Study of Glass Transition and Crystallization Behavior in $Ga_{15}Se_{85-x}Pb_x$ ($0 \leq x \leq 6$) Chalcogenide Glasses

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There has been a growing interest in the synthesis and characterization of amorphous chalcogenide glasses due to their importance in preparing electronic memories, grating, switching devices and their optical applications as good IR transmitting materials. The study of the glass transformations and crystallization processes in the amorphous systems is interesting not only from the fundamental aspect of establishing the reaction mechanism of crystal nucleation and growth, but also from a technological point of view. The present research work is concentrated on the study of glass transition and crystallization behavior in $Ga_{15}Se_{85-x}Pb_x$ with $x = 0$, 3, and 6 chalcogenide glasses by differential scanning calorimetry. Their amorphous nature has been verified by X-ray diffraction. The differential scanning calorimetry experiments were performed at different continuous heating rates (5 to 25 K/min). The glass transition temperature (T_g) and crystallization temperature (T_c) of these glasses has been determined from differential scanning calorimetry thermograms. The dependence of T_g and T_c on the heating rate (β) has been used for the determination of different crystallization parameters such as the activation energy of crystallization (ΔE_c), the activation energy for structural relaxation (ΔE_t) and the order parameter (n). The results of crystallization were discussed on the basis of different models such as Kissinger's approach and modification for non-isothermal crystallization in addition to Johnson, Mehl, Ozawa and Avrami.

1. Introduction

Studies of glass transition and crystallization behavior in chalcogenide glasses are of particular interest because they are connected with such important phenomena as memory type of switching, reversible optical recording, etc. Thermal analysis is a very useful tool for describing the glass transition and crystallization kinetics as it is rapid and convenient.

One of the most important problems in the area of chalcogenide glasses is the understanding of glass transition mechanism. The nature of glass transition is complex and even today remains poorly understood [1]. For 186 binary and ternary chalcogenide glasses, a good correlation between the glass transition temperature (T_g) and the overall mean bond energy of a covalent network of a glass was found [2]. Chalcogenide glasses are often called lone-pair semiconductors. The chemical bonds with lone-pair electrons are characterized by electron flexibility [3]. The lone-pair electrons have an important role in chalcogenide glass formation [4, 5]. Because of the electrostatic repulsion and the repulsion caused by the Pauli exclusion principle, the valence electrons tend to avoid one another [6]. Therefore, it is easier to distort a bond with lone-pair electrons than a bond with no unshared electrons. The glass transition is exhibited as an endothermic peak in differential scanning calorimetry

(DSC) due to change in specific heat. The heating rate dependence of T_g is well known, which makes possible the study of glass transition kinetics.

The glass transition and crystallization studies in chalcogenide glasses upon heating can be performed by two basic methods: isothermal and non-isothermal methods [7–9]. Non-isothermal measurements using a constant heating rate are more commonly used in the study of the crystallization of amorphous solids and possess several advantages such as the quick performance of these experiments and the rapid information they provide about the glass transition temperature [10–12]. Discovery of new materials, whose properties can be tailored constitute the core of development of solid state technology. Continuous variation of discrete structural, thermal, optical and electronic properties, if achieved in semiconducting materials in a controlled manner, could enhance their employability in the fabrication of devices with predetermined characteristics. Ternary alloy semiconductors do provide such a class of materials. Non-isothermal analysis of the crystallization kinetics of glass forming alloys has become increasingly attractive. Although the isothermal experiments are, in most cases, more definitive but non-isothermal experiments are preferable due to the following advantages: (i) The rapidity of performing these experiments makes them attractive,
(ii) they provide rapid information about the glass transition temperature, transformation enthalpy and temperature and activation energy over a wide range of temperature,

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(iii) non-isothermal techniques are suitable for the determination of the stability of the amorphous alloys and for the investigation of nucleation and growth processes that occur during transformation of the metastable phases in the glassy alloy as it is heated at constant heating rates.

The study of glass transition and crystallization kinetics in amorphous materials by DSC methods has been widely discussed in the literature by various workers [13–22]. Abu-Sehly [23] has studied kinetics studies of crystallization of Te–As–Cu chalcogenide glasses, Elabbar et al. [24] have studied the crystallization kinetics of Pb–Se chalcogenide glasses using DSC techniques, Soltan [25] has studied the pre-crystallization kinetics of Pb–Se glass, Mehta et al. [26] have studied the glass transition phenomena in Se–Te and Se–Ge based ternary chalcogenides glasses, Abd Elnaeim et al. [27] have studied the glass transition and crystallization kinetics in In–Se–Te chalcogenide glasses. The work on glass transition temperature and thermal stability of Se–Sn chalcogenide glass by Omar et al. [28], study of the glass transition in amorphous Se by Abu-Sehly et al. [29], calorimetric studies of Se–Te–Cd and Se–Te–Cd–In multicomponent chalcogenide glasses by Kumar and Singh [30], phase transformation kinetics of Se–Ge–Pb chalcogenide glass by Praveen et al. [31], determination of crystallization parameters of Ge–Te glasses by El-Oyoun [32] are also worth mentioning. The studies on preparation and characterization of chalcogenide materials by non-isothermal DSC measurements are also available in the literature by various workers [33–40].

In the present work, the study of glass transition and crystallization behavior in $Ga_{15}Se_{85-x}Pb_x$ $(0 \leq x \leq 6)$ chalcogenide glasses and the evaluation of the activation energies were carried out by means of non-isothermal DSC measurement. In the present system, we have used Se as a major content because it is widely used as a typical glass-former. Here we have chosen Ga as an additive to Se. There is a strong tendency for Ga to super cool below its freezing point. So, seeding may be necessary to initiate solidification. We have incorporated lead in Ga–Se system. Metallic additive such as Pb and Bi in chalcogenide glasses enter the network as charged species, altering the concentration of positively and negativity of valence alternation pairs [41–43]. One of their most important properties is their ion selectivity, thanks to the fact that the Pb and Bi change the concentration of positively and negativity of valence alternation pairs. Namely, because of this specific feature, the Se–Pb chalcogenides are used. Selenium–lead chalcogenides are considered to be mainly utilized for detecting hydrocarbon pollutant in atmosphere, higher solution spectroscopy, trace gas analysis, optical fiber analysis and optical communication system over super long distances [44–46].

2. Experimental

Bulk material of $Ga_{15}Se_{85-x}Pb_x$ $(0 \leq x \leq 6)$ chalcogenide glasses were prepared by the well-established melt-

-quench technique. Amorphous materials produced in this manner have been termed as glasses, which exhibit glass transition temperature phenomena. High purity (99.999%) Ga, Se and Pb in appropriate proportions were sealed in a quartz ampoule under a vacuum of 10^{-5} Torr. The contents were heated in a microprocessor-controlled programmable muffle furnace, where the temperature was increased at 3 K/min up to 1273 K and kept at that temperature for 14 h with frequent rocking to ensure the homogenization of the melt. During the melting, the tube was frequently shaken to homogenize the resulting alloy. The melt was then rapidly quenched by ice water. After quenching, ingots of the sample were removed by breaking the ampoules. A Philips Model PW 1710 X-ray diffractometer was employed for studying the structure of the material. The copper target was used as a source of X-rays with $\lambda = 1.5404$ Å (Cu K_{α_1}). The scanning angle was in the range of 20°–100°. A scan speed of 2°/min and a chart speed of 1 cm/min were maintained.
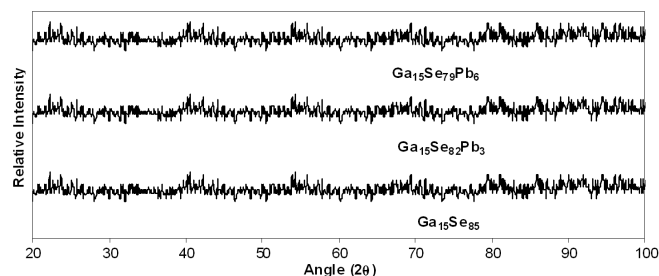

Fig. 1. X-ray pattern of $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses.

The X-ray diffraction traces of $Ga_{15}Se_{85-x}Pb_x$ with $x = 0$, 3, and 6 chalcogenide glasses were taken at room temperature and found to show similar trends and are shown in Fig. 1. The absence of sharp structural peak confirms the amorphous nature of the samples. The study of glass transition and crystallization behavior of $Ga_{15}Se_{85-x}Pb_x$ with $x = 0$, 3, and 6 chalcogenide glasses were studied under non-isothermal measurements by using a Shimadzu DSC-60 instrument. Typically, 10 mg of sample in powder form was sealed in standard aluminum sample pans and heated at different rates ranging from 5 to 25 K/min. The glass transition temperature, crystallization temperature and melting temperatures were measured by the DSC thermograms. The temperature precision of this equipment is ±0.1 K with an average standard error of about 1 K in the measured values of T_g and T_c. The DSC equipment was calibrated prior to measurements, using high purity standards Pb, Sn and In with well-known melting points.

3. Results and discussion

Figure 2 shows the DSC curves of $Ga_{15}Se_{79}Pb_6$ glass at various heating rates of 5, 10, 15, 20, and 25 K/min, while Fig. 3 shows the DSC curves of $Ga_{15}Se_{85-x}Pb_x$

glasses at 25 K/min. Similar curves were obtained for other glassy alloys (not shown here). The characteristic phenomena (endothermic and exothermic peaks) are evident in the DSC curves in the temperature range of investigation. From the analysis point of view, the DSC curve is divided into three parts, the first one corresponds to the glass transition region which appears as endothermic reaction at temperature, T_g, the second part is related to the crystallization process of the considered glass indicated by one exothermic crystallization peak, T_c, and the last corresponds to the melting region which appears as an endothermic reaction at temperature, T_m.
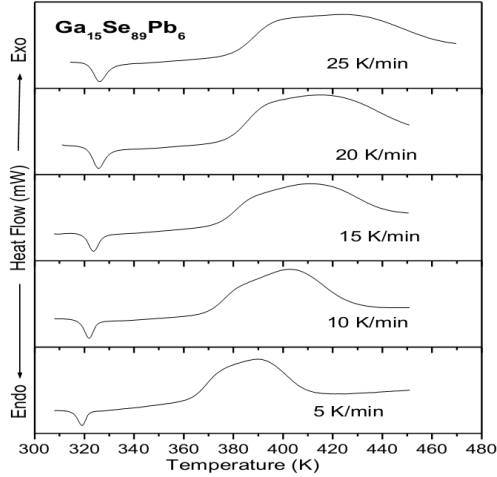

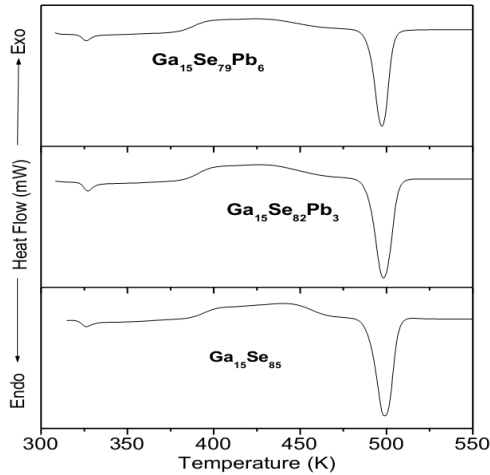Fig. 2. DSC plot for $Ga_{15}Se_{89}Pb_6$ glass at different heating rates.

Fig. 3. DSC plot for $Ga_{15}Se_{85-x}Pb_x$ glasses at 25 K/min.

The values of glass transition temperature, T_g, for all the glassy alloys at different heating rates are given in Table I. It reveals that the glass transition temperature is shifted to the higher values by increasing the heating rates from 5 to 25 K/min for all the samples of $Ga_{15}Se_{85-x}Pb_x$ glasses. The glass temperature T_g as defined by the endothermic change in the DSC trace indicates a large change of viscosity, marking a transformation from amorphous solid phase to supercooled liquid state. The pronounced variation of T_g with heating rate is a manifestation of the kinetic nature of the glass transition. The relatively large endothermic peaks observed in the present work are most likely due to aging effect. The exothermic peak temperature T_c is used to identify the crystallization process. It is evident from Table I that both T_c and T_g shift to higher temperatures with increasing heating rate. The shift of T_c arises from the dependence of the induction time associated with nucleation process. Crystallization is controlled by nucleation and there exist an induction time for nucleation. As the heating rate increases, the temperature at which induction time becomes zero increases leading to the observed shift of crystallization to higher temperatures.

TABLE I

Compositional dependence of T_g (K) and T_c (K) of $Ga_{15}Se_{85-x}Pb_x$ glasses from non-isothermal DSC experiments.

Heating rate [K/min]	$Ga_{15}Se_{85}$		$Ga_{15}Se_{82}Pb_3$		$Ga_{15}Se_{79}Pb_6$	
	T_g	T_c	T_g	T_c	T_g	T_c
5	317.27	397.75	316.52	393.22	317.79	390.36
10	319.64	410.25	318.95	404.34	320.32	402.74
15	321.28	422.81	322.55	411.96	321.89	411.13
20	322.35	433.79	323.9	423.03	323.53	415.07
25	323.7	440.21	324.78	426.34	324.79	424.45

This variation of glass transition temperature takes the form of a power law behavior and may be represented by the following expression [47]:

$$T_g = T_0[\beta]^y, \tag{1}$$

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. (1) the exponent y is given by

$$y = \log_{10}\left[(T_g)_{10}/(T_g)_1\right], \tag{2}$$

where $(T_g)_{10}$ stands for the T_g values at a heating rate of 10 K/min. Equation (1) 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 T_g is an experimentally observed [48, 49] 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 [47] as the relaxation time. With increasing heating rate, τ_{obs} decreases and hence the glass transition temperature increases.

The kinetics of isothermal crystallization involving nucleation and growth is usually analyzed using the Kolmogorov–Johnson–Mehl–Avrami (KJMA) model [50, 51]. According to this model, the volume fraction of crystallites (α) is given by [52–54]:

$$\alpha(t) = 1 - \exp\left(-(kt)^n\right), \qquad (3)$$

where $\alpha(t)$ is the volume fraction crystallized after time t, n is the Avrami exponent that is associated with the nucleation and growth mechanisms and k is the reaction rate constant.

In this thermally activated process the reaction rate constant k is related to temperature T and is given by

$$k = \nu \exp(-\Delta E_c / RT), \qquad (4)$$

where ΔE_c is the activation energy of crystallization, ν is the pre-exponential factor and R is the gas constant. In the framework of KJMA model, the kinetic parameters n, A and E are assumed to be constant during the crystallization process.

However, as pointed out by Vyazovkin [55], the crystallization process is generally determined by nucleation and growth, which are likely to have different activation energies. It is also possible that different growth mechanisms are operating at different degree of crystallization leading to temperature-dependent activation energy. The activation energy for crystallization as well as the Avrami exponent can be obtained using a method suggested specifically for non-isothermal experiments by Matusita et al. [56].

The fraction "α" crystallized at any temperature "T" is given as $\alpha = A_T / A$, where "A" is the total area of exotherm between the onset crystallization temperature T_1, where crystallization just begins and the temperature T_2 where the crystallization is completed. "A_T" is the partial area of exothermic peak between the temperature "T_1" and "T_2". The temperature T is selected between T_1 and T_2.

In non-isothermal crystallization, the existence of a constant heating rate condition is assumed. The relation between the sample temperature and the heating rate can be written as

$$T = T_0 + \beta t, \qquad (5)$$

where T_0 is the initial temperature.

As the temperature constantly changes with time, k is no longer a constant but varies with time in a more complicated form and Eq. (4) becomes

$$\alpha(t) = 1 - \exp\left(-\{k(T - T_0)/\beta\}^n\right). \qquad (6)$$

After rearranging and taking logarithms of Eq. (6), Ozawa [57, 58] obtained

$$\ln(-\ln(1 - \alpha)) = n \ln k(T - T_0) - n \ln \beta. \qquad (7)$$

According to Eq. (7), a plot of $\ln(-\ln(1 - \alpha))$ versus $\ln \beta$ yield a straight line with slope equal to n. Figure 4 shows the variation of $\ln(-\ln(1 - \alpha))$ against $\ln \beta$ for $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses.

The value of n for these compositions is listed in Table II. When the liquified compound is cooled in the glass transition region, the relaxation times for molecular movements become comparable to the experimental time scale. Therefore, the diffusive movements become comparable to the experimental timescale, the diffusive motion of the liquid is trapped and the system falls out of thermal equilibrium. At this moment, the size of the
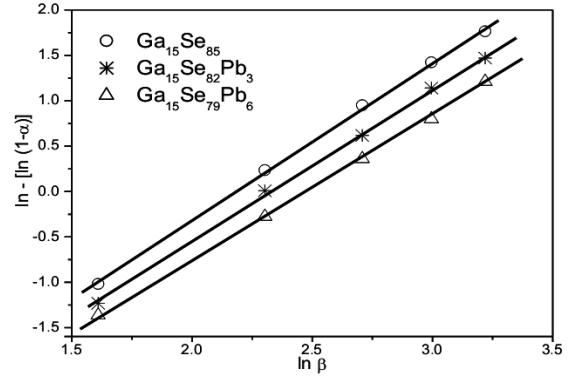

Fig. 4. Plot of $\ln(-\ln(1 - \alpha))$ as a function of $\ln \beta$ of $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses.

nuclei does not reach the critical size required to initiate the nucleation process and hence the glass is assumed to have no nuclei (of critical size). When the glass is heated in the DSC furnace, the rate of crystal nucleation reaches the maximum at a temperature somewhere higher than the glass transition temperature and then decreases rapidly with increasing temperature, while the rate of crystal growth reaches a maximum at a temperature much higher than the temperature at which the nucleation rate is the highest. When the glass is heated at a constant rate, the crystal nuclei are formed only at lower temperatures and crystals grow in size at higher temperature without any increase in number.

TABLE II

Compositional dependence of order parameter (n) and enthalpy released(ΔH_c) of $Ga_{15}Se_{85-x}Pb_x$ glasses from non-isothermal DSC experiments.

Sample	n	ΔH_c [J/mg]				
		5 K/min	10 K/min	15 K/min	20 K/min	25 K/min
$Ga_{15}Se_{85}$	1.7376	6587.14	5727.86	6841.21	7630.71	6788.57
$Ga_{15}Se_{82}Pb_3$	1.6787	3844.29	4425.01	4352.14	4958.57	4551.43
$Ga_{15}Se_{79}Pb_6$	1.5857	2929.29	3171.43	3192.86	3285.25	3336.43

It is well known that crystallization of chalcogenide glasses is associated with nucleation and growth processes and the extent of crystallization increases with an increase in temperature. Due to these order pa-

rameter (n) changes. Since for the sample prepared by melt quenching technique, the value of n may be 4, 3, 2 or 1, which can be related to different crystallization mechanism; $n = 4$ represents volume nucleation, three--dimensional growth; $n = 3$ represents volume nucleation, two-dimensional growth; $n = 2$ represents volume nucleation, one-dimensional growth; $n = 1$ represents surface, one-dimensional growth from surface to inside. In our present system of $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses, the value of n is equal to 2, which represents volume nucleation, one-dimensional growth.

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

$$\Delta H_c = KA/M, \tag{8}$$

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 for $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses at different heating rates are shown in Table II. The enthalpy release is related to the metastability of the glasses and the least stable glasses are supposed to have maximum ΔH_c. It is observed that $Ga_{15}Se_{85}$ glass has more enthalpy than other glasses at all heating rates and hence $Ga_{15}Se_{85}$ glass is the least stable glass than the other glasses of $Ga_{15}Se_{85-x}Pb_x$.

The interpretation of the experimental crystallization data is given on the basis of Kissinger's, Matusita's and modified Ozawa's equations for non-isothermal crystallization. The activation energy (ΔE_c) for crystallization can therefore be calculated by using Kissinger's equation [59],

$$\ln(\beta/T_c^2) = -\Delta E_c/RT_c + D. \tag{9}$$

The plot of $\ln(\beta/T_c^2)$ versus $1000/T_c$ for $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses are shown in Fig. 5, which come to be straight lines. The value of ΔE_c may be calculated from the slope of each curve and is given in Table III.
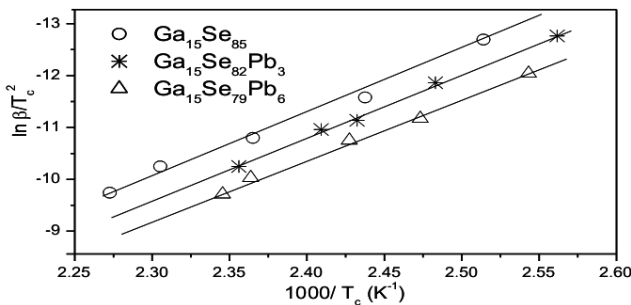

Fig. 5. Plot of $\ln(\beta/T_c^2)$ as a function of $1000/T_c$ [K^{-1}] of $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses.

The activation energy of crystallization can also be obtained from the variation of the onset crystallization temperature with heating rate by using Ozawa's [58] relation

as

$$\ln\beta = -\Delta E_c/RT_c + C, \tag{10}$$

where C is a constant.

Compositional dependence of ΔE_c (kJ/mol) and ΔE_g (kJ/mol) of $Ga_{15}Se_{85-x}Pb_x$ glasses from non-isothermal DSC experiments.

Sample	ΔE_g [kJ/mol]		ΔE_c [kJ/mol]	
	$\ln\beta$ versus $1000/T_g$	$\ln(\beta/T_g^2)$ versus $1000/T_g$	$\ln\beta$ versus $1000/T_c$	$\ln(\beta/T_c^2)$ versus $1000/T_c$
$Ga_{15}Se_{85}$	160.63	157.04	95.88	98.02
$Ga_{15}Se_{82}Pb_3$	183.43	172.81	113.73	108.89
$Ga_{15}Se_{79}Pb_6$	208.89	197.97	122.98	114.97

Figure 6 shows $\ln\beta$ versus $1000/T_c$ dependences, which come to be linear. The value of ΔE_c is calculated from the slope of each line for $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses and is shown in Table III. The values of the activation energies calculated from Eqs. (9) and (10) are in good agreement with each other. It is clear from Table III that the activation energy of crystallization increases in both methods with increasing Pb content in Ga–Se system, indicating that the rate of crystallization is higher as the Pb content increases in Ga–Se system. The increase in activation energy of crystallization may be interpreted in terms of increased hopping conduction in impurity induced states [60]. At higher concentration, alloying effect was observed which could change the mobility gap and various other parameters of the original materials.
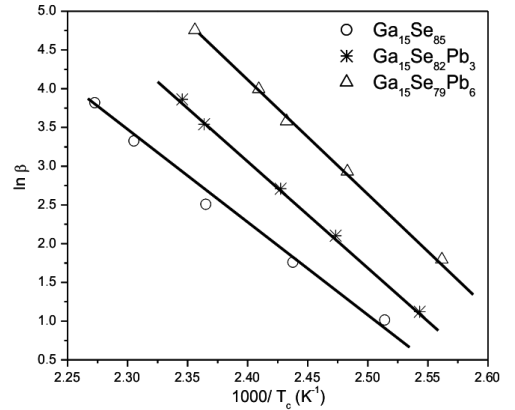

Fig. 6. Plot of $\ln\beta$ as a function of $1000/T_c$ [K^{-1}] of $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses.

The activation energy of glass transition (ΔE_g) for $Ga_{15}Se_{85-x}Pb_x$ chalcogenide glasses can be calculated by using Kissinger's Eq. [59] as,

$$\ln(\beta/T_g^2) = -\Delta E_g/RT_g + \text{constant}. \tag{11}$$

It is evident from this equation that a plot of $\ln(\beta/T_g^2)$ against $1000/T_g$ should be straight line (shown in Fig. 7) and that the activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot and are shown in Table III.
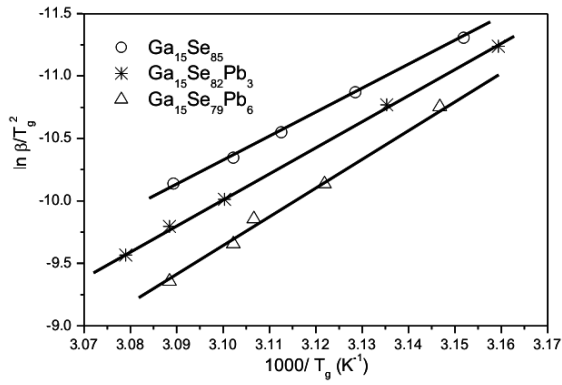
Fig. 7. Plot of $\ln(\beta/T_g^2)$ as a function of $1000/T_g$ [K^{-1}] of Ga$_{15}$Se$_{85-x}$Pb$_x$ chalcogenide glasses.
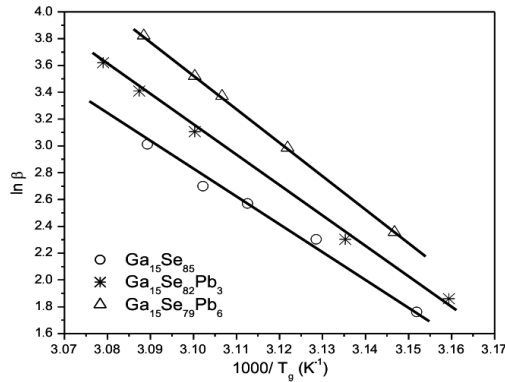

Fig. 8. Plot of $\ln\beta$ as a function of $1000/T_g$ [K^{-1}] of Ga$_{15}$Se$_{85-x}$Pb$_x$ chalcogenide glasses.

The heating rate (β) dependence of the glass transition temperature in chalcogenide glasses may be interpreted in terms of thermal relaxation phenomena and it has been shown by Moynihan et al. [61] that the activation energy of structural relaxation (ΔE_g) can be related to T_g and β by

$$\mathrm{d}\ln\beta/\mathrm{d}(1/T_g) = -\Delta E_g/R. \qquad (12)$$

It is evident from this equation that a plot of $\ln\beta$ against $1000/T_g$ should be straight line (shown in Fig. 8) and that the activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot and are shown in Table III. It is clear from this table that the activation energy of glass transition (structural relaxation) increases with increasing Pb content in Ga–Se system in both methods. The activation energy of glass transition (structural relaxation) depends on T_g and heating rate (β). The glass transition temperature is known to depend on several independent parameters such as the band gap, bond energy, effective molecular weight, the type and fraction of various structural units formed, cohesive energy, the average heats of atomization and the average coordination number [62–64]. From Table II, it is observed that the

activation energy of glass transition calculated using the two models is in good agreement with each other.

4. Conclusion

The glass transition behavior and crystallization kinetics of Ga$_{15}$Se$_{85-x}$Pb$_x$ chalcogenide glass have been investigated by non-isothermal DSC measurements. The value of order parameter (n) for studied glasses indicates that there is volume nucleation with one-dimensional growth. The interpretation of the experimental crystallization data is given on the basis of Kissinger's, Matusita's and modified Ozawa's equations. By employing different methods, the activation energy of crystallization (ΔE_c) and activation energy of structural relaxation (ΔE_g) were determined from the heating rate dependence of crystallization and glass transition temperature. The results of crystallization kinetics indicate that the degree of crystallization under non-isothermal conditions fits well with the theory of Matusita, Sakka and Kissinger. A multiple scanning technique was used to calculate ΔE_c and ΔE_g, it was found that the value of ΔE_c and ΔE_g by both techniques are in good agreement with each other. The values of ΔE_c and ΔE_g are found to increase with compositions indicating a structural change due to the addition of Pb. The enthalpy released is found to be maximum for Ga$_{15}$Se$_{85}$ glass as compared to other glasses under investigation at all heating rates.

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