



Pelagia Research Library

Advances in Applied Science Research, 2011, 2 (2): 109-116



Kinetic Investigations of Glass Transition in Bulk $\text{Te}_x(\text{Bi}_2\text{Se}_3)_{1-x}$ Chalcogenide Glasses

Manish Saxena^{a*}, Shilpa Gupta^b and Animesh Agarwal^a

^aMoradabad Institute of Technology, Moradabad, INDIA

^bDepartment of Physics, Singhania University, Jhunjhunu, INDIA

ABSTRACT

The crystallization studies are carried out under non-isothermal conditions with samples heated at several uniform rates. Variation in some important parameters namely glass transition temperature T_g , glass forming ability K_{gl} and reduced glass transition temperature T_{rg} have been studied with variation in Te content at various heating rates. From the heating rate dependence of T_g , the activation energy E_t for glass transition has been evaluated. This analysis helps in finding the suitability of an alloy to be used in phase transition optical storage media/ switches. The optical media point the way for the most significant advances in recording for this century and beyond. Simply put, optical technologies offer enormous capacities and extremely high resolution, making them ideal for every purpose, from audio recording to information storage on machines not yet invented.

Keywords: Chalcogenide Glasses, Glass-thermal properties; Glass-optical materials, Activation energy, Thermal Stability.

INTRODUCTION

Chalcogenide glasses have their vast electrical, optical and technological applications, such as in reversible phase change optical recording, memory devices, optical fibers, xerography, photolithography, infrared lenses, optical amplifiers, blue laser diodes and in solar cells, make them more attractive for their investigation [1–7]. Erasable recording is usually considered to be a potential replacement for conventional recording due to its high storage density and archival stability. The chalcogenides used for recording medium must be easy to amorphize and crystallize, and there should be a high optical contrast between the amorphous and crystalline states. Furthermore, the writing and erasing must be fast and the material should be stable to an adequate number of write and erase cycles and have good oxidation resistance [8]. The concept

of phase change optical recording is, that some physical property of microscopic area of recording layer on disc surface is altered. In this technique, spots of a crystalline material are melted momentarily by short laser pulses for recording and the recorded marks are erased through annealing process during which long laser pulses heat the amorphous spot to return it to crystalline phase. Threshold switches are made in those glasses near the center of the glass-forming region where the glasses are stable and show little or no tendency to crystallize when heated or cooled slowly. Memory switches come from the boundaries of the glass-forming region where the glasses are more prone to crystallization [9].

The properties of chalcogenide materials like optical, electrical and physical can be controlled by changing their chemical composition [9]. Chalcogenide glasses are vitreous materials whose composition contains one or more chalcogen elements S, Se or Te, as well as elements of the groups IV and V of periodic classification. These glasses are interesting materials because of their technological applications and commercial importance [10, 11]. Especially selenium alloys exhibit a unique property of reversible transformation which makes these systems very useful for optical memory, X-ray imaging and photonics. Among amorphous chalcogenide alloys, selenium based melt are characterized by a high viscosity. This feature favours the glass formation in bulk form by air-quenching or water-quenching as well as in evaporated thin film forms. Since tellurium based melts with the same elements generally have low viscosity, a high cooling rate is required to prevent nucleation and growth during quenching and to obtain bulk glasses. Among chalcogenide glasses, Se-Te based alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and smaller ageing effects as compared to pure Se glass [12, 13, 14]. The addition of tellurium (Te) has a catalytic effect on the crystallization of selenium. The presence of Te in Se chains probably favors their thermal dissociation as the Se-Te bond being weaker than Se-Se bond [15]. Binary Se-Te alloys are found useful in practical application. From technology point of view these glasses should be stable with time and temperature. The addition of Bi 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. The series of Se-Te has been used as a base material for the incorporation of Bi [16, 17, 18]. The addition of Bi to the Se-Te system is expected to modify the material properties to make it more suitable for reversible optical recording with an erase time less than 1 μ sec. Thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses.

In chalcogenide glass systems, the glasses which exhibit no exothermic crystallization reaction above the glass transition temperature T_g could possibly be used in threshold switching systems whereas glasses exhibiting an endothermic crystallization reaction above T_g show a memory type of switching [8]. It has been shown that the amorphous films with composition outside the glass-forming region are more suitable for memory devices because of their fast crystallization during the application of a suitable electric pulse or by the heat of a focused laser beam. In this paper, we report our studies on Bi-Se-Te ternary glasses. A fundamental observation recently made for the rapidly quenched metal alloys is that they do not usually indicate a sharp glass liquid transition characteristic of amorphous material. Crystallization studies are carried out under non-isothermal conditions with samples heated at several uniform rates. In the non-isothermal method, the sample is heated at a fixed rate (β) and the heat evolved is recorded as a function of temperature or time [19]. For phase change optical switching systems, it is important to optimize various

parameters like, the glass transition temperature T_g , the crystallization temperature T_c and the melting temperature T_m by varying the composition and heating rate [15]. From the heating rate dependence of T_g , the activation energy for glass transition (E_t) has been evaluated.

MATERIALS AND METHODS

Experimental Details

For the preparation of Te-Bi-Se glasses, high purity elements (99.999 %) in appropriate atomic percentage were weighed in to quartz ampoules. The ampoules, sealed under high vacuum conditions (10^{-5} Torr) were suspended in a vertical furnace at 900°C for 24 hours, shaken vigorously for homogeneous mixing. The temperature was raised at a rate of 3 to 4 K/min. The melt was rapidly quenched in ice-water mixture. The quenched samples were removed from the ampoule by dissolving the ampoule in a mixture of $\text{HF}+\text{H}_2\text{O}_2$ for about 20 hours. The samples were then kept at room temperature in dark for about one month for attainment of thermodynamic equilibrium as stressed by Abkowitz in chalcogenide glasses [20]. Amorphous nature of the samples was ensured by the absence of any sharp peaks in the X-ray diffractograms.

The prepared solid solution in powder form has been used for thermal analysis using the Differential Thermal Analysis (DTA). This material was first sealed in a standard aluminium pan and the calorimetric thermo grams of various compositions of the samples were obtained with a RIGAKU DTA 8150 calorimeter in the temperature range $50\text{-}700^\circ\text{C}$ at various heating rates ($10\text{-}20\text{ K min}^{-1}$). Calorimetric measurements were made under non-isothermal conditions and a multi-scan technique has been used for crystallization studies. The activation energy for glass transition (E_t) has been determined by using Kissinger's equation in different forms.

RESULTS AND DISCUSSION

The transformation to a glass does not take place at one, strictly defined temperature, but within a temperature range, representing the transformation region [21]. The width of the later depends on the properties of the material studied (low-temperature edge) and on the thermal history of the sample (high-temperature edge). It has been shown that for a given uniform heating rate, the glasses show a single glass transition endothermic peak and a single exothermic crystallization peak. By the time crystallization start-taking place, the temperature goes up owing to the higher heating rates. DTA curves, indicating the glass transition peaks, for Te at 30% for different heating rates, ranging from 10 K/min to 20 K/min have been shown in fig (1).

The single endothermic glass transition peak indicates the homogeneity of the glass. T_g represents the "strength" or the "rigidity" of the glass structure. Therefore, drastic changes in T_g cannot be expected by increase in Te content, which results in isostructural units of nearly same bond strength. The slight increase in T_g with heating rates, observed is probably due to the increase in mean molecular weight of the glasses with Te content. In the present Te-Bi-Se glass system, the glass transition temperature was found to decrease with increasing the amount of Te. The values of glass transition temperature were also found to increase with the increase in heating rates as shown in fig (2). This may be attributed to the fact that when heating rate is high, the system doesn't get sufficient time for nucleation and crystallization.

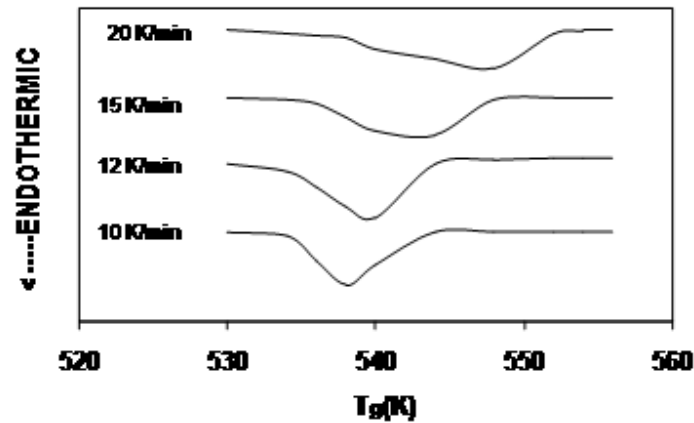


Fig. 1 DTA curves for Te at 30% for different heating rates.

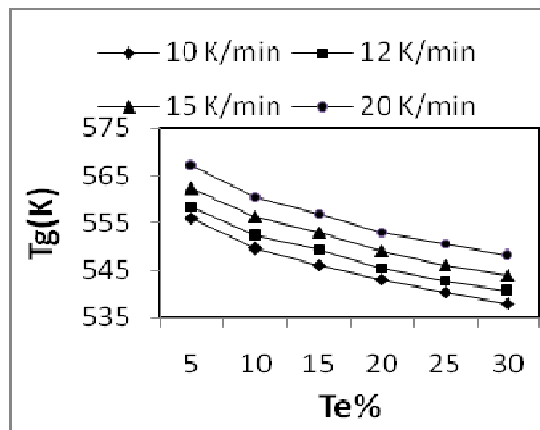


Fig 2: Variation of T_g with Te content

The kinematical studies are always connected with the concept of the activation energy. In general, separate activation energies must be identified with individual nucleation and growth steps in a transformation, although they usually have been combined in to activation energy representative of the overall crystallization process. The activation energy for glass transition, E_t , were analysed using the Kissinger relation given as follows, [22],

$$\ln (T_g^2/\beta) + \text{const} = E_t/kT_g \tag{1}$$

Where k is Boltzmann's constant.

The plots of $\ln (T_g^2/\beta)$ versus $10^3/T_g$ as shown in fig (3) are seen to be linear for these glasses up to a heating rate of 20K/min. The graph is found to be linear for all the samples. The glass transition activation energy is the amount of energy that is absorbed by a group of atoms in the glassy region so a jump from one metastable state to another [23]. In other words, the activation energy is involved in the molecular motions and rearrangements of the atoms around the glass transition temperature [24]. When the sample is reheated during DTA heating, the atoms undergo infrequent transitions between the local potential minima separated by different energy barriers

in the configuration space where each local minimum represents a different structure. The most stable local minimum in the glassy region has lower internal energy. Accordingly, the atoms in a glass having minimum activation energy have a higher probability to jump to the metastable state (or local) of lower internal energy and hence is the most stable [23]. Therefore, one can argue that the addition of Te increases the stability of the glasses under investigation. The activation energy, E_t , for the glass transition, was calculated from the slopes of the linear fits to the experimental data in fig (3) using equation 1. The activation energy is found to increase from 1.567 eV to 1.895 eV with the increase in Te content for these samples. The variation of activation energy for glass transition E_t , with Te content is illustrated in fig (4).

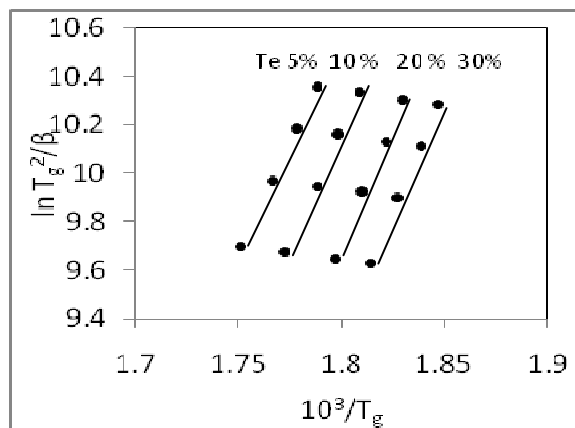


Fig. 3: Plots of $\ln T_g^2 / \beta$ versus $10^3/T_g$ for different Te content.

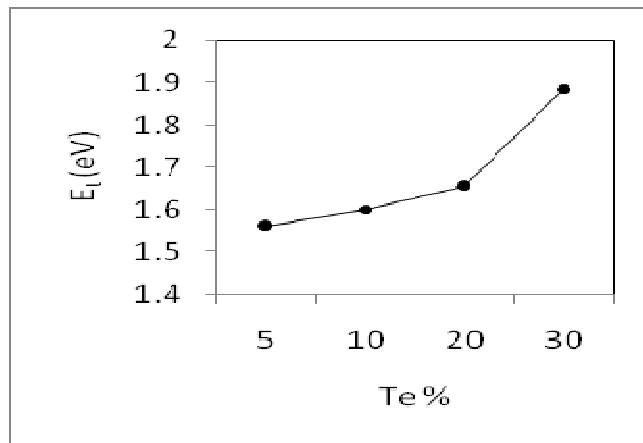


Fig. 4: Variation of activation energy, E_t , with Te content.

Since there is no absolute criterion to parameterize the glass formation, the empirical parameters extensively used for its quantitative characterization have been evaluated. For a given uniform heating rate, the glasses show a single glass transition endothermic peak and a single exothermic crystallization peak. The single endothermic glass transition peak indicates the homogeneity of the glass. For a memory/switching material, the thermal stability and ease of glass formation are of crucial importance. The value of $T_c - T_g$ is found to increase with increase in Te concentration as shown in fig (5). This indicates a increase in thermal stability of glass with an increase in Te concentration in the Te-Bi-Se glass system.

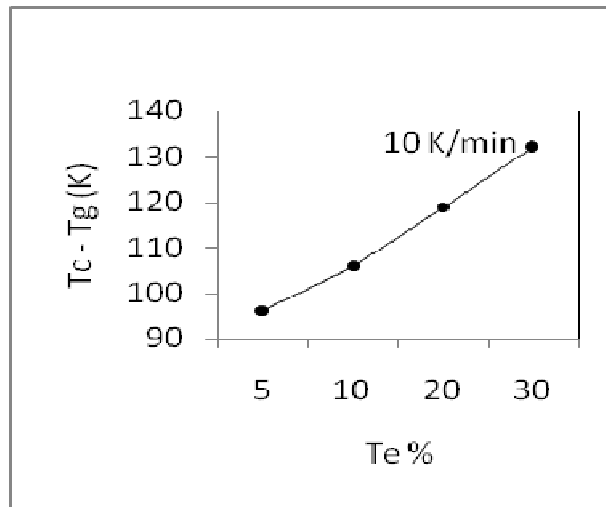


Fig 5: Variation of $T_c - T_g$ with Te content

The glass forming ability can be calculated using the following relation as given by Hurby [25].

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c} \quad 2$$

The values of K_{gl} are found to increase from 0.3837 to 0.6044 with an increase in Te content as shown in fig. (6). It is noticed that the glasses with higher Te content are easy to form compared to those with lower Te content.

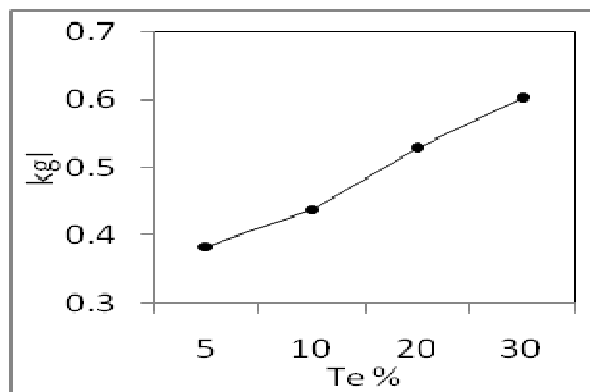


Fig. 6: Variation of K_{gl} with Te content.

The ease of glass formation is determined by calculating the reduced glass transition temperature $T_{rg} = T_g/T_m$ [26]. The values of T_{rg} is found to be of the order of 2/3 for all the samples thus indicating good glass forming tendency for all the compositions of the material as depicted in fig. (7).

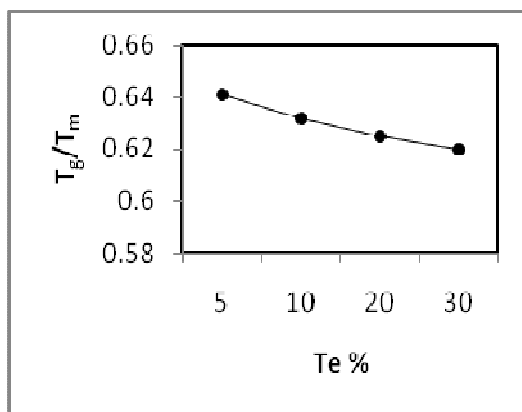


Fig. 7: Variation of T_g/T_m with Te content.

CONCLUSION

A systematic investigation of crystallization kinetics of Te- Bi-Se glass system reveals a heating rate dependence of T_g . The glass transition temperature T_g is found to increase with the increase in heating rates. The slight increase in T_g observed, with the variation of Te content from 5% to 30%, is probably due to the increase in mean molecular weight of the glasses with increasing Te content. The activation energy for glass transition E_t was found to increase with increase in Te content. The increase of T_c-T_g at higher Te concentration leads to conclusion that stable glasses can be obtained with higher Te concentration. Thermal stability of these glasses is also found in good command to form the glasses with ease. Analyzing the results with the increase in Te content, the glass forming ability K_{gl} was found to be increased. It is concluded that the glasses with higher Te content are easy to form compared to those with lower Te content.

REFERENCES

- [1] G. Kaur and T. Komatsu, *J. Mater. Sci.*, **2001**, 36, 453.
- [2] Z. Abdel-Khalek Ali, G.H. Adel, A.S. Abd-rbo. *Chalcogenide Letters*, **2009**, 6, 125.
- [3] V. Trnovcona, I. Furar, D. lezal, *J. Non-Cryst. Solids*, **2007**, 353, 1311.
- [4] Anup Kumar, P. B. Barman, Raman Sharma, *Adv. in Appl. Sci. Research*, **2010**, 1(2), 47.
- [5] T. Wagner, *J Optoelectron Adv. Mater*, **2002**, 4, 717.
- [6] M. S. Kamboj, R. Thangaraj, *Eur Phys J App Phys*, **2003**, 24, 33.
- [7] A. El-Korashy, N. El-Kabany, H. El-Zahed, *Physica* , **2005**, B 55, 365.
- [8] A. Singh, A. Kumar and A. K. Nagpal, *J. Mater. Sci.*, **2000**, 35, 191.
- [9] N. Mehta, M. Zulfequar, A. Kumar, *J. Optoelectron. Adv. Mater*, **2004**, 6, 441.
- [10] K. Tanaka, *Physics Rev*, **1989**, B39, 1270.
- [11] M. Leh Deli, D. Houphouet Boigny, G. Kra , *Journal of Non-Oxide Glasses*, **2010**, 1(1) 59.
- [12] N. Suri, K.S. Bindra and R. Thangaraj, *J. Phys: Conens. Matter*, **2006**, 18, 9129.
- [13] M. Ilyas, M. Zulfequar and M. Husain, *Optical Materials*, **2000**, 13, 397.
- [14] M. A. Majeed Khan, M. Zulfiquar, M. Husain, *J. Materials Sci.*, **2003**, 38, 549.
- [15] Manish Saxena, *J. Physics D: Applied Physics*, **2005**, 38, 460.
- [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] L. C. Chen and F. Spaepen, *Nature (London)*, **1988**, 336, 366.
- [20] M. A. Abkowitz in “*The Physics of Se and Te*”, edited by E. Ferlach and P. Grosse, *Springer, Berlin*, **1979** p. 178.
- [21] N. Afify, *J. Non Crystalline Solids*, **1990**, 126, 130.
- [22] H. E. Kissinger, *J. Res. Nat. Bur. Stand.*, **1956**, 57, 217.
- [23] M. M. A. Imran, D. Bhandari, N. S. Saxena, *Physica*, **2001**, B 293, 394.
- [24] P. Agarwal, S. Goel, J. S. P. Rai, A. Kumar, *Physica Status Solidi*, **1991**, (a) 127, 363.
- [25] A. Hurby, *Czech J. Phys. B*, **1972**, 22, 1187.
- [26] W. Kauzmann, *Chem Rev.*, **1948**, 43, 219.