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EFFECT OF THERMAL HISTORY ON CRYSTALLIZATION AND GLASS TRANSITION IN Se AND $Se_{90}Te_{10}$ CHALCOGENIDE GLASSES

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The effect of thermal history on cold crystallization and glass transition in glassy Se and $Se_{90}Te_{10}$ was studied using differential scanning calorimetry (DSC) technique. The amorphous Se and $Se_{90}Te_{10}$ materials were prepared using standard melt quench technique. The aged samples were stored in the dark for prolonged period of time (~ 5 years) at room temperature. All samples were thermally treated to remove thermal history using a rejuvenated procedure and then the same kinetic parameters were determined. A significant shift of the glass transition temperature along with the large endothermic signal was observed indicating of the important effect of thermal history on glass transition. No such effect was observed in the crystallization exothermic peaks. The activation energies for glass transition and crystallization thermal events in glassy Se and $Se_{90}Te_{10}$ were determined using Moynihan *et al* and Ozawa methods, respectively. It is found that the activation energy for glass transition decreases with aging in both glasses. The pronounced changes observed in the characteristics of the glass transition in aged samples as compared to the rejuvenated samples are due to structural relaxation of the glassy phase.

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Keywords: Crystallization, Glass transition, DSC, Se-Te chalcogenide glass, Thermal history

1. Introduction

It is well known that physical aging plays an important role in the thermal and structural behaviour of glassy materials. Due to this effect many physical properties of a glass will be affected by the thermal history as well as the structural relaxation of the glass [1]. Physical aging has been widely investigated in chalcogenide glasses [2-6]. This interest arises from the wide range of applications of these glasses in optical and phase-change memory devices. The physical aging phenomenon in chalcogenide glasses can also provide vital information on the glassy state and glass transition. Among many properties that can be affected by the thermal history were the glass transition temperature (T_g) and the activation energy of the glass transition (E_g). In this paper, in addition to T_g and E_g, the corresponding parameters for the crystallization process (i.e., the crystallization temperature and the activation energy of crystallization) were determined in Se and Se-Te samples having different thermal histories using differential scanning calorimetry. The activation energies of the two processes will be determined for both systems using well established kinetic models. In order to observe significant variation of these kinetic parameters the samples with long-term aging were investigated.

2. Experimental details

Bulk amorphous Se and $Se_{90}Te_{10}$ samples were prepared by the well-established melt-quench technique. High purity (99.999%) Se and Te in appropriate atomic percentage proportion were weighed and sealed in a quartz glass ampoule under a vacuum of 10^{-5} Torr. The contents were heated to about 450 K for 36 h. During the melt process, the tube was frequently shaken to homogenize the resulting alloy. DSC experiments were performed using TA Q2000 instrument,

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with a temperature accuracy of ±0.1 K under dry nitrogen supplied at a rate of 35 ml/min. Samples of 5mg were encapsulated in standard aluminium pans. Nonisothermal DSC curves were obtained at selected heating rates between 2–30 K/min. The temperature and enthalpy calibrations were checked with indium (T_m = 429.75 K, ΔH_m = 28.55 Jg^{-1}) as a standard material supplied by TA.

3. Results and discussions

A thermal procedure known as rejuvenation is used to remove any previous thermal history of the samples. This is achieved by heating the aged samples to 10 ^oC above the glass transition temperature, after a holding time of 5 minutes at this temperature; the samples are cooled very quickly to the initial temperatures of the nonisothermal scans.

Figs. 1 and 2 show DSC scans for the rejuvenated and aged glassy Se. Three characteristic thermal events are evident: the glass transition as indicated by an endothermic change, the exothermic crystallization peak and melting. Possible assignments for the characteristics temperatures for these three thermal events (denoted by T_g, T_p, and T_m) are indicated in Fig. 1. The glass transition region in the rejuvenated sample is marked by a small endothermic step. In the aged sample, the enthalpic recovery is indicated by a pronounced endothermic event (see the inset of Fig. 2) superimposing the glass transition step. Similar overall behaviour of glass transition and crystallization was observed in the aged and rejuvenated $Se_{90}Te_{10}$ glass as shown in Figs. 3 and 4.

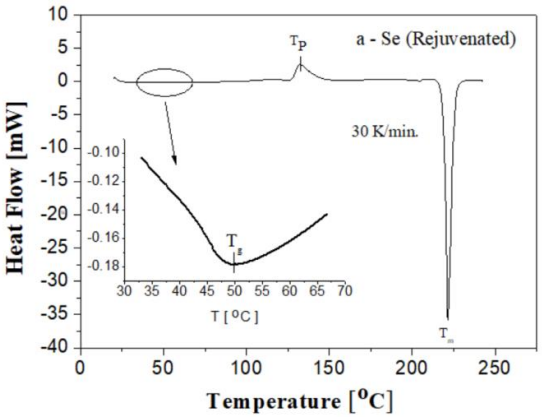

Fig. 1. DSC scan for rejuvenated glassy Se conducted at heating rate of 30 ^oC/min.

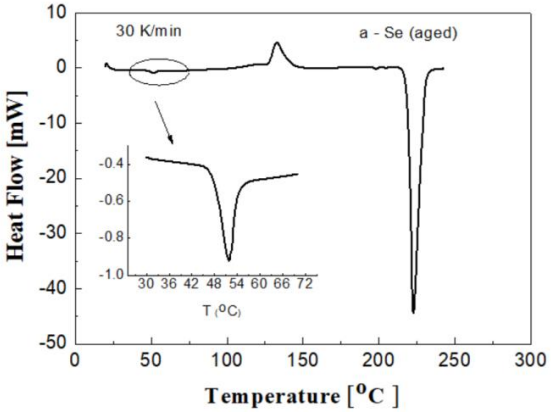

Fig. 2. DSC scan for aged glassy Se conducted at heating rate of 30 ^oC/min.

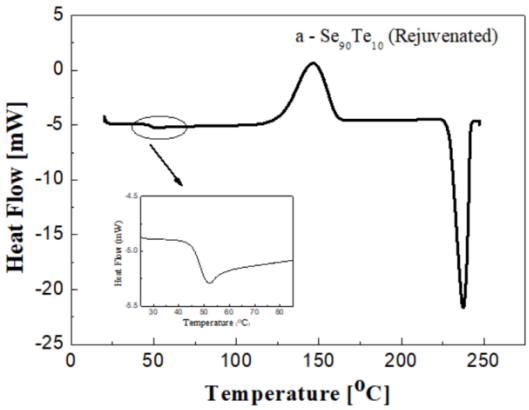

Fig. 3. DSC scan for rejuvenated glassy $Se_{90}Te_{10}$ conducted at heating rate of 30 °C/min.

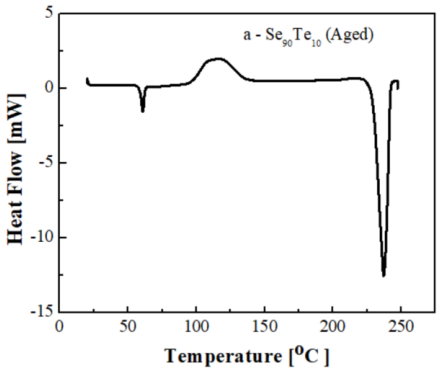

Fig. 4. DSC scan for aged glassy $Se_{90}Te_{10}$ conducted at heating rate of 30 °C/min.

The transformation from the glassy to the supercooled phase at temperature T_g is strongly affected by physical aging. Fig. 5 clearly illustrates the effect of prolonged physical aging on the glass transition phenomenon.

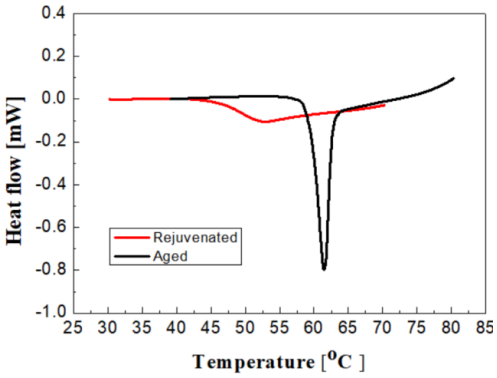

Fig. 5. A comparison between the endothermic peaks of the glass transition region for aged and rejuvenated glasses.

It is well known that T_g and T_p both shift to higher temperatures with increasing heating rates. An example of the heating-rate dependence is shown in Fig. 6 for the glass transition peak in $Se_{90}Te_{10}$ glass.

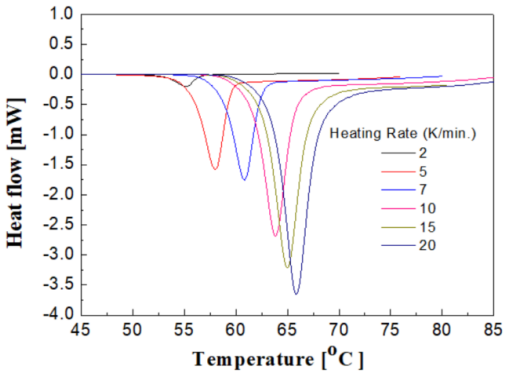

Fig. 6. The heating rate dependence of the glass transition endothermic peaks for the $Se_{90}Te_{10}$ glass.

The heating-rate dependence of the crystallization peak temperature T_p can be used to determine the activation energy for the crystallization process. It has been shown by Ozawa [7] that the effective activation energy of crystallization, E_c, can be estimated using the following equation:

$$ln\beta = -\frac{E_c}{RT_p} + constant \quad (1)$$

where β is the heating rate and R is the gas constant. Eq. (1) indicates that the plot of lnβ against $1/T_p$ should be a straight line. From the slope, of the activation energy of crystallization can be obtained. As evident from Fig. 7, the crystallization process is not affected by aging as similar slopes are obtained in both aged and rejuvenated Se glasses. As can be seen in Table 1, similar values of the crystallization activation energies, E_c, are obtained for the aged and rejuvenated Se glasses.

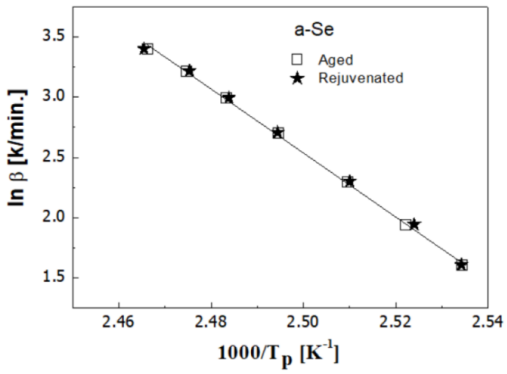

Fig. 7. Ozawa plot showing the heating rate dependence of crystallization temperature for aged and rejuvenated Se glass.

The heating rate dependence of T_g can also be used to determine the activation energy of glass transition (E_g) as originally suggested by Bartenev [8] and Ritland [9] and adopted by Moynihan et al [10] and others [11-12]. According to this method, the glass transition activation energy, E_g, is obtained using the following relationship:

$$ln\beta = -\frac{E_g}{RT_g} + constant \quad (2)$$

The plot of lnβ against $1/T_g$ for aged and rejuvenated Se glasses is shown in Fig. 8. It is evident from Fig. 8 that physical aging causes a significant shift of T_g as well as change in the slope in the plot of lnβ against $1/T_g$. The calculated activation energy of the glass transition for aged and rejuvenated Se glasses listed in Table 1 shows a decrease in E_g due to aging.

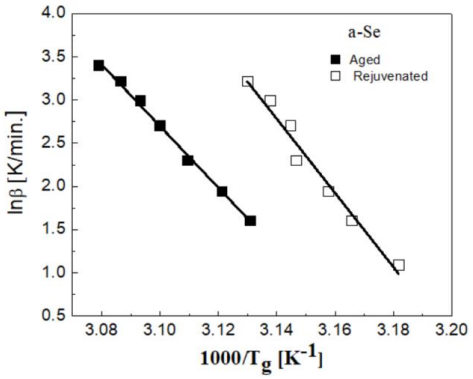

Fig. 8. Moynihan plot showing the heating rate dependence of glass transition temperature for aged and rejuvenated Se glass.

Similar behaviour was observed for the $Te_{10}Se_{90}$ glasses as shown in Figs. 9 and 10 from which the activation energies for crystallization and glass transition processes were determined and depicted in Table 1.

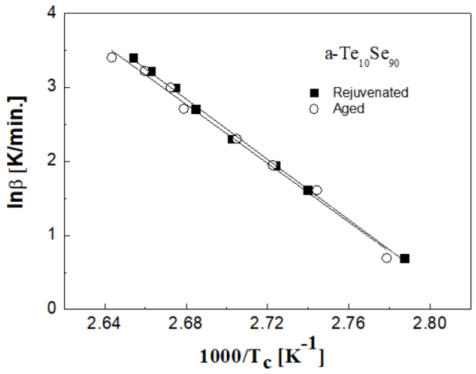

Fig. 9. Ozawa plot showing the heating rate dependence of crystallization temperature for aged and rejuvenated $Te_{10}Se_{90}$ glass

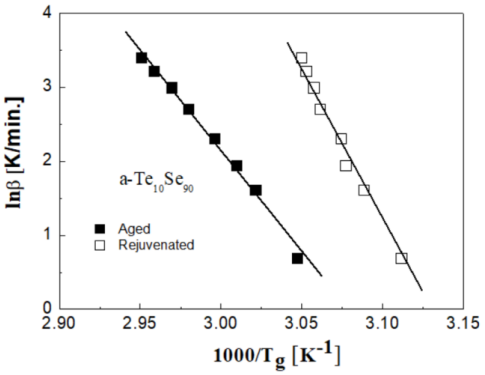

Fig. 10. Moynihan plot showing the heating rate dependence of glass transition temperature for aged and rejuvenated $Te_{10}Se_{90}$ glass.

The values of the activation energies for glass transition and crystallization processes for aged and rejuvenated samples are depicted in Table 1. As can be seen in Table 1, no significant change is observed in the activation energies for crystallization in the aged and rejuvenated glasses in both systems investigated in this study. For the glass transition event, a noticeable increase in the activation energy occurred when the a-Se was rejuvenated as compared with the aged glass.

Table 1. The values of the activation energies for aged and rejuvenated samples

	Activation Energy (kJ/mole)			
	Crystallization		Glass Transition	
	Aged	Rejuvenated	Aged	Rejuvenated
a-Se	217 ± 0.16	220 ± 0.07	296 ± 2.1	337 ± 2.1
a-$Te_{10}Se_{90}$	165 ± 0.23	170 ± 0.11	229 ± 2.5	362 ± 2.5

A more pronounced increase in the activation energy was observed in the case of a-$Te_{10}Se_{90}$ when the thermal history was removed by rejuvenation. The decrease of the activation energy of the glass transition as a result of aging can be attributed to the slow structural relaxation associated with the physical aging leading to a structural rearrangement of the glass network in its tendency towards equilibrium.

It is evident from the present study that although significant changes of the kinetics of the glass transition due to physical aging was found, the crystallization process is unaffected by prolonged aging. This is an indication that a long- term aging at temperatures well below the onset of glass transition does not lead to formation of new nuclei or produce any significant changes in the nucleation mechanism in the present glasses. It has been suggested by Svoboda [6] that the long-term aging in glassy SeTe led to formation of a significant number of nuclei. This suggestion is not supported by the present study and further investigations on the affect of physical aging on crystallization are required.

It is worth mentioning that despite the fact that glass transition and crystallization are quite different phenomena, their similar kinetic behaviour as evident from the strong heating rate dependence is remarkable. This similarity is also indicated by the two methods (Eqs. 1 & 2) used to evaluate the activation energies of the two processes which are mathematically identical. Similar observation was reported in Ref. 13. This is a strong indication that the glass transition is a kinetic process and does not involve a thermodynamic phase transition.

4. Conclusions

The present work showed that while crystallization process is not affected by physical aging, the glass transition is strongly affected. A significant decrease of the glass transition activation energy due to physical aging was found in both Se and $Se_{90}Te_{10}$ glasses. The glassy state below T_g being a non-equilibrium state tends to evolve to the equilibrium via structural relaxation. This structural relaxation leads to various physical changes of the glassy materials including the observed increase in T_g and the decrease in the activation energy.

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