

# Theoretical Analysis of Thermal Behaviour with Structural Change in Ge-Se-Te Glasses

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## ABSTRACT

In the present article we have studied the thermal behaviour of  $\text{Ge}_x\text{Se}_{50}\text{Te}_{50-x}$  ( $x = 10, 20, 30, 40$ ) alloy, for different combinations with changing heating rate ( $\alpha$ ) have been studied on the theoretical background. The values of the glass transition temperature,  $T_g$ , the crystallization temperature,  $T_c$ , and the crystallization peak temperature  $T_p$ , were found varying with change in composition as well as heating rate. The glass transition energy  $E_g$  was also calculated. On the basis of determined parameters glass, forming ability of the present system has been discussed.

**Keywords :** Glass transition temperature  $T_g$ , Crystallization temperature  $T_c$ , Glass transition energy  $E_g$  and Peak crystallization temperature  $T_p$ , Glass forming ability.

## I. INTRODUCTION

Due to potential applications of electrical, optical and technological field, chalcogenide glasses are widely used in reversible phase change optical recording, memory devices, optical fibers, xerography, photolithography, infrared lenses and optical amplifiers. These are multipurpose utility material and are used in the fabrication of technological important devices. Due to having an important role in research fields, the researchers have shown a lot of interests in these materials [1-4]. The properties of these glasses are influenced with the structural change which is most dependent on thermal effect [5, 6]. The structural change helps in studying practical applications and thermal stability in the material. The studies of glass transition and crystallization behaviour in chalcogenide glasses are the area of particular interest due to important phenomena such as switching and reversible optical recording, etc.

There are various techniques available to study the structural change in glass such as X ray diffraction, electron microscopy and scanning calorimetric [7]. In calorimetric measurements, two methods are used, which are isothermal and non-isothermic. It is well-known that in the isothermal method the sample is

brought quickly to a temperature above the glass transition temperature and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time while in the non-isothermal method, the sample is heated at a fixed rate and heat evolved is recorded as a function of temperature or time. Since Practical processes occur under dynamic and non-isothermal conditions, the non-isothermal experiments have been suggested for the analysis of the DTA data [8-11]. By the study of crystallization kinetics, the crystallization activation energy and crystallization exponent can be determined. Metallic amorphous alloys are very well-known to possess unique physical, mechanical, magnetic and corrosion properties compared to conventional crystalline metals. These alloys are kinetically metastable. Most of them are stable at low temperatures and can crystallize at high temperatures [8], therefore thermal and thermodynamic characteristic during crystallization process used to vary substantially [12]. Hence, the understanding of thermally-induced crystallization process in such systems is important from the application point of view.

Chalcogenide glasses which are selenium rich exhibit a unique property of reversible transformation and makes these systems very useful for applications like optical

memory, X-ray imaging and photonics. Among chalcogenide glasses, Se-Te based alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and lesser ageing effects as compared to pure Se glass [13-15]. The addition of third element like Ge in Se-Te system affects the electrical and optical properties and leads to cross linking of chains results in the increase of glass transition temperature of system [16- 18]. The addition of Ge to the Se-Te system is expected to modify the material properties to make it more suitable for reversible optical recording. Thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses. It has been reported that the effect of the heat treatment on the structure and electrical resistivity of amorphous  $\text{Ge}_{20}\text{Se}_x\text{Te}_{80-x}$  alloys (where  $x = 15, 30$  and  $50$  at %) [4]. The crystallization kinetics of chalcogenide glasses is always connected with the concept of activation energy, which is associated with the nucleation and growth [19-23].

The effect of the annealing temperature ( $T < T_p$ ) on the optical energy gap had been reported by earlier researchers [24].

The crystallization kinetics of Ge-Se-Te glasses with the increasing heating rate with the result of crystallization kinetics for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  for  $x = 10, 20, 30, 40$  at % are reported earlier [25]. The composition dependence as well as the effect of heating rate on the glass transition temperature ( $T_g$ ), the crystallization extrapolated onset temperature ( $T_c$ ) and the crystallization peak temperature ( $T_p$ ) were investigated by the earlier researchers. Information on some aspects of the crystallization mechanism was discussed.

This present research work is based on a theoretical study of the thermal behaviour with the structural change in Ge-Se-Te glasses with various compositions.

## II. Result and Discussion

To analyze the dependence of  $T_g$  on the heating rate two approaches are used. The first is the empirical relationship, which has originally been suggested by Lasocka [26];

$$T_g = A + B \ln \alpha \quad (1)$$

Where A and B are constants for a given glass compositions.

When this study is made for the temperature 2.5 to 22.5 then the results are shown in the table 1.

Plots of  $T_g$  versus  $\ln \alpha$  for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  glasses are shown in figure 1, which indicates the validity of eq. (1) for our compositions. It is clear from figure 1,  $T_g$  is increasing with heating rates as well as with increase in composition. This indicates that system is more suitable to form glass.

The corresponding  $T_c$ - $T_g$  result is given in figure 2 and their values listed in Table 2.

Both  $T_c$  and ( $T_c$ - $T_g$ ) represent the thermal stability of the glass [27, 28]. The values of ( $T_c$ - $T_g$ ) for the studied compositions at different heating rates are given in table 2. It is clear that the composition  $\text{Ge}_{20}\text{Se}_{50}\text{Te}_{30}$  has the highest value of ( $T_c$ - $T_g$ ) which indicates the composition  $\text{Ge}_{20}\text{Se}_{50}\text{Te}_{30}$  is most stable and the composition  $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$  is less stable.

These studies may be connected with the concept of activation energy. Hence the activation energy should be identified. So the second approach is being considered which is connected with glass transition activation energy  $E_g$ , and can be calculated using the well-known Kissinger's equation [29];

$$\ln(\alpha / T_g^2) + \text{const} = -E_g / RT_g \quad (2)$$

Where  $\alpha$  is the heating rate,  $E_g$  is the activation energy for the transition and  $R$  is the gas constant. Fig (3) shows the variation between  $\ln(\alpha / T_g^2)$  and  $(1000/T_g^2)$  for the investigated compositions.

Glass transition energy  $E_g$  can also be deduced by using approximation [30];

$$\ln \alpha = -E_g / RT_g + \text{const} \quad (3)$$

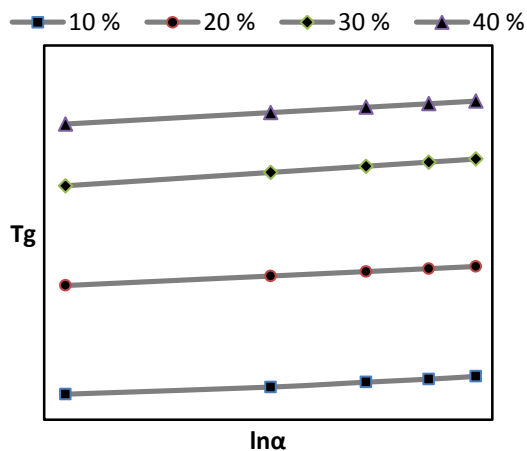
The relation between and for the studied compositions is shown in Fig. 4

The calculated value of  $E_g$  is shown in the table 3 for all compositions from the table it is clear that the values  $E_g$  (glass transition energy) decreases with the increase in Te content which results in apparent decrease in the glass transition temperature  $T_g$ .

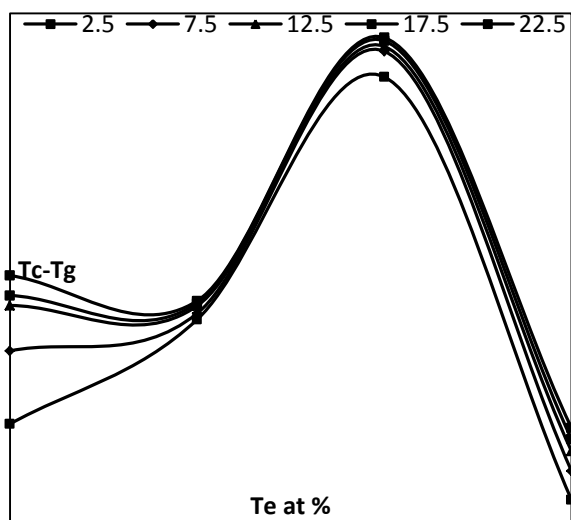
This result is in good agreement with the result obtained by earlier researchers [25]. The decrease of  $T_g$  was attributed to the decrease in the coordination number ( $Z$ ), bond energies and the mean atomic masses of these

glasses with increasing Te. The values of Tc and (Tc-Tg) represent the thermal stability of the glass.

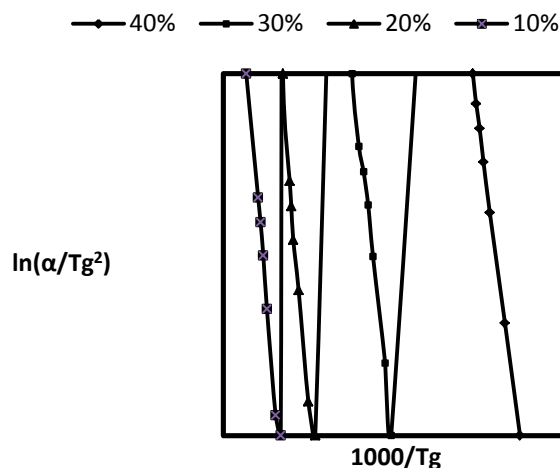
### III. Figures and Tables



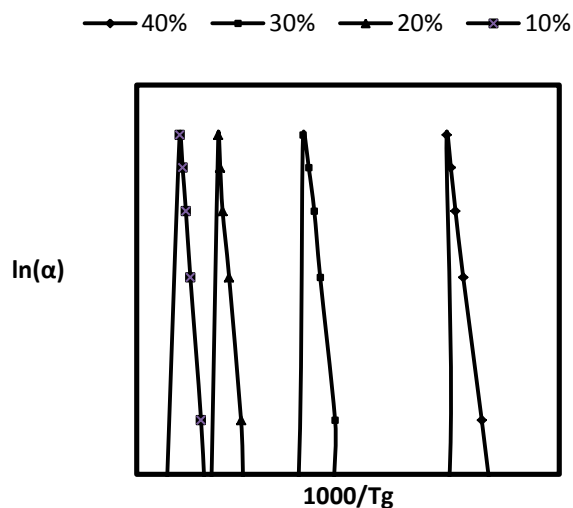
**Figure 1:** The dependence of Tg on different heating rate  $\ln \alpha$



**Figure 2:** Variations of Tc-Tg with Te atomic percentage



**Figure 3:** Graph between  $\ln(\alpha/Tg^2)$  versus  $1000/Tg$



**Figure 4:** Graph between  $\ln(\alpha)$  versus  $1000/Tg$

**Table 1:** The glass transition temperature (Tg), the onset crystallization temperature (Tc), the crystallization temperatures (Tp) and (Tc-Tg) for all compositions at different heating rates.

$\alpha$	$\ln \alpha$	Tg	Tc	Tp	Composition
2.5	0.9163	370.39	416.29	460.42	$Ge_{10}Se_{50}Te_{40}$
7.5	2.0149	376.11	428.76	472.06	
12.5	2.5257	380.039	437.33	480.05	
17.5	2.8622	382.45	442.59	484.95	
22.5	3.1135	384.68	447.45	489.48	
2.5	0.9163	449.66	594.73	601.7	$Ge_{20}Se_{50}Te_{30}$
7.5	2.0149	464.89	615.98	623.64	
12.5	2.5257	467.75	619.97	627.76	
17.5	2.8622	471.07	624.6	632.54	

22.5	3.1135	472.99	627.28	635.31	Ge <sub>30</sub> Se <sub>50</sub> Te <sub>20</sub>
2.5	0.9163	541.34	629.49	635.27	
7.5	2.0149	547.14	636.73	646.71	
12.5	2.5257	554.19	645.54	653.71	
17.5	2.8622	556.82	648.82	658.31	
22.5	3.1135	558.95	651.48	663.82	
2.5	0.9163	578.75	642.4	646.54	Ge <sub>40</sub> Se <sub>50</sub> Te <sub>10</sub>
7.5	2.0149	599.67	680.47	685.7	
12.5	2.5257	597.32	688.78	698.86	
17.5	2.8622	601.58	695.38	713.95	
22.5	3.1135	605.41	703.88	719.15	

**Table 2:** Variation of the values of Tc-Tg at different heating rates with varying Te atomic %

Te at %	Tc-Tg at 2.5K/Mi	Tc-Tg at 7.5K/Mi	Tc-Tg at 12.5K/M in	Tc-Tg at 17.5K/M in	Tc-Tg at 22.5K/M in
40	45.9	52.65	57.29	60.14	62.77
30	145.07	151.09	152.22	153.53	154.29
20	88.15	89.59	91.35	92	92.53
10	63.65	80.8	91.46	93.8	98.47

**Table 3:** The coordination number (Z) and the activation energy (Eg) and using eq. (2) & (3) for various compositions

Parameters	Ge <sub>10</sub> Se <sub>50</sub> Te <sub>40</sub>	Ge <sub>20</sub> Se <sub>50</sub> Te <sub>30</sub>	Ge <sub>30</sub> Se <sub>50</sub> Te <sub>20</sub>	Ge <sub>40</sub> Se <sub>50</sub> Te <sub>10</sub>
Coordination number (Z)	2.2	2.4	2.6	2.8
Eg{Eq. 2}kcal/min	39.01	45.20	57.27	67.91
Eg{Eq. 3}kcal/min	40.37	46.87	59.15	69.70

#### IV. CONCLUSION

Systematic investigation of crystallization kinetics of Ge-Se-Te glass system reveals a heating rate dependence of Tg. It is found that the glass transition temperature Tg increases with the increase in heating

rates. The little increase in Tg was observed, with the variation of Te content from 10% to 40%. There is increase of Tc-Tg at higher Te concentration upto 30%, which leads to more stable glass and at 40% becomes less stable. Thermal stability of these glasses is also found in good agreement to form the glasses with ease.

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#### VI. REFERENCES

- [1]. S.R. Ovshinsky and H. Fritzsche, Met. Trans. 2 (1971) 641
- [2]. RG. Neale, D.L. Nelson and G.E. Moore, Electronics 49 (1970) 56.
- [3]. D. Adler, Electronics 49 (1970) 61
- [4]. M.M. Hafiz, M.M. Ibrahim, M. Dongol and F.H. Hammad, J. Appl. Phys. 54 (1983) 1950.
- [5]. M.N. Abdel-Rahim, A.H. Moharram, M. Dongol and M.M. Hafiz, J. Phys. Chem. Solids 51 (1990) 355.
- [6]. F.H. Hammad, A.A. Ammar, M.M. Hafiz and E1-Nadi, Recent Adv. Sci. Technol. Mater. 1 (1974) 171.
- [7]. C.B. Thomas, A.F. Frat and J. Bosnell, Philos. Mag. 26(1972) 617.
- [8]. T.L. Shanker Rao, K.N. Lad and A.Pratap: J. Therm. Anal. Vol. 78 (2004), p. 769.
- [9]. Z.Z. Yuan, X.D. Chen, B.X. Wang and Y.J. Wang: J. Alloys Compd. Vol. 407 (2006), p. 163.
- [10]. K. Song, X. Bian, J. Guo, X. Li, M. Xie and C. Dong: J. Alloys Compd. Vol. 465 (2008), p. L7.
- [11]. J. Vazquez, P.L. Lopez-Aleman, P. Villares and R. Jimenez-Garay: Mater. Chem. Vol. 57 (1998), p. 162.
- [12]. H.F. Li and R.V. Ramanujan: Mater. Sci. A 375–377 (2004), p. 1087.
- [13]. N. Suri, K.S. Bindra and R. Thangaraj, J. Phys: Conens. Matter, 2006, 18, 9129.
- [14]. M. Ilyas, M. Zulfeqar and M. Husain, Optical Materials, 2000, 13, 397.
- [15]. M. A. Majeed Khan, M. Zulfiqar, M. Husain, J. Materials Sci., 2003, 38, 549.
- [16]. M. Saxena and P. K. Bhatnagar, Bull. Mater. Sci., 2003, 26, 547

- [17]. Nikhil Suri, K.S. Bindra, P. Kumar, M. S. Kamboj, R. Thangaraj, Journal of Ovonic Research, 2006, 2(6), 111.
- [18]. N. Mehta, S. K. Agrahari and A. Kumar, Phys. Scr., 2006, 74, 579
- [19]. D.J. Sarrah, J.P. De Neufville and W.L. Haworth J. Non-Cryst. Solids 22(1976) 245.
- [20]. N. Afify, M.A. Abdel-Rahim, A.S. Abd El-Halim and M.M. Hafiz, J. Noncryst.Solids 128 (1991) 269
- [21]. N. Afify J. Non-Cryst. Solids 128 (1991) 279
- [22]. H.E. Kinssinger, Anal. Chem. 29 (1957) 1702
- [23]. N. Rysava, T. Spasov and L. Tichy, J. Therm. Anal. 32 (1987) 1015.
- [24]. A. Shamshad Khan, M. Zulfquar, M. Husain, Physica B 324 (2002) 336-343.
- [25]. M. Abdel-Satar, M. A. Abdel-Rahim and A. El-Korashy, International J. of Pure and Applied Physics Volume 3 Number 1 (2007) 59–68
- [26]. M. Lasocka, Mater. Sci. Eng. 23 (1976) 173.
- [27]. S. Mohadevan, A. Giridhar, A.K. Singh, J. Non-Cryst. Solids 88 (1986) 11.
- [28]. M. A. Abdel-Rahim, J. Mater Sci. 97 (1992) 1757.
- [29]. H.E. Kissinger, J. Res. Nat. Bur. Stan. 57(1956) 217
- [30]. A. Giridhar and S. Mahadeven, J. Non-Cryst. Solids 51 (1982) 283.