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Non-isothermal crystallization kinetic study on $Ga_{15}Se_{85-x}Ag_x$ chalcogenide glasses by using differential scanning calorimetry

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ABSTRACT

At different heating rates, the glass transition temperature (T_g) and the crystallization temperature (T_c) are obtained from the non-isothermal differential scanning calorimetry (DSC) measurements of bulk $Ga_{15}Se_{85-x}Ag_x$ ($x = 0$, 2, 4, 6 and 8) chalcogenide glasses prepared by melt quenching technique. Their amorphous state was verified by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was observed that the glass transition temperature and crystallization temperatures both increase with increasing heating rates and also by increasing Ag concentration in Ga–Se system. The activation energy of crystallization (E_c), activation energy of glass transition (E_g), crystallization enthalpy (ΔH_c) and the Avrami exponent (n) have been determined from the dependence of T_g and T_c on the heating rate (β). The obtained value of the n indicates that the volume nucleation with two dimensional growth is responsible for amorphous-crystallization phase transformation. On the basis of the obtained experimental data, the temperature difference ($T_g - T_c$) and the enthalpy released (ΔH_c) are found to be maximum and minimum, respectively, for $Ga_{15}Se_{77}Ag_8$ glass, which indicate that this glass is thermally most stable in the composition range under investigation. The crystallization kinetic study of $Ga_{15}Se_{85-x}Ag_x$ glass was studied by using the modified Kissinger and Ozawa equations.

1. Introduction

Amorphous semiconductors especially chalcogenide glasses have been investigated largely due to its important technological applications, such as switching, electrophotography, X-ray imaging, photonics, thermal imagining, ultra-high-density phase-change storage and memory, integrated fiber optics, infrared photo-detectors, photo-voltaic, biosensors [1–5]. The considerable interest of researchers in these glasses is due to the possibility of their various applications in different fields of electronics that based on the fact that they combine the characteristic features of the disordered systems and some properties of the crystalline semiconducting materials. Recently, chalcogenide glasses have been investigated as infrared transmitting materials to replace single-crystalline germanium for fabricating infrared optical lenses.

The differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are extremely popular tools for studying the kinetics of non-isothermal transformation. The appeal of these methods is their simplicity and their flexibility in the selection of heating rates. Between these techniques, DSC is particularly important, since it is easy to be carried out and is quite sensitive [6]. In DSC two basic methods are used: isothermal and non-isothermal. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature (T_g) and the heat evolved during the crystallization process is recorded as a function of time, whereas in non-isothermal method, the sample is heated at fixed rate and the heat evolved is recorded as a function of temperature or time. The isothermal experimental analysis techniques are more definite but on the other hand non-isothermal thermo-analytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed, makes these techniques more attractive. Further, this technique can be used to extend the temperature range of measurements for an advantage over the isothermal experiments. The 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. Many phase transformations occur too rapidly to be measured under isothermal conditions because of transitions inherently associated with the experimental apparatus. Industrial processes often depend on the kinetic behavior of systems undergoing phase transformation under non-isothermal conditions. In this respect, a definitive measurement of non-isothermal transformation kinetic is desirable. The DSC has widely been used to investigate the glass transformations in glassy materials. It is very quick and needs very small

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quantities of glass samples to acquire kinetic parameters of the crystallization [7].

Over the past several decades, many experimental results of non-isothermal kinetics have been fitted with the Johnson–Mehl–Avrami (JMA) model [8,9]. JMA equation plays a central role in studies of transformations, where nucleation and growth mechanism operate. So many experimental results of phase transformation kinetics have been fitted with a JMA equation. The JMA equation can only be validated under certain conditions [7,10–14], specially when the nucleation process takes place. Under this conditions, the Avrami exponent (n) and the effective activation energy (E_c) should be constant during the transformation process. Several studies of crystallization kinetics in binary and ternary chalcogenide glasses by non-isothermal DSC methods have been widely discussed in the literature [15–27]. For example, Mehta et al. [20] have studied a comparative analysis of thermal crystallization in Cu–Ti and Cu–Zr metallic glasses. Elabbar et al. [21] and Srivastava et al. [22] have studied the crystallization kinetics of Pb–Se and Se–Te–Zn glasses by using DSC, respectively. The work on crystallization kinetics of Si–Te chalcogenide glasses by Zhang et al. [23], the studies of the glass transition in amorphous Se using DSC by Abu-Sehly et al. [24], thermal stability and crystallization kinetics of As–Ge–Se–Sb glasses by Dahshan [25], studies of thermal properties of chalcogenide glasses in the $GeSe_2$–As_2Se_3–CdSe system by Zhao et al. [26] and kinetics study of Se–Te–Pb using non-isothermal crystallization by Khan et al. [27] are also worth mentioning.

In this article, the crystallization kinetics and the evaluation of the activation energies of $Ga_{15}Se_{85-x}Ag_x$ chalcogenide glasses are studied by using the non-isothermal method. There has been a growing interest in the synthesis and characterization of selenides due to their unique properties in electronics, magnetism and optics, and also wide applications in various fields such as sensors, laser materials, solar cells, infrared detectors, and thermoelectric cooling materials [28,29]. 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, 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 [30]. In the present system, we have incorporated silver in Ga–Se system. Ag-doped chalcogenide glasses have become attractive materials for fundamental research of their structure, properties, and preparation. They have many current and potential applications in optics, optoelectronics, chemistry, and biology (optical elements, gratings, memories, microlenses, waveguides, bio and chemical-sensors, solid electrolytes, batteries, etc.). The Ag doped chalcogenide glasses can be used as optical memory and materials for holography [31] and also be used as sensitive electrochemical electrodes or their membranes for sensors for potentiometric determination [32,33].

2. Experimental

The investigated glasses were synthesized from high purity (99.999%) Ga, Se and Ag elements by using melt quenching techniques. The desired amounts of elements were weighed according to their atomic percentage and put into ultrasonically cleaned quartz ampoules. The ampoules were evacuated and sealed under a vacuum of 10^{-3} Pa to exclude reaction of glasses with oxygen at high temperature. The bunch of sealed ampoules was heated in a Microprocessor Controlled Programmable Muffle Furnace and raised the temperature up to 1323 K. The temperature of the furnace was raised at the rate of 4 K/min. and kept it at that temperature for 12 h. During the melting process the ampoules were frequently rocked to ensure the homogeneity of molten materials. After achieving desired time, the ampoules with molten materials were rapidly quenched into ice cooled water. Then ingots of glassy materials were removed from the ampoules. The crystallization kinetics of $Ga_{15}Se_{85-x}Ag_x$ (x = 0, 2, 4, 6 and 8) glasses were investigated by using Differential Scanning Calorimeter (Model-DSC plus, Rheometric Scientific Company, UK). The instrument was calibrated with indium, lead and tin standards. Each sample was heated at a constant heating rate (β) of 5, 10, 15 and 20 K/min and the changes in heat flow with respect to temperature were measured. The glass transition temperature (T_g) and the crystallization temperature (T_c) were determined using the microprocessor of thermal analyzer. A Regaku X-ray diffractometer Ultima IV was employed for studying the structure of the material. Copper target was used as the X-ray source with λ = 1.54178 Å (Cu Kα_1). The scanning angle was in the range of 10–100°. A scan speed of 2°/min and a chart speed of 1 cm/min were maintained. The X-ray diffraction traces of all samples were taken at room temperature and found to show similar trends and hence only one of them is shown in Fig. 1. The absence of sharp structural peak confirms the amorphous state of the samples. The surface morphology of $Ga_{15}Se_{81}Ag_4$ powder was examined by means of JEOL JSM-6360LV, Japan, scanning electron microscopy (SEM), shown in Fig. 2, which also confirms the amorphous state of the samples.

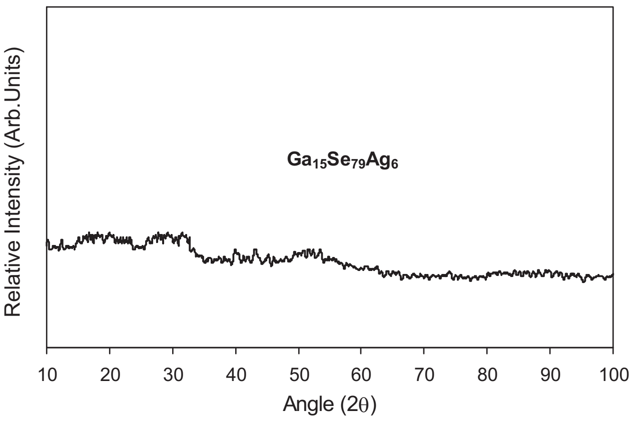

Fig. 1. X-ray pattern of $Ga_{15}Se_{79}Ag_6$ sample.

3. Theoretical background

Studies of crystallization kinetics 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 crystallization phenomena as it is rapid and convenient. The kinetics of first-order phase transformation are important in physics, chemistry, ceramic and material science. The fraction 'α' crystallized at any temperature 'T' is defined 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.

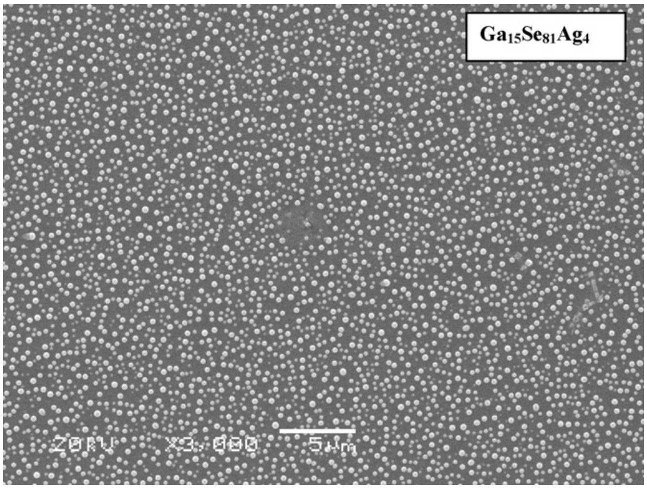

Fig. 2. SEM of $Ga_{15}Se_{81}Ag_4$ sample.

The crystallization fraction (α) which is a function of time t, have been extensively studied using the classical Johnson–Mehl–Avrami (JMA) [8,9,35] theoretical model

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

where n is the Avrami exponent (order parameter), which depends on the mechanism of growth and dimensionality of the crystal and K is the effective (overall) reaction rate constant which is given by

$$K = K_0\, exp\left(-\frac{E_c}{RT}\right), \tag{2}$$

where E_c is the activation energy for crystallization and K_0 is the frequency factor.

The crystallization process is generally well characterized, when the three kinetic parameters E_c, n and K_0 are determined. Based on the JMA model, different authors [6,36–38] have developed very diverse methods for calculating these parameters. Their developments are carried out under the hypothesis that the temperature is constant during the crystallization reaction, which means that the methods are strictly applicable to isothermal experiments. However, under some approximations, it is shown [39] that the application of these methods to non-isothermal experimental data leads to satisfactory conclusions. 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,

$$T = T_0 + \beta t, \tag{3}$$

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. (1) becomes,

$$\alpha(t) = 1 - exp\left[-\left\{K\frac{T - T_0}{\beta}\right\}^n\right]. \tag{4}$$

After rearranging and taking logarithms of Eq. (4), Ozawa [40,41] obtained

$$ln[-ln(1-\alpha)] = n\,ln\,k(T - T_0) - n\,ln\,\beta. \tag{5}$$

According to Eq. (5), a plot of $ln[-ln(1-\alpha)]$ *versus* $ln\,\beta$ yield a straight line with slope equal to n.

The crystallization rate is obtained by taking the time derivative of expression (1) bearing in mind that the reaction rate constant is a time function through its Arrhenius temperature dependence, resulting in,

$$\left(\frac{d\alpha}{dt}\right) = n(Kt)^{n-1}\left[K + t\left(\frac{dK}{dt}\right)\right](1-\alpha). \tag{6}$$

The time derivative of K can be obtained from Eqs. (2) and (3) as follows:

$$\frac{dK}{dt} = \left(\frac{dK}{dT}\right)\left(\frac{dT}{dt}\right) = \left(\frac{\beta E_c}{RT^2}\right)K. \tag{7}$$

Then Eq. (6) becomes,

$$\left(\frac{d\alpha}{dt}\right) = nK^n t^{n-1}[1 + at](1-\alpha), \tag{8}$$

where $a = (\beta E_c/RT^2)$.

Now adopting the most commonly used Kissinger approach [42], where it is assumed that $\beta E_c/RT^2 \ll 1$, the term 'at' in above equation is neglected in comparison to unity and so Eq. (8) reduces to

$$\left(\frac{d\alpha}{dt}\right) = nK^n t^{n-1}(1-\alpha). \tag{9}$$

Expressing t in term of α from Eq. (1), the crystallization rate becomes

$$\left(\frac{d\alpha}{dt}\right) = \varphi nK(1-\alpha), \tag{10}$$

where $\varphi = [-ln(1-\alpha)]^{(n-1)/n}$. Since the crystallization temperature, T_c is identified as the temperature of maximum crystallization, i.e. the temperature at which $(d^2\alpha/dt^2) = 0$, we differentiate Eq. (8) with respect to time assuming that $[-ln(1-\alpha)]^{(n-1)/n}$ is a constant near the crystallization peak [43] and equating the resulting expression at $T = T_c$ to zero we get

$$\left(\frac{d^2\alpha}{dt^2}\right)\bigg|_{T=T_c} = \varphi nK(1-\alpha)\left[\left(\frac{\beta E_c}{RT_c^2}\right) - \varphi nK\right] = 0 \tag{11}$$

or,

$$\left(\frac{\beta}{T_c^2}\right) = C\,exp\left(\frac{-E_c}{RT_c}\right), \tag{12}$$

where $C = \varphi RnK_0/E_c$. Now taking the logarithm of the above equation, we can get,

$$ln\left(\frac{\beta}{T_c^2}\right) = (constant) - \left(\frac{E_c}{RT_c}\right). \tag{13}$$

A slightly different form of Eq. (13) but probably more accurate expression has been derived by Augis and Bennett [44] for determining crystallization parameters. By substituting a variable u for Kt in Eq. (8) they proceed as follows:

$$\left(\frac{d\alpha}{dt}\right) = nKu^{n-1}[1 + at](1-\alpha)$$

or,

$$\left(\frac{d\alpha}{dt}\right) = n\left(\frac{du}{dt}\right)u^{n-1}(1-\alpha) \tag{14}$$

with

$$\frac{du}{dt} = u\left[\left(\frac{1}{t}\right) + a\right]. \tag{15}$$

As before, since T_c is identified as the temperature of maximum crystallization, we differentiate Eq. (14) with respect to time and equating the resulting expression at $T = T_c$ to zero we get

$$\left(\frac{d^2\alpha}{dt^2}\right)\bigg|_{T=T_c} = \left[\left(\frac{d^2u}{dt^2}\right)u - \left(\frac{du}{dt}\right)^2(nu^n - n + 1)\right]nu^{n-2}(1-\alpha) = 0. \tag{16}$$

The time derivative of Eq. (15) is given by,

$$\left(\frac{d^2u}{dt^2}\right) = \left(\frac{du}{dt}\right)\left[\frac{1}{t} + a\right] + u\left[\left(-\frac{1}{t^2}\right) + \left(\frac{da}{dt}\right)\right]. \tag{17}$$

Now since $a = (\beta E_c/RT^2)$ and $T = T_0 + \beta t$, we get $da/dt = -(2\beta/T)a$, and hence Eq. (17) becomes

$$\left(\frac{d^2u}{dt^2}\right) = u\left[a^2 + \left(\frac{2aT_0}{tT}\right)\right]. \tag{18}$$

As $T_0 \ll T$, the last term in the above equation is neglected [44] and so Eq. (18) reduces to a simple form

$$\left(\frac{d^2u}{dt^2}\right) = ua^2. \tag{19}$$

Substituting the values of du/dt and d^2u/dt^2 from Eqs. (15) and (19) into Eq. (16) we get

$$nu^n - n + 1 = \left[\frac{at}{(1 + at)}\right]^2. \tag{20}$$

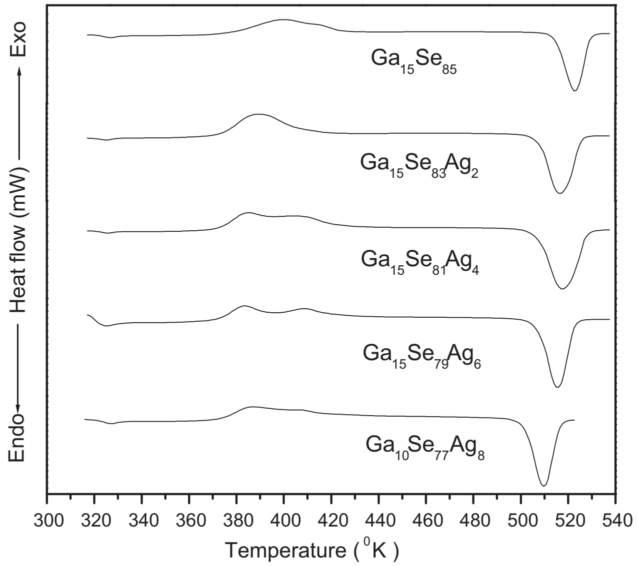

Fig. 3. DSC plot of $Ga_{15}Se_{85-x}Ag_x$ glasses recorded at heating rates 20 K/min.

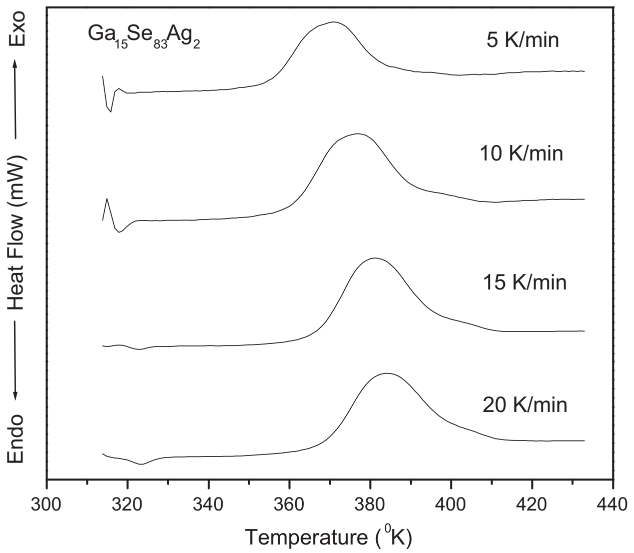

Fig. 4. DSC plot of $Ga_{15}Se_{83}Ag_2$ glass at different heating rates 5, 10, 15 and 20 K/min.

For $E_c/RT \gg 1$, the value of right hand side of above equation approaches to its maximum limit and consequently u at the peak = 1, that is

$$u = (Kt)_{peak} = K_0\, exp\left(-\frac{E_c}{RT_c}\right)\left[\frac{T_c - T_0}{\beta}\right] \approx 1. \tag{21}$$

Since $T_0 \ll T_c$, we have,

$$ln\left(\frac{\beta}{T_c}\right) \approx \left(-\frac{E_c}{RT_c}\right) + ln\, K_0. \tag{22}$$

The value of E_c can be calculated by the plotting $ln(\beta/T_c)$ against $1000/T_c$.

The activation energy of crystallization can also be obtained from the variation of the onset crystallization temperature T_c with heating rate by using relation [43] as

$$ln\, \beta = constant - \left(\frac{E_c}{RT_c}\right). \tag{23}$$

So E_c can be evaluated from this equation using plots of $ln\, \beta$ against $10^3/T_c$.

4. Results and discussion

Fig. 3 represents the DSC thermograms of $Ga_{15}Se_{85-x}Ag_x$ chalcogenide glasses recorded at heating rates 20 K/min. A typical DSC trace of $Ga_{15}Se_{83}Ag_2$ glasses at different heating rates 5, 10, 15 and 20 K/min. are also shown in Fig. 4. Three characteristic phenomena are evident in these DSC thermograms: (1) endothermic-like phenomenon indicating the glass transition region, (2) an exothermic phenomenon that manifest the crystallization process and (3) the endothermic phenomenon corresponds to the melting of the sample. The crystallization kinetics of alloys is characterized by measuring the exothermic peak temperature 'T_c'. The values of glass transition (T_g), crystallization (T_c) and melting temperatures(T_m) with Ag contents at the heating rate 15 K/min for all the samples of $Ga_{15}Se_{85-x}Ag_x$ are given in Table 1. It is clear from this table that T_g increases with increasing Ag contents in the Ga–Se system. The increase in T_g could be attributed either to the increase in effective molecular weight with increasing Ag content or to the increase in concentration of long polymeric chains of Ga–Se. The T_g of a multi-component glass is known to be dependent on several independent parameters such as band gap, co-ordination numbers, bond energy, effective molecular weight, the type and fraction of various structural units formed [34,45–47]. In our study T_g increases with increasing Ag concentration. 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 [48] as the relaxation time. With increasing Ag concentration, τ_{obs} decreases and hence the glass transition temperature increases.

Both $(T_c - T_g)$ and T_c represent the thermal stability of the glass. The values of $(T_c - T_g)$ for different compositions are given in Table 1. It is clear from this table that $(T_c - T_g)$ is highest for the composition of 8% of Ag. Hence the glass with 8% of Ag is most stable.

The crystallization enthalpy ΔH_c was evaluated for all composition using the formula:

$$\Delta H_c = \frac{kA}{m}, \tag{24}$$

where k (=1.5) is the constant of the instrument, A is the area of crystallization peak and m is the mass of sample.

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. The values of the ΔH_c for various compositions at different heating rates are also quoted in Table 1. The enthalpy release is related to the meta-stability of the glasses. It is obvious from this table that minimum heat is released for the composition with 8% of Ag in Ga–Se system, which confirms the maximum stability of the glass.

In addition to the evaluation of the activation energy of crystallization, the order parameter has been evaluated by using Eq. (5).

Table 1
Compositional dependence of crystallization parameters T_c, T_g, T_m, $(T_c - T_g)$ and crystallization enthalpy (ΔH_c) of $Ga_{15}Se_{85-x}Ag_x$ from non-isothermal DSC experiments at a heating rate of 15 K/min.

Sample	T_g (K)	T_c (K)	T_m (K)	$T_c - T_g$ (K)	ΔH_c (J/mg)
$Ga_{15}Se_{85}$	316.41	384.12	509.42	63.71	3135.43
$Ga_{15}Se_{83}Ag_2$	319.66	380.26	505.21	60.60	4243.52
$Ga_{15}Se_{81}Ag_4$	320.21	376.53	503.38	56.32	2002.56
$Ga_{15}Se_{79}Ag_6$	321.16	374.34	502.12	53.18	1405.45
$Ga_{15}Se_{77}Ag_8$	322.79	388.24	508.64	65.45	862.29

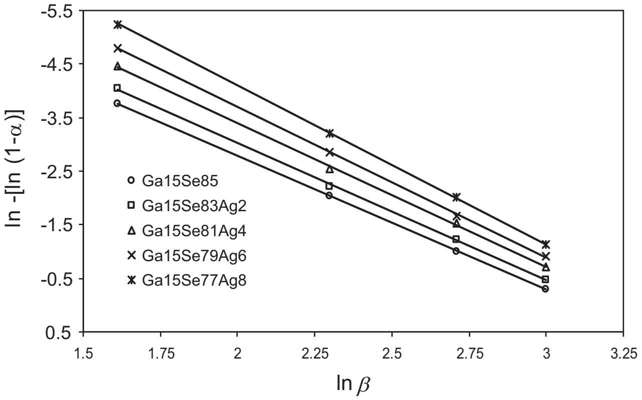

Fig. 5. Plot of $ln[-ln(1-\alpha)]$ as a function of $ln\,\beta$ of $Ga_{15}Se_{85-x}Ag_x$ glass.

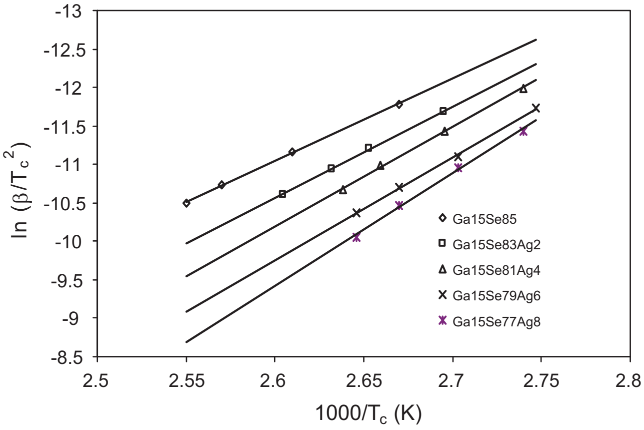

Fig. 6. Plot of $ln(\beta/T_c^2)$ as a function of $1000/T_c$ (K) for $Ga_{15}Se_{85-x}Ag_x$ glass.

Fig. 5 shows the variation of $ln[-ln(1-\alpha)]$ with $ln\,\beta$ for glassy alloys $Ga_{15}Se_{85-x}Ag_x$. The values of n have been determined from the slope of these curves and are given in Table 2. When the liquefied 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. And so, the diffusive motion of the liquid is trapped and the system falls out of thermal equilibrium [49]. At this moment, the size of the 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). According to Matusita et al. [50], 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 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. It is clear from Table 2 that the values of n increases with increasing Ag contents in the Ga–Se system. It is also well known that crystallization of chalcogenide glasses is associated with nucleation and growth processes whereas the extent of crystallization (α) increases with an increase in temperature. Due to these, order parameter (n) increases. 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 with three dimensional growth; $n=3$ represents volume nucleation with two dimensional growth; $n=2$ represents volume nucleation with one dimensional growth and finally $n=1$ represents surface nucleation with one dimensional growth from surface to inside [51]. In our study the value of n is approximately three for all the samples of $Ga_{15}Se_{85-x}Ag_x$ indicating volume nucleation with two dimensional growth during amorphous-crystallization phase transformation.

The activation energy of crystallization (E_c) can be calculated by using Kissinger's model, Eq. (13) of $Ga_{15}Se_{85-x}Ag_x$ chalcogenide glasses. The kinetics of phase transformations resulting in a microstructure formation is driven by nucleation and growth steps. Nucleation and crystallization rates are some times measured directly in the microscope but Differential Scanning Calorimeter is valuable for the quantitative study of crystallization in different glassy systems [52]. It is well known that T_c and E_c are important parameters for characterization of the thermal stability of amorphous alloys and they are considered to be related to the glass forming ability. So it is necessary to study the dependence of T_c and E_c on the composition of amorphous alloys [53].

Fig. 6 shows the plot of $ln(\beta/T_c^2)$ *versus* $1000/T_c$ for all the samples of $Ga_{15}Se_{85-x}Ag_x$ chalcogenide glasses, which appears to be straight lines. The E_c can be calculated from the slope of each curve and the values are reported in the Table 2. The activation energy of crystallization can also be obtained from the variation of the onset crystallization temperature T_c with heating rate by using Ozawa's Eq. (23). Fig. 7 shows $ln\,\beta$ *versus* $1000/T_c$ curves, which come to be linear for the entire heating rate. The value of E_c is calculated from the slope of each curve and are shown in Table 2.

It is clear from the table that the activation energy of crystallization increases with increasing Ag content in the present system in both methods, indicating that the rate of crystallization is faster as the Ag content increases. The activation energy of crystallization is an indication of the speed of rate of crystallization. It is useful for the characterization of glassy alloys for different applications. It is obvious from the Table 2 that the value of E_c is maximum for $Ga_{15}Se_{77}Ag_8$, which indicates that speed of rate of crystallization, is faster with Ag at 8% in the present system.

The activation energy of glass transition (E_g) for $Ga_{15}Se_{85-x}Ag_x$ chalcogenide glasses can be calculated by using Kissinger's Eq. (13) as,

$$ln\left(\frac{\beta}{T_g^2}\right) = -\left(\frac{E_g}{RT_g}\right) + (constant). \tag{25}$$

Table 2
Compositional dependence of order parameter (n), activation energy of crystallization (E_c) and activation energy of glass transition (E_g) of $Ga_{15}Se_{85-x}Ag_x$ ($x=0$, 2, 4, 6 and 8) from non-isothermal DSC experiments.

Sample	Avrami index (n)	E_c (kJ/mol)		E_g (kJ/mole)	
		$ln(\beta/T_c^2)$ versus $1000/T_c$	$ln\,\beta$ versus $1000/T_c$	$ln(\beta/T_g^2)$ versus $1000/T_g$	$ln\,\beta$ versus $1000/T_g$
$Ga_{15}Se_{85}$	2.4977	89.1727	94.6187	120.0859	130.2213
$Ga_{15}Se_{83}Ag_2$	2.5579	98.6179	100.6716	129.3566	137.0391
$Ga_{15}Se_{81}Ag_4$	2.6836	107.2484	115.2885	132.6158	141.3959
$Ga_{15}Se_{79}Ag_6$	2.8041	113.3429	121.0919	139.9242	153.4852
$Ga_{15}Se_{77}Ag_8$	2.9587	121.6739	132.5826	142.8842	157.3098

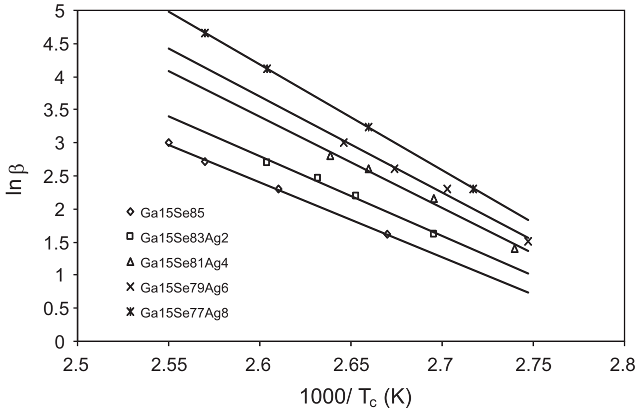

Fig. 7. Plot of $ln\,\beta$ as a function of $1000/T_c$ (K) for $Ga_{15}Se_{85-x}Ag_x$ glass.

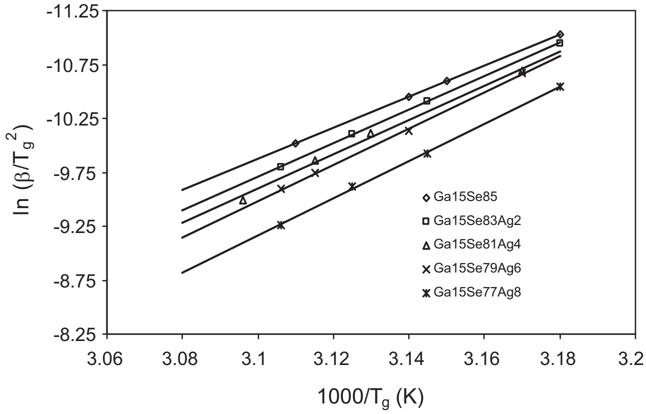

Fig. 8. Plot of $ln(\beta/T_g^2)$ as a function of $1000/T_g$ (K) for $Se_{80}Te_{20-x}Zn_x$ glass.

It is evident from this equation that a plot of $ln(\beta/T_g^2)$ against $1000/T_g$ should be a straight line, which is 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 tabulated in Table 2.

Since the change of $ln(T_g^2)$ with β is negligibly small as compared with the change of $ln(\beta)$, then Eq. (25) can be simplified as,

$$ln(\beta) = -\left(\frac{E_g}{RT_g}\right) + (constant). \qquad (26)$$

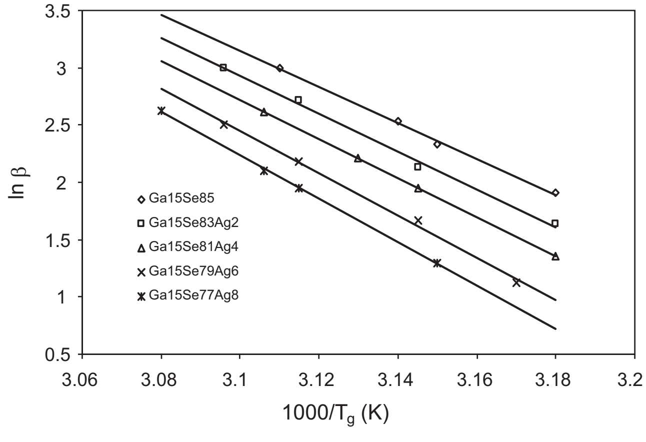

Fig. 9. Plot of $ln\,\beta$ as a function of $1000/T_g$ (K) for $Se_{80}Te_{20-x}Zn_x$ glass.

Fig. 9 shows a plot of a plot of $ln\,\beta$ against $1000/T_g$ and the activation energy of glass transition (E_g) can also be calculated from the slope of this plot (values of E_g are shown in Table 2). It is clear from this table that the activation energy of glass transition (structural relaxation) increases with increasing Ag content in the present system in both methods. The activation energy of glass transition (structural relaxation) depends on T_g as well as on the heating rate (β). This activation energy of structural relaxations is 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. It is observed that $Ga_{15}Se_{85}$ has a minimum value of activation energy of glass transition, which indicates that this particular glass has a larger probability to jump to a state of lower configurationally energy.

5. Conclusion

In the present research work, a systematic investigation on the crystallization kinetic of $Ga_{15}Se_{85-x}Ag_x$ ($x = 0$, 2, 4, 6 and 8) chalcogenide glasses has been performed using non-isothermal DSC measurements, which indicate that the glass transition and crystallization temperatures depend on the heating rates. The results indicate that the degree of crystallization (α), fit well with the theory of Matusita, Sakka and Kissinger. From both Ozawa and Kissinger relation, it was found that values of E_c are in good agreement with each other. The activation energy is found to vary with composition indicating a structural change due to the addition of silver. The value of E_c increases with increasing Ag contents in Ga–Se system, which indicates that the speed of rate of crystallization, is faster with increasing Ag concentration in the present system. The temperature difference ($T_c - T_g$) is highest for the samples with 8% of Ag. Hence, the glass with 8% of Ag is most stable and also the minimum release of enthalpy further confirms its maximum stability. It has also been observed that $Ga_{15}Se_{85}$ has a minimum value of activation energy of glass transition, which indicates that this particular glass has a larger probability to jump to a state of lower configurational energy.

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