma_{SP}$ is simple pair contribution.

Theoretical calculation of ac conductivity in case of Se$_{85-x}$ Te$_x$ Ge$_x$ ($x = 6, 10, 15$) have been done using (2), (3), (6) and (7) and the parameters obtained for best fits are listed in Table 1.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\kappa$</th>
<th>$W_M$(eV)</th>
<th>$W_1$(eV)</th>
<th>$W_2$(eV)</th>
<th>$U_{eff}$(eV)</th>
<th>$N_1$(m$^3$)</th>
<th>$W$(eV)</th>
<th>$\tau_0$(s)</th>
<th>$N_s^2\tau_0$(m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{83}$ Te$</em>{15}$ Ge$_2$</td>
<td>7.5</td>
<td>2.78</td>
<td>0.78</td>
<td>1.74</td>
<td>0.26</td>
<td>$2*10^{20}$</td>
<td>-</td>
<td>1.0*10$^{-13}$</td>
<td>-</td>
</tr>
<tr>
<td>Se$<em>{79}$ Te$</em>{15}$ Ge$_6$</td>
<td>7.0</td>
<td>2.70</td>
<td>0.80</td>
<td>1.52</td>
<td>0.38</td>
<td>$9*10^{19}$</td>
<td>1.10</td>
<td>1.8*10$^{-13}$</td>
<td>1.60*10$^{7}$</td>
</tr>
<tr>
<td>Se$<em>{75}$Te$</em>{15}$ Ge$_{10}$</td>
<td>6.0</td>
<td>2.40</td>
<td>0.90</td>
<td>1.02</td>
<td>0.48</td>
<td>$4*10^{19}$</td>
<td>1.34</td>
<td>1.0*10$^{-14}$</td>
<td>1.44*10$^{7}$</td>
</tr>
<tr>
<td>Se$<em>{70}$Te$</em>{15}$ Ge$_{15}$</td>
<td>5.5</td>
<td>2.24</td>
<td>0.80</td>
<td>1.12</td>
<td>0.40</td>
<td>$9*10^{18}$</td>
<td>1.06</td>
<td>2.0*10$^{-14}$</td>
<td>7.84*10$^{6}$</td>
</tr>
</tbody>
</table>

Figs. 4, 5, 6 show the experimental data and calculated curves (from CHB model plus simple pair contribution fitting) for Se$_{79}$ Te$_{15}$ Ge$_6$, Se$_{75}$ Te$_{15}$ Ge$_{10}$ and Se$_{70}$ Te$_{15}$ Ge$_{15}$ respectively. In each case, the two results are in good agreement with each other.

**Fig. 4. Temperature dependence of ac conductivity for Se$_{79}$ Te$_{15}$ Ge$_6$**
An agreement between theoretical and experimental results clearly indicates that the behaviour of $S_{85-x} \ Te_{15} Ge_x$ ($x = 6, 10, 15$) seems to be well explained by introducing the concept of simple paired states. From the fits it is clear that single polaron hopping is dominant in case of $Se_{83} \ Te_{15} Ge_2$ and $Se_{70} \ Te_{15} Ge_6$ in the studied temperature range and simple pair contribution to conductivity is very small due to lack of sufficient number of paired states. But the sufficient numbers of paired states are available in case of $Se_{75} \ Te_{15} Ge_{10}$ and $Se_{70} \ Te_{10} Ge_{15}$ to contribute significantly to the ac conductivity in addition to polaron hopping in the studied temperature and frequency range.

4. Conclusion

The ac conductivity behaviour of $Se_{85} \ Te_{15}$ and $Se_{85} \ Te_{15} Ge_2$ has been explained well by CBH model. But higher doping of Germanium leads to the formation of simple pairs in the band
gap which contribute significantly to the ac conductivity in addition to the polaron hopping as suggested by CBH model.

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References