J Mater Sci (2007) 42:490–494
DOI 10.1007/s10853-006-1065-9

Pre-exponential factor of Arrhenius equation for the isothermal crystallization of some Se–Ge, Se–In and Se–Te chalcogenide glasses

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Received: 14 July 2005 / Accepted: 18 January 2006 / Published online: 14 November 2006
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Abstract Compensation law or Meyer–Neldel rule is observed in 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. In the present paper, we have reported the compensation effect for the isothermal crystallization of some Se–Ge, Se–In and Se–Te chalcogenide glasses. We have observed Meyer–Neldel rule between pre-exponential factor K_0 and activation energy of crystallization E_c in the present case.

Introduction

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 law or Meyer–Neldel rule. The Meyer–Neldel rule or MN rule (also known as compensation effect) is an empirical law known since 1937 [1]. This rule is observed in wide range of 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:

$$X = X_0 \exp(-\Delta E/kT) \tag{1}$$

Here X is the absolute rate of a thermally activated process, X_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 ($\Delta E/k$) of an Arrhenius plot of ln X 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:

$$X_0 = X_{00} \exp(\Delta E/E_{MN}), \tag{2}$$

where X_{00} and E_{MN} are positive constants. E_{MN} is known as Meyer–Neldel energy for the process in question. Since then, the origin of this relation is referred to as the Meyer–Neldel relation or MN rule and the physical interpretation of X_{00} and E_{MN} has been the subject of speculations. The discussion of whether there is one universal explanation for the MNR in different systems is not yet settled. Various plausible models have been proposed.

The hallmarks 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

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glassy alloys [12–19] in a specific glassy system or by the variation of intensity of light [19, 20]. In our laboratory also, different glassy systems were prepared by quenching technique and the observation of MN rule were reported in some of these glassy systems in a series of papers [12–15].

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 isothermal crystallization of some chalcogenide glasses of $Se_{100-x}Ge_x$, $Se_{100-x}In_x$ and $Se_{100-x}Te_x$ ($5 \le x \le 30$) glassy systems. A strong correlation between the pre-exponential factor K_0 and activation energy of crystallization E_c has been observed in the present study.

Experimental

Glassy alloys used in the present study were prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed (~5 g) using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} g. The material was then sealed in evacuated (~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 h. The temperature of the furnace was raised slowly at a rate of 3–4 °C/min. 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 h, 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 Differential Scanning Technique (DSC) technique. For this purpose, DSC patterns of all the samples were taken at a heating rate of 5 K/min using DSC 2910 Differential Scanning calorimetry (T. A. instruments, USA). Each sample (10–20 mg) in powdered form was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. The DSC patterns of glassy $Se_{90}M_{10}$ (M = Ge, In, Te) alloy are shown in Fig. 1. From Fig. 1, it is clear that well-defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperatures (T_c) respectively. Similar DSC patterns were obtained for the other glassy alloys.

The glasses, thus prepared, were ground to make fine powder and the pellets (dia ~ 6 mm and thickness ~ 0.5–1 mm) were obtained after compressing the powder in a die at a load of 3–4 × 10^4 N.

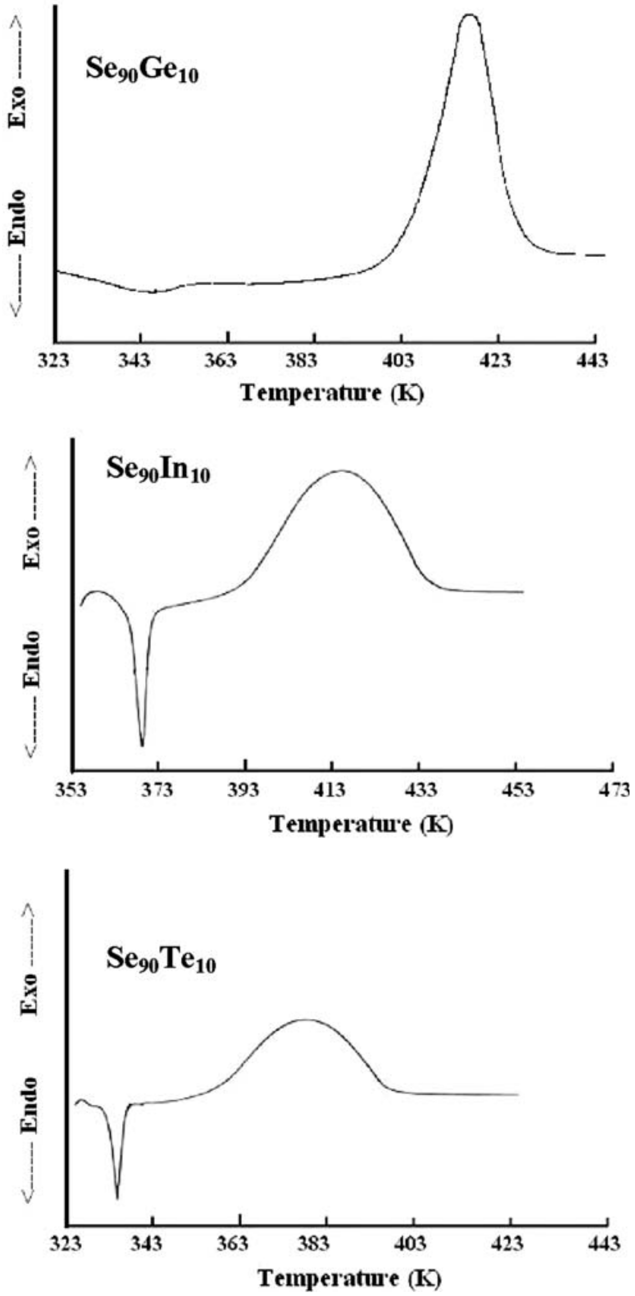

Fig. 1 DSC patterns of glassy $Se_{90}M_{10}$ (M = Ge, In, Te) alloys at heating rate of 5 K/min

The isothermal amorphous to crystalline (a–c) phase transformation was studied by measuring the d.c. conductivity σ as a function of time (1–2 min intervals) at various annealing temperatures between the glass transition temperature and crystallization temperature. The annealing temperature T was kept constant during the a–c phase transformation period. The remarkable increase of σ implies that σ at any time t is the result of two conductivities σ_a and σ_c corresponding to a double phase system, amorphous and crystalline.

The conductivity measurements were taken in a vacuum ~ 10^{-2} Torr by mounting the samples in a specially designed sample holder. The resistance was measured using Kiethely Electrometer (model 614). The temperature was measured using a calibrated constantan thermocouple. Different pellets were taken for each value of T. The annealing temperature T was attained at a fast heating rate and then maintained constant till saturation in the resistance was obtained.

Results

During the isothermal transformation, the extent of crystallization (α) of a certain material is represented by the Avrami's equation [21]:

$$\alpha(t) = 1 - \exp[-(K\,t)^n] \tag{3}$$

where 'K' is rate constant and 'n' is the order parameter which depends upon the mechanism of crystal growth.

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:

$$K = K_0 \exp(-E_c/kT) \tag{4}$$

where E_c is called the activation energy of crystallization and K_0 is called the pre-exponential factor.

The above equation is termed as Arrhenius law and is used to determine the activation energy of crystallization. The extent of crystallization (α) has been calculated using the isothermal d.c. conductivity measurements [22, 23]. The details of the method can be obtained from the literature [24–28]. Once the values of α are known at different isothermal annealing times [22, 23], the value of ln K as a function of temperature can be calculated using Eq. 3 in the following form:

$$\ln[\ln(1 - a)^{-1}] = \ln K + n \ln t \tag{5}$$

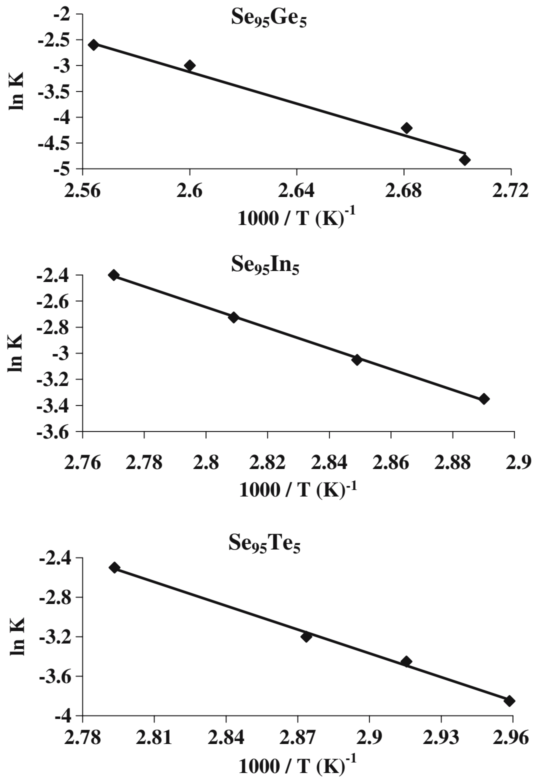

Fig. 2 Plots of ln K vs. 1000/T for glassy $Se_{95}M_5$ (M = Ge, In, Te) alloys

According to Eq. 5, the plot of ln[ln $(1 - \alpha)^{-1}$] vs. ln t leads to a straight line of intercept ln K.

The values of the temperature dependent crystallization rate constant K, evaluated from the intercepts of ln [ln $(1 - \alpha)^{-1}$] vs. ln t curves were plotted as a function of temperature for glassy Se–Ge, Se–In and Se–Te alloys. The plots of ln K vs. $10^3/T$ curves for glassy $Se_{95}M_5$ (M = Ge, In, Te) alloys are shown in Fig. 2. The straight line, thus obtained, confirms the validity of Eq. 4. Similar plots are obtained for the other glassy alloys. The values of E_c and ln K_0 for various alloys obtained from the slopes of ln K vs. $10^3/T$ curves are given in Table 1.

Discussion

It is clear from this table that E_c and K_0 are composition dependent and K_0 is not a constant but depends on E_c. Figure 3 shows the plots of ln K_0 vs. E_c for glassy $Se_{100-x}Ge_x$, $Se_{100-x}In_x$ and $Se_{100-x}Te_x$ systems. Curve fitting is done by least square method and the square of coefficient of correlation (R^2) of the ln K_0 vs. E_c plot is indicated in these figures. It is clear from these figures that each ln K_0 vs. E_c plot is a

Table 1 Values of E_c and K_0 evaluated from isothermal method for $Se_{100-x}M_x$ (M = Ge, In, Te) chalcogenide glasses

Glassy system	E_c (eV)	K_0 (min)$^{-1}$	$K_0 = K_{00}$ exp $[E_c/kT_0]$ (min)$^{-1}$
$Se_{100-x}Ge_x$			
$x = 5$	1.32	9.00×10^{15}	4.00×10^{14}
$x = 10$	0.50	2.60×10^{3}	6.36×10^{2}
$x = 15$	1.13	3.00×10^{10}	8.30×10^{11}
$x = 22$	0.87	4.00×10^{7}	1.40×10^{8}
$Se_{100-x}In_x$			
$x = 5$	0.68	3.09×10^{8}	2.10×10^{8}
$x = 10$	0.82	1.17×10^{10}	1.92×10^{10}
$x = 20$	0.91	4.40×10^{11}	4.10×10^{11}
$x = 30$	1.01	1.32×10^{13}	1.21×10^{13}
$Se_{100-x}Te_x$			
$x = 5$	0.69	4.57×10^{8}	4.39×10^{8}
$x = 10$	0.90	3.26×10^{11}	4.02×10^{11}
$x = 20$	1.07	1.61×10^{14}	1.08×10^{14}
$x = 30$	1.16	1.54×10^{15}	1.94×10^{15}

straight line of good correlation coefficient indicating that K_0 varies exponentially with E_c following the relation:

$$\ln K_0 = \ln K_{00} + E_c/k\,T_0 \tag{6}$$

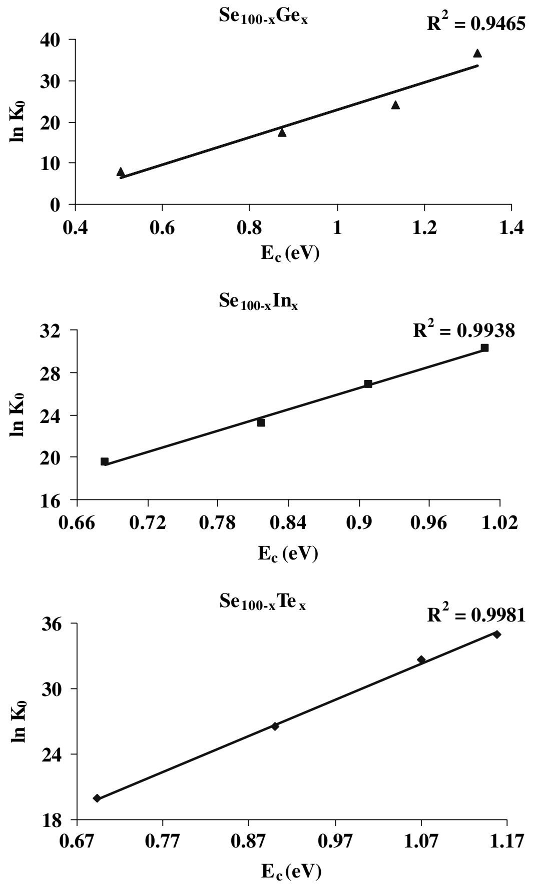

Fig. 3 ln K_0 vs. E_c plots for glassy $Se_{100-x}Ge_x$, $Se_{100-x}In_x$ and $Se_{100-x}Te_x$ systems

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 the glassy $Se_{100-x}Ge_x$, $Se_{100-x}In_x$ and $Se_{100-x}Te_x$ systems and compared with the reported values (see Table 1). An overall good agreement between these two values confirms the validity of MN Rule in glassy $Se_{100-x}Ge_x$, $Se_{100-x}In_x$ and $Se_{100-x}Te_x$ systems for isothermal crystallization.

Various workers have provided different models or assumptions [29–32] to explain the MN rule for such kinetic phenomena, as we have observed for some chalcogenide glasses of Se–M (M = Ge, In, Te) system in the present study. The applicability of MN rule for isothermal crystallization of some chalcogenide glasses in Se–Ge–Sb system has been reported by Bordas et al. [29, 30]. On annealing some Se–Ge–Sb glasses, they have observed two crystalline phases: Sb_2Se_3 and $GeSe_2$. For the glass samples located in the crystallization region of Sb_2Se_3, they state that the compensation effect is related to the crystallization of Sb_2Se_3. In any case, they attribute the compensation effect to the primary and secondary crystallization of different phases. Fang [31] has proposed a model for MN rule in activated processes. According to this model, the annealing time parameter obeys the MN rule. Koga and Sestak [32] 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. As the rate constant K is also annealing time dependent parameter, our results confirm the validity of the model proposed by Fang [31].

Conclusion

Chalcogenide glasses of glassy $Se_{100-x}Ge_x$, $Se_{100-x}In_x$ and $Se_{100-x}Te_x$ systems have been prepared by quenching technique. Temperature dependence of crystallization rate constant $K(T)$ has been studied for various glassy alloys. It has been find that $K(T)$ is thermally activated. The activation energy, however, depends on the composition.

The activation energy and pre-exponential factor satisfies the MN rule for all the glassy systems. This shows 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 the crystallization in chalcogenide glasses.

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