



## Crystallization kinetics of glassy $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ alloys: Observation of Mayer-Neldel rule

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### Abstract

Glassy alloys of  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  were prepared using melt quenching technique. Non-isothermal differential scanning calorimetric (DSC) studies were done on  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$  at.%) glassy alloys at four different heating rates ( $\beta = 5, 10, 15, 20$  °C/min). Well defined endothermic and exothermic peaks were obtained at glass transition ( $T_g$ ) and crystallization temperature ( $T_c$ ), respectively. Augis and Bennett's method was used to obtain the composition dependent crystallization activation energy ( $E_c$ ) and the pre-exponential factor ( $\eta_0$ ) of the Arrhenius expression. A linear dependence between  $\ln \eta_0$  and  $E_c$  was observed showing the existence of compensation effects of the Meyer-Neldel type. These compensation effects confirm the applicability of Meyer-Neldel (MN) rule for the non-isothermal crystallization in the present case.

**Keywords:** chalcogenide glasses, crystallization kinetics, activation energy, Meyer-Neldel rule

### I. Introduction

Applicability of amorphous semiconductors has truly emerged in various directions. Chalcogenide glasses are used to fabricate solid state devices which are helpful both in scientific and technological fields. Different techniques have been used to study the structure of chalcogenide glasses e.g. electron microscopy, X-ray diffraction and differential scanning calorimetry [1]. Studies of the crystallization kinetics of a glass by differential scanning calorimetry can be performed by using either isothermal or non-isothermal method. In the isothermal method, a sample is first heated up to the crystallization temperature and then change of physical quantity is measured as a function of time. However, in the non-isothermal method, the sample is heated at a fixed heating rate and change of physical parameter is measured as a function of temperature. The non-isothermal method is considered to be advantageous over isothermal method because in isothermal method there is a problem of reaching a test temperature instantaneously. Also during the time in which the system needs to stabilize, no measurements can be recorded in

isothermal method.

These days, due to their structure, properties and preparation [2–12], Ag doped chalcogenide glasses have become attractive materials for fundamental study. Their application is widely spread over optics and optoelectronics such as optical imaging, photo doping, photo lithography and phase change optical recording [2–12]. Another important reason for popularity of Ag doped chalcogenide glasses is the low free energy of crystallization of Ag (48 kcal/mol) which is helpful in phase change optical recording [10,11]. This helps in good optical recording-high phase transformation rate. Thus, the research based on the Ag doped chalcogenide glasses is of great importance from basic science point of view and its application.

When one heats the amorphous system, crystallization takes place near crystallization temperature. During crystallization process crystallization rate constant ( $\eta$ ) increases exponentially with the increase in temperature. This shows that crystallization is a thermally activated process. Mathematically, it is written as:

$$\eta = \eta_0 \exp \frac{-E_c}{k \cdot T} \quad (1)$$

where  $\eta$  is the absolute rate of a thermally activated pro-

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cess,  $\eta_0$  is the pre-exponential factor,  $E_c$  is the activation energy and  $k$  is the Boltzmann constant.

Activation energy for glass to crystal transformation ( $E_c$ ) and pre-exponential factor ( $\eta_0$ ) for each composition can be obtained by using the Augis and Bennett's [13] method which is based on the Johnson Mehl Avrami (JMA) model [14–16]. The Augis and Bennett's equation is [13]:

$$\ln \frac{\beta}{T_c} = -\frac{E_c}{k \cdot T_c} + \ln \eta_0 \quad (2)$$

where  $T_c$  stands for the peak crystallization temperature and  $k$  is the Boltzmann constant. This method has an advantage that the plot between  $\ln(\beta/T_c)$  and  $1/T_c$  gives the value of pre-exponential factor  $\eta_0$  of Arrhenius equation.

It has been observed by various researchers that the pre-exponential factor  $\eta_0$  correlates with the activation energy  $E_c$  [17]:

$$\ln \eta_0 = \ln \eta_{00} + \frac{E_c}{E_{MN}} \quad (3)$$

where  $\eta_{00}$  and  $E_{MN}$  are positive constants,  $E_{MN}$  is Meyer-Neldel energy,  $\eta_0$  and  $E_c$  are directly dependent. This is known as Meyer-Neldel rule or MN rule (also referred as compensation effect). This is an empirical law known since 1937 [18]. The effect was first observed by Meyer-Neldel [18] in electronic conductivity of oxide semiconductors ( $\text{WO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$ ). Though it is observed in two main fields that are diffusion processes and semiconductor conduction, MN rule has wide range of applicability in various phenomena of physics, chemistry, biology and electronics [17,19–26].

Though, universally single MN rule explanation for different system is found to be controversial [27,28]. Work done for the testing of compensation effect in different thermally activated processes in the same type of materials and in the same thermally activated process in different types of materials (such as polymers, amorphous solids, glasses, crystalline solids, etc.) is successful. The latest study includes number of activated phenomenon such as solid-state diffusion in crystals and polymers, dielectric relaxation and conduction in polymers, thermally stimulated processes in polymers and electronic conduction in amorphous semiconductors [19–25,29–34]. There are also reports of MN rule in kinetic processes, such as amorphous to crystal transition [26,35,36].

In our earlier paper [37], we have reported the temperature dependence of AC conductivity for bulk samples of glassy  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$ ) at different frequencies. From these measurements activation energy and pre-exponential factor were calculated. It is found that pre-exponential factor does not remain constant but varies with activation energy. This verifies the validity of MN rule. The experiment was carried out in the temperature range 289–402 K and frequency range 20–500 kHz. We have also calculated the activation en-

ergy of glass transition phenomenon and crystallization process of these glassy samples. Along with the study of thermal stability of  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ , composition dependence of thermal stability and activation energy of glass transition have also been reported in our previous work [38,39].

Our present work reports the activation energy of crystallization using Augis and Bennett's method. A strong correlation between the pre-exponential factor  $\eta_0$  and activation energy of crystallization  $E_c$  is reported in the paper.

## II. Experimental

Glassy alloys of  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$  at.%) were prepared using the conventional quenching technique. High-purity (99.999%) Se, In and Ag in appropriate atomic proportions were weighed using an electronic balance (LIBROR, AEG-120) with the least count of  $10^{-4}$  g and sealed in a quartz ampoule under a vacuum of  $10^{-5}$  Torr. The ampoules were then heated in the furnace at  $1000^\circ\text{C}$  for about 12 h. The ampoules were continuously rotated to facilitate homogenization of the sample. The molten samples were rapidly quenched in ice cooled water to obtain the glassy state. The ingot so produced was ground gently using a pestle and mortar to obtain fine powder.

The thermal characterization was investigated using differential scanning calorimeter (TA instrument, USA, model auto Q20) using an accuracy of  $\pm 0.1^\circ\text{C}$ . DSC measurements were taken at four different heating rates, i.e. 5, 10, 15 and  $20^\circ\text{C}/\text{min}$  on accurately weighed samples in aluminium pan under non-isothermal conditions.

## III. Results and discussion

The glassy nature of the samples was ascertained by X-ray diffraction (XRD). Figure 1 shows the diffractograms of the  $\text{Se}_{90}\text{In}_8\text{Ag}_2$  composition. The absence of sharp diffraction peaks indicates that the samples exhibit glassy nature. Similar results were also obtained for other compositions.

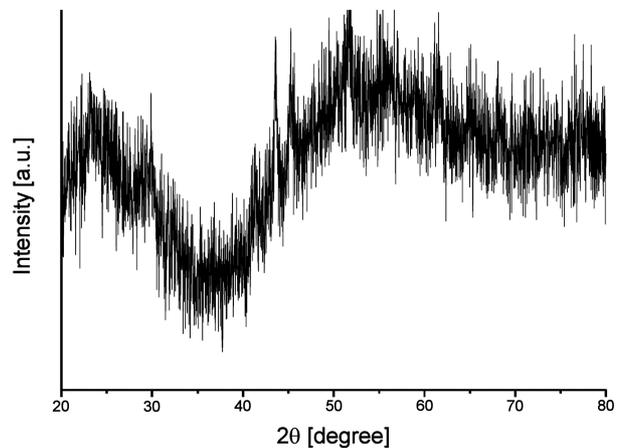


Figure 1. XRD pattern of  $\text{Se}_{90}\text{In}_8\text{Ag}_2$  chalcogenide glass

**Table 1. Peak crystallization temperature  $T_c$  of glassy  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$ ) alloys at different heating rate**

Heating rate [°C/min]	Peak crystallization temperature, $T_c$ [°C]				
	$\text{Se}_{90}\text{In}_{10}$	$\text{Se}_{90}\text{In}_8\text{Ag}_2$	$\text{Se}_{90}\text{In}_6\text{Ag}_4$	$\text{Se}_{90}\text{In}_4\text{Ag}_6$	$\text{Se}_{90}\text{In}_2\text{Ag}_8$
5	111.5	113.0	112.3	91.2	99.0
10	119.0	119.0	120.3	101.8	108.6
15	123.4	125.0	124.3	97.8	110.1
20	127.3	136.0	129.9	99.4	113.1

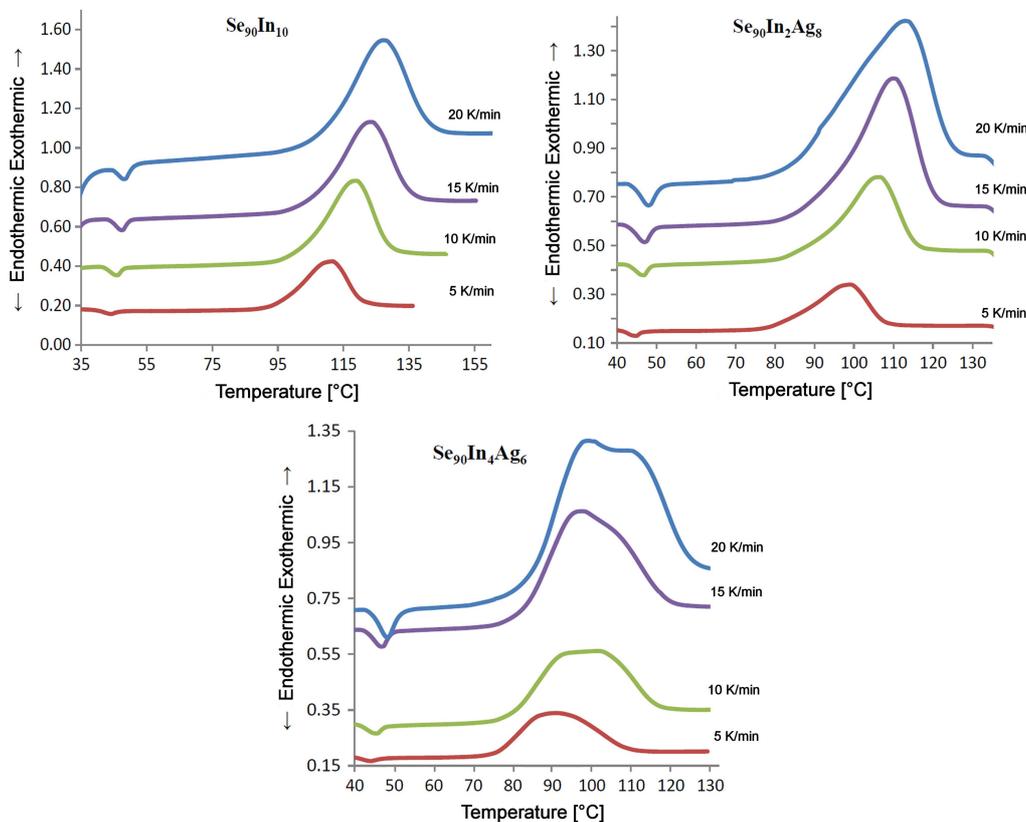
Figure 2 shows DSC thermograms of the samples  $\text{Se}_{90}\text{In}_{10}$ ,  $\text{Se}_{90}\text{In}_4\text{Ag}_6$  and  $\text{Se}_{90}\text{In}_2\text{Ag}_8$  for all heating rates (i.e. 5, 10, 15, 20 °C/min). Similar results are obtained for other glassy alloys, as well. The presence of single crystallization peak shows existence of single phase in crystallization of each alloy. Peak crystallization temperatures for the samples at different heating rates (5, 10, 15, 20 °C/min) are given in Table 1.

Activation energy for glass to crystal transformation ( $E_c$ ) and pre-exponential factor ( $\eta_0$ ) for each composition were obtained by using the Augis and Bennett’s

[13] equation (Eq. 2). Linear plots were obtained from the graph of  $\ln(\beta/T_c)$  against  $1000/T_c$  and thus the values of  $E_c$  were calculated from the obtained slopes. The pre-exponential factor ( $\eta_0$ ) in the Arrhenius equation is obtained from the vertical intercepts of the plots. The resultant plots are shown in Fig. 3. The calculated values of  $E_c$  and exponential factor of the Arrhenius relation  $\ln \eta_0$  are listed in Table 2. From the obtained results it can be concluded that both  $E_c$  and  $\ln \eta_0$  are composition dependent and  $\eta_0$  is not constant but instead  $\ln \eta_0$  depends on  $E_c$ . By plotting a graph between  $\ln \eta_0$  and  $E_c$ , presence of compensation effect is shown in the non-isothermal crystallization process in glassy alloy of  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  (Fig. 4). With high regression factor ( $R^2 = 0.974$ ) a strong correlation between  $\ln \eta_0$  and  $E_c$  shows that MN rule is applicable for the non-isothermal crystallization process. It should be mentioned here that crystallization process may be complex, but in the present analysis we have calculated activation energy considering a simple process giving an average value of activation energy in each case.

**Table 2. Values of  $E_c$  and  $\ln \eta_0$  for  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$ ) glassy alloys**

Alloy	$E_c$ [eV]	$\ln \eta_0$
$\text{Se}_{90}\text{In}_{10}$	1.14	29.98
$\text{Se}_{90}\text{In}_8\text{Ag}_2$	0.76	18.64
$\text{Se}_{90}\text{In}_6\text{Ag}_4$	1.05	27.20
$\text{Se}_{90}\text{In}_4\text{Ag}_6$	1.07	30.05
$\text{Se}_{90}\text{In}_2\text{Ag}_8$	1.19	32.77



**Figure 2. DSC thermograms of  $\text{Se}_{90}\text{In}_{10}$ ,  $\text{Se}_{90}\text{In}_4\text{Ag}_6$  and  $\text{Se}_{90}\text{In}_2\text{Ag}_8$  alloys**

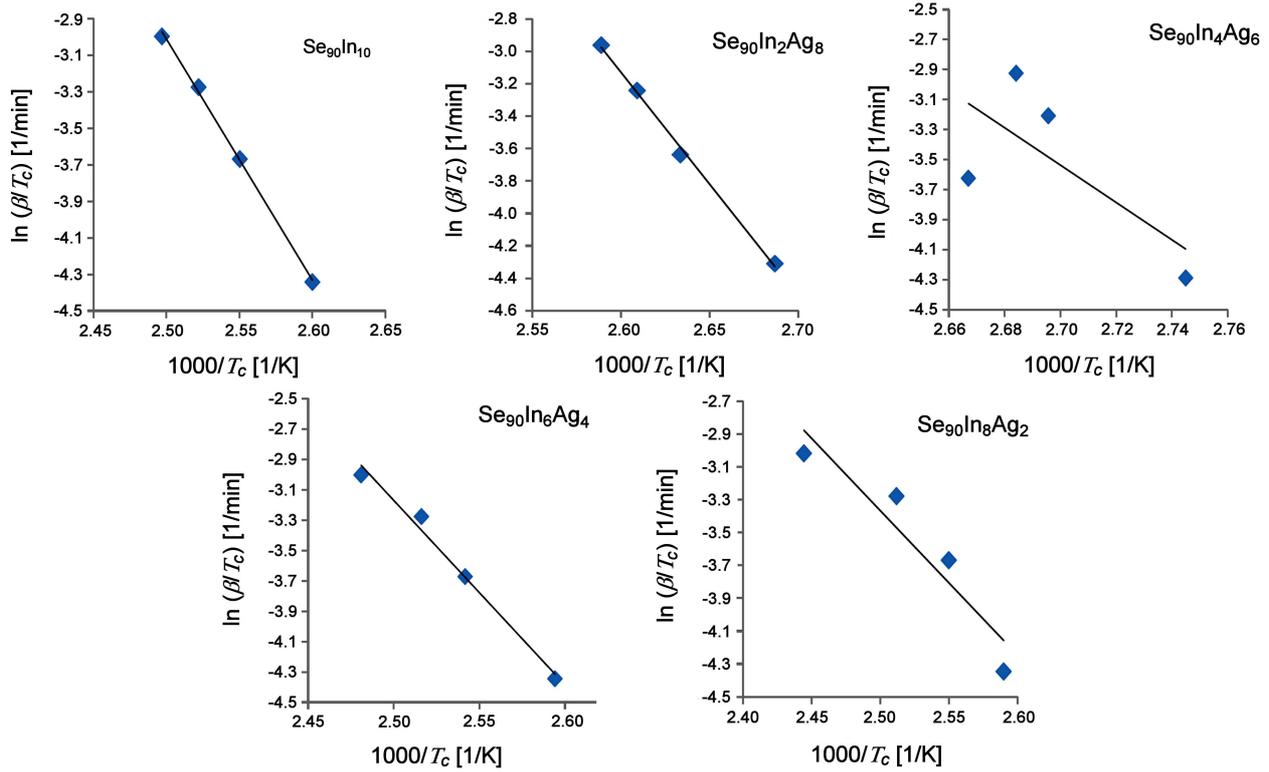


Figure 3. Plots of  $\ln(\beta/T_c)$  with  $1000/T_c$  for  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$ ) glassy alloys

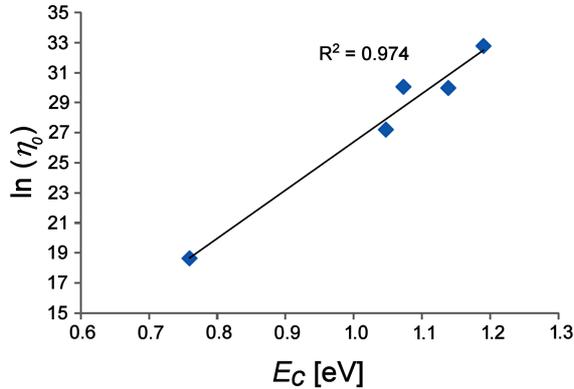


Figure 4. Plot of  $\ln \eta_0$  against  $E_c$  for  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$

Koga and Sestak [40] have mathematically shown that the effect due to the kinetic compensation is the resultant of exponential form of the rate constant. Thus, a change in activation energy ( $E_c$ ) is compensated by the same change in the logarithm of the pre-exponential factor ( $\eta_0$ ) or temperature, which is shown in the present study. The information thus obtained has good application from the research point of view. However, it is difficult to have any quantitative information from it. The present results are in the favour of applicability of MN rule for thermally activated processes in  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$  at.%) glassy alloys.

#### IV. Conclusions

Non-isothermal method was used to study the crystallization process in  $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$  ( $x = 0, 2, 4, 6, 8$  at.%)

glassy alloys. The pre-exponential factor ( $\ln \eta_0$ ) was found to depend on activation energy ( $E_c$ ) and linear correlation between  $\ln \eta_0$  and  $E_c$  was observed. Linear dependence shows the presence of a compensation effect for the non-isothermal crystallization process in the present sample.

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