# KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION IN $Ga_{15}Se_{76}Pb_9$ CHALCOGENIDE GLASSES BY DIFFERENTIAL SCANNING CALORIMETER (DSC)

ZISHAN H. KHAN, NUMAN SALAH, SAMI HABIB,
SHAMSHAD A. KHAN[a]
*Center of Nanotechnology, King Abdulaziz University, Jeddah, Saudi Arabia*
*[a]Department of Physics, St. Andrew's, College, Gorakhpur, UP 273001, India*

Bulk sample of $Ga_{15}Se_{76}Pb_9$ chalcogenide glass was prepared by melt quenching technique. The amorphous nature was verified by XRD. A study of crystallization kinetics of this glass was investigated using non-isothermal DSC measurements. The glass transition temperature and crystallization temperature of $Ga_{15}Se_{76}Pb_9$ glass was determined at different heating rate of 5, 10, 15, 20 and 25 K/min. The dependence of $T_g$ and $T_c$ on the heating rate ($\beta$) has been used for the determination of different crystallization parameters such as the activation energy for structural relaxation ($\Delta E_t$) and activation energy of crystallization ($\Delta E_c$). The area analysis of crystallization peaks were used to determine the order parameter (n) and the crystallization enthalpy ($\Delta H_c$). The order parameter is found to be 1.18 which represent one dimensional growth from surface to inside in $Ga_{15}Se_{76}Pb_9$ chalcogenide glass. The results of crystallization was discussed on the basis of different models.

## 1. Introduction

Chalcogenide glasses have drawn a great attention due to the fact that these materials show certain unusual switching properties that could be important in modern technological applications such as switching, electrophotography and memory devices [1–4]. The glass transition is exhibited as an endothermic peak in differential scanning calorimetry (DSC) due to change in specific heat. The glass transition and crystallization studies in chalcogenide glasses upon heating can be performed by two basic methods: isothermal and non-isothermal methods. 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.

The study of crystallization kinetics in amorphous materials by DSC methods has been widely discussed in the literature [5-14]. Mehta et al [ 15] have studied the glass transition phenomena in Se-Te and Se-Ge based ternary chalcogenides glasses, Abd Elnaeim et al [16] 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 [17], study of the glass transition in amorphous Se by Abu-Sehly et al [18], calorimetric studies of Se-Te-Cd and Se-Te-Cd-In multicomponent chalcogenide glasses by Kumar et al [19], phase transformation kinetics of Se-Ge-Pb chalcogenide glass by Praveen et al [20] 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 [21-29].

In the present work, kinetics of non-isothermal crystallization in $Ga_{15}Se_{76}Pb_9$ chalcogenide glass was carried out by DSC measurement. Selenium–lead chalcogenides are considered to be mainly utilized for detecting hydrocarbon pollutant in atmosphere, higher solution spectroscopy,

---

*Corresponding author:  zishan_hk@yahoo.co.in

trace gas analysis, optical fiber analysis and optical communication system over super long distances [30-32].

## 2. Experimental

High-purity (99.999%) Ga, Se and Pb in different proportions was weighted and sealed in quartz ampoule under a vacuum of $10^{-5}$ Torr.. The ampoule was 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 hours with frequent rocking to ensure the homogenization of the melt. During the melting, the ampoule was frequently shaken to homogenize the resulting alloy. The melt was then rapidly quenched in ice water. After quenching, ingot of the sample was removed by breaking the ampoules. The study of crystallization kinetics in $Ga_{15}Se_{76}Pb_9$ chalcogenide glass was 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 and 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

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$\alpha_1$). The scanning angle was in the range of $10^0$-$120^0$. A scan speed of $2^0$/min and a chart speed of 1 cm/min were maintained.



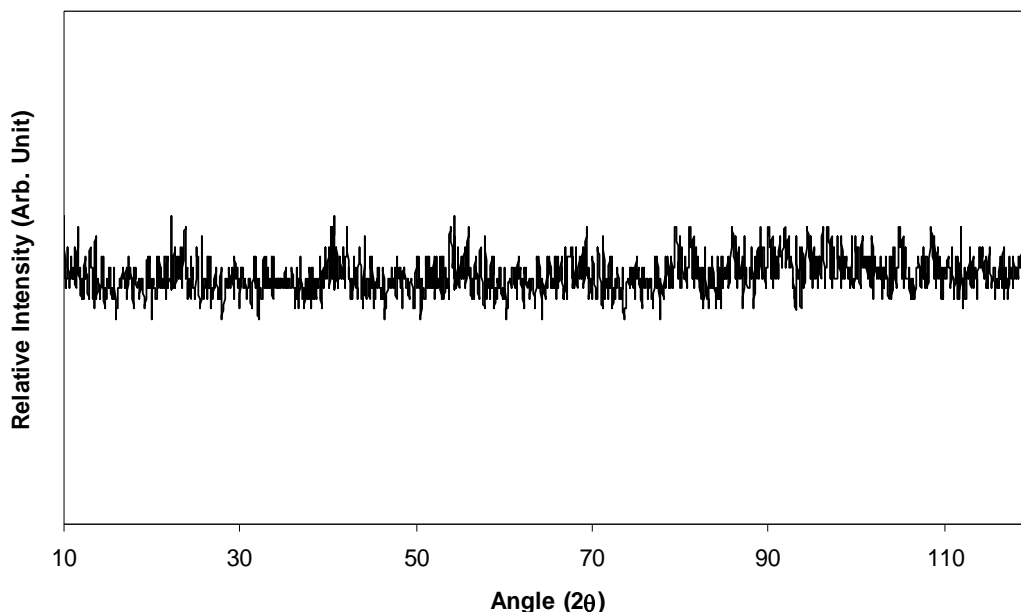*Fig. 1  :  X-ray pattern of $Ga_{15}Se_{76}Pb_9$ chalcogenide glass.*

The X-ray diffraction trace of $Ga_{15}Se_{76}Pb_9$ chalcogenide glass 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. 2 shows the typical continuous DSC curves of the crystallization process for $Ga_{15}Se_{76}Pb_9$ glass at various heating rates of 5, 10, 15, 20 and 25 K/min. The characteristic phenomena (endothermic and exothermic peaks) are evident in the DSC curves in the temperature

range of investigation. The values of glass transition temperature ($T_g$) $Ga_{15}Se_{76}Pb_9$ glassy alloy at different heating rates are given in Table 1. It is found that the glass transition temperature is shifted to the higher values by increasing the heating rates from 5 to 25 K/min.. The glass transition temperature is 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.
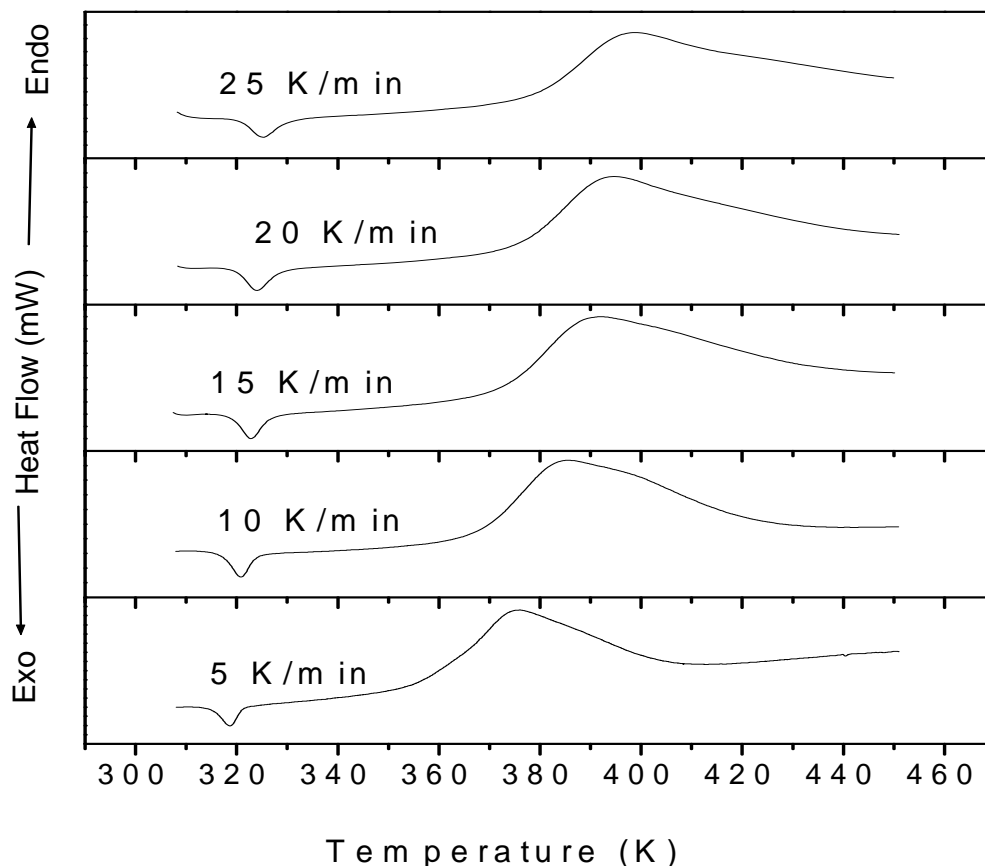


*Fig. 2 : DSC plot for $Ga_{15}Se_{76}Pb_9$ glass at different heating rates.*

The exothermic peak temperature ($T_c$) is used to identify the crystallization process. It is evident from the Table-1 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.

The kinetics of isothermal crystallization involving nucleation and growth is usually analyzed using Kolmogorov–Johnson–Mehl–Avrami (KJMA) model [33-34]. According to this model, the volume fraction of crystallites ($\alpha$) is given by [35-37]:

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

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,

$$k = \nu \exp. (-\Delta E_c / RT) \tag{2}$$

where, $\Delta E_c$ is the activation energy of crystallization, *A* is the pre-exponential factor and *R* is the gas constant.

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 $T_2$.

The volume fraction of crystallites (α) precipitated in a glass heated at constant heating rate (β) is related to the effective activation energy for crystallization (E) through the following expression:

$$\ln [- \ln (1-\alpha)] = - n \ln (\beta) - 1{:}052 \, mE/RT + \text{constant} \qquad (3)$$

where, m is an integer which depends on the dimensionality of the crystal and n being a numerical factor depending on the nucleation process.

Fig. 3 shows the variation of *ln [-ln(1-α)]* against *ln β* for $Ga_{15}Se_{76}Pb_9$ chalcogenide glass. The value of n for $Ga_{15}Se_{76}Pb_9$ chalcogenide glass is found to be 1.18 which represents one dimensional growth from surface to inside.



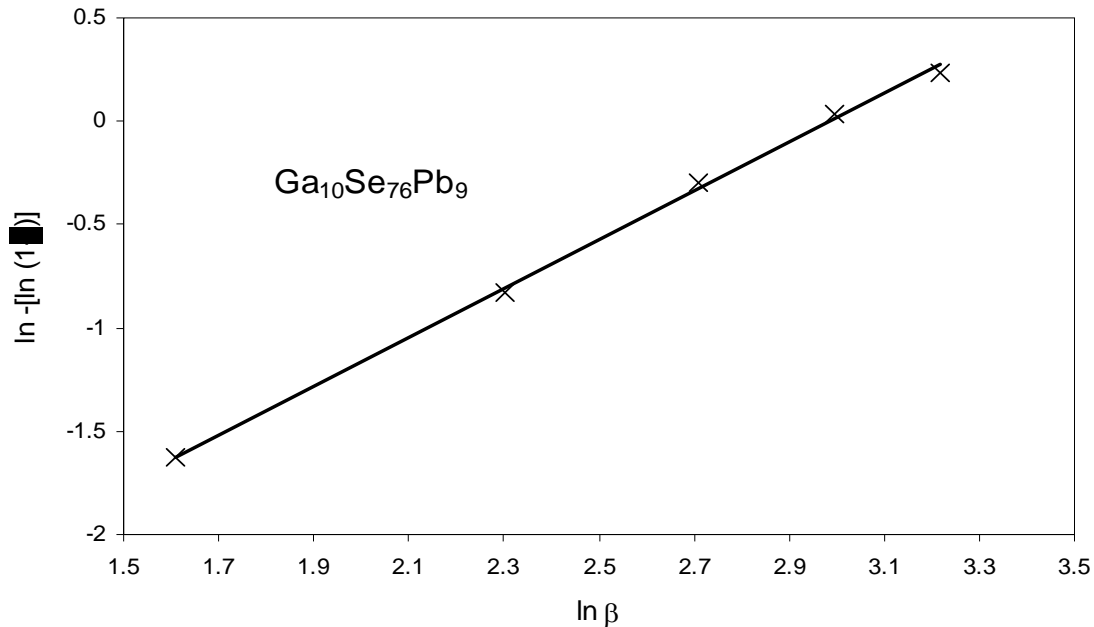*Fig. 3. Plot of ln [-ln(1-α)] as a function of lnβ of $Ga_{15}Se_{76}Pb_9$ glass.*

The crystallization enthalpy ($\Delta H_c$) is evaluated by using the formula,

$$\Delta H_c = K A / M \qquad (4)$$

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 values of $\Delta H_c$ for $Ga_{15}Se_{76}Pb_9$ chalcogenide glass at different heating rates are shown in Table-1.

The activation energy ($\Delta E_c$) for crystallization can be calculated by using Kissinger's equation [38],

$$\ln (\beta/T_c^2) = - \Delta E_c / RT_c + D \qquad (5)$$

The plot of *ln (β/$T_c^2$)* versus 1000/$T_c$ for $Ga_{15}Se_{76}Pb_9$ chalcogenide glass is shown in figure 4. The value of $\Delta E_c$ may be calculated from the slope of the curve and is given in Table-1.
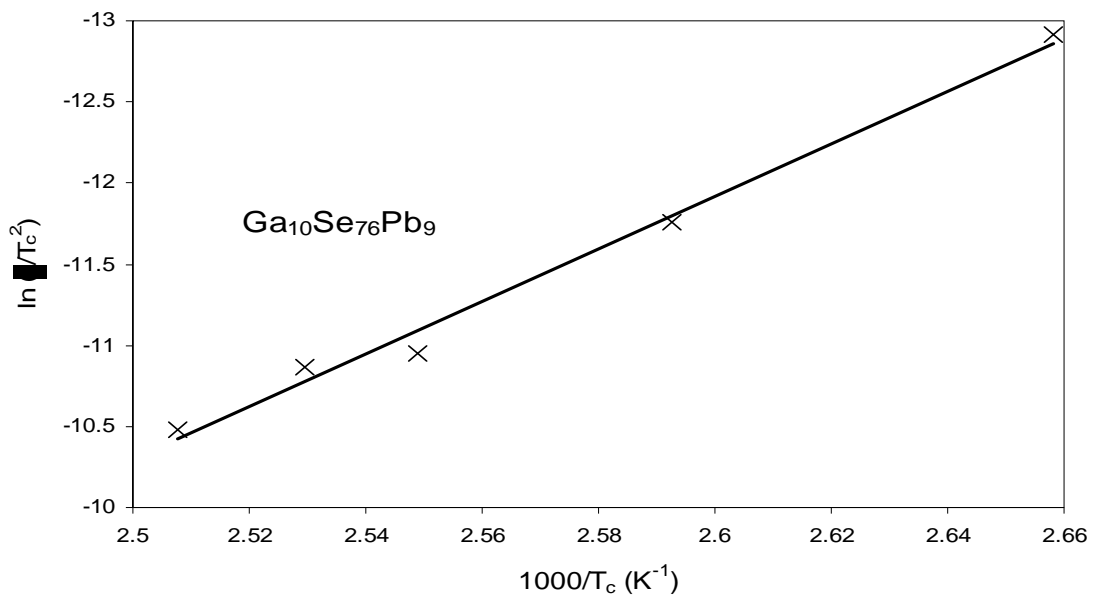
*Fig. 4. Plot of ln ($\beta/T_c^2$) as a function of 1000/$T_c$ ($K^{-1}$) of Ga$_{15}$Se$_{76}$Pb$_9$ glass.*

The activation energy of crystallization can also be obtained from the variation of the onset crystallization temperature with heating rate by using Ozawa's [39] relation as,

$$\ln \beta = -\Delta E_c / RT_c + C \qquad (6)$$

Figure 5 shows ln $\beta$ versus 1000/$T_c$ curves. The value of $\Delta E_c$ is calculated from the slope of this curve for Ga$_{15}$Se$_{76}$Pb$_9$ chalcogenide glass and is given in table 1.
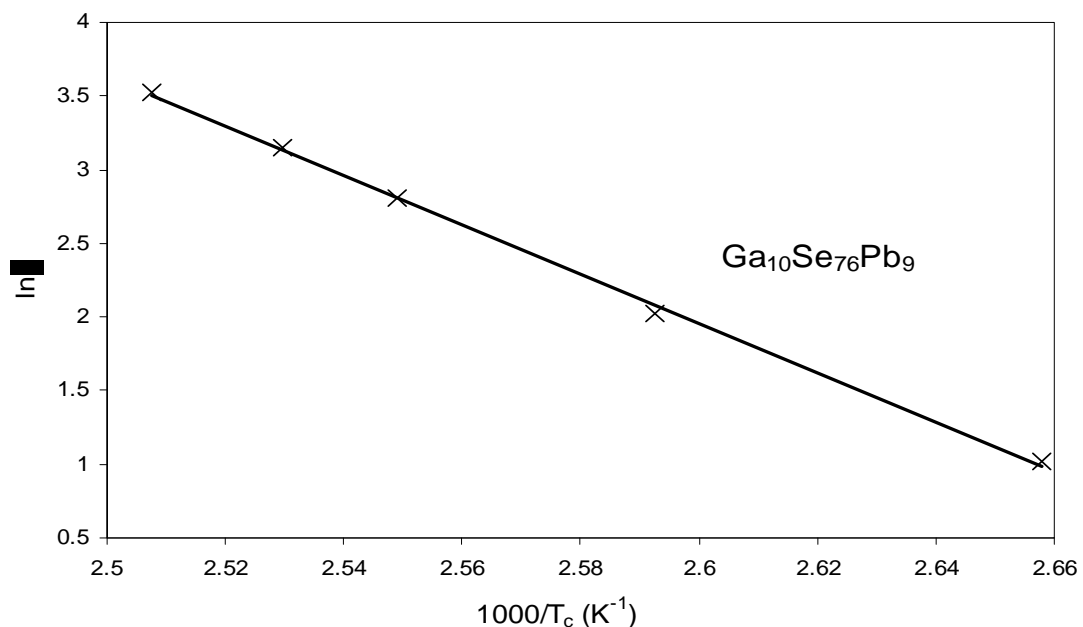


*Fig. 5 : Plot of ln $\beta$ as a function of 1000/$T_c$ ($K^{-1}$) of Ga$_{15}$Se$_{76}$Pb$_9$ glass.*

The activation energy of glass transition ($\Delta E_g$) for Ga$_{15}$Se$_{76}$Pb$_9$ chalcogenide glass can be calculated by using Kissinger's Eq. [38] as,

$$\ln (\beta/T_g^2) = -\Delta E_g /RT_g + \text{constant} \qquad (7)$$

A plot of ln $(\beta/T_g^2)$ against $1000/T_g$ should be straight line (shown in Fig. 6) and $\Delta E_g$ can be calculated from the slope of this plot and are shown in Table 1.

*Table 1. Heating rate dependence of ($\Delta H_c$) , $T_g$ (K) and $T_c$ (K); $\Delta E_c$ ( kJ/mole) and $\Delta E_g$ ( kJ/mole) of $Ga_{15}Se_{76}Pb_9$ glass from non-isothermal DSC experiments:*

| | $\Delta H_c$ ( J/mg) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5 K/min | | 10 K/min | | 15 K/min | | 20 K/min | | 25 K/min | |
| | 2067.86 | | 2121.43 | | 1928.57 | | 2348.57 | | 1988.57 | |
| **$Ga_{15}Se_{76}Pb_9$** | $T_g$ | $T_c$ | $T_g$ | $T_c$ | $T_g$ | $T_c$ | $T_g$ | $T_c$ | $T_g$ | $T_c$ |
| | 317 | 376 | 319 | 385 | 321 | 392 | 322 | 395 | 325 | 399 |
| | $\Delta E_g$ ( kJ/mole) | | | | $\Delta E_c$ ( kJ/mole) | | | | | |
| | ln$\beta$ versus 1000/Tg | | ln$(\beta/Tg^2)$ versus 1000/Tg | | ln$\beta$ versus 1000/Tc | | | ln$(\beta/Tc^2)$ versus 1000/Tc | | |
| | 237.35 | | 230.24 | | 139.47 | | | 134.73 | | |

The heating rate ($\beta$) 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 [40] that the activation energy of structural relaxation ($\Delta E_g$) can be related to $T_g$ and $\beta$ by,

$$d \, ln \, \beta \, / \, d \, ( \, 1/T_g) \, = \, - \Delta E_g \, / \, R \qquad (8)$$
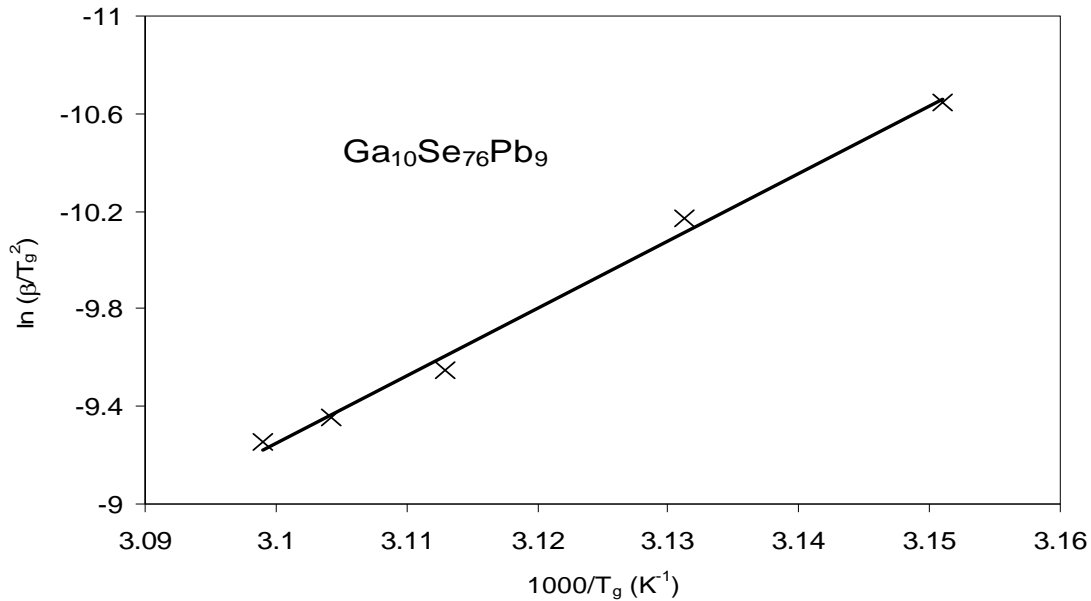


*Fig. 6. Plot of ln ($\beta/T_g^2$) as a function of $1000/T_g$ ($K^{-1}$) of $Ga_{15}Se_{76}Pb_9$ glass.*

A plot of ln$\beta$ against $1000/T_g$ should be straight line (shown in figure 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 1.
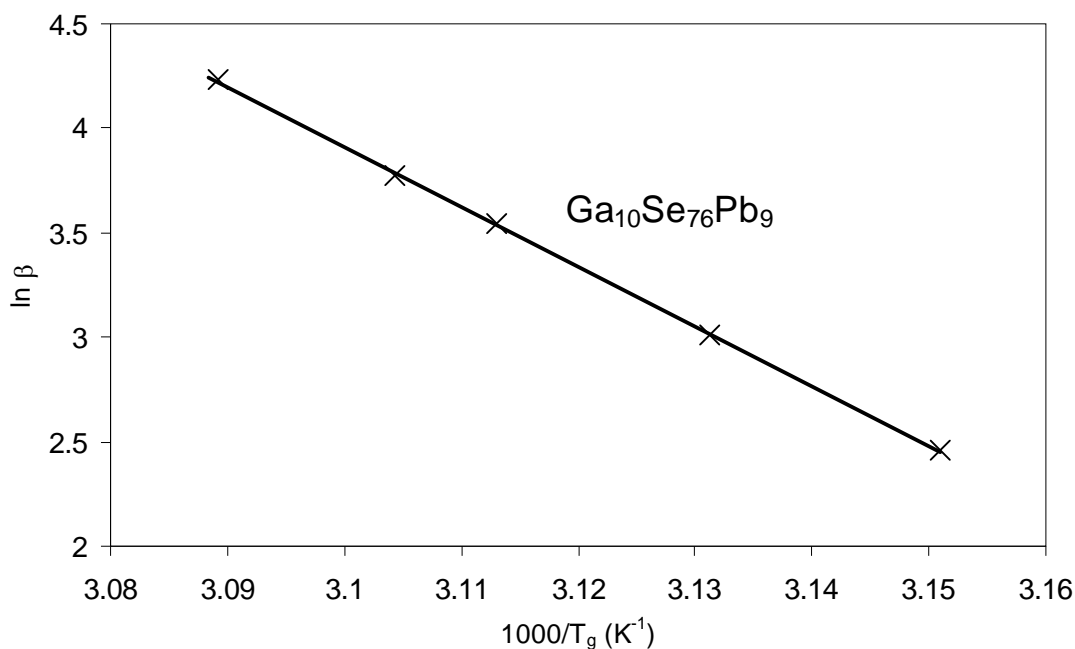
*Fig. 7. Plot of ln β as a function of 1000/T$_g$ (K$^{-1}$) of  Ga$_{15}$Se$_{76}$Pb$_9$ glass.*

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 [41-43]. From Table-1, 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 structure and kinetics of crystallization of Ga$_{15}$Se$_{76}$Pb$_9$ glass was investigated. The X-ray diffraction measurements confirmed the amorphous nature of the sample. The crystallization kinetics of Ga$_{15}$Se$_{76}$Pb$_9$ chalcogenide glass have been investigated by non-isothermal DSC measurements The value of order parameter (n) for studied glasses is found to be 1.18 which indicates that there is one dimensional growth from surface to inside. 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.

### Acknowledgement

# References

[1] T. Ohta, J. Optoelectron. Adv. Mater. **3,** 609 (2001).

[2] S.A. Khan, M. Zulfequar, M. Husain, J. Phys. Chem. Solids **63** ,1787 (2002).

[3] M. Popescu, J. Optoelectron. Adv. Mater. **7**,2189 (2005).

[4] N. Mehta, J. Sci. Ind. Res. **65**, 777 (2006).

[5] S.M. El-Sayed, Mater. Chem. Phys. **78**, 262 (2002) .

[6] Mousa M.A. Imran, Omar A. Lafi, Materials Chem. and Phy. **129**, 1201 (2011).

[7] J. M. Saiter, J. Ledru, A. Hamou, G. Saffarini, Physica B **245**, 262 (1998).

[8] M. Abu El-oyoun, J. Phys. Chem.Solids **61**, 1653 (2000).

[9] A. H. Moharram, M. Abu El-Oyoun, J. Phys. D: Appl.Phys.**33**, 700 (2000).

[10] N. Afify, J. Non-Cryst.Solids **126**, 130 (1990).

[11] A.A. Othman, K. Tahon, M. A. Osman, Physica B **311**, 356 (2002).

[12] A.H. Khafagy, M.S. Abo-Ghazala, M.M. El-Zaidia, A.A. El- Shourbagy, J. Non-Cryst. Solids **278**, 119 (2000).

[13] M.H. El-Fouly, L.A. Wahab, M.F. Kotkata, J. Thermal Anal. **42**, 1285 (1994).

[14] M.F. Kotkata, M.H. El-Fouly, S.A. El-Hakim, Semicond.Sci.Technol.**1**, 313(1986).

[15] N. Mehta, K. Singh, A. Kumar Physica B **404**, 1835 (2009).

[16] A.M. Abd Elnaeim, K.A. Aly, N. Afify, A.M. Abousehlly, J. Alloys and Compounds, **491**, 85 ( 2010).

[17] Omar A. Lafi, Mousa M.A. Imran, Radiation Phy. and Chem. **79**, 104 (2010).

[18] A.A. Abu-Sehly, M. Abu El-Oyoun, A.A. Elabbar, Thermochimica Acta **472**, 25 (2008) 25.

[19] Sunil Kumar, Kedar Singh, Physica B **405**, 3135 ( 2010).

[20] Deepika, Praveen, K. Jain, K.S. Rathore, N.S. Saxena, J. of Non-Cryst.Solids **355**,1274 (2009).

[21] M. Abu El-Oyoun, J. of Alloys and Comp. **486**, 1 (2009).

[22] M.M. Abd El-Raheem, H.M. Ali , J. Non-Crys. Solids **356**, 77(2010).

[23] M.S. Rasheedy, A.A.I. Abd-Elmageed, J. Alloys and Comp. **472**, 581 (2009).

[24] Mousa M.A. Imran, Ali F. Al-Shawabkeh, J. Alloys and Comp. **500**, 237 (2010).

[25] Muneer Ahmad, R. Thangaraj, Physica B **404**, 1553 (2009).

[26] K.A. Aly, A.A. Othman, A.M. Abousehly, J. Alloys and Comp. **467**, 417(2009).

[27] J. Rocca, M. Erazu, M. Fontana, B. Arcondo, J. Non-Cryst. Solids **355**, 2068 ( 2009) .

[28] Roman Svoboda, Pavla Honcova, Jiri Malek, J. Non-Crys. Solids **356**, 447(2010).

[29] Roman Svoboda, Pavla Honcova, Jiri Malek, J. Non-Cryst. Solids **356**, 165 (2010).

[30] S. Abbe, Y. Furukawa, K. Mochizuki, K. Masumato, J. Jpn. Inst. Met. **58**, 346 (1994).

[31] A. Lambrecht, R. Kurbel, M. Agne, Mater. Sci. Eng. **21**, 217 (1993).

[32] M. Agne, A. Lambrecht, U. Schiessl, M. Tacke, Infrared Phys. Tech. **35**, 47 (1994).

[33] A.N. Kolmogorov, Bull. Acad. Sci. USSR. Phys. Ser. **3**, 555 (1937).

[34] W.A. Johnson, P.A. Mehl, Trans. Am. Inst. Min. Metall. Eng. **135**, 416 (1939).

[35] M. Avrami, J. Chem. Phys. **7**, 1103(1939).

[36] M. Avrami, J. Chem. Phys. **8**, 212 (1940).

[37] M. Avrami, J. Chem. Phys. **9**, 177 (1941).

[38] H. E. Kissinger, Anal. Chem. **29**, 1702 (1957).

[39] T. Ozawa, Bull. Chem. Soc. Jpn. **38**, 188 (1965).

[40] C. T. Moynihan, A. J. Easteal, J. Wilder, J. Tucker, J. Phys. Chem. **78**, 2673(1974).

[41] A. Giridhar, S. Mahadevan, J. Non-Cryst. Solids **151**, 245 (1992).

[42] A.F. Ioffe, A.R. Regel, Prog. Semicond. **4**, 239 (1960).

[43] M. K. Rabinal, K.S. Sangunni, E.S.R. Gopal, J. Non-Cryst. Solids **188**, 98(1995).