

FURTHER MEYER-NELDEL RULE IN a- $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ THIN FILMS

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Temperature dependence of conductivity is measured in dark as well as in presence of light in amorphous thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ in the temperature range 290 –365 K and in the intensity range 0-1190 Lux. We have investigated further Meyer Neldel rule by two different approaches. In first approach, the different sets of Meyer Neldel pre-factor σ_{00} and Meyer Neldel energy E_{mn} are obtained by keeping composition constant. In the second approach, the different sets of Meyer Neldel prefactor σ_{00} and Meyer Neldel energy E_{mn} are obtained by changing the composition. A strong correlation between Meyer Neldel pre-factor σ_{00} and Meyer Neldel energy E_{mn} has been observed in both the cases.

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1. Introduction

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:

$$\sigma = \sigma_0 \exp (- \Delta E / kT) \quad (1)$$

where, ΔE is called the activation energy and σ_0 is called the pre-exponential factor. The above equation is termed as Arrhenius law and is used to determine the activation energy for electrical conduction.

In many organic and amorphous materials, σ_0 is found to increase exponentially with ΔE [1-18] following a relation:

$$\sigma_0 = \sigma_{00} \exp (\Delta E / kT_0) \quad (2)$$

Recently, the Meyer Neldel relation has been applied to various thermally activated phenomena in chalcogenide glasses [19-28]. Activated phenomena, such as d. c. conduction, a. c. conduction and thermal crystallization, are examples for which MNR has been demonstrated in various chalcogenide glassy systems [19-32].

Thus, the observation of MNR in various thermally activated phenomena for different materials is well known. Shimakawa and Abdel-Waheb [33], found a strong correlation between σ_{00} and kT_0

$$\ln \sigma_{00} = A + B k T_0 \quad (3)$$

where A and B are constants.

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A strong co-relation between σ_{00} and kT_0 has also been reported by Wang and Chen [34] in fullerenes. A similar correlation has also been reported in the case of a-Si:H by varying composition techniques[35].

In the present paper we report the evidence of further Meyer-Neldel rule in a- $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($x = 0, 2, 4, 6$ and 8) thin films in two cases. In first approach, σ_{00} is obtained from temperature dependence of conductivity at different illumination intensities and tried to investigate whether there is a correlation or not between Meyer Neldel conductivity pre-factor σ_{00} and the characteristic energy kT_0 in Se-Te-Zn glassy system. In second approach, we have tried to investigate whether there is a correlation or not between Meyer Neldel conductivity pre-factor σ_{00} and the characteristic energy kT_0 by varying the composition of glassy system. We have observed a correlation between σ_{00} and the characteristic energy kT_0 in the MN rule in both the cases. Our results may be helpful as an additional guideline to understand the long standing puzzle of the origin of the MN rule.

2. Experimental procedure

Glassy alloys of $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($0, 2, 4, 6,$ and 8) were prepared by quenching technique. Highly pure materials (5 N pure) were weighed according to their atomic percentages and were sealed in a quartz ampoule under a vacuum of 10^{-5} Torr. Ampoules were kept inside the furnace at an appropriate temperature (where the temperature was raised to 900°C at a rate of $4\text{-}5^\circ\text{C}/\text{min.}$). The ampoules were rocked frequently for 11 hrs at the maximum temperature to make the melt homogeneous. Quenching was done in liquid nitrogen and the glassy nature of alloys was checked by x-ray diffraction technique.

Thin films of glassy alloys were prepared by vacuum evaporation technique at a base pressure of 10^{-5} Torr, using a standard coating unit (IBP-TORR: EPR- 002), keeping the glass substrate at room temperature. Vacuum- evaporated indium electrodes were used for electrical contacts. The thickness of the films was about 5000 \AA . A coplanar structure (length ~ 1.3 cm and electrodes separation ~ 0.5 mm) was used for present measurements.

Steady - state photoconductivity measurements were performed by mounting the film in a specially designed sample holder in which light could be shown through a transparent window. A vacuum of about 10^{-2} Torr was maintained during these measurements. The temperature of these films was controlled by a heater mounted inside the sample holder and was measured using a copper - constantan thermocouple mounted very near to the films. The light source for these measurements was a 200 W tungsten lamp, the intensity of which was measured by a lux meter (Testron, model LX-101). The photoconductivity was measured by a digital electrometer (Keithley, model 614). Before measurement, the films were first annealed at their glass transition temperature ($T_g \sim 360$ K) for two hours in a vacuum $\sim 10^{-3}$ Torr. The present measurements were made by applying only 10 V across the films.

3. Results

The temperature dependence of conductivity was studied in amorphous thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($0, 2, 4, 6$ and 8) at different intensities ($0\text{-}1190$ lx) in the temperature range $290\text{-}365$ K. In σ_{ph} vs $1000/T$ curves were found to be straight lines in all the cases. Results of only two alloys are shown in Figs.1 and 2. Such a behavior is consistent with Eq. (1). From the slopes and the intercepts of these lines the values of ΔE and σ_0 are calculated for each glassy alloy. Fig.3 shows the plot of $\ln \sigma_0$ vs ΔE for $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ thin films for the first approach. In all the cases, $\ln \sigma_0$ vs ΔE curves were found to be straight lines. Curve fitting is done by least square method and the correlation coefficients (R^2) of such lines are indicated in Fig.3 and also mentioned in Tables 1-5.

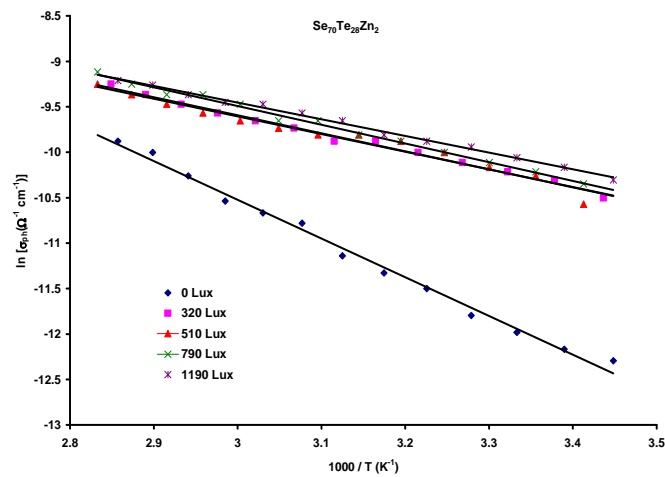


Fig.1. $\ln \sigma$ vs $1000/T$ at different level of illumination intensities in amorphous $Se_{70}Te_{28}Zn_2$ thin films

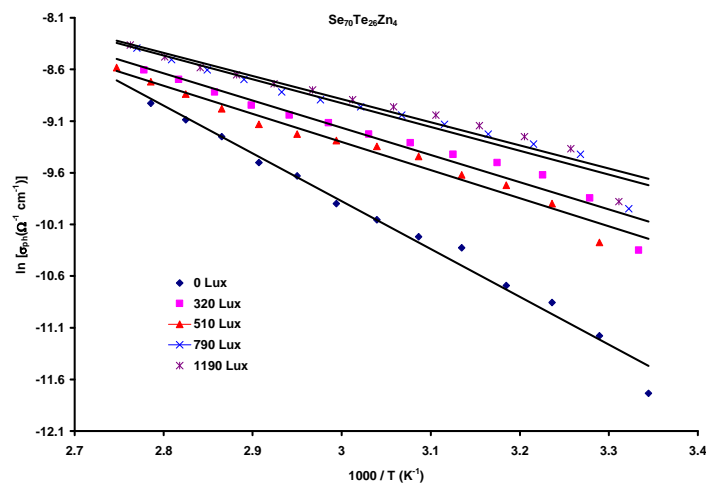


Fig.2. $\ln \sigma$ vs $1000/T$ at different level of illumination intensities in amorphous $Se_{70}Te_{26}Zn_4$ thin films

Table 1. Semiconduction parameters in a- $Se_{70}Te_{30}$ thin films at various intensity (according to first approach).

S. No.	F (Lux)	ΔE (eV)	$\ln \sigma_0$ ($\Omega^{-1} \text{ cm}^{-1}$)	Square of Correlation coefficient (R^2) for $\ln \sigma_0$ vs ΔE
1	0	0.39	5.63	0.9939
2	320	0.3	2.8281	
3	510	0.28	2.1588	
4	790	0.27	2.0153	
5	1190	0.27	2.1755	

Table 2. Semiconduction parameters in $Se_{70}Te_{28}Zn_2$ thin films at various intensity of Light (according to first approach)

S. No.	F (Lux)	ΔE (eV)	$\ln \sigma_0$ ($\Omega^{-1} \text{ cm}^{-1}$)	Square of Correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	320	0.17	-3.6352	0.9348
2	510	0.17	-3.7705	
3	790	0.18	-3.3129	
4	1190	0.16	-3.9508	

Table 3. Semiconduction parameters in $Se_{70}Te_{26}Zn_4$ thin films at various intensity of light (according to first approach)

S. No.	F (Lux)	ΔE (eV)	$\ln \sigma_0$ ($\Omega^{-1} \text{ cm}^{-1}$)	Square of correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	320	0.23	-1.2491	0.9896
2	510	0.23	-1.1423	
3	790	0.2	-2.0206	
4	1190	0.19	-2.1733	

Table 4. Semiconduction parameters in $Se_{70}Te_{24}Zn_6$ thin films at various intensity of light (according to first approach)

S. No.	F (Lux)	ΔE (eV)	$\ln \sigma_0$ ($\Omega^{-1} \text{ cm}^{-1}$)	Square of correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	0	0.32	3.8056	0.9622
2	320	0.3	3.4629	
3	510	0.29	3.1883	
4	1190	0.29	3.0975	

Table 5. Semiconduction parameters in $Se_{70}Te_{22}Zn_8$ thin films at various intensity of light (according to first approach).

S. No.	F (Lux)	ΔE (eV)	$\ln \sigma_0$ ($\Omega^{-1} \text{ cm}^{-1}$)	Square of correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	0	0.34	4.7982	0.9864
2	320	0.28	3.2222	
3	510	0.26	2.3996	
4	790	0.25	2.3084	
5	1190	0.27	2.983	

We have calculated the values of $(kT_0)^{-1}$ and σ_{00} from the slopes and intercepts of these lines for each individual case. It is interesting to note that the value of MN conductivity pre-factor σ_{00} is different at different compositions. The value of the characteristic energy (kT_0) is also different at these compositions (see Table 6). On plotting $\ln\sigma_{00}$ as function of kT_0 , a straight line is obtained (see Fig. 4) which indicates that a strong correlation exists between these quantities which can be described by the following relation:

$$\sigma_{00} = \sigma_{00'} \exp(kT_0 / \varepsilon) \quad (4)$$

where ε is a constant.

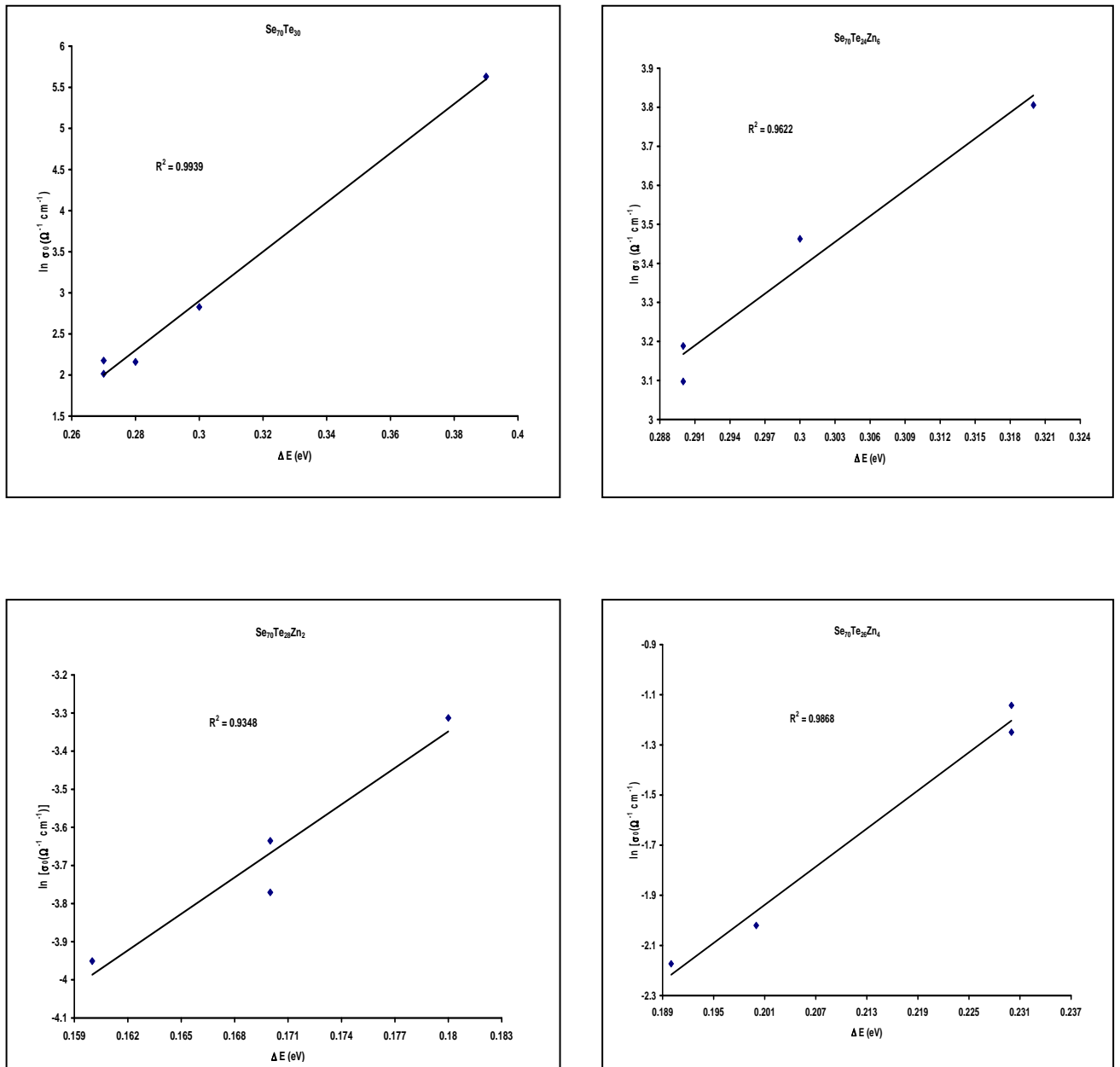


Fig.3. $\ln\sigma_0$ vs ΔE for a- $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ thin films for the first approach (different composition with illumination as a variable)

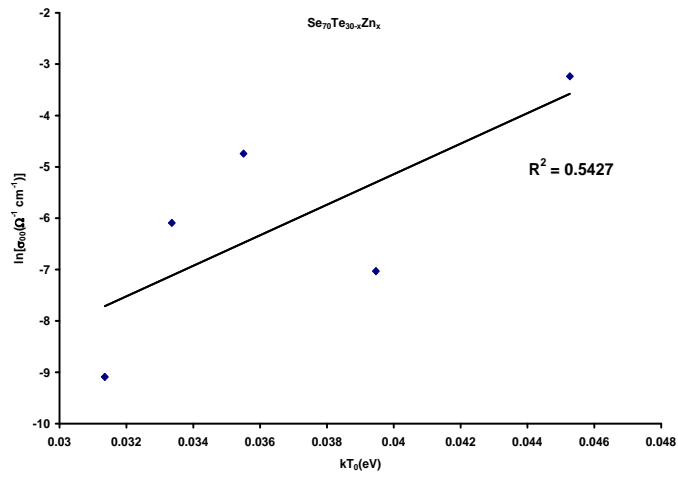


Fig. 4. $\ln \sigma_0$ vs kT_0 plot for a - $Se_{70}Te_{30-x}Zn_x$ thin films for the first approach (different composition with illuminations variable).

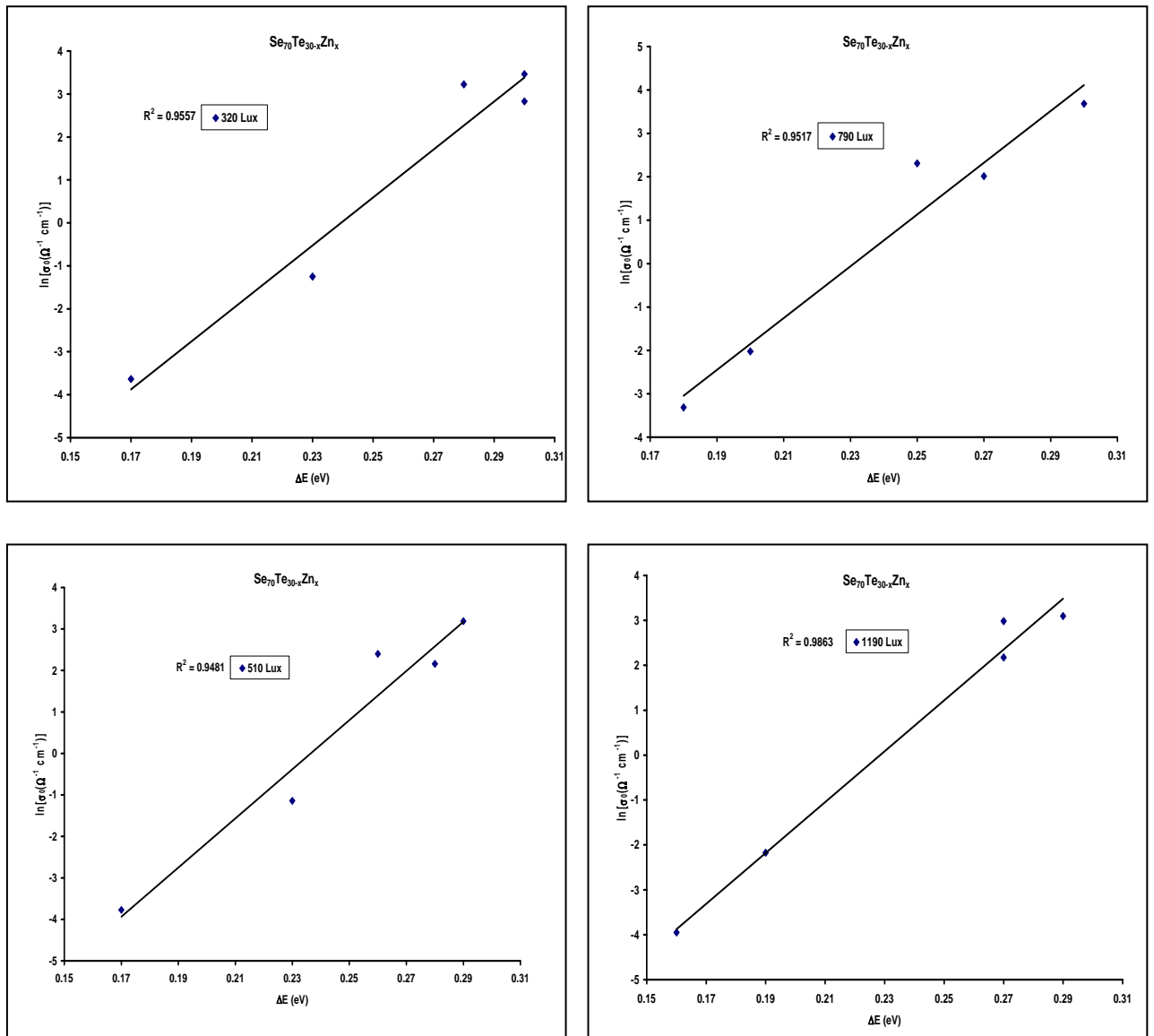


Fig.5 $\ln \sigma_0$ vs ΔE for a - $Se_{70}Te_{30-x}Zn_x$ thin films for the second approach (various levels of illumination with composition(x as a variable)).

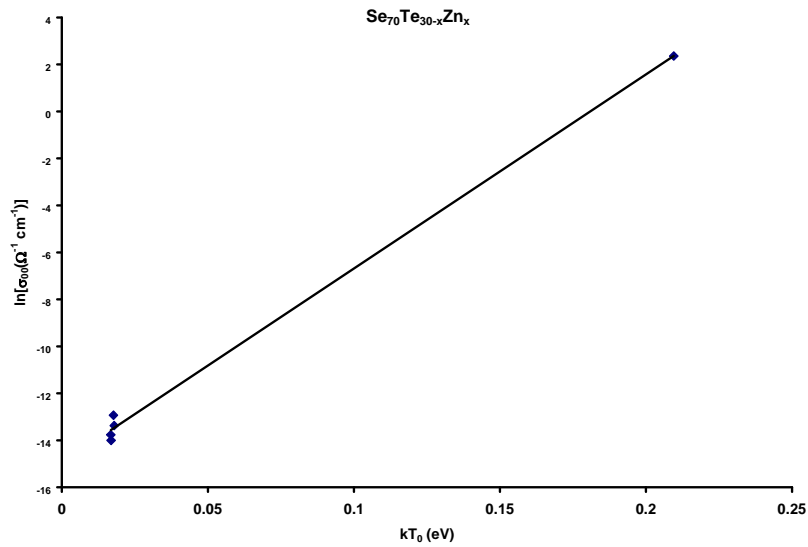


Fig. 6. $\ln\sigma_{00}$ vs kT_0 for a - $Se_{70}Te_{30-x}Zn_x$ thin films for the second approach (various levels of illumination with composition(x) as a variable)

In the second approach, ΔE and σ_0 are collected at a particular intensity for different compositions (see Tables 7-11) and plotted in Fig.5. From the slopes and intercepts of these curves, the values of $(kT_0)^{-1}$ and σ_{00} are obtained at different intensities. The values of $\sigma_{00} kT_0$ are given in Table 12. On plotting $\ln\sigma_{00}$ as function of kT_0 , a straight line is obtained (see Fig.6) which indicates that a strong correlation exists between these quantities in this approach also.

Table 6. $\ln\sigma_{00}$ and kT_0 parameters for a - $Se_{70}Te_{30-x}Zn_x$ thin films for the first approach (different composition with illumination as variable).

S. No.	Series	kT_0 (eV)	$\ln[\sigma_{00}(\Omega^{-1} \text{ cm}^{-1})]$
1	$x = 0$	0.033357	-6.0921
2	$x = 2$	0.031353	-9.0895
3	$x = 4$	0.039465	-7.0309
4	$x = 6$	0.045269	-3.2384
5	$x = 8$	0.035506	-4.7435

Table 7. Semiconduction parameters in $Se_{70}Te_{30-x}Zn_x$ thin films in dark for second Approach.

S. No.	Series	ΔE (eV)	$\ln[\sigma_0(\Omega^{-1} \text{ cm}^{-1})]$	Square of Correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	$x = 0$	0.39	5.63	0.0162
2	$x = 2$	0.37	2.25	
3	$x = 4$	0.4	4.0083	
4	$x = 6$	0.32	3.8056	
5	$x = 8$	0.34	4.7982	

Table 8. Semiconduction parameters in $Se_{70}Te_{30-x}Zn_x$ thin films at 320 Lux for second approach

S. No.	Series	ΔE (eV)	$\ln[\sigma_0(\Omega^{-1} \text{cm}^{-1})]$	Square of Correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	x = 0	0.3	2.8281	0.9557
2	x = 2	0.17	-3.6352	
3	x = 4	0.23	-1.2491	
4	x = 6	0.3	3.4629	
5	x = 8	0.28	3.2222	

Table 9. Semiconduction parameters in $Se_{70}Te_{30-x}Zn_x$ thin films at 510 Lux for second approach

S. No.	Series	ΔE (eV)	$\ln[\sigma_0(\Omega^{-1} \text{cm}^{-1})]$	Square of Correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	x = 0	0.28	2.1588	0.9481
2	x = 2	0.17	-3.7705	
3	x = 4	0.23	-1.1423	
4	x = 6	0.29	3.1883	
5	x = 8	0.26	2.3996	

Table 10. Semiconduction parameters in $Se_{70}Te_{30-x}Zn_x$ thin films at 710 Lux for second approach

S. No.	Series	ΔE (eV)	$\ln[\sigma_0(\Omega^{-1} \text{cm}^{-1})]$	Square of Correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	x = 0	0.27	2.0153	0.9517
2	x = 2	0.18	-3.3129	
3	x = 4	0.2	-2.0206	
4	x = 6	0.3	3.6828	
5	x = 8	0.25	2.3084	

Table 11. Semiconduction parameters in $Se_{70}Te_{30-x}Zn_x$ thin films at 1190 Lux for second approach

S. No.	Series	ΔE (eV)	$\ln[\sigma_0(\Omega^{-1} \text{cm}^{-1})]$	Square of Correlation coefficient(R^2) for $\ln \sigma_0$ vs ΔE
1	x = 0	0.27	2.1755	0.9863
2	x = 2	0.16	-3.9508	
3	x = 4	0.19	-2.1733	
4	x = 6	0.29	3.0975	
5	x = 8	0.27	2.983	

Table 12. $\ln\sigma_{00}$ and kT_0^{-1} parameters for $a\text{-Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ thin films for the second approach (different composition with illumination as variable)

S. No.	F (Lux)	$(kT_0)^{-1}$ (eV) ⁻¹	$\ln[\sigma_{00}(\Omega^{-1} \text{ cm}^{-1})]$
1	Dark	4.7734	2.3609
2	320	55.85	-13.372
3	510	59.24	-14.006
4	790	59.603	-13.77
5	1190	56.622	-12.937

The correlation between σ_{00} and kT_0 has also been reported by Shimakawa and Abdel-Waheb [2] in the case of chalcogenide glasses. In their case, ε has a value 1.7 meV. Wang and Chen [34] have also reported strong correlation between σ_{00} and kT_0 in fullerenes. They have shown that conductivity in fullerenes obeys the Meyer-Neldel rule. They found that the correlation between σ_{00} and kT_0 can be approximately described by an expression

$$\sigma_{00} = \sigma_{00'} \exp(-E_h / kT_0) \quad (5)$$

where $\sigma_{00'}$ and E_h are constants.

In addition, Wang and Chen [34] have shown that the set of values of σ_{00} and kT_0 obtained for a group of glassy systems by Shimakawa and Wahab [2] can be well fitted to Eq. (5) and hence they have concluded that the model proposed by Crandall [36] and Chen [5] can be used to describe the MN conductivity pre-factor in chalcogenide glasses very well.

Following the above described facts, we have tried to investigate whether the set of values of σ_{00} and kT_0 obtained in our case for $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($0 \leq x \leq 8$) thin films can be fitted or not in Eq. (5). This is found true in the present case for both the approaches (Figs are not shown here). These results confirm the fact that conclusion made by Wang and Chen [34] for chalcogenide glasses is correct and can be well understood by the model given by Crandall [36] and Chen [5] to interpret the MN conductivity behavior in chalcogenide glasses.

4. Conclusion

To observe the presence of Meyer Neldel rule in $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($0 \leq x \leq 8$) thin films, two sets of data are collected. In first approach, variation of activation energy is observed at different intensities for a particular amorphous thin film. The pre-exponential factor σ_0 changed with activation energy for all glassy alloys. In second approach, we have used the second data set, in which activation energy is changed by varying the composition at a fixed intensity of light. It is found that σ_0 varies with ΔE in both the approaches. In both the cases, a further MN rule is also observed where a co-relation between σ_{00} and kT_0 is observed. The results of further MN rule is similar to the model given by Wang and Chen, which is based on the explanation given by Crandall [36] and Chen [5] to interpret the MN conductivity behaviour in chalcogenide glasses.

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