Journal of Ovonic Research Vol. 11, No. 4, July - August 2015, p. 183 - 188

# ENTHALPY AND ENTROPY CHANGE DURING GLASS/CRYSTAL PHASE TRANSFORMATION FOR $Ge_ySe_{94-y}In_6$ (y= 10, 15 and 20) GLASSES

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A study of thermodynamic parameters enthalpy and entropy change during glass/crystal phase transformation of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses have been carried out by Differential Scanning Calorimetery (DSC) under non-isothermal conditions. DSC scans have been recorded at heating rate 20K/min. Specific heat measurements are required to study the variation of enthalpy and entropy during glass/crystal phase transformation. DSC scans have been used for specific heat measurements. As $\Delta H_{gc}$ and $\Delta S_{gc}$ both are the criteria of glass stability; the stability of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses has been accounted for the values of $\Delta H_{gc}$ and $\Delta S_{gc}$ during glass/crystal phase transformation.

(Received June 12, 2015; Accepted August 12, 2015)

*Keywords:* DSC, Specific heat, Enthalpy, Entropy, Chalcogenide glass

## 1. Introduction

Amorphous chalcogenide glasses are emerging as new interesting materials from technological point of view because of their wide range of applications in electronics and optoelectronics field [1-6]. Amorphous Se, due to high glass forming ability, represents a good host matrix for the investigation of chalcogenide glasses. But in pure state, it has disadvantages like short life time and low sensitivity. To overcome these difficulties certain additives Bi, Te, Ge, As, Ga etc. are used. Ge-Se binary chalcogenide glasses have easy synthesis requirements, good chemical stability and ready glass formations [7, 8]. Addition of In as the third element to Ge-Se glassy system expands glass forming region, creates compositional and configurational disorder in system, which results in large effect on their structural, electrical, optical and thermal properties [9-11]. Ge-Se-In system is of interest as it forms glasses over a wide domain of composition [12].

For practical applications, thermal stability of glasses prior to crystallization is important to be known. Change in thermodynamic parameters during glass/ crystal transformation gives important information about the thermal stability of glasses. From the thermodynamic point of view, glass is a non- equilibrium frozen system. During the process of glass formation, the liquid is cooled at sufficiently high rate to avoid crystallization. When glassy samples are heated in DSC at constant heating rate, the frozen structure relaxes. In such procedures, a transition is observed from non-equilibrium glassy state to equilibrium crystalline state. To study these phase transformation, the investigation of thermodynamic parameters of glassy and crystalline state is essential. In the present study, the thermodynamic parameters which have been studied, using DSC, are enthalpy and entropy during glass/ crystal transformation for $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses. Many researchers have used Differential Scanning Calorimetery to study thermodynamics of glasses [13-17].

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## 2. Material preparation and experimental procedure

Preparation of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy system has been carried out using rapid quenching of melt technique. High purity (99.999%) constituent materials Ge, Se and In have been taken in elemental power form in proper atomic weight percentage and sealed in quartz ampoule under a vacuum of $10^{-5}$ torr. The sealed ampoules have been subjected to a heat treatment inside a programmable furnace whose temperature has been raised to 940°C and maintained at 940°C for 15 hrs. Quenching has been carried out in ice-cooled water to obtain glassy state. Amorphous nature of, so, produced glassy samples has been confirmed by X-ray diffraction.

Differential scanning calorimetery (DSC) Netschz 204 F1 Phoenix has been used to record thermograms under non iso- thermal conditions. DSC scans have been recorded at a heating rate of 20 K/min on accurately weighted samples sealed in aluminium pans from room temperature to 550°C.

## 3. Results and discussion

Sudden change in specific heat at glass transition is a characteristic feature of all glasses. Measurement of specific heat as function of temperature provides an easy method for determination of glass transition under different compositions and heating rates. Specific heat measurements are necessary for calculating other thermodynamic parameters such as enthalpy and entropy [18-25]. Using DSC data, specific heat of the sample can be calculated using the following relation;

$$C_P = \frac{M_r \Delta_s}{M_s \Delta_r} C_r \tag{1}$$

where, $M_r$ and $M_s$ are masses of reference material (sapphire) and sample, respectively and $\Delta_s$ and $\Delta_r$ are the shifts for sample and reference material with respect to base line. $C_r$ is specific heat of reference material, which has been taken from standard literature.

Fig. 3.1 (a, b, c) show the specific heat curves of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy alloys at heating rate of 20 K/min. These thermograms have been recorded from room temperature to 550°C

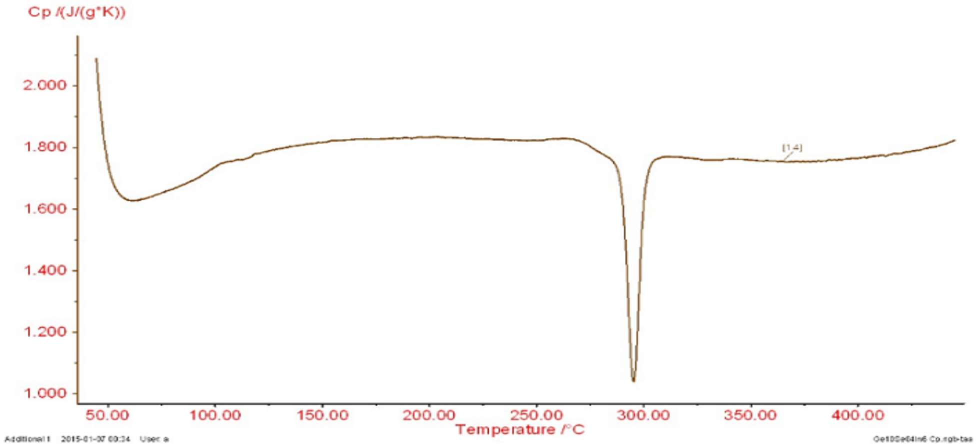

*Fig.3.1 (a): Variation of specific heat ($C_p$) with temperature of $Ge_{10}Se_{84}In_6$ glass.*

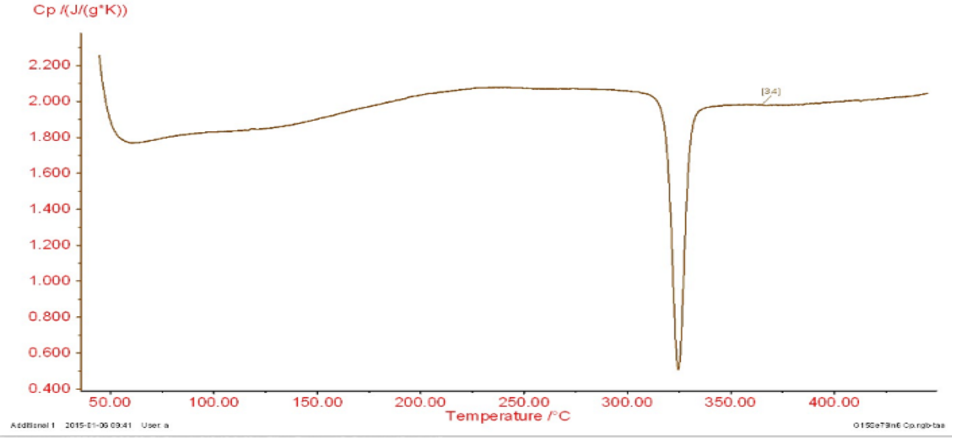

*Fig3.1 (b): Variation of specific heat ($C_p$) with temperature of $Ge_{15}Se_{79}In_6$ glass.*

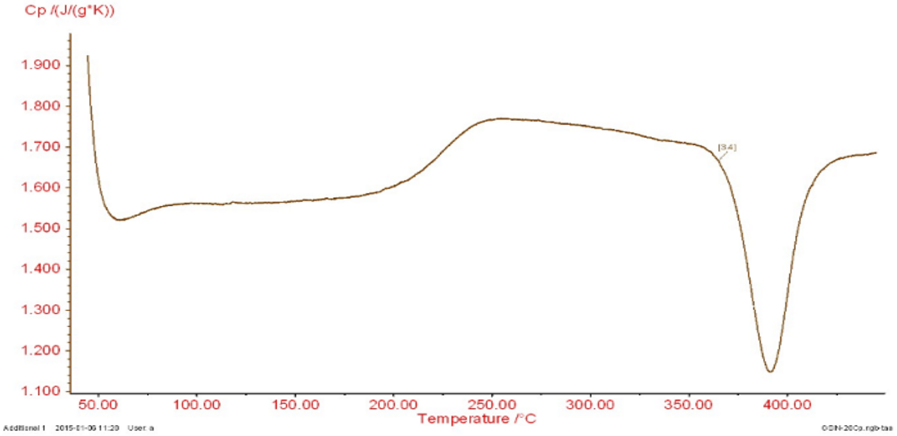

*Fig.3.1(c): Variation of specific heat ($C_p$) with temperature of $Ge_{20}Se_{74}In_6$ glass.*

From the figures, it is evident that below glass transition temperature specific heat is weekly temperature dependent. At $T_g$ Specific heat shows an abrupt jump due to addition configurational degrees of freedom of motion (rotational and translation) [26] of the atoms which were locked when the structure was frozen in glassy state [27]. An endothermic peak is observed in specific heat curve at crystallization temperature. This may be due to vestiges of short range order that still remain above on -set crystallization temperature and are disappeared when temperature is further increased [28].

### 3.1 Enthalpy released during glass/crystal phase transformation

Enthalpy released during transformation from glassy to crystalline state is given by relation;

$$\Delta H_{gc} = \Delta H_g - \Delta H_c \tag{2}$$

Where, $\Delta H_g$ and $\Delta H_c$ represents enthalpy released per unit mass of the sample during relaxation and crystallization process respectively.

$\Delta H_c$ has been measured by calculating area under crystallization peak.

$$\Delta H_g = \int C_p dT \tag{3}$$

And, $\Delta H_g$ is the area under the curve of specific heat verses temperature in glass transition region. $\Delta H_{gc}$ is an important parameter for determining stability of glasses. Fig. 3.2 shows the variation of $\Delta H_{gc}$ as a function of Ge concentration for glass/crystal phase transformation of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses.

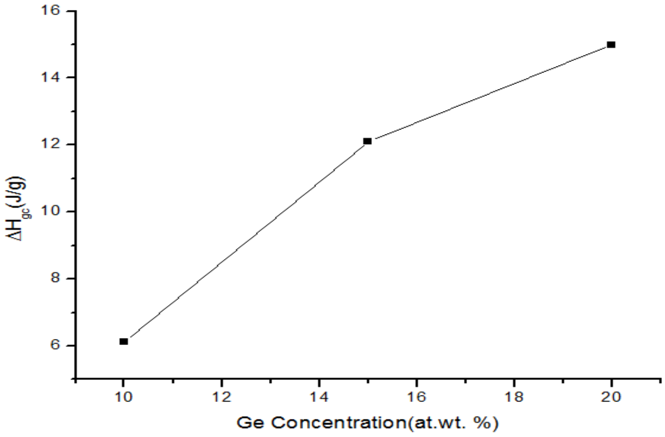

*Fig. 3.2: Variation of $\Delta H_{gc}$ as function of Ge concentration for $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses.*

From fig. 3.2, it is evident that $\Delta H_{gc}$ increases with increase of Ge concentration in $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses. Enthalpy released during the phase transformation from glassy to crystalline state is related with stability of Sample. Glass being a metastable state releases excess enthalpy during phase transformation (glass/ crystal) and tries to gain stability. The sample that releases least value of $\Delta H_{gc}$ will be most stable as it already posses least energy stable atomic configuration. As the composition with minimum value of $\Delta H_{gc}$ is most stable, in $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy series $Ge_{10}Se_{84}In_6$ glass has minimum value of $\Delta H_{gc,}$ hence most stable among all composition of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy series. The stability can also be explained on the basis of bond theory. The total bond energy of system decreases with increase of Ge concentration in $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glasses. Because of fixed amount of In in system the number of In-Se bonds are fixed and the variation in average bond strength is only due to the variation in Ge and Se concentration in the samples. For Ge rich compositions the strong heteropolar Ge-Se bonds (bond energy = 234.9 kJ/mol) are replaced by weaker homopolar Ge-Ge bonds (bond energy = 205.2 kJ/mol), results in decrease of bond energy of system resulting in maximum stability of $Ge_{10}Se_{84}In_6$ glass as compare to other compositions of series.

### 3.2 Entropy difference between glassy and crystalline state

Entropy is associated with disorder present in system. Entropy difference between glassy and crystalline state is another parameter which tells the stability of glass. Difference in entropy of glass and crystalline state is given by thermodynamic relation.

$$\Delta S_{gc}=\Delta S_g-\Delta S_c \qquad (4)$$

The thermodynamic relation describing the entropy of glassy state is given by equation;

$$S = S_{cof.} + \int_0^T \left(\frac{C_p}{T}\right) dT \qquad (5)$$

Where, $S_{cof.}$ is configuration entropy. Configurational entropy is that part of entropy which is due to configuration rather than vibrational degree of freedom [29].

$$S_{cof.} = -K \ln (w) \tag{6}$$

Where, 'K' is Boltzmann constant, 'w' is the total number of different ways in which atoms can arrange themselves in a particular fashion and is given by relation;

$$W = \frac{N!}{\{(A_x N)!(B_y N)!(C_z N)!\}} \tag{7}$$

Where 'N' is the total number of atoms present in the system. $A_x$ is fraction of 'x' atom, $B_y$ is the fraction of 'y' atom, $C_z$ is number of 'z' atoms.

When calculating the entropy of crystalline state, configuration entropy is taken equal to zero because there is only one way to arrange the atoms in the correct ordered array (w=1). So, the entropy of crystalline state is [30];

$$S_c = \int_0^T \left(\frac{C_p}{T}\right) dT \tag{8}$$

The area of $C_p/T$ verses T curve gives the entropy of crystalline state. Fig. 3.3 shows the variation of $\Delta S_{gc}$ with Ge concentration of $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) compositions.

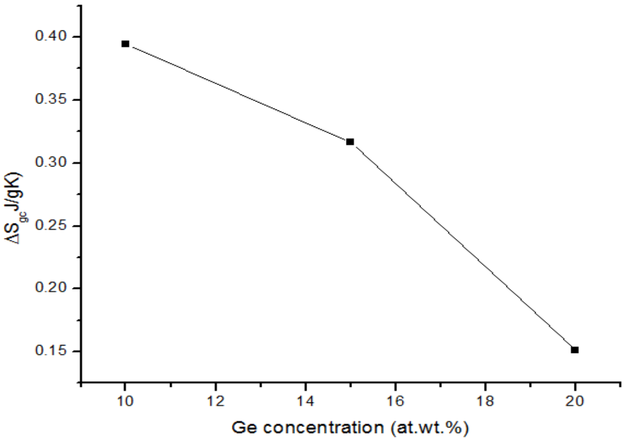

*Fig. 3.3: Variation of $\Delta S_{gc}$ with Ge concentration.*

$\Delta S_{gc}$ is also a parameter to determine stability of glasses. Higher value of $\Delta S_{gc}$ is an indicator of stable glassy state. From fig. 3.3, it is evident that entropy difference between glassy and corresponding crystalline state decreases with increase of Ge Concentration in $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy system. As $\Delta S_{gc}$ is a parameter of glass stability, $Ge_{10}Se_{84}In_6$ glass having maximum value of $\Delta S_{gc}$ is most stable in series.

## 4. Conclusions

In $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy alloys the study of thermodynamic parameters (enthalpy & entropy) indicates that stability of samples of $Ge_ySe_{94-y}In_6$(y=10, 15, 20) glassy alloys decreases with increase of Ge concentration. The enthalpy released during glass/crystal phase transformation is minimum for $Ge_{10}Se_{94-y}In_6$ glass, indicating maximum stability of sample as compare to other compositions of series.

The values of entropy difference between glassy and crystalline state decreases with increase of Ge concentration in $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy alloys, confirming the fact that stability decreases with increase of Ge concentration in $Ge_ySe_{94-y}In_6$ (y = 10, 15 and 20) glassy series. $Ge_{10}Se_{84}In_6$ glass having maximum value of $\Delta S_{gc}$ is most stable composition in series.

## Acknowledgement

Authors are thankful to Banasthali University and DST, New Delhi. Banasthali University is a member university in DST's CURIE scheme.

## References

[1] A. S. Kumar, J. Non-oxide glasses **3**, 1 (2012).
[2] V. K. Saraswat, V. Kishore, N. S. Saxena, K. Sharma, T. P. Sharma, A. Misra, J. Optoelectron. Adv. Mater. **8**, 1349 (2006).
[3] V. K. Saraswat, N. Tanwar, N. S. Saxena, J. Non-oxide glasses **4**, 55 (2012).
[4] V. K. Saraswat, V. Kishor, N. S. Saxena, T. P. Sharma, J. of Pure and Applied physics **44**, 196 (2006).
[5] V. K. Saraswat, K. Singh, N. S. Saxena, V. Kishore, T. P. Sharma, P. K. Saraswat, Current Applied Physics **6**, 14 (2006).
[6] N. Tanwar, V. K Sarwaswat, J. Non-Cryst. Solids **394**, 1 (2014).
[7] D. N. Tafen, D. A. Drafold, Phys. Review B **72**, 054206 (2005).
[8] J. Sharma, S. Kumar, J. Non-oxide glasses **2**, 120 (2009).
[9] R. Kumar, A. Kumar, V. S. Rangra, J.Optoelec. & Adv. Mater.**4**, 1554 (2010).
[10] M. S. Kamboj, R.Thangaraj, Eur. Phy. J. Appl. Phys. **24**, 33 (2003).
[11] S. Mahadevan, A. Giridhar, J. Non - Cryst. Solids **162**, 294 (1993).
[12] Z. U. Borissova, "Glassy Semiconductors", Plenum Press, New York (1998).
[13] P. Preedeep, N. S. Saxana, M. P. Saxena, A. Kumar, Phys. Stat. Sol (a) **155**, 333 (1996).
[14] M. A. Imran Mousa, D. Bhandari, N. S. Saxena, J. Mater. Sci. Engg. A **292,** 56 (2000).
[15] Deepika, N. S. Saxena, J. Phys. Chem. B **114**, 28 (2010).
[16] R. S. Tiwari, N. Mehta, R. K. Shukla, A. Kumar, J. Ovon. Res. **2**(4) (2006).
[17] P. Jain, K. S. Rathore, N. Jain, N. S. Saxena, Chalcogenide letters **6**, 97 (2009).
[18] O. P. Cao, J. Zhana, A. Harsewell, J. Jiang, Y. H Zhow, J. Physics condensed matter **19**, 246205 (2007).
[19] R. C. Tiwari, N. Mehta, R. K. Shukla, P. Aggarwal, A. Kumar, Indian J. pure and applied Physics **43**, 363 (2005).
[20] G. R. Kolarkar, J. T Devaraju, S. Asokan, International J. Engineering Research & Technology **1,** 9 (2012).
[21] A. K Singh, The European physical J. & applied Physics **55**, 11103 (2011).
[22] D. Chaudhary, K. S Rathore, N. S. Saxena, J. Therm. Anal. Calorim. **98**, 725 (2009).
[23] KE Hai-Bo, ZHA-Zuo-Feng, WE Ping, WANG Wei-Hua, China. Phys. Lett. **29,** 046402 (2012).
[24] T. Wagner, M. Frumar, S. O. Kasap, J. Non-Crst. Solids **256**, 160 (1999).
[25] S. Saraswat, S. D. Sharma, New J. Glass and Ceramic **4**, 66 (2014).
[26] C. A. Angell, Pure Appl. Chem. **63**, 1387 (1991).
[27] G. Saffarini, J. M Saiter, J. Materi. Sci. **39**, 6141 (2004).
[28] J. P. Neufville, J. Non. Cryst. Solids **353**, 2443 (2007).
[29] M. D. Ediger, C. A. Angell, S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).
[30] K. T. Jacob, P. Sagar, R. M. Mallya, Bull. Mater. Sci **33**, 603 (2010).