Observation of further MN rule in a- $Se_{100-x}Bi_x$ thin films at high electric fields

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In the present paper, we report temperature dependence of conductivity in a- $Se_{100-x}Bi_x$ thin films at different electric fields. It is observed that conductivity is thermally activated with single activation energy at all the electric fields applied. However, the pre-exponential factor and activation energy are found to be dependent on electric field applied. A correlation is observed between pre-exponential factor and activation energy which is similar to Meyer-Neldel rule. The paper also reports the further MN rule in the present glassy system.

(Received March 5, 2011; accepted March 16, 2011)

Keywords: Chalcogenide glasses, Activation energy, Pre-exponential factor

1. Introduction

Chalcogenide glasses generally exhibit p-type electrical conduction due to the pinning of the Fermi level arising from the trapping of the charge carriers at localized gap states [1, 2]. But in 1979, Tohge et al. [3, 4] reported for the first time p-to n-type transition in Bi doped Ge-Se glasses at higher concentration of Bi (more than 7 atomic %). Due to this reason, the Bi doping becomes important in chalcogenide glasses.

Recently, many attempts have been made to investigate the MN rule in electrical conductivity without changing the composition of a chalcogenide glass in some different thermally activated electrical conduction phenomena [5-7].

Singh et al and Kushwaha et al [8, 9] observed Meyer-Neldel(MN) rule in amorphous thin films of $Se_{90}Ge_{10-x}In_x$ and $Se_{100-x}Sb_x$ respectively in presence of light by varying intensity of light. Moreover, they found that the characteristic energy (E_{MN}) is also different at different intensities and there exists a strong correlation between the MN conductivity pre-factor and characteristic energy which is known as further MN rule.

In the present paper we have made an attempt to see the applicability of further MN rule by measuring d. c. conductivity at different electric fields. Conductivity is found to vary exponentially with temperature at all electric fields with an activation energy ΔE. The values of ΔE and pre-exponential factor (σ_0) are calculated at various electric fields for each composition. σ_0 and ΔE follow MN rule for all the glasses studied here. Further MN rule is also observed between $\ln\sigma_{00}$ and E_{MN} in the present glassy system.

2. Experimental details

2.1. Synthesis of materials

Glassy alloys of $Se_{100-x}Bi_x$(x = 0.5, 2.5, 4) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Bi 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 material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 800 ^{0}C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{0}C / minute. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous glassy alloys. After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule.

2.2. Thin films preparation

Thin films of the glassy material were prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom were used for electrical contacts. The thickness of the films was ~ 500 nm. The coplanar structures (length ≈ 1.2 cm and electrode separation ≈ 0.12 mm) were used for the present measurements. The films were kept in the deposition chamber in the dark for 24 hours before mounting them in the sample holder. This was done to allow sufficient annealing at room temperature so that a

metastable thermodynamic equilibrium may be attained in the samples.

For the measurements of high field conduction, thin film samples were mounted in a specially designed metallic sample holder. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper - constantan thermocouple kept very near to the films. A vacuum ~ 10^{-3} Torr was maintained throughout the measurements. A d. c voltage (0 to 250 V) was applied across the sample and the resultant current was measured by digital Pico-ammeter. I-V characteristics were measured at various fixed temperatures (308-348 K) in these films. Before measuring I-V characteristics, thin films were annealed in a vacuum ~ 10^{-3} Torr near glass transition temperature for two hours in the same sample holder that was used for the above measurements.

3. Results and discussion

Temperature dependence of d. c. conductivity (σ) has been measured in a-$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4) thin films at different electric fields. The ln σ vs 1000 / T curves are found to be straight lines in the temperature range (308 K-348 K) at all the electric field for each sample studied here. Figs. 1-3 show such plots at different electric fields in a-$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4) thin films. These figures illustrate that conductivity behavior is consistent with Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \qquad (1)$$

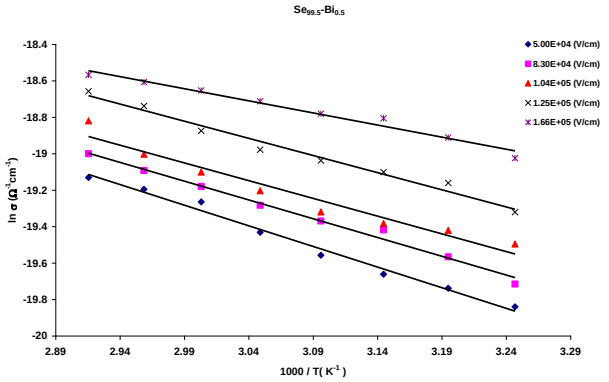

Fig. 1. ln σ versus 1000 / T plots for a-$Se_{99.5}Bi_{0.5}$ thin films at different electric fields.

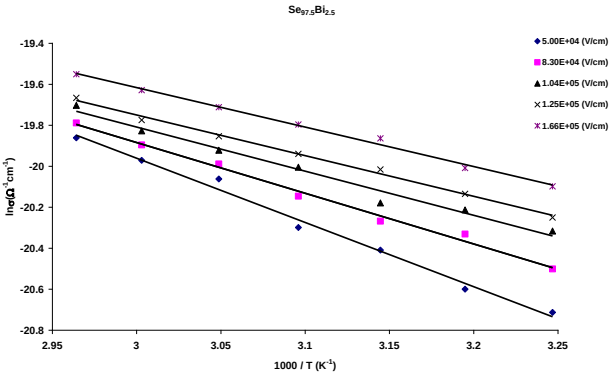

Fig. 2. ln σ versus 1000 / T plots for a-$Se_{97.5}Bi_{2.5}$ thin films at different electric fields.

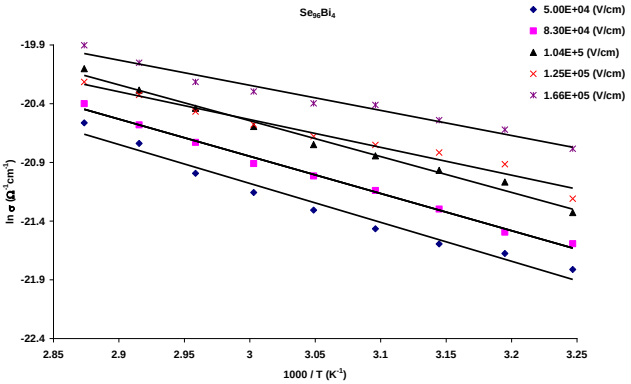

Fig. 3. ln σ versus 1000 / T plots for a-$Se_{96}Bi_4$ thin films at different electric fields.

From the slopes and the intercepts of these lines the values of ΔE and σ_0 are calculated at different electric fields for each sample. The values of these parameters are given in Table 1 in case of a- $Se_{100-x}Bi_x$. It is clear from the table that pre-exponential factors σ_0 is not constant for all the electric fields. We have checked the presence of MN Rule in the present glassy system by plotting ln σ_0 vs. ΔE curves. Fig. 4 shows such plot for a-$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4) thin films. These are straight lines with high correlation coefficient (R^2) showing an exponential relation between σo and ΔE following the equation which is given by Meyer and Neldel [10]:

$$\sigma_0 = \sigma_{00} \exp\left(\frac{\Delta E}{E_{MN}}\right) \qquad (2)$$

where E_{MN} is the characteristic energy and σ_{00} is constant.

Table 1. Conducting parameters ΔE (in eV) and σ_0 (Ω^{-1} cm^{-1}) for a-$Se_{100-x}Bi_x$ thin films.

Electric Field (V/cm)	$Se_{99.5}Bi_{0.5}$		$Se_{97.5}Bi_{2.5}$		$Se_{96}Bi_4$	
	ΔE	σ_0	ΔE	σ_0	ΔE	σ_0
5.00E+04	0.195	3.68E-06	0.277	2.59E-05	0.285	1.45E-05
8.30E+04	0.177	2.30E-06	0.213	3.85E-06	0.273	1.18E-05
1.04E+05	0.167	1.81E06	0.185	1.59E-06	0.263	1.14E-05
1.25E+05	0.162	1.18E-06	0.171	1.01E-06	0.204	1.48E-06
1.66E+05	0.112	4.25E-07	0.166	9.85E-07	0.184	9.85E-07

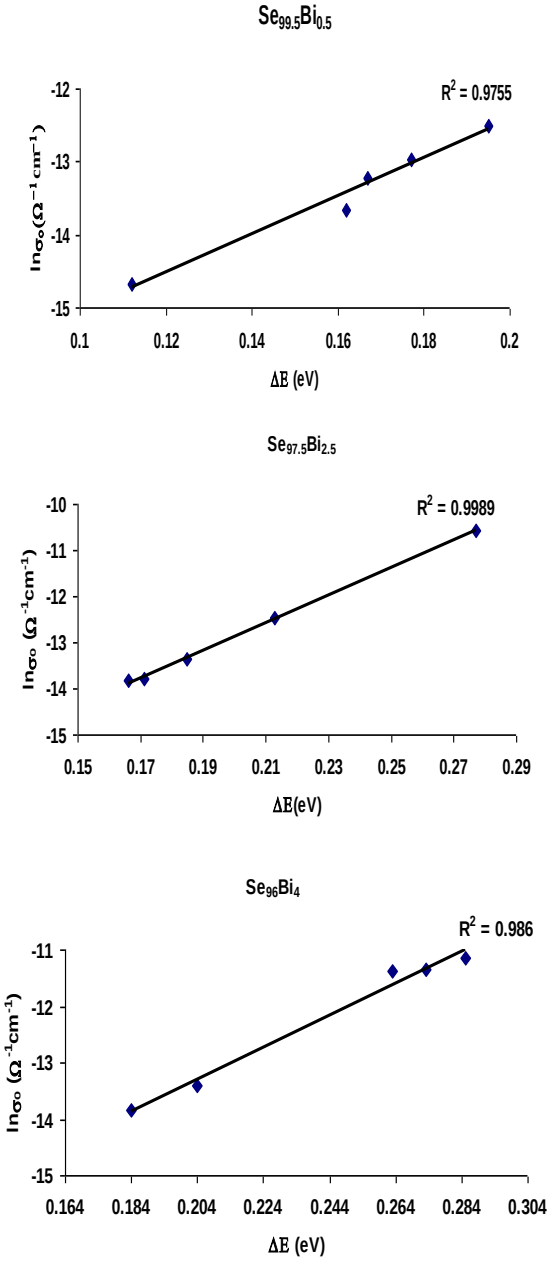

Fig. 4. ln σ_0 versus ΔE plot for a-$Se_{100-x}Bi_x$ thin films.

From the slopes and intercepts of the lines of ln σ_0 vs. ΔE curves, we have calculated the values of E_{MN} and σ_{00}. These values are given in Table 2. It is clear from this table that the characteristic energy (E_{MN}) is different at different electric field and there exists a strong correlation between the MN conductivity pre-factor and characteristic energy as shown in Fig. 5. This figure indicates that σ_{00} varies exponentially with E_{MN}, which can be expressed as:

$$\ln \sigma_{00} = \alpha + \beta E_{MN} \qquad (3)$$

where α and β are constants.

Table 2. The values of ln σ_{00} and MN Energy (E_{MN}) for glassy a-$Se_{100-x}Bi_x$ thin films.

Composition	E_{MN} (meV)	σ_{00} (Ω^{-1} cm^{-1})
$Se_{99.5}Bi_{0.5}$	38.01	2.18E-08
$Se_{97.5}Bi_{2.5}$	33.20	6.31E-09
$Se_{96}Bi_4$	34.96	8.78E-09

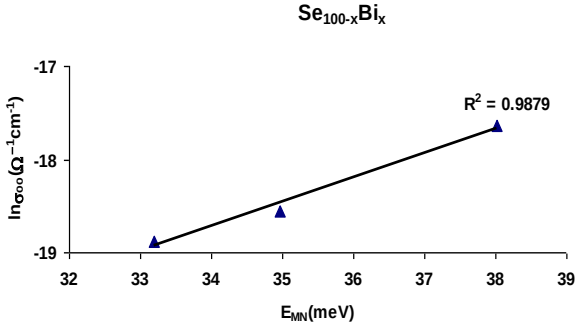

Fig. 5. ln σ_{00} versus E_{MN} plot for a-$Se_{100-x}Bi_x$ thin films to the see applicability of further MN rule.

The above relation between σ_{00} and E_{MN} given by Equation (3) is called "Further MN Rule" [11, 12].

To explain MN rule, Yelon and Movaghar has proposed a model, called YM model [13, 14]. According to this model, the MN rule 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 et al. suggest that the optical phonons are the source of the excitation energy in such process. It is assumed that many phonons are involve in trapping and de-trapping of electrons, either by cascade or by multi-phonon process. They have explained MN Rule with entropy term, which may vary the pre-factor by many orders of magnitude. It applies equally well to crystalline or amorphous materials.

In this model, Emin [15] has calculated the hopping rates due to multi-phonon effects, using small polaron theory and the Kubo–Greewood formula. The result is

$$R(\Delta E) \propto \exp\left[\left(\frac{\Delta E}{h\upsilon_0}\right)\ln S\right]\exp\left(\frac{-\Delta E}{kT}\right) \qquad (4)$$

where $h\upsilon_0$ is the optical phonon energy. That is,

$$E_{MN} = \frac{h\upsilon_0}{\ln S} \qquad (5)$$

where

$$S = \frac{2E_b}{h\upsilon_0} \qquad (6)$$

In Eq. (6), E_b is the small-polaron binding energy, so that S represents a normalized coupling strength. In Eq. (5), if ln S is of the order 1 in all these cases, the typical value of optical phonon energies in materials is about 25 and 50 meV [16].

In order to understand the variation of E_{MN} with $\ln\sigma_{00}$ observed by Shimakawa and Abdel-Wahab, we start by assuming that electron hopping induced by optical phonons and the associated variation in σ_{00}, must be due to variation in ln S. Actually, Emin's model predicts that the hopping rate, and as a result, the conductivity, will be extremely sensitive to variation in ln S. The most complete expression for the hopping rate at low temperatures is presented by Emin [15]. If we limit our consideration to hops upward in energy, and use the present notation, this may be written as

$$R(\Delta E) = \frac{2\pi}{\omega_0}\left(\frac{J}{h}\right)^2 e^{-s}\frac{\exp\left(\frac{-\Delta E}{E_{MN}}\right)\exp\left(\frac{-\Delta E}{kT}\right)}{\left(\frac{\Delta E}{h\upsilon_0}\right)!} \times\left[\sum_{\pi-\infty}^{\infty}(A_n)^{\frac{\Delta E}{h\upsilon_0}}\times\cos\left(\frac{\Delta E\phi_n}{h\upsilon_0}\right)\right] \qquad (7)$$

Where J is the electron transfer integral connecting the initial and final sites, A_n is a lattice-relaxation amplitude function and ϕ_n is the lattice relaxation phase shift. As can be easily seen the MN energy depends upon ln S, whereas the hopping rate depends upon the exp (-S). Combining, Eqs. (5) and (7) leads the prediction that

$$\ln\sigma_{00} = r - \exp\left(\frac{h\upsilon_0}{E_{MN}}\right), \qquad (8)$$

Here it has been assumed that 'r' is a constant.

Using the data of σ_{00} and E_{MN}, curves are plotted between σ_{00} and E_{MN}, (see Figs. 6). The value of $h\upsilon_0$ for the above case is 17.4 meV. The lower values of $h\upsilon_0$ may be due to high field electric conduction in the present case, whereas Yelon et al developed above theory without using high electric field. The present results, therefore supports the model given by Yelon and Movaghar to explain the observation of MN rule between σ_{00} and E_{MN} for high field conduction.

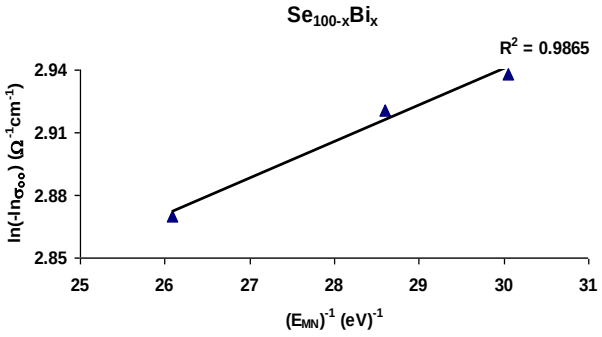

Fig. 6. ln(-ln σ_{00}) versus $(E_{MN})^{-1}$ plot for a-$Se_{100-x}Bi_x$ thin films.

4. Conclusions

In the present paper, we report the observation of the further Meyer-Neldel rule (MNR) in thermally activated high field conduction in a-$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4) thin films. For this purpose the temperature dependence of d. c. conductivity is studied at different electric fields for all samples used in the present study.

We found that the conductivity obeys the Meyer-Neldel rule as the pre-exponential factor depends on activation energy. We also found a strong correlation between pre-factor σ_{00} and Meyer Neldel energy (E_{MN}). The observation of the correlation between pre-factor σ_{00} and Meyer Neldel energy can be described by multiple excitations stimulated by phonon energy as described by Yelon and Movaghar.

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