

APPLICABILITY OF MEYER-NELDEL RULE FOR NON ISOTHERMAL CRYSTALLIZATION IN GLASSY $\text{Se}_{90}\text{M}_{10}$ ($\text{M} = \text{Cu, Bi, In, Sb, Te}$) ALLOYS

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Many activated phenomena, including solid state diffusion in crystals and polymers, dielectric relaxation, conduction and thermally stimulated processes in polymers, and electronic conduction in amorphous semiconductors obey the compensation rule or Meyer-Neldel rule. In the present paper, we report the applicability of this rule in the non-isothermal crystallization in glassy $\text{Se}_{90}\text{M}_{10}$ ($\text{M} = \text{Cu, Bi, In, Sb, Te}$) alloys. We have observed Meyer-Neldel rule between pre-exponential factor K_0 and activation energy of crystallization E_c in the present case.

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1. Introduction

The Meyer–Neldel rule or MN rule is an empirical law, which was developed by W. Meyer and H. Neldel in 1937 [1]. This rule is applicable in broad range of thermally activated phenomena in physics, chemistry, biology and electronics [2-8]. It appears to be a fundamental property of many families of activated processes following an Arrhenius dependence on temperature:

$$\psi = \psi_0 \exp\left(-\frac{\Delta E}{k T}\right) \quad (1)$$

Here ψ is the absolute rate of a thermally activated process, ψ_0 the pre-exponential factor, ΔE the activation enthalpy and k the Boltzmann constant. Commonly, by the evaluation of experimental data, the activation enthalpy is determined from the slope of $(\Delta E / k)$ of an Arrhenius plot of $\ln \psi$ vs $1 / T$. It is frequently found that, when ΔE is varied with a family of processes (for example, related chemical reaction), then pre-exponential factor X_0 obeys the following empirical relation:

$$\psi_0 = \psi_{00} \exp\left(\frac{\Delta E}{E_{MN}}\right) \quad (2),$$

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where ψ_{00} and E_{MN} are positive constants. E_{MN} is known as Meyer-Neldel energy for the process in question. This empirical relation is known as MN rule or compensation effect.

The features of the MN rule, linear behavior of the Arrhenius plot and a characteristic temperature where the compensation is exact, are often recognized. This rule is generally observed in disordered materials. In the class of amorphous semiconductors, the MN rule has been reported in a-Si:H films in which ΔE is varied by doping, by surface absorption, light soaking or by preparing films under different conditions [9-11].

In case of chalcogenide glasses also, MN rule is observed by the variation of activation energy ΔE of d.c. conduction on changing the composition of the glassy alloys [12-15] in a specific glassy system or by the variation of intensity of light [16, 17].

Though evidence of MN rule has been reported for a number of activated phenomena 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 [2-8], a less effort has been done to observe MN rule in kinetic phenomena such as crystallization phenomenon. In this paper, we have reported the observation of MN rule for the non-isothermal crystallization in glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloys. A strong correlation between the pre-exponential factor K_0 and activation energy of crystallization E_c has been observed in the present study.

2. Experimental

Glassy alloys of $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te, Bi, In and Sb 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 ($\sim 10^{-5}$ Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm). The ampoules containing material were heated to 1000°C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of $3 - 4^\circ\text{C} / \text{minute}$. During heating, the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by X-ray diffraction (XRD) technique. The XRD pattern of $\text{Se}_{90}\text{Sb}_{10}$ alloy is shown in Fig. 1. Absence of any sharp peak in XRD pattern in Fig. 1 confirms the glassy nature of $\text{Se}_{90}\text{Sb}_{10}$ alloy. Similar XRD patterns were obtained for the other glassy alloys.

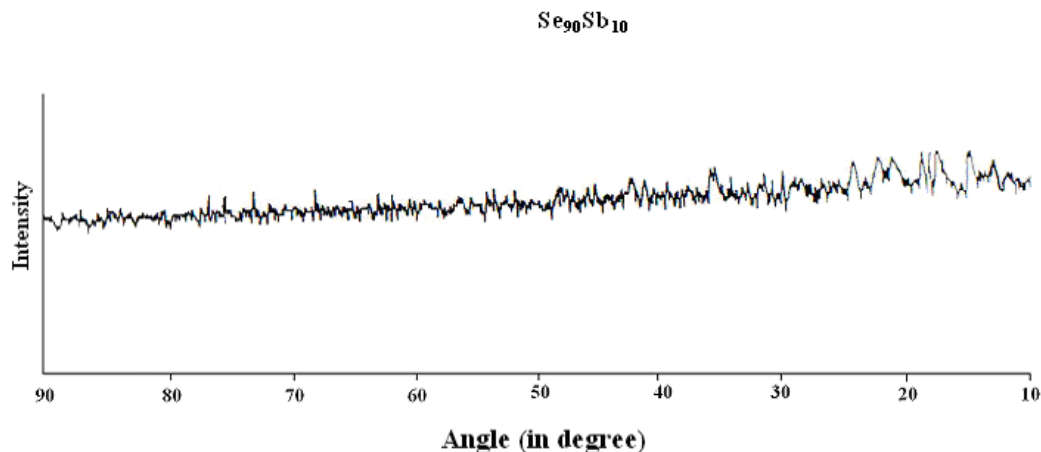


Fig. 1. XRD pattern of glassy $\text{Se}_{90}\text{Sb}_{10}$ alloy

The glasses, thus prepared, were ground to make fine powder for DSC studies. Constant heating rates were used for DSC scans. Before DSC experiment, the Thermogravimetric Analysis has been made on each glassy sample. Perkin Elmer TGA7 Thermogravimetric is used for this purpose. In Thermogravimetric Analysis, the percent weight loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment (inert-nitrogen gas). The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. The TGA curve for $\text{Se}_{90}\text{Sb}_{10}$ alloy is shown in Fig. 2, which is a plot of percent weight loss versus temperature. From this figure, it is clear that there is no drastic loss in the weight of the sample over the entire temperature range. Similar TGA curves are obtained for the other glassy alloys.

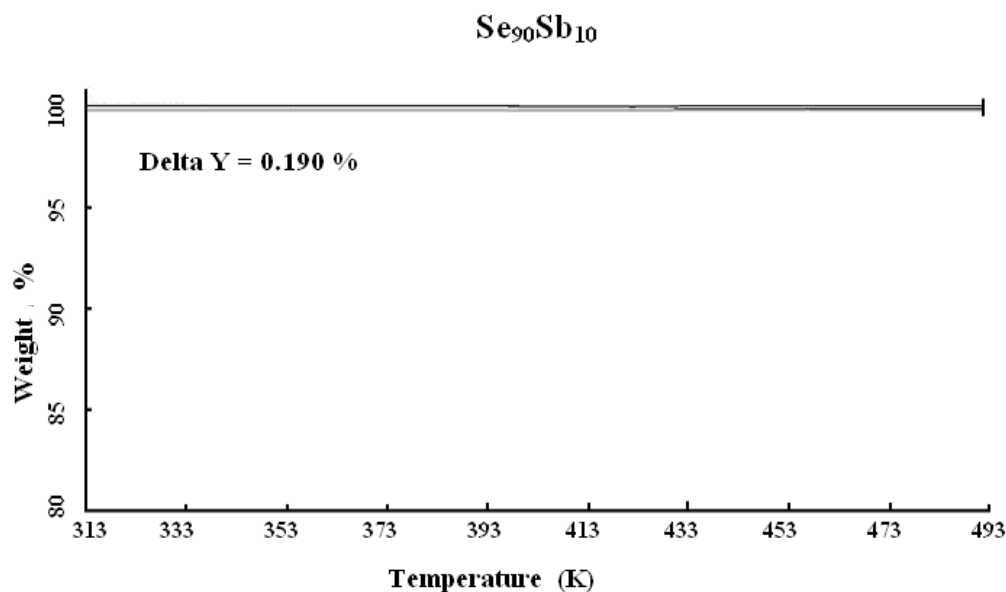


Fig. 2. TGA curve for glassy $\text{Se}_{90}\text{Sb}_{10}$ alloy.

The thermal behaviour was investigated using differential scanning calorimeter (Model-DSC plus, Rheometric Scientific Company, UK). The temperature precision of this equipment is ± 0.1 K with an average standard error of about ± 1 K in the measured values (glass transition and crystallization temperatures).

3. Theoretical basis

In general, crystallization rate constant K increases exponentially with temperature indicating that the crystallization is a thermally activated process. Mathematically, it can be expressed as:

$$K = K_0 \exp\left(-\frac{E_c}{kT}\right) \quad (3)$$

where E_c is the activation energy of crystallization, K_0 the pre-exponential factor and k the Boltzmann constant. In equation (3), E_c and K_0 are assumed to be practically independent of the temperature (at least in the temperature interval accessible in the calorimetric measurements). The values of activation energy of crystallization E_c and the pre-exponential factor K_0 can be evaluated by the equation

$$\ln\left(\frac{\beta}{T_c}\right) = -\frac{E_c}{k T_c} + \ln K_0 \quad (4)$$

The above equation is derived by Augis and Bennett [18] from the classical JMA model [19-21]. This method has an extra advantage that the intercept of $\ln \beta/T_c$ vs. $1/T_c$ gives the value of pre-exponential factor K_0 of Arrhenius equation.

4. Results and discussion

Fig. 3 shows the typical DSC thermograms for $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloys at the heating rate of 10 K/min. Similar thermograms were obtained for other heating rates also (not shown here). It is clear from Fig. 3 that well defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperatures (T_c) respectively.

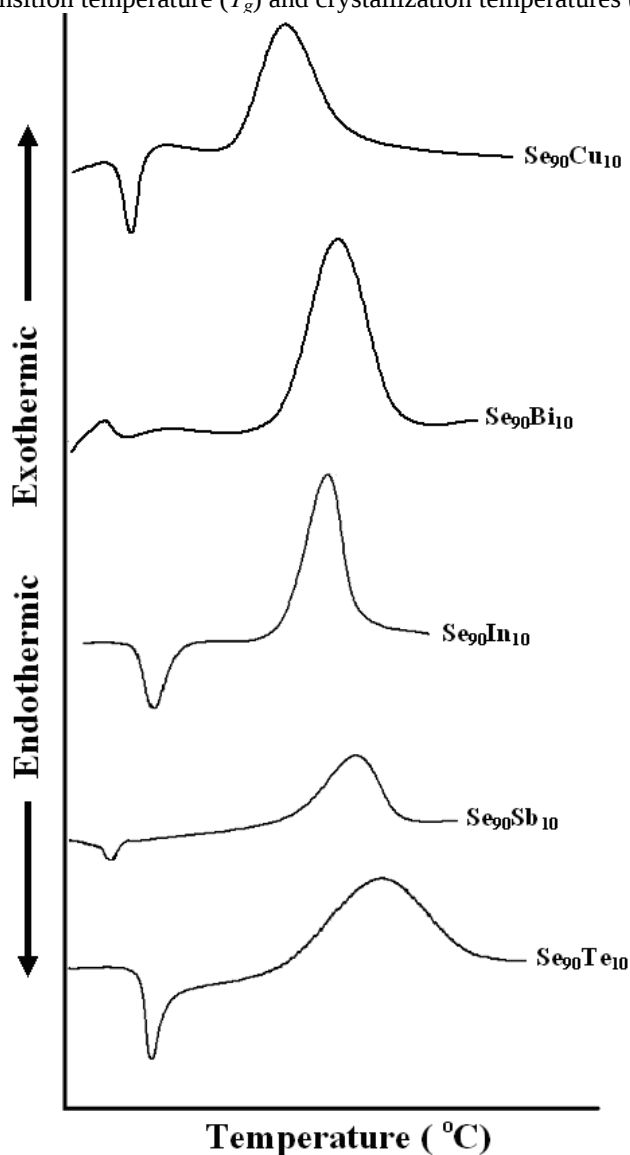


Fig. 3. DSC Thermograms for glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloys at heating rate of 10 K / min

According to eqn. (4), the plot of $\ln (\beta / T_c)$ vs $10^3 / T_c$ leads to a straight line. This has been verified for glassy $\text{Se}_{90}\text{In}_{10}$ alloy in Fig. 4. Similar plots curves are obtained for the other glassy alloys.

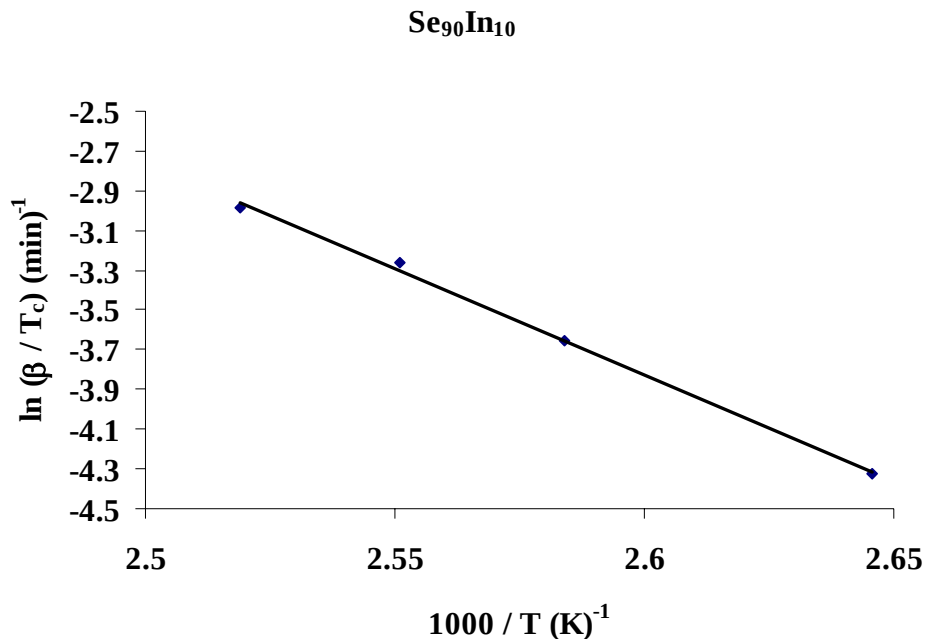


Fig. 4. $\ln (\beta / T_c)$ vs $10^3 / T_c$ plots for glassy $\text{Se}_{90}\text{In}_{10}$ alloy

The activation energy of crystallization E_c and pre-exponential factor K_0 of the glassy alloys have been calculated from the slopes and intercepts of the plots of $\ln (\beta / T_c)$ vs $10^3 / T_c$. The values of E_c and $\ln K_0$ for various binary glassy alloys obtained from equation (4) are given in Table 1.

Table 1. Values of E_c and $\ln K_0$ for glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu}, \text{Bi}, \text{In}, \text{Sb}, \text{Te}$) alloys

Composition	E_c (e V)	$\ln K_0$	$\ln K_0 = \ln K_{00} + [E_c / k T_0]$
$\text{Se}_{90}\text{Cu}_{10}$	0.75	19.9	18.4
$\text{Se}_{90}\text{Bi}_{10}$	0.92	24.0	23.4
$\text{Se}_{90}\text{In}_{10}$	1.41	37.8	37.8
$\text{Se}_{90}\text{Sb}_{10}$	0.97	25.2	24.8
$\text{Se}_{90}\text{Te}_{10}$	0.89	22.1	22.4

It is obvious from Table 1 that E_c and K_0 are composition dependent and K_0 is not a constant but depends on E_c . Fig. 5 shows the plot of $\ln K_0$ vs E_c for glassy $\text{Se}_{90}\text{In}_{10}$ ($M = \text{Cu}, \text{Bi}, \text{In}, \text{Sb}, \text{Te}$) alloys. Curve fitting is done by least square method and the square of coefficient of correlation (R^2) of $\ln K_0$ vs E_c plot is indicated in the Fig. 5. Microsoft Excel program is used in the present measurements for determination of R^2 . It is clear from the Fig. 5 that $\ln K_0$ vs E_c plot is a straight line of good correlation coefficient indicating that K_0 varies exponentially with E_c following the relation:

$$\ln K_0 = \ln K_{00} + \frac{E_c}{k T_0} \quad (5)$$

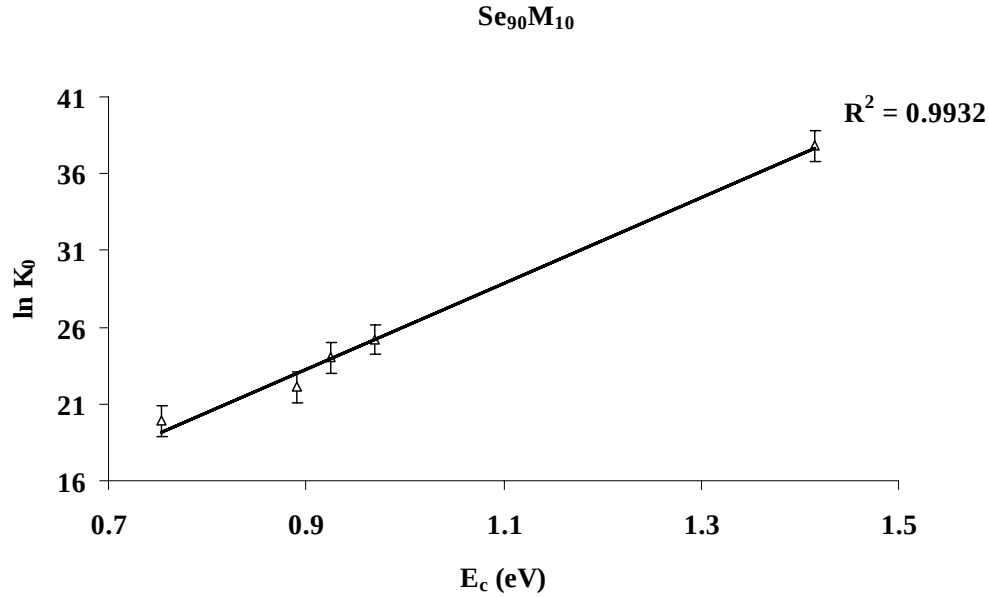


Fig. 5. Plot of $\ln K_0$ versus E_c for glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloy

From the slope and intercept of the line, we have calculated the values of $(kT_0)^{-1}$ and K_{00} . Using these values, the expected $\ln K_0$ values have been calculated for glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloys and compared with the reported values (see Table 1). An overall good agreement between these two values confirms the validity of MN rule in the present glasses.

Koga and Sestak [22] have shown that the kinetic compensation effect mathematically results from the exponential form of the rate constant. A change of activation energy is thus compensated by the same change in temperature or in the logarithm of the pre-exponential factor. In the present study also, the increase in E_c is compensated by the increase in the pre-exponential factor K_0 . However, it should be noted that the above observation is highly qualitative and it is difficult to get any quantitative information from such observation. Future experiments in this direction could reveal the exact origin for the observation of MN rule for non-isothermal crystallization of amorphous semiconductors such as we have observed for glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloys in the present study.

5. Conclusion

Glassy $\text{Se}_{90}\text{M}_{10}$ ($M = \text{Cu, Bi, In, Sb, Te}$) alloys have been prepared by quenching technique. The results show that the activation energy and pre-exponential factor satisfies the MN rule for the present glassy system. This indicates that the MN rule, which is generally observed for solid state diffusion in crystals and polymers, dielectric relaxation and conduction in polymers, thermally stimulated processes in polymers and electronic conduction in amorphous semiconductors; is also observed for non-isothermal crystallization in chalcogenide glasses.

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