PHYSICAL AGEING EFFECT IN Se$_{75}$Te$_{20}$In$_5$ CHALCOGENIDE GLASS

M. M. A. IMRAN[a], O. A. LAFI[a*], N. MEHTA[b], A. F. ALSHWABKEH[c],
A. A. SHAHEEN[d], A. ALBQOOR[a]
[a]*Department of Physics, Faculty of Science, Al-Balqa Applied University, Al-Salt-19117, Jordan*
[b]*Glass Science Laboratory, Department of Physics, Banaras Hindu University, Varanasi - 221005, India*
[c]*Department of Applied Sciences, Faculty of Engineering Technology, Al-Balqa Applied University, Amman, Jordan*
[d]*Department of Physics, Faculty of Science, Hashemite University, Zarka, Jordan*

Investigation of physical ageing effect induced by natural storage up to 11 yr of Se$_{75}$Te$_{20}$In$_5$ glass has been carried out using differential scanning calorimeter. It is observed that10-years of natural storage increase both the glass transition temperature T_g and the endothermic peak area A, which represents the enthalpy loss Δh of structural relaxation. The estimated value of A of the 10-years aged glass (27.1 ± 2.1) J/g is greater than that of as-prepared glass (11.3 ± 1.7) J/g, indicates that a significant natural ageing effect is evident in the studied glass and a structural relaxation process towards a more thermodynamically equilibrium state has been attained. This was also confirmed through calculation of the enthalpy loss, during the relaxation process, from the knowledge of the excess specific heat ΔC_p. However, after one additional year of storage of the 10-years aged glass (that is 11-years of natural storage), thermal parameters of structural relaxation namely: T_g, Δh, ΔC_p and the value of A do not significantly differ from those of the 10-years aged sample. Thus, after 10-years of natural storage the glass reached its ageing plateau and further additional structural relaxation of glass network towards a more thermodynamic equilibrium state is not expected to occur. In addition, calculation of the relaxation activation energy E_t and heteropolar bond energies of the studied glass reveals that structural relaxation occurs due to bond interchange rather than sliding of atomic layers.

1. Introduction

Physical ageing is one of the most important phenomena for glassy disordered solids such as chalcogenide glasses. The promising applications of chalcogenide glasses are limited by their structural instability, resulting from the production process, in which the liquid phase is quenched to the ambient temperature. The process of thermal ageing of as-quenched material leads to the achievement of the metastable state characteristic of the supercooled liquid. To avoid the changes in physical properties caused by physical aging, a material with completely saturated ageing should be used in chalcogenide-based devices. However, natural physical ageing requires years at low temperatures; therefore, γ-irradiation, photo-exposure, and thermal annealing are usually applied to accelerate the relaxation process [1-3]. The ageing process can be predicted on the basis of thermodynamic relaxation, induced by structural rearrangements in amorphous matrices, which is responsible for changes (as a function of time) in many physical properties of such kind of materials. The reason is that the glassy disordered solids are conventionally obtained in a metastable state frozen near glass transition and therefore they aspire to the extrapolated states of the thermodynamic equilibrium of undercooled liquid. In other words, the prepared glasses kept

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*Corresponding author: olafi66@yahoo.com

far below glass transition temperature (T_g) lose their excess of configurational entropy, enthalpy or free volume to reach a more favorable thermodynamic state [1]. This effect was observed experimentally in many binary and ternary systems of chalcogenide glasses and can be evaluated by using differential scanning calorimetry (DSC) through distinguishable changes in the glass transition region [2–6].

The physical ageing effects are characterized by the glass transition temperature T_g and the change in the relaxation enthalpy Δh that can be detected from the endothermic DSC curves. The observed endothermic peak is normally associated with structural relaxation of glass network owing to glass-to-supercooled liquid phase transition [7]. Besides, it is mentioned that the corresponding area A under this endothermic peak in the DSC curve represents the enthalpy loss Δh: the greater A, the greater Δh and thus the glassy material is closer to equilibrium state of undercooled liquid [5, 8, 9].

Thermal stability represents the resistance to devitrification of glassy alloy through the nucleation and growth processes [10]. The relaxation activation energy E_t is a good indication on thermal stability. This activation energy is the amount of energy, which is absorbed by a group of atoms in the glassy region so that a jump from one metastable state to another is possible. This means, this activation energy is involved in the molecular motion and rearrangements of atoms around the glass transition temperature. When the sample is reheated in the DSC furnace, the atoms undergo infrequent transitions between the local potential minima separated by different energy barriers in the configuration space where each local minimum represents a different structure. The most stable local minimum in the glassy region has lower internal energy. This activation energy of thermal relaxation could be monitored through the knowledge of the enthalpy loss during the relaxation process in the aged glass [11, 12].

The objective of the present work is to monitor the effect of physical ageing induced by natural storage on the glass transition region in $Se_{75}Te_{20}In_5$ glass using differential scanning calorimeter (DSC). In this regard, the glass transition temperature, excess specific heat and enthalpy loss of as-prepared, 10-years aged and 11-years aged $Se_{75}Te_{20}In_5$ glass have been studied. Besides, the relaxation activation energy E_t was calculated from the dependence of the glass transition temperature on heating rate and compared with bonds energies of the constituent elements of the investigated glass.

2. Experimental details

$Se_{75}Te_{20}In_5$ glass was prepared on September 2005 by melt quenching technique. High purity (5N) In, Te, and Se in appropriate atomic weight percentage (at. wt %) proportions were weighed into a quartz ampoules and sealed at a vacuum of 10^{-5}Torr. The ampoules were then heated at 900 ℃ for about 15 h with continuous rotation to facilitate homogenization of the sample. The molten sample was rapidly quenched in icecooled water to produce a glassy state. The ingot of the so-produced glassy sample was taken out of the ampoule by breaking the ampoule and then grinded gently in a mortar and pestle to obtain a powder form. The as-prepared sample is divided into three parts. One part of the sample is subjected to the DSC immediately after preparation. The second and the third parts were packed in sealed containers with ambient atmosphere and stored under normal conditions for 10 and 11-years. The calorimetric measurements, at different heating rates of 5, 10, 15, and 20, were carried out in a Perkin-Elmer DSC7 calorimeter with an accuracy of $\pm$ 0.1°C. This equipment is calibrated prior to measurements, using high purity standards Pb, Sn and In with well-known melting points. For each heating rate, about (10 $\pm$ 0.5) mg of each of the investigated glassy samples in powder form were sealed in a standard aluminum pans and scanned from room temperature up to 100℃ (around the glass transition region). The operation of DSC is based on measurement of the thermal response of an unknown specimen as compared with a standard when the two are heated uniformly. A typical differential scanning calorimeter consists of two sealed pans; a sample pan and an empty reference pan. These pans are often covered by or composed of aluminum, which acts as a radiation shield. The two pans are heated, or cooled, uniformly while the heat flow difference between the two is monitored. This can be done at a constant temperature

(isothermally), but is more commonly done by changing the temperature at a constant rate (non-isothermally) as in this work.

3. Results and discussion

The enthalpy Δh recovered as a result of structural relaxation during physical ageing is dependent on the ageing time. The kinetics for the enthalpy relaxation have been extensively studied in amorphous materials [5-9, 13]. The enthalpy recovery increases with ageing time, but approaches a plateau when a sufficient time is given. The time rate of increased enthalpy increase ($d\Delta h/dt$) gradually decreases with ageing, because the mobility of polymer chains is reduced as the systemreaches the metastable equilibrium state [14]. The glass transition temperature T_g (the temperature at which the endothermic peak (enthalpy recovery) appears on the DSC thermogram) increases with ageing time. It has been previously reported that T_g increased in a linear fashion, relative to the logarithmic values of ageing time [5].

Typical DSC endothermic curves of as-prepared $Se_{75}Te_{20}In_5$ glass at the heating rates of 5, 10, 15, and 20K/min are shown in Fig.1, as an example. Similar thermograms (not shown in the text) were recorded for the 10-years aged and 11-years aged $Se_{90}In_4Sn_6$ glass. Depending on these figures, the glass transition temperatures (T_g) have been deduced from the intersection of the two linear portions adjoining the transition elbow in the DSC trace in the endothermic direction [15]. In addition, DSC data for three $Se_{75}Te_{20}In_5$ samples, one just after preparation, the second after 10-years of natural storage, and the third after 11-years of natural storage, are shown in Fig. 2 at a heating rate of 20K/min. The increase in T_g and endothermic peak area in the vicinity of the glass to undercooled liquid transition testifies to the significant natural physical ageing effect in this glass. As mentioned before, the endothermic peak area represents the enthalpy losses occurred during prolonged natural storage of the samples. The two parameters T_g and A are determined from the DSC endothermic peaks that are shown in Fig. 2 for as-prepared, 10-years aged and 11-years aged $Se_{75}Te_{20}In_5$ glass at a heating rate of 20K/min and listed in Table1. It is clear from this table that both T_g and the area A under the endothermic peak increase after 10-years of natural storage. After one additional year (11-years of natural storage), the value of A do not differ significantly from that of the 10-years of natural storage sample. From this result, one can say that additional structural relaxation of glass network towards thermodynamic equilibrium of super-cooled liquid after this period of time is not expected and the glass reached its ageing plateau. Thus, the 10-years aged sample is in a glassy state that is as close to the thermodynamic equilibrium states of supercooled liquid as possible under the natural conditions.
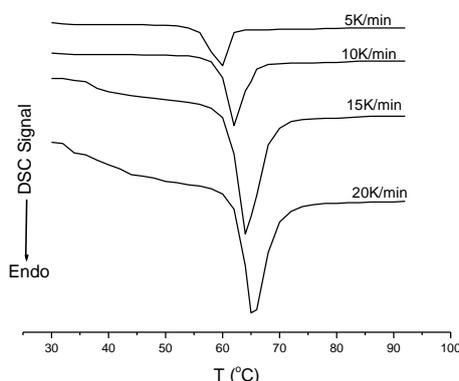

Fig.1. DSC endothermic curves, obtained at heating rates of 5, 10, 15 and
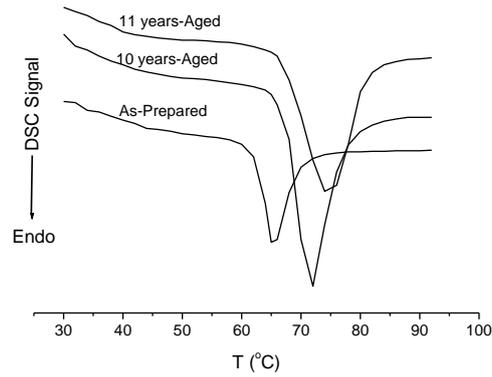*20K/min for as-prepared Se$_{75}$Te$_{20}$In$_5$ glass*

Fig.2. DSC endothermic curves, obtained at a heating rate of 20K/min, of as-prepared,
10-years aged and 11-years aged $Se_{75}Te_{20}In_5$ glass

Table 1: Glass transition temperature T_g, and the area under endothermic peak A (converted into unit
of energy) of $Se_{75}Te_{20}In_5$ glass with different characteristics at a heating rate of 20K/min

Sample characteristic ↓	T_g (^{o}C)	A (J / g)
As-prepared	60.8	11.3 ± 1.7
10-years aged	66.5	27.1 ± 2.1
11-years aged	67.1	28.2 ± 3.2

Physical aging is a phenomenon that is kinetically and thermodynamically controlled, and is generally thought to occur in a nonlinear and nonexponential fashion [13, 14]. Nonlinearity is resultant from the dependence of relaxation time (τ) on both the temperature (T) and the structure of glassy matrices. Among the expressions widely used to describe this phenomenon is the Tool-Narayanaswamy-Moynihan equation, which is applicable at a temperature near the glass-transition temperature [16-18]:

$$\tau = \tau_o\exp(-E_t/RT)\exp(-c(h-h_e)) \tag{1}$$

where τ_o and c are constants, R is the universal gas constant (= 8.314 $JK^{-1}mol^{-1}$), $\Delta h= h-h_e$ is the enthalpy loss during the relaxation process and E_t is the relaxation activation energy. It is mentioned earlier that the endothermic peak area represents the enthalpy loss Δh during thermal relaxation. However, in the present case since natural storage time is so long therefore one can calculate the value of Δh from the knowledge of the specific heat difference $\Delta C_p=C_{pe}- C_{pg}$ versus temperature curve, through the use of the well known formula $\Delta h = \Delta C_p [T^c_g- T_a]$ as described in [19] and the references therein. Here C_{pe} is the equilibrium specific heat obtained at a temperature after the glassy region is completed where the glass attains equilibrium liquid like structure and C_{pg} is the specific heat of the material just before jumping at T_g takes place. The temperature difference $[T^c_g- T_a]$ is considered as the difference between the glass transition temperature obtained when the glass is cooled through the transition region at a rate of 20K/min and the ageing temperature T_a (which was taken as room temperature = 298 K). The variation of specific heat as a function of temperature for as-prepared, 10-years aged and 11-years aged $Se_{75}Te_{20}In_5$ glass at a heating rate of 20K/min is shown in Fig. 3. It is clear that C_p is weakly temperature dependent except in the glassy region where it exhibits a sudden jump at T_g which is attributed to additional degrees of freedom that are available for the atoms to formulate complete short range order in the liquid state [20]. The C_p against temperature curves were used to calculate ΔC_p and Δh values, which are listed in Table 2, for the studied glass. The obtained values of Δh indicate that drastic relaxation occurs due to natural storage and that the aged glass reached almost equilibrium state.

The observed increase in the values of Δh with ageing time at ageing temperature below the glass transition is an indication of the fact that atomic rearrangement becomes more cooperative in relaxation process in which more enthalpy is released with an increase in ageing time [19].
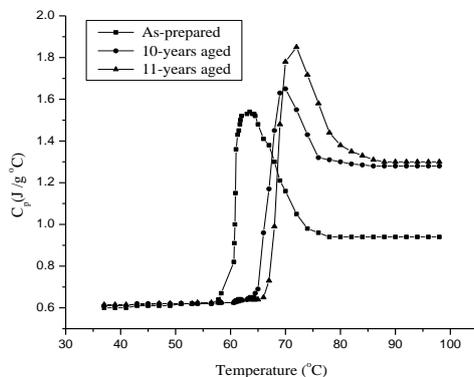

Fig. 3. The variation of specific heat as a function of temperature for as-prepared, 10-years aged and 11-years aged $Se_{75}Te_{20}In_5$ glass

Table 2: Specific heat difference ΔC_p and the enthalpy loss during natural storage of $Se_{75}Te_{20}In_5$ glass at room temperature (at a heating rate of 20 K/min)

Sample characteristic ↓	ΔC_p (J / g $^{\circ}$C)	Δh (J / g)
As-prepared	0.31	10.9 ± 1.1
10-years aged	0.62	25.4 ± 1.4
11-years aged	0.65	26.8 ± 1.7

Depending on equ.(1), Moynihan and co-workers [17] derived the following relation, from which E_t can be calculated from the variation of T_g with the heating rate β:

$$d(\ln \beta) / d(1/T_g) = -E_t /R \qquad (2)$$

Fig.4 shows plots of $\ln\beta$ vs. $10^3/T_g$ for all samples. The values of the relaxation activation energy E_t are calculated from the slopes of the resulting straight lines and found to be 2.33, 2.24, and 2.22 eV for as-prepared, 10-years aged, and 11-years aged glass, respectively. It is clear that E_t decreases after 10 years of natural storage which is an indication that the state of equilibrium is almost reached. In addition, a comparison between the estimated value of E_t for 11 years of natural storage and that of 10 years of natural storage reveals that no noticeable change in the stability of the studied glass. This agrees fairly well with the above result obtained from the relaxation enthalpy (endothermic peak area) calculations.
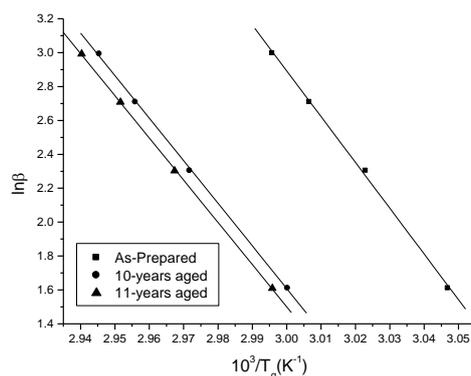
Fig.4. Plot of lnβ vs. $10^3/T_g$ for as-prepared, 10-years aged and 11-years aged $Se_{75}Te_{20}In_5$ glass.

The studied glass is a chalcogen rich alloy in which the structural configuration consists of rings or chains held together by Van der Waals interaction [21] with bonds have energies in the range 0.12-0.40 eV. However, the bond energies between constituent atoms for the glass under investigation were calculated following the procedures reported in [12] and the references therein. These bond energies found to be 1.76, 1.71, and 1.39 eV for Se-In, Se-Te, and Te-In, respectively. Comparing the obtained values of the relaxation activation energy E_t with Van der Waals energies, one can say that the relaxation is not possible to occur due to sliding of the atomic layers. However, the values of E_t for as-prepared, 10-year aged, and 11-years aged are higher than the above calculated heteropolar bonds energies. Hence, it is reasonable to believe that the relaxation process in the sample under study is due to bonds interchange.

4. Conclusions

Physical ageing effect and thermal stability of $Se_{75}Te_{20}In_5$ glass have been studied using differential scanning calorimeter (DSC) and the following conclusions may drawn:

Firstly, the estimated enthalpy loss during relaxation process measured from the endothermic peak area agrees fairly well with the calculated value for the studied glass with different characteristics.

Secondly, the obtained values of the thermal parameters T_g, Δh, and ΔC_p, indicate that the process of relaxation is terminated in almost 10-years of natural storage.

Finally, the calculations of the relaxation activation energy and bonds energies of the constituent elements of the studied glass reveal that the structural relaxation occurs due to breaking of interchain bonds which must reform after completion of relaxation process.

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