

Crystallization kinetics of amorphous $\text{Te}_x(\text{Bi}_2\text{Se}_3)_{1-x}$ glasses

^{1*} Lovely Sabat, ² Sambit Acharya

^{1*} Asst. Professor, Dept. Of Civil Engineering, NIT BBSR,

² Asst. Professor Dept. of Civil Engineering, SSEC, BLSR

^{1*} lovelysabot@gmail.com, acharya.sambit91@gmail.com

Abstract. The activation energy plays a dominant role in deciding the utility of the material for the specific purpose—here storage. The dependence of the peak temperature of crystallization (T_p) on the composition and heating rate (b) has been studied here. From the heating rate dependence, T_p , the activation energy for crystallization (E_c) has been evaluated. The activation energy, E_c , calculated using three different approaches is found to decrease with the increase in Bi content. This analysis helps in finding the suitability of an alloy to be used in phase transition optical memories/switches. The results have been analysed using Kissinger's equation for non-isothermal crystallization of materials.

Keywords : Glasses—thermal properties; thermal analysis; glass—optical materials; activation energy.

1. Introduction

Chalcogenide glasses have been investigated intensively because of their promising technological applications in reversible phase change optical recording, optical fibres, photoresists, photoconductors, etc (Kaur and Komatsu 2001). There has been considerable interest in amorphous semiconductors because of their interesting physical properties like threshold and memory switching. An optical storage system is a particularly attractive component of this hierarchy because it provides data access times that are an intermediate solution between a hard disk drive and a tape drive. Access time is the time, including latency, required to start retrieving a random block of data and typically ranges from < 10 ms for a hard disk drive, to 30–50 ms for an optical disk drive, and several seconds for a tape drive. It becomes an important link in the chain as data are staged up and down between cpu, memory, and storage. Our need for storage is explosive; fueled by multimedia requirement for text, images, video and audio, storage requirements are growing at an exponential rate and are expected to exceed 10^{20} bits in the coming years. Erasable recording is usually considered to be a potential replacement for conventional recording due to its high storage density and archival stability. 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 (Sripathi *et al* 1992). Thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses (Abu-Sehly 2000). In order to view the suitability of a material for the above applications, it is necessary to investigate the crystallization behaviour of the material concerned. In the present work, a systematic investigation of the crystallization kinetics of amorphous $\text{Te}_x(\text{Bi}_2\text{Se}_3)_{1-x}$ system has been made. The thermal stability and crystallization kinetics have been reported for the Te–Bi–Se system for different Bi contents. The studies of crystalline kinetics of a glass upon heating can be performed in several different ways. In calorimetric measurements, two basic methods can be 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 at a constant temperature is recorded as a function of time. In the non-isothermal method, the sample is heated at a fixed rate (b) and the heat evolved is recorded as a function of temperature or time (Saxena and Bhatnagar 2003). Here, calorimetric studies were made under non-isothermal conditions at different heating rates. The kinematical investigations are always connected with the concept of the activation energy. In glass-crystallization phenomena, the values of these investigations are associated with the nucleation and growth processes, which dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with individual nucleation and growth steps in a transformation, although they usually have been combined into a single activation energy representative of the overall crystallization process. Selenium based melts are characterized by a high viscosity among amorphous chalcogenide alloys (Khan *et al* 1997; Ilyas *et al* 2000). 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. The tellurium alloys have often been used for the active layer of those devices because of low melting point. Te-based alloys, which contain a small amount of As, Bi, Sb or Ge, exhibit fast crystallization processes after switching (Saxena *et al* 2003). However, several problems like segregation and low crystallization temperature arises with these alloys. The segregation limits the reversible transition between amorphous and crystalline states, because the compositional deviation is likely to continue in the active layer in every crystallization process. The answer to the above problems may be a ternary solid alloy with relatively low melting point because no compositional changes occur in a solid solution when it is cycled between amorphous and crystalline states. In this paper, we report our studies on Te–Bi–Se ternary glasses with the variation in Bi content. From the heating rate dependence of T_p , the

activation energy for crystallization, E_c , has been evaluated.

2. Experimental

For the preparation of Te–Bi–Se glasses, high purity elements (99.999%) in appropriate atomic percentage were weighed into quartz ampoules. The ampoules, sealed under high vacuum conditions (10^{-5} Torr) were suspended in a vertical furnace at 900°C for 24 h, shaken vigorously for homogeneous mixing. The temperature was raised at a rate of 3–4 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 HF + H_2O_2 for about 20 h. The samples were then kept at room temperature in dark for about one month for attainment of thermodynamic equilibrium as stressed by Abkowitz (1979) in chalcogenide glasses. 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 differential thermal analysis (DTA). This material was first sealed in a standard aluminium pan and the calorimetric thermograms 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 ($10\text{--}20^\circ\text{C min}^{-1}$). Calorimetric measurements were made under non-isothermal conditions and a multi-scan technique was used for crystallization studies. The activation energy for crystallization (E_c) was determined by using Kissinger's equation in different forms.

3. Results and discussion

In the Te–Bi–Se system the various bonds involved are Bi–Te, Bi–Se, Te–Se, Se–Se, Te–Te, etc. The chemical bonds approach predicts that only three types of bonds, viz. Bi–Te, Bi–Se and Se–Se, are expected to form for the investigated compositions. In other words, the Te–Se, Te–Te and Bi–Bi bonds are not present. Addition of Bi leads to the formation of Bi–Se bonds at the expense of the Se–Se bonds. When the atomic percentage of Bi is increased in Te–Bi–Se glass system, Bi is expected to combine preferably with Se because the bond energy of Bi–Se (170.4 kJ/mol) is greater than that of Bi–Te (125.6 kJ/mol).

This results in decreasing Se–Se bonds. The number of the Bi–Se bonds increases with increasing Bi content (El-Shazly and Hafiz 2001). This explains the increase in T_g with the increase in Bi content due to the formation of large number of heteropolar Bi–Se bonds and decrease in homopolar Se–Se, Te–Te and Te–Se bonds. The results are similar to those obtained by earlier workers (Rahman *et al* 1991). In memory devices using different electrical and optical properties in the crystalline and amorphous states, a lower melting point is preferable, because the crystalline state can be converted to the amorphous state by laser beam or electrical pulse with relatively lower energy. Moreover, those solids forming a solid solution are preferable, because phase separation or segregation does not occur in the transition from amorphous to crystalline state. The phase separation or segregation in crystallization processes cause degradation of memory devices. A higher crystallization temperature is also necessary for memory devices.

It is well known that thermal relaxation occurs in a glassy substance following an instantaneous change in temperature, during the quenching process, as it relaxes from a state of higher enthalpy towards a metastable equilibrium state of lower enthalpy. This type of thermal relaxation depends upon the annealing temperature and may be quite fast near the glass transition temperature. The glass transition is exhibited in differential thermal analysis or differential scanning calorimeter traces as an endothermic peak or a shift in the base line due to a change in specific heat. However, in chalcogenide glasses, such an endothermic peak can also be observed due to a fast change in enthalpy when the glassy system relaxes quickly due to a decrease in viscosity at the glass transition temperature. DTA or DSC technique can, therefore, be quite useful in the study of thermal relaxation in 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. DTA curves for Bi at 28% for different heating rates, ranging from 10–20 K/min have been shown in figure 1. The variation of T_p with Bi content at different heating rates ranging from 10–20 K/min has been shown in figure 2. It is deduced from the figure that the value of T_p decreases with the increase in Bi content whereas it is found to be increasing with the increase in heating rates from 10–20 K/min.

Theoretical aspects for calculating E_c

The activation energies to be considered in a crystalline process are the activation energy for nucleation (E_n), activation energy for crystal growth (E_g) and that for the whole process of crystallization, called the activation energy for crystallization, denoted by E_c . The thermal analysis methods enable the determination of E_c (Ranganathan and Heimendahl 1981). It has been pointed out that in non-Crystallization kinetics of amorphous $\text{Te}_x(\text{Bi}_2\text{Se}_3)_{1-x}$ glasses isothermal measurements, generally due to a rapid temperature rise and big differences in the latent heats of nucleation and growth of the crystalline phase from the amorphous matrix, nucleation is more or less calorimetrically unobservable at temperatures below the crystallization exotherm, or it takes place very rapidly and immediately after overheating of the

material in the initial stages of crystallization exotherm, which results in the deformed beginning of the measured exotherm (Illekova 1984). Based on the experimental results, the theoretical approach is set up on three models to exhibit how the activation energy associated with crystallization is modified with respect to the different parameters.

First Model: The activation energy, E_c , of the amorphous to crystalline transformation is calculated by using the equation derived by Kissinger (Kissinger 1957; Abdel-Rahim 1992)

$$\ln (T_p^2/b) = (E_c/kT_p) + \text{constant.} \quad (1)$$

Figure 3 shows the relations between $\ln (T_p^2/b)$ and $10^3/T_p$ for different compositions of $Te_x(Bi_2Se_3)_{1-x}$ system. The data are well fitted by straight lines, which show that the crystallization obeys the above-mentioned relation. It is evident from figure 6 that the value of activation energy, E_c , decreases from 2.467 eV to 1.870 eV with the increase in Bi content, using (1), for $Te_x(Bi_2Se_3)_{1-x}$ system.

Second Model: The activation energy of the amorphous to crystalline transformation, E_c , can be calculated also from the following relation, which correlates the shifts in T_p values of DTA with the heating rate (Mahadevan *et al* 1986; Abdel-Rahim 1992)

$$\ln b = -E_c/kT_p + \text{constant.} \quad (2)$$

Figure 4 shows the plots of $\ln b$ with $10^3/T_p$ for $Te_x(Bi_2Se_3)_{1-x}$ system. The data are well fitted by straight lines, which show that the crystallization obeys (2). The values of E_c are found to decrease from 2.49 eV to 1.83 eV with the increase in Bi content using (2) as shown in figure 6.

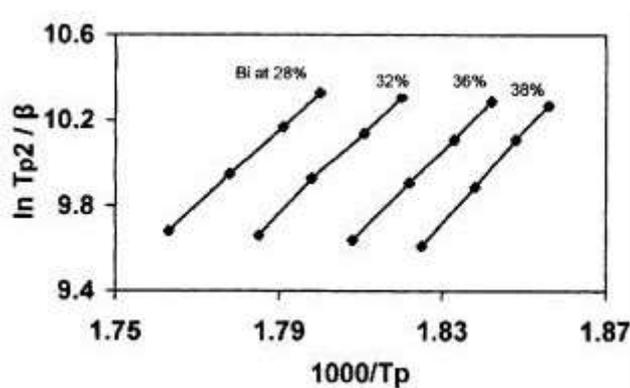
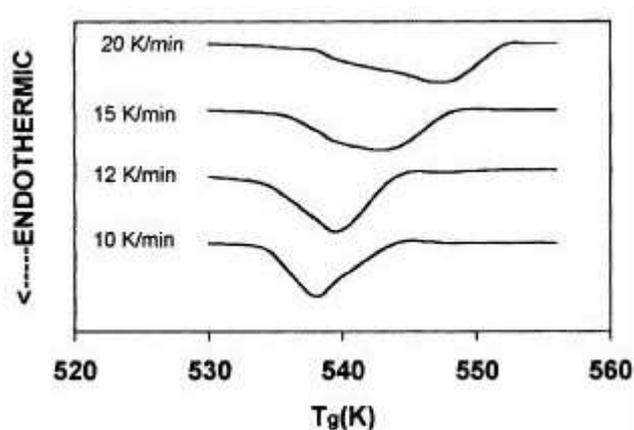


Figure 3. Relation between $\ln (T_p^2/b)$ and $10^3/T_p$

for various

Figure 1. DTA curves for Bi at 28% for different heating rates.

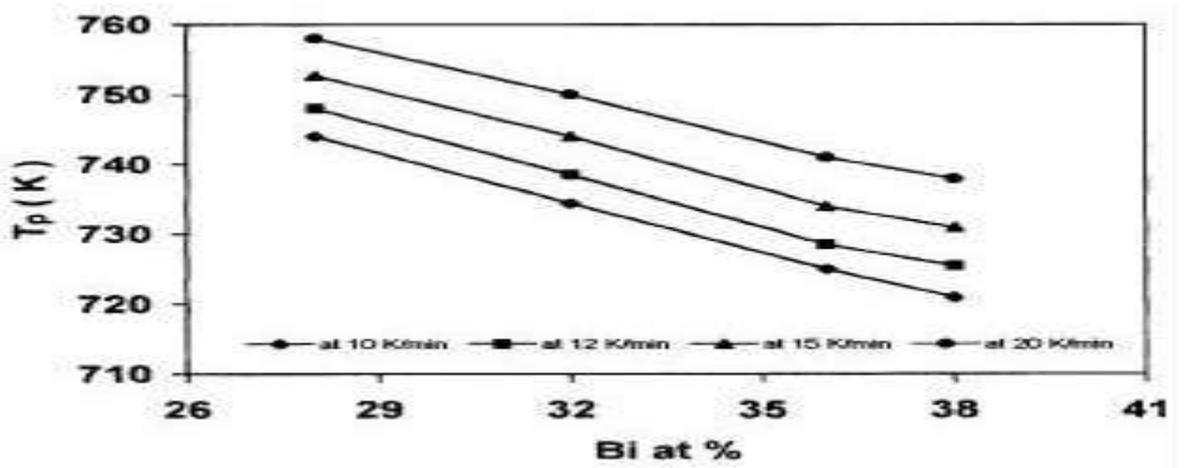


Figure 2. Variation of T_p with Bi content at various heating rates.

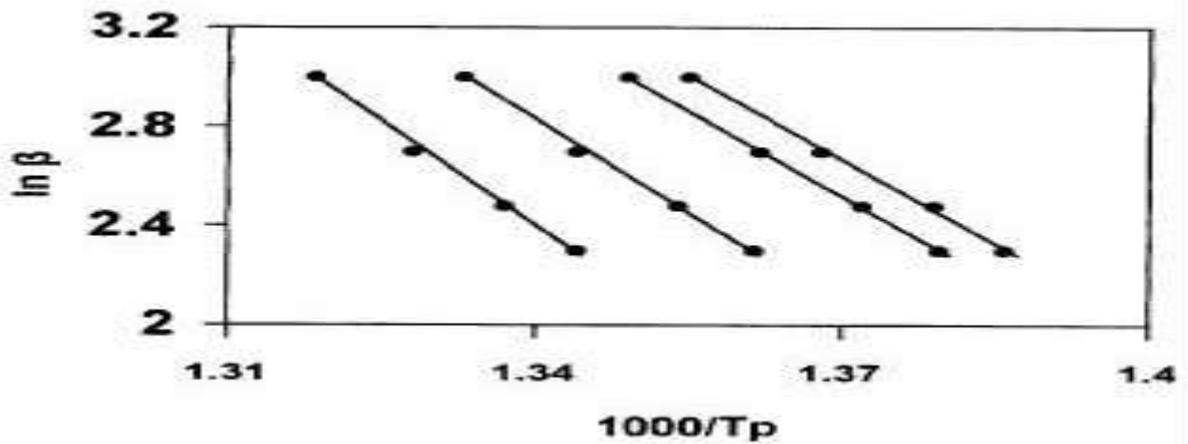


Figure 4. Relation between $\ln b$ and $10^3/T_p$ for various compositions.

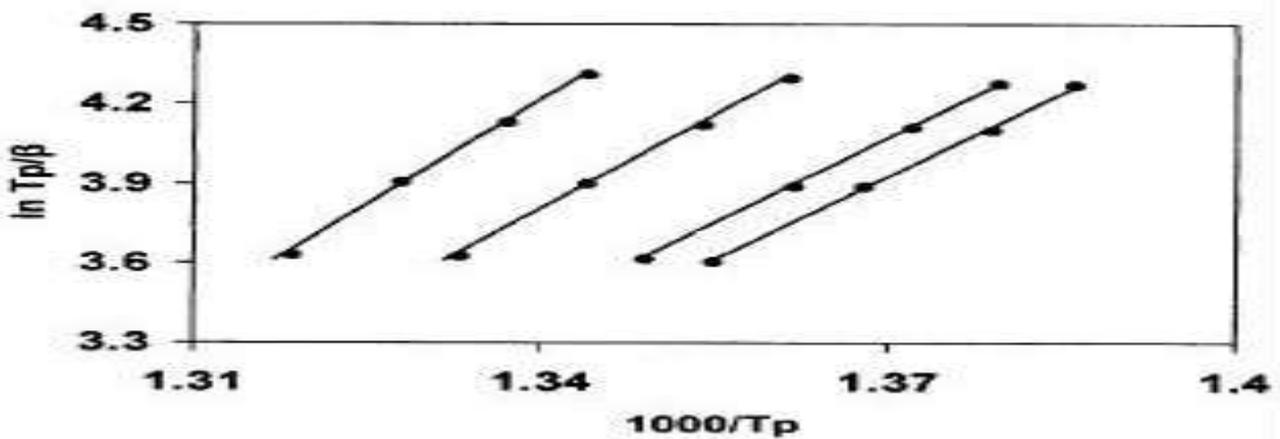


Figure 5. Relation between $\ln (T_p/b)$ and $10^3/T_p$ for various compositions.

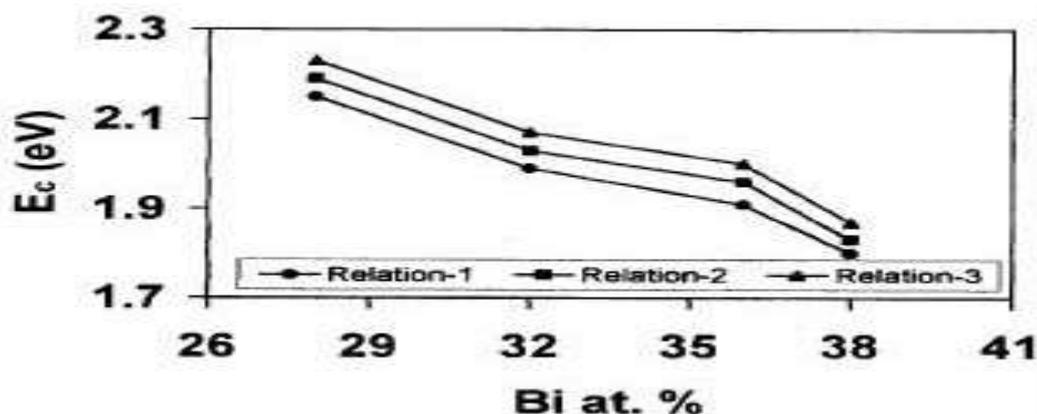


Figure 6. E_c with variation of Bi for relations (1, 2, 3).

Third Model: The third model, used to calculate the values of E_c , is based on Marseglia's theory (Marseglia 1980; Atmani 1988), which admits that

$$\ln T_p/b = E_c/kT_p + \text{constant.}$$

Plots of $\ln T_p/b$ vs $10^3/T_p$ for different compositions of $\text{Te}_x(\text{Bi}_2\text{Se}_3)_{1-x}$ system are shown in figure 5. A straight line could be fitted to give the activation energies. The values of E_c , obtained by using (3), are also shown in figure 6 with the variation of Bi content. It is clear from figure 6 that the value of E_c decreases from 2.23 eV to 1.87 eV with the increase in Bi content of $\text{Te}_x(\text{Bi}_2\text{Se}_3)_{1-x}$ system. For all the three relations, the E_c decreases with increase in Bi content. There is not much difference in the values of E_c obtained using these relations.

Conclusions

The effect of addition of Bi to Se–Te on the crystallization kinetics and activation energy of the Te–Bi–Se system has been investigated. It is found that the glass transition temperature shows little variation with the addition of Bi. The value of peak of crystallization, T_p , is found to decrease with the increase in Bi content. From the heating rate dependence of T_p the activation energy for the crystallization has been evaluated. The results are discussed on the basis of Kissinger's approach and Marseglia's theory for non-isothermal crystallization. The activation energy, E_c , calculated using three different approaches decreases with increase in Bi content. For all the three relations, the E_c decreases with increase in Bi content. There is not much difference between the obtained values of E_c , so it can be concluded that any of these models can be taken to calculate E_c as the values of activation energies, using three different models, are in good agreement with each other. It is suggested that the addition of Bi leads to the formation of Bi–Se bonds at the expense of the Se–Se bonds. The number of the Bi–Se bonds increases with increasing Bi content.

References

- Abdel-Rahim M A 1992 *J. Mater. Sci.* **27** 1757
 Abkowitz M A 1979 in *The physics of Se and Te* (eds) E Ferlachand P Grosse (Berlin: Springer) p. 178
 Abu-Sehly A A 2000 *J. Mater. Sci.* **35** 2009
 Atmani H 1988 *Mater. Chem. & Phys.* **19** 255
 El-Shazly O and Hafiz M M 2001 *J. Mater. Sci.: Mater. Electron.* **12** 395
 Illekova E 1984 *J. Non-Cryst. Solids* **68** 153
 Ilyas M, Zulfeqar M and Husain M 2000 *Opt. Mater.* **13** 397 Kaur G and Komatsu T 2001 *J. Mater. Sci.* **36** 453
 Khan Z H, Zulfeqar M and Husain M 1997 *Mod. Opt.* **44** 55 Kissinger H E 1957 *Anal. Chem.* **29** 1702
 Mahadevan S, Giridhar A and Singh A K 1986 *J. Non-Cryst. Solids* **88** 11
 Marseglia E A 1980 *J. Non-Cryst. Solids* **41** 31
 Rahman S, Ramana M V and Sastry G S 1991 *J. Mater. Sci. Lett.* **10** 192
 Ranganathan S and Heimendahl M V 1981 *J. Mater. Sci.* **16** 2401 Saxena M and Bhatnagar P K 2003 *Bull. Mater. Sci.* **26** 547 Saxena M, Rastogi N, Agarwal A and Bhatnagar P K 2003