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Dependence of activation energy and pre-exponential factor on audio frequency in glassy $Se_{80-x}Te_{20}Sn_x$ alloys

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ABSTRACT

In the present paper, we have studied the temperature and frequency dependence behaviours of ac conductivity in glassy system $Se_{80-x}Te_{20}Sn_x$ ($x = 0$, 2, 4, and 6). All the measurements have been done in the frequency range (1–500 KHz) and in the temperature range from room temperature to glass transition temperature T_g. We have found that activation energy and pre-exponential factor both vary with audio frequency according to Meyer–Neldel's relation (MNR).

We have investigated MNR by two different approaches. In first approach, the temperature dependence of ac conductivity is studied at four different audio frequencies without changing the composition of the glassy system. In the second approach, the composition itself varies at a particular audio frequency. The results are explained in terms of compensation effect in relaxation time and the multi-excitation character of the processes suggested by Yelon and Movaghar responsible for MNR in chalcogenide glasses.

1. Introduction

MNR [1] is observed in many processes in nature. The two mainstream fields that are most affected by it are diffusion processes and semiconductor conduction [2–5].

According to this relation, in the case of a thermally activated electrical conduction, the conductivity (σ) obeys the equation

$$\sigma = \sigma_0 \exp\left[\frac{-\Delta E}{kT}\right], \tag{1}$$

Here ΔE is called the activation energy and σ_0 is called the pre-exponential factor. In most of the semiconducting materials, σ_0 does not depend on ΔE. However in some cases σ_0 correlates with the activation energy ΔE as

$$\sigma_0 = \sigma_{00} \exp\left[\frac{\Delta E}{kT_0}\right], \tag{2}$$

where σ_{00} and kT_0 are constants for a given class of materials. σ_{00} is often called as MN pre-exponential factor and kT_0 is expressed as MN characteristic energy E_{MN}. Eq. (2) is frequently referred to as MNR.

The validity of MNR has been reported in the case of chalcogenide glasses for different thermally activated process in recent past [11–20]. Initially, in case of these glasses this rule was observed by the variation of ΔE on changing the composition of the glassy alloys [6–9] in a specific glassy system. Later, MNR is observed in chalcogenide glasses by varying the intensity of light [10–14]. Most recently, it is observed by our group by changing ΔE by varying electric field across a particular sample in dark in glassy $Se_{70}Te_{30-x}Zn_x$ system [15]. The application of the MNR in case of ac conductivity studies has not been studied in detail.

Recently, Ielmini et al. [16,17] have reported that structural relaxation and crystallization in phase-change memory (PCM) devices are interpreted by the MNR allowing for (i) the development of a new temperature dependent analytical model for structural relaxation and (ii) a unified interpretation of structural relaxation and crystallization, allowing for a physical interpretation of the pre-exponential Arrhenius time by many-phonon thermal excitation. Thus, the significance of MNR appears for technological applications in addition to theoretical studies.

In the present work, we have observed MNR in the ac conductivity measurements in $Se_{80-x}Te_{20}Sn_x$ ($x = 0$, 2, 4, and 6) chalcogenide glasses. For this, we have measured the temperature dependence of ac conductivity at different frequencies in audio frequency range. The reason for the selection of Sn as a chemical modifier in Se–Te system is based on the fact that the glass-formation region of binary and ternary chalcogenide glasses with tin as chemical modifier is very narrow and corresponds to a small amount of tin in the alloy. Hence, no sufficient studies are reported in literature on tin-based chalcogenide glasses. Hence, the present study of tin-based chalcogenide glasses will be useful for the glass physicists working on new phenomena and the application of chalcogenide glasses.

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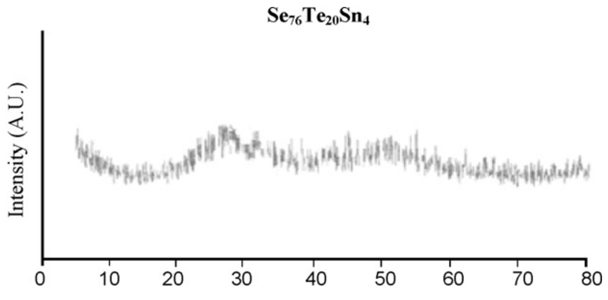

Fig. 1. XRD pattern of glassy $Se_{76}Te_{20}Sn_4$ alloy.

2. Experimental

2.1. Material preparation

Glassy alloys of $Se_{80-x}Te_{20}Sn_x$ (x = 0, 2, 4, and 6) system were prepared by the quenching technique. High purity Se, Te and Sn materials (5 N) were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~5 cm and internal diameter ~8 mm), with a vacuum ~10^{-5} Torr. The sealed ampoules were kept inside a furnace where the temperature was raised to 1000 °C, at a rate of 3–4 °C/min. The ampoules were frequently rocked for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature was verified by X-ray diffraction. The XRD pattern of as prepared sample of ternary $Se_{76}Te_{20}Sn_4$ alloy is shown in Fig. 1. The absence of any sharp peak confirms the glassy nature of the sample. Similar XRD patterns were obtained for the other samples.

2.2. Ac conductivity measurements

The glassy alloys thus prepared were ground to a very fine powder and pellets (diameter ~10 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 vacuum evaporated indium film to ensure good electrical contact between the sample and the electrodes.

The pellets were mounted in between two steel electrodes of a metallic sample holder for dielectric measurements. The temperature measurement was made easy by a copper-constantan thermocouple mounted in close proximity to the sample. A vacuum of ~10^{-3} Torr was maintained over the entire temperature range.

For calculating ac conductivity, conductance and capacitance were measured using a digital LCR meter (Wayne Kerr Electronics, Model: 4255). The parallel conductance was measured and ac conductivity was calculated. The experimental results for the temperature dependence of the ac conductivity $\sigma_{ac}(\omega)$ are obtained by subtracting the dc conductivity from the total measured conductivity σ_T. Three terminal measurements were performed to avoid the stray capacitances.

3. Results

The temperature dependence (above the room temperature) of ac conductivity in glassy $Se_{80-x}Te_{20}Sn_x$ (x = 0, 2, 4, and 6) alloys is studied at different audio frequencies. It has been found that above the room temperature, $\ln\sigma_{ac}$ vs. $1000/T$ curves are almost straight lines at different frequencies. Such a plot is shown for glassy $Se_{78}Te_{20}Sn_2$ alloy in Fig. 2. Similar results were obtained for other glassy alloys.

The above results show that, the variation of ac conductivity with temperature can approximately be expressed by an exponential relation in the high temperature range:

$$\sigma_{ac} = \sigma_0 \exp\left[\frac{-\Delta E_{ac}}{kT}\right], \tag{3}$$

where ΔE_{ac} is called the activation energy for ac conduction and σ_0 is called the pre-exponential factor.

As evident from Eq. (3), the pre-exponential factor σ_0 and ac activation energy ΔE_{ac} can be obtained from the semi-logarithmic plots of the ac conductivity vs. reciprocal temperature. Hence, the activation energy ΔE_{ac} is determined from the slope of the approximate straight lines in the resulting plots at different frequencies (see Fig. 2). These straight lines are obtained by the best fit to the experimental data using the least squares method. The intercept of line gives the value of $\ln\sigma_0$.

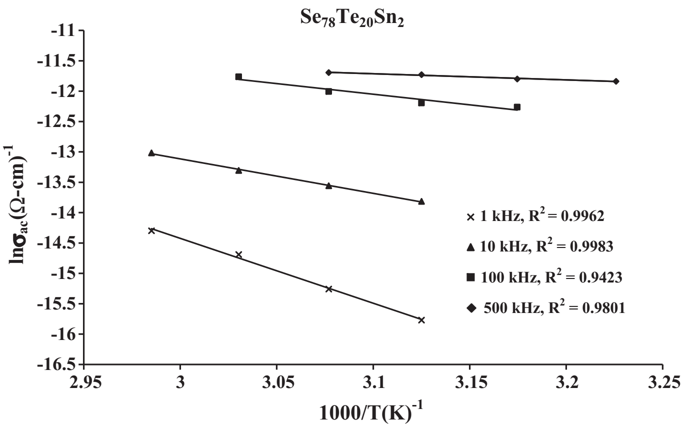

Fig. 2. Linear plots of $\ln\sigma_{ac}$ vs. $1000/T$ at different audio frequencies for glassy $Se_{78}Te_{20}Sn_2$ alloy.

As described earlier, we have checked the presence of MNR in the present glassy system by plotting $\ln\sigma_0$ vs. ΔE_{ac} curves by changing audio frequency keeping the composition constant. Fig. 3 shows such plots of $\ln\sigma_0$ vs. ΔE_{ac} for bulk samples of glassy $Se_{80-x}Te_{20}Sn_x$ (x = 0, 2, 4, and 6) alloys at each value of x.

In second approach, we have checked the presence of MNR in the present glassy system by plotting $\ln\sigma_0$ vs. ΔE_{ac} curves by changing composition keeping the audio frequency constant. Fig. 4 shows such plots of $\ln\sigma_0$ vs. ΔE_{ac} for bulk samples of glassy $Se_{80-x}Te_{20}Sn_x$ (x = 0, 2, 4, and 6) alloys at each value of applied audio frequency.

Figs. 3 and 4 show the straight lines with high correlation coefficients (R^2). This gives the evidence of MNR [Eq. (2)] in the present glassy alloys for thermally activated high field conduction for both cases.

The slope of $\ln\sigma_0$ vs. ΔE_{ac} curves in Figs. 3 and 4 yields the values of $(kT_0)^{-1}$ and $\ln\sigma_{00}$ for the present glasses. Using these values of $(kT_0)^{-1}$ and $\ln\sigma_{00}$, the theoretical values of $\ln\sigma_0$ have been calculated for the glassy $Se_{80-x}Te_{20}Sn_x$ (x = 0, 2, 4, and 6) alloys for both cases and compared with the experimental values (see Figs. 5 and 6). An overall good agreement between the theoretical and experimental values of $\ln\sigma_0$ also confirms the validity of MNR for the two cases.

From Figs. 5 and 6, it is also clear that the variation of $\ln\sigma_0$ is not monotonic for some cases. Mott suggested [18] that the pre-exponential factor σ_0 is of significance to differentiate two conduction mechanisms: (i) conduction in localized states and (ii) conduction in the extended states. For conduction in the extended states, the values of σ_0 reported for various chalcogenide glasses [19] are of the order of $10^4\ \Omega\,cm^{-1}$, while in the present case, the values of σ_0 are of the order of 10^{-3}–$10^3\ \Omega\,cm^{-1}$. Thus, the random change in conduction mechanism at a particular frequency or composition is probably the reason of the non-monotonic behaviour of σ_0.

4. Discussion

The chalcogenide glassy material during ac conduction can be considered as a medium consisting of network of resistors and capacitors [20]. If the local conductivity is thermally activated, and all capacitors are assumed to be equal, then the resistance and capacitance between pairs of sites are given by:

$$R = R_0 \exp\left(\frac{W}{kT}\right) \tag{4}$$

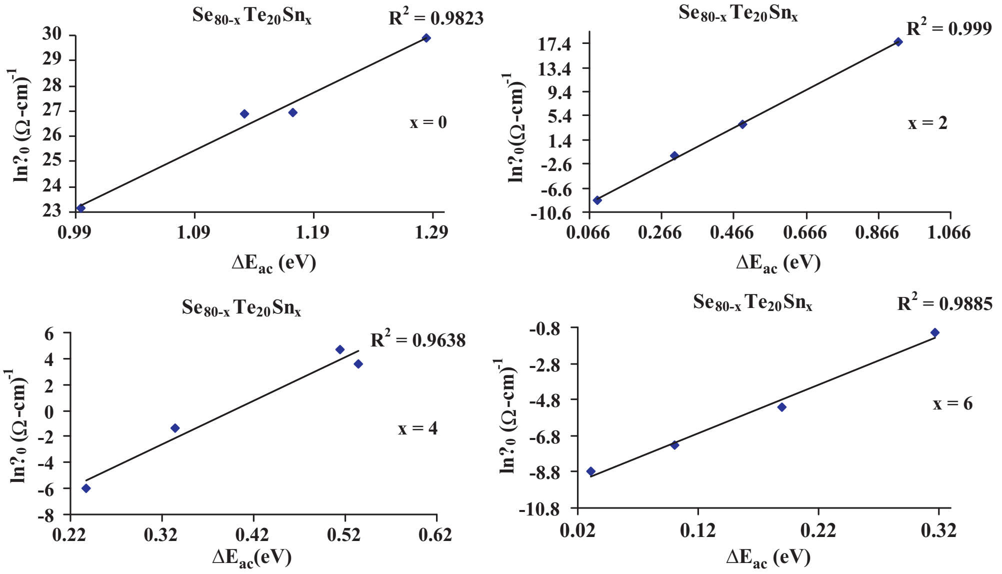

Fig. 3. Plots of pre-exponential factor $\ln \sigma_0$ vs. activation energy ΔE for first case.

and

$$C = C_0 \tag{5}$$

Here R_0 and C_0 are constant. For the whole system, a broad distribution of energy barriers [20] $P(W)$ can be anticipated, and the resistance of the sample is given by:

$$R = R_0 P(W) \exp\left(\frac{W}{kT}\right) \tag{6}$$

The time constant of the circuit is:

$$\tau = RC = R_0 C_0 P(W) \exp\left(\frac{W}{kT}\right) = \tau_0 P(W) \exp\left(\frac{W}{kT}\right) \tag{7}$$

Here

$$\tau_0 = R_0 C_0 \tag{8}$$

For $P(W)$ = constant, the relaxation time has an Arrhenius form (Eq. (7)).

If the distribution of the energy barriers has an exponential form [20–22]:

$$P(W) \approx \exp\left(-\frac{W}{kT_0}\right) \tag{9}$$

Here T_0 is the characteristic temperature, then Eq. (7) yields:

$$\tau = \tau_0 \exp\left(\frac{W}{kT}\right) \exp\left(-\frac{W}{kT_0}\right) \tag{10}$$

This is exactly the same as MNR. However, it should be noted that conduction occurs by percolation in presence of a broad distribution of resistance in a 3D network. The overall resistance depends on the specific random distribution of barriers and on the size of the resistor (e.g. very long and narrow, or very short and wide) [23].

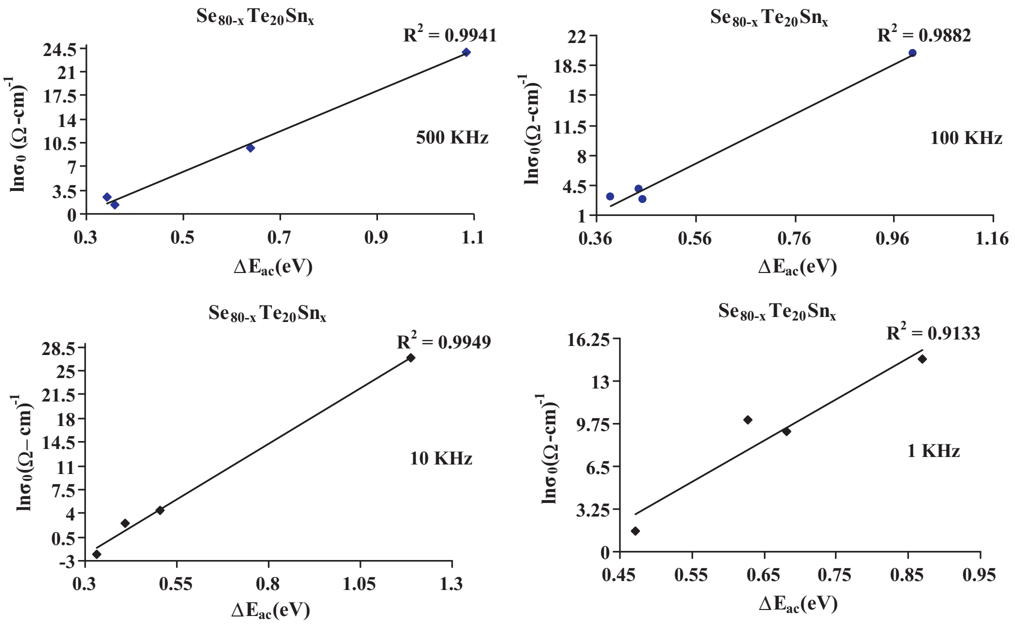

Fig. 4. Plots of pre-exponential factor $\ln \sigma_0$ vs. activation energy ΔE_{ac} for second case.

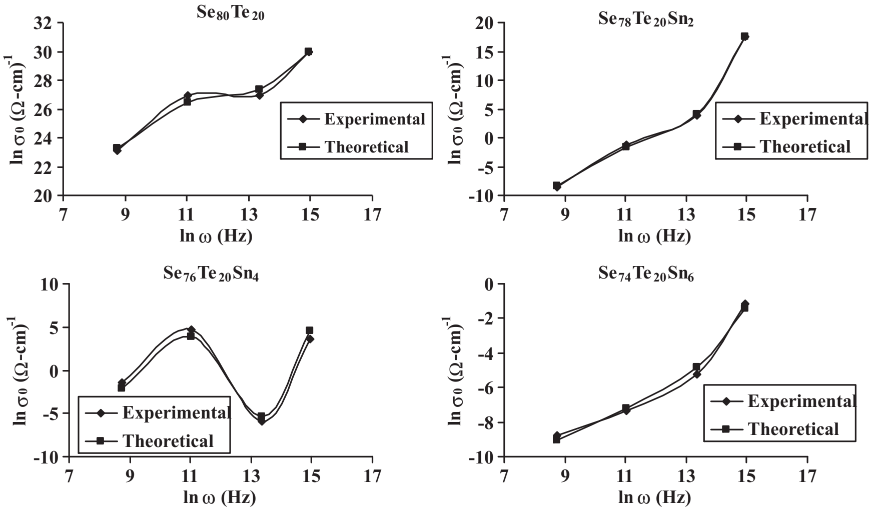

Fig. 5. Theoretical and experimental values of $\ln\sigma_0$ for first case.

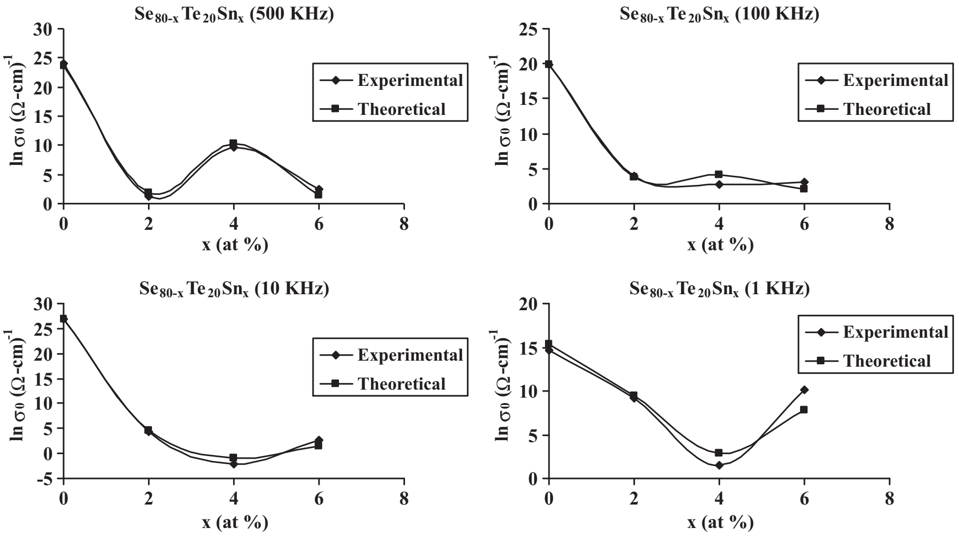

Fig. 6. Theoretical and experimental values of $\ln\sigma_0$ for second case.

Yelon and Movaghar [24–26] have proposed a model of multi-phonon excitation to explain the MNR in amorphous as well as in crystalline materials. The model suggests that the optical phonons are the source of the excitation energy in such process. According to this model, the MNR may be understood as arising naturally when the activation energy for a process is significantly larger than the typical excitations available and *kT* both. Yelon and Movaghar suggested that many phonons involve in trapping and detrapping of electrons, either by cascade or by multi-phonon process. Various authors have adopted the YM model for explanation of MNR in many chalcogenide glassy systems [12,13,27]. One common thing in these data is the value of E_{MN} that is shown to be between 25 and 50 meV for different samples. The values of E_{MN} for present glassy alloys are given in Table 1 for the first and second case. From these tables, it is clear that the value of E_{MN} shows the excellent agreement of the experimental data observed by other workers.

Table 1
Values of E_{MN} for first and second case.

E_{MN} (meV)			
First case		Second case	
$x = 0$	43.5	500 kHz	31.6
$x = 2$	32.0	100 kHz	30.6
$x = 4$	29.9	10 kHz	34.5
$x = 6$	37.4	1 kHz	33.3

5. Conclusion

Bulk samples of glassy $Se_{80-x}Te_{20}Sn_x$ ($x = 0$, 2, 4, and 6) alloys have been prepared by quenching technique. Temperature dependence of ac conductivity is studied at different frequencies. We have found that ac conductivity shows strong temperature dependence and can be considered to be thermally activated with single activation energy. The activation energy, however, depends on the applied audio frequency. The detailed study shows that activation energy and pre-exponential factor for ac conduction satisfies the MNR. The results are explained in terms of MNR rule in the activated form of the relaxation time. The Meyer–Neldel characteristic energy, E_{MN}, lies in the range 25–45 meV which seems to be too small for band transport.

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