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KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION IN $Ga_{10}Se_{90}$ CHALCOGENIDE GLASS

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The present research work deals with the thermal behavior of $Ga_{10}Se_{90}$ chalcogenide glass prepared by melt quenching technique. The kinetics of crystallization of $Ga_{10}Se_{90}$ glassy alloy at different heating rates 5, 10, 15, 20, 25, 30 K/min was studied by differential scanning calorimetry (DSC) using non-isothermal means. DSC experimental method is currently employed for determining the kinetic parameters of crystallization in $Ga_{10}Se_{90}$ glassy alloy. These parameters include the activation energy of crystallization (E_c), activation energy of glass transition temperature (E_g) and crystallization enthalpy (ΔH_c). The average value of E_c is found to 96.06 kJ/mol and E_g is found to be 151.17 kJ/mol respectively. The results of crystallization have been discussed on the basis of different models such as Kissinger's approach and modification for non-isothermal crystallization in addition to Ozawa and Avrami.

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1. Introduction

In the past three decades, one of the most important discovery in modern technology is the phase change memory in chalcogtenide glasses. This was made by Ovshinsky [1-3] in the binary and ternary glasses. Since that time, chalcogenide glasses have attracted much attention in the field of electronics as well as infrared optics which are applicable for solid state devices such as electrical switches, reversible phase change memory, image storage, photo resistors, optical fibers, photoconductors, and optical recording [4–8]. The increasing use of thermal analysis techniques such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) has offered a great promise of obtaining applicable data with simple methods [9]. The utilization of thermal analysis techniques depends in turn on the development of methods for analyzing the experimental data with this objective. A large number of mathematical treatments are based on the formal theory of transformation kinetics.

The crystallization of a glass upon heating can be performed in several ways. In caloimetric measurements, two basic methods can be used, isothermal and non-isothermal. However, the results of crystallization process can be interpreted in terms of several theoretical models [10-11].

In the present work, the thermal properties of $Ga_{10}Se_{90}$ glassy alloy has been studied. Our aim is to explore the glass transition region, crystallization and thermal stability in the Ga-Se system. Many studies have been reported on the Se based metallic glasses regarding their crystallization kinetics, optical and electrical properties [12-19]. In view of these, in the present system, we use Se because of its wide commercial applications. Glassy selenium has some shortcomings from the point of view of practical application, e.g. low sensitivity and thermal instability. These properties can be improved by alloying some elements into selenium matrix,

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such as gallium. There is a strong tendency for Ga to super cool below its freezing point. So, seeding may be necessary to initiate solidification [20].

2. Experimental

Bulk chalcogenide $Ga_{10}Se_{90}$ sample was prepared by the conventional melt-quenching technique. High purity materials (99.999 % pure) Ga and Se in appropriate atomic percentage proportions were weighted and sealed in an evacuated (10^{-3} Pa) quartz ampoules. The sealed quartz ampoules were kept inside a furnace, where the temperature was raised to 1073 K and it was maintained for 18 hours with frequent rocking to ensure the homogenization of the melt. The ampoules were subsequently quenched in iced water (very fast quenching). The ingots of the sample were taken out by breaking the quartz ampoules. These ingots were then grinded into a fine powder. The amorphous nature of the samples was confirmed by X-ray diffraction. The crystallization studies were done by using Differential Scanning Calorimeter (Model DSC Plus, Reheometric 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). The DSC was calibrated prior to the measurement using high purity standard Pb, Sn and In with well known melting points. The crystallization experiments were carried out through continuous heating rate of 5,10, 15, 20, 25 and 30 K/min. The glass transition (T_g) and crystallization (T_c) were determined using the microprocessor of thermal analyzer.

3. Theoretical consideration

The study of the crystallization kinetics in glass-forming liquids under non-isothermal conditions was made in the frame of two theories. The first one is based on Johnson–Mehl–Avrami [21-22] (JMA) equation:

$$\alpha(t) = 1 - \exp -(Kt)^n \tag{1}$$

where α (t) is the volume fraction of the initial material transformed at time t, n is the Avrami exponent (the exponent which reflects the nucleation rate and/or the growth morphology) and *K* is the reaction rate constant and is usually assigned as:

$$K = K_0 \exp(-E_c / k_B T) \tag{2}$$

In this equation, E_c is the activation energy for the crystallization reaction, which describes the overall crystallization process, k_B is the Boltzmann constant, T is the isothermal temperature, and K_0 is the frequency factor.

The activation energy of crystallization (E_c) can be obtained from the variation of the onset crystallization temperature T_c with heating rate by using Ozawa's [23] relation as,

$$\ln \beta = -E_c / RT_c + C \tag{3}$$

where C is a constant.

The plot of ln β versus $1000/T_c$ curves comes to be linear and the value of E_c is calculated from the slope of these curve.

The interpretation of the experimental crystallization data is also be given on the basis of Kissinger's, Matusita's and modified Ozawa's equations for non-isothermal crystallization. The activation energy (E_c) for crystallization can therefore be calculated by using Kissinger's equation [24],

$$\ln(\beta/T_c^2) = -E_c / RT_c + D \tag{4}$$

From the slope of the plot of *ln* (β/T_c^2) versus $1000/T_c$ the activation energy for crystallization can be determined.

The heating rate (β) dependence of the glass transition (T_g) in chalcogenide glasses may be interpreted in terms of thermal relaxation phenomena and it has been shown by Moynihan et al [25] that the activation energy of glass transition (structural relaxation) (E_g) can be related to T_g and β by,

$$d \ln \beta / d(1/T_g) = -E_g / R \tag{5}$$

It is evident from this equation that a plot of lnβ against $1000/T_g$ should be straight line and that the activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot.

4. Results and discussion

A Regaku X-ray diffractometer Ultima IV was employed for studying the structure of $Ga_{10}Se_{90}$ sample. Copper target was used as the X-ray source with λ = 1.54178 Å ($CuK\alpha_1$). The scanning angle was in the range of 20^0-80^0. A scan speed of 2^0/min and a chart speed of 1 cm/min were maintained. The X-ray diffraction traces of $Ga_{10}Se_{90}$ sample was taken at room temperature and is shown in Fig. 1. The absence of sharp structural peak confirms the amorphous nature of the sample.

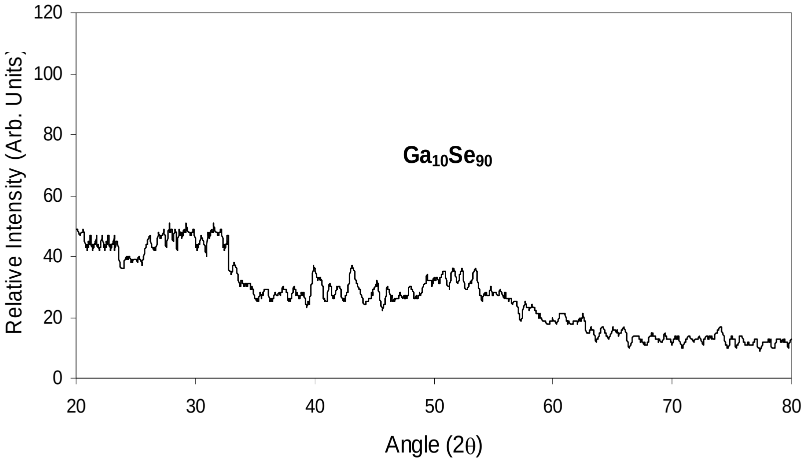

Fig. 1. X-ray pattern of $Ga_{10}Se_{90}$ sample.

The surface morphology of $Ga_{10}Se_{90}$ powder was examined by means of JEOL JSM-6360LV, Japan, scanning electron microscope (SEM), shown in Fig. 2, which also confirms the amorphous nature of the sample.

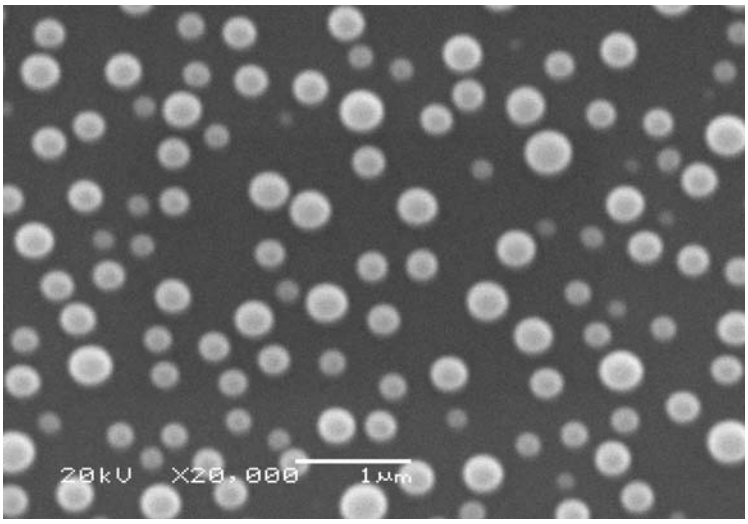

Fig. 2. SEM of $Ga_{10}Se_{90}$ chalcogenide glass.

Fig. 3 shows typical DSC curves obtained when $Ga_{10}Se_{90}$ chalcogenide glass was heated at constant heating rates of 5, 10, 15, 20, 25, 30 K/min. Some characteristic features are observed in the studied temperature ranges. The first endothermic-like peak correspond to the glass transition temperatures (regions) T_g, while the second are exothermal peaks indicate to crystallization temperatures T_c. It is observed that both T_g and T_c shift towards higher temperature as the heating rate is increased from 5 to 30 K/min.

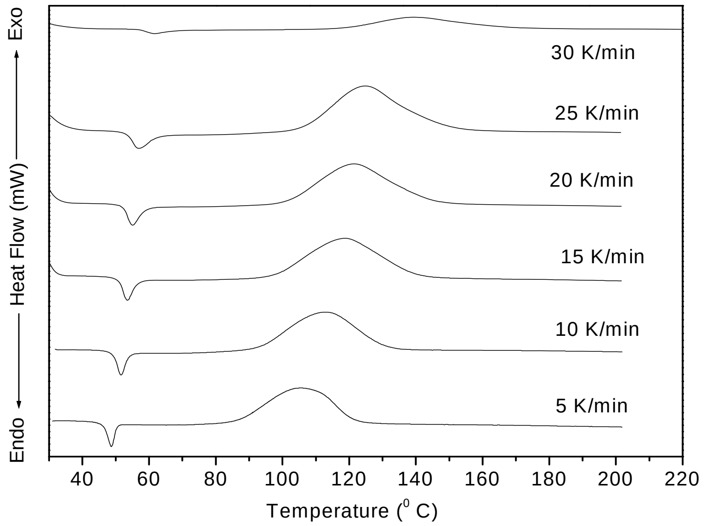

Fig. 3: DSC plots of $Ga_{10}Se_{90}$ at different heating rates.

The dependence of glass transition temperature (T_g) and crystallization temperature (T_c) on the heating rate for $Ga_{10}Se_{90}$ sample is given in Table 1 and the variation of T_g with heating rate is shown in Fig. 4.

The value of T_g and therefore the rigidity of the lattice increase with increasing heating rates. This variation takes the form of a power law behavior and may be represented by the following expression [26]:

$$T_g = T_0 [\beta]^y \tag{6}$$

where β is normalized heating rate and T_0 is T_g of the glass at a heating rate of 1 K/ min, i.e. $T_0 = (T_g)_1$. Normalization has been done with respect to a heating rate of 1 K/min. Using Eq. (6) the exponent y is given by,

$$y = \log_{10} [(T_g)_{10} / (T_g)_1] \tag{7}$$

where $(T_g)_{10}$ stands for the T_g values at a heating rate of 10 K/ min. Equation (6) gives an excellent description of the dependence of T_g which increases with increasing heating rate, and the maximum deviation in the theoretical and experimentally measured values is within the average standard error. The heating rate dependence of glass transition temperature is an experimentally observed [27-28] fact. Theoretically, T_g is defined as the temperature at which the relaxation time τ becomes equal to the relaxation time of observation τ_{obs}. At the same time, T_g varies inversely [26] as the relaxation time. With increasing heating rate, τ_{obs} decreases and hence the glass transition temperature increases.

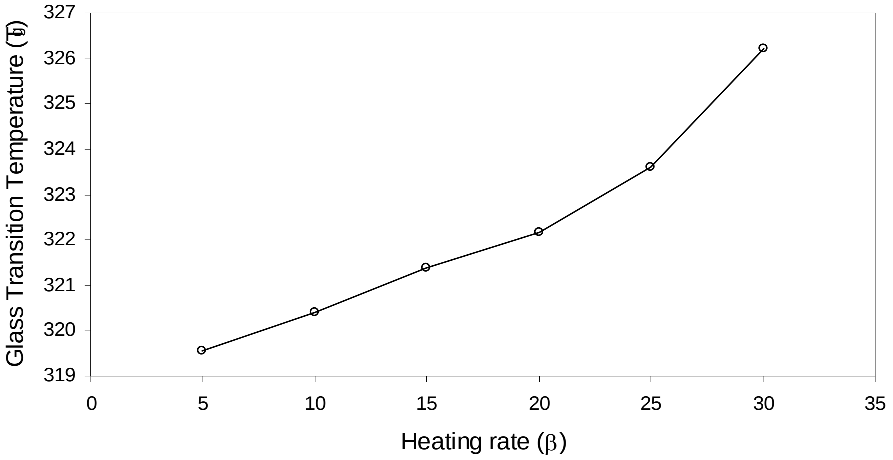

Fig. 4. Plot of T_g versus heating rate (β) of $Ga_{10}Se_{90}$ glass.

The crystallization enthalpy (ΔH_c) is evaluated by using the formula,

$$\Delta H_c = K A / M \tag{8}$$

Where K (= 1.5) is the constant of the instrument used. The value of K was deduced by measuring the total area of the complete melting endotherm of high purity tin and indium and used the well known enthalpy of melting of these standard materials. A is the area of the crystallization peak and M is the mass of the sample. The value of ΔH_c at different heating rates of $Ga_{10}Se_{90}$ chalcogenide glass are shown in Table 1. The enthalpy release is related to the metastability of the glasses and the least stable glasses are supposed to have maximum ΔH_c.

Table 1. Glass transition, crystallization temperature and Enthalpy released (ΔH_c) of $Ga_{10}Se_{90}$ chalcogenide glass from non-isothermal DSC experiments:

Heating rate β (K/min)	T_g (K)	T_c (K)	ΔH_c (joule/gm)
5	319.56	378.48	7.90
10	320.42	386.04	8.33
15	321.38	391.78	8.42
20	322.18	394.63	8.15
25	323.61	398.21	9.32
30	326.23	401.49	7.02

Figs. 5 and 6 illustrates the plot ln(β) versus $1000/T_c$ and $\ln(\beta/T_c^2)$ versus $1000/T_c$ by using Eq (3) and (4) respectively. The slope of the resulting line, corresponds to the value of activation energy of crystallization. The value of activation energy of crystallization (E_c) by using Ozawa's model (Fig. 5) is equal to 99.29 kJ/mole and by using Kissinger's methods (Fig. 6) is equal to 92.82 kJ/mole. From both Ozawa and Kissinger relation, it was found that values of E_c are in good agreement with each other.

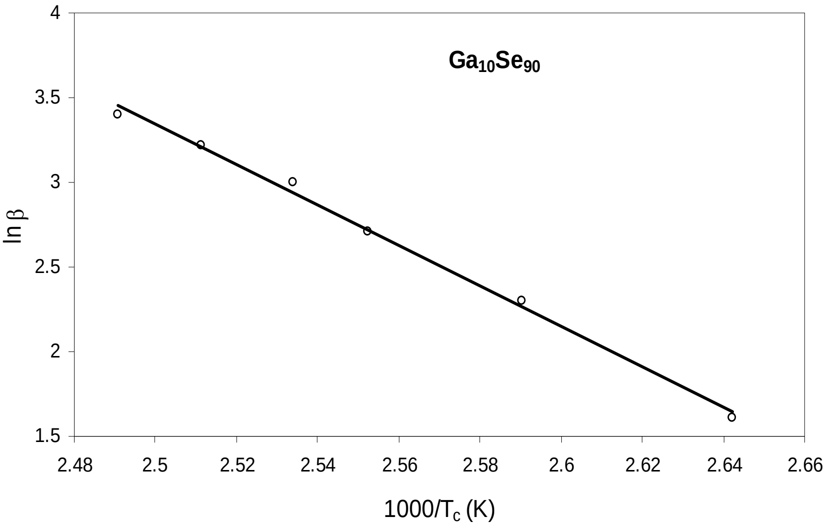

Fig. 5: Plots of ln β as a function of 1000/ T_c for $Ga_{10}Se_{90}$ chalcogenide glass.

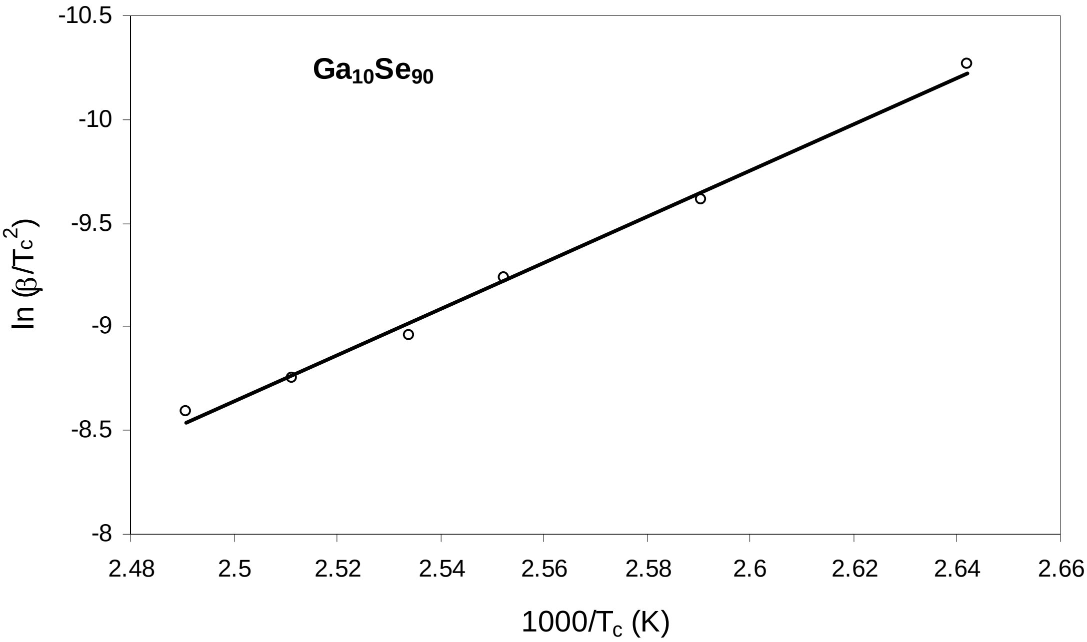

Fig. 6. Plots of ln (β /T_c^2) as a function of 1000/ T_c for $Ga_{10}Se_{90}$ chalcogenide glass.

The activation energy of glass transition (E_g) for $Ga_{10}Se_{90}$ chalcogenide glass can be calculated by using Eq. (5). Fig. 7 shows the variation of ln (β) against 1000/T_g. The activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot.

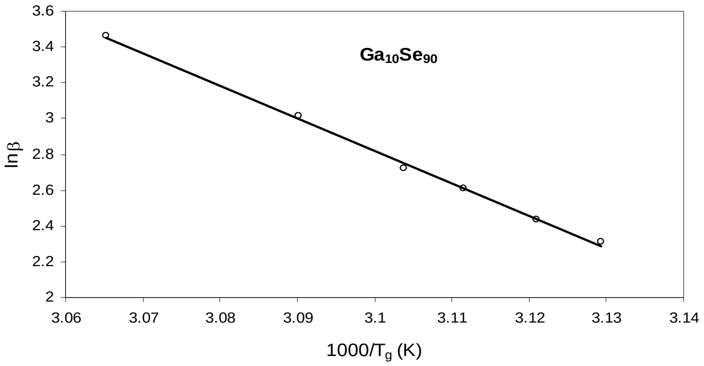

Fig. 7. Plots of ln β as a function of 1000/ T_g for $Ga_{10}Se_{90}$ chalcogenide glass.

The value of the activation energy of glass transition (E_g) deduced from Fig. 7 is 151.17 kJ/mole. The activation energy of glass transition (structural relaxation) depends on T_g and heating rate (β). The activation energy of structural relaxations involved in the molecular motions rearrangements of atoms around glass transition temperature. When the sample is heated, in DSC furnace, the atom undergoes infrequent transitions between the local potential minima separated by different energy barriers in the configurationally space where each local minimum represent a different structure. The most stable local minima in the glassy region have lower internal energy. Accordingly, the atoms in a glass having minimum activation energy have higher probability to jump to the meta-stable (or local minimum) state of lower internal energy.

5. Conclusions

A study of non-isothermal crystallization for $Ga_{10}Se_{90}$ by differential scanning calorimetry (DSC) shows a glass transition temperature followed by a crystallization peaks. The kinematics studies indicate that the glass transition and crystallization temperatures depend on the heating. Such studies can be used to determine the activation energies for molecular motions and rearrangement around the glass transition temperature which, in turn, are useful in the understanding of thermal relaxation phenomena in these glasses. The crystallization was followed in the frame of Kissinger and Ozawa models. The activation energy of crystallization has been determined and it was found that the value of E_c by both techniques is in good agreement with each other. The average value of E_c of the investigated glass is 96.06 kJ/mole and the activation energy of glass transition temperature (E_g) is found to be 151.17 kJ/mole.

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