First Order Phase Transformation in Amorphous $Ge_{25}Se_{75-x}Sb_x$ Glasses

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Non-isothermal Differential scanning calorimetry (DSC) technique was used to study the kinetics of first order phase transformation in $Ge_{25}Se_{75-x}Sb_x$ glasses. The X-ray diffraction (XRD) technique was employed to investigate the amorphous and crystalline phases in $Ge_{25}Se_{75-x}Sb_x$ glasses. From the heating rate dependences of crystallization temperature; the activation energy for crystallization and other kinetics parameters were derived. The temperature difference $(T_c - T_g)$ and T_c is highest for the samples with 6 % of Sb. Hence, $Ge_{25}Se_{69}Sb_6$ glass is most stable. The enthalpy released is found to be less for $Ge_{25}Se_{69}Sb_6$ glass which further confirms its maximum stability. The activation energy of crystallization (ΔE_c) is found to vary with compositions indicating a structural change due to the addition of Sb. The crystallization data are interpreted in terms of recent analyses developed for non-isothermal conditions. The present investigation indicates that both the glass transition and the crystallization processes occur in a single stage.

Keywords: Glass transition temperature, Crystallization kinetics, X-Ray diffraction, Phase transformation.

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1. INTRODUCTION

Amorphous chalcogenide glasses have been investigated extensively over the past few decades. These glasses have been widely used in device technology and the current interest in these materials centers on X-ray imaging and photonics [1]. The relevance of studying the phase transformation in these materials has a technological aspect, since several physical properties change in the temperature range of utilization of the materials. It is also of fundamental scientific interest, since one can obtain useful information on the elementary processes, which modify the structure of an amorphous system, eventually producing stable phases on crystallization. The study the first order phase transformation in chalcogenide glasses by the differential scanning calorimetry (DSC) method has been widely discussed in literatures [2-8]. The first order phase separation effects are of general interest in chalcogenide glasses. It is a term used to describe a phenomenon where an initially homogeneous system, such as a liquid, will unmix into two or more finely mixed chemically or structurally different, component or phases. Such structural effects produce usually pronounced changes in glass physical properties including a lowering of the glass transition temperature, a lowering of the optical band gap, an increase of molar volumes [9]. The phase transformation can exist on a variety of length scales from nanometers to micrometers or millimeters [9]. For the purpose of photonic applications, it is important that phase separation be eliminated or at least minimized to length scales much smaller than that the wavelengths of light being used. Apart from the technical importance, the knowledge of crystallization kinetics is very important for a better understanding of amorphous structure of such chalcogenide glasses.

The study of glass transition kinetics in chalcogenide glasses is of great importance to establish the thermal stability, glass-forming ability and ultimately to determine the useful range of operating temperatures for a specific technological application before the eventual crystallization takes place. The glass forming tendency of the glassy alloys is related to ease by which melt can be cooled with the avoidance of crystal formation. Meanwhile, the thermal stability indicates the resistance of crystallization of glassy alloy through the nucleation and growth process. To evaluate the glass forming tendency and thermal stability of chalcogenide glasses, different simple quantitative methods are usually used. The most commonly used methods are those suggested by Kissinger [10] and Ozawa [11], which are based on some characteristic temperatures such as the glass transition and crystallization temperatures monitored by the differential scanning calorimeter (DSC).

The present work reports first order phase transformation in amorphous $Ge_{25}Se_{75-x}Sb_x$ glasses by using non-isothermal DSC measurements. The effect of variation of Sb content on the thermal stability and glass forming tendency has also been studied. In the present system, we have used Se as a major content because it is widely used as a typical glass-former. The choice of selenium is due to its wide commercial importance. Its device applications like rectifiers, photocells and switching memory, etc. have made it attractive. But the pure selenium has low sensitivity and short lifetime. In order to overcome this difficulty, several workers have used certain additives (Ga, Ge, Bi, etc.) for alloying Se to some extent. We have chosen germanium as an additive material. Germanium is also known to contribute to long-term room temperature stability [12]. We have incorporated Sb as the third element in Ge-Se alloys. The continued scientific interest in Sb based chalcogenide glasses is due to its potential use in phase change optical recording [13-18]. In phase change optical recording, the recording of information is based on writing and erasing of amorphous marks in a crystallization layer of a phase change material. Since the optical properties of the amorphous phases are different from those of the crystallization phase, the written mark can be read out as a contrast in the reflectance. Besides sufficient optical contrast between the crystalline and amorphous state, the thermal stability and

glass forming tendency are one of the most important issues in developing phase change materials. In chalcogenide glasses, glass forming tendency and thermal ability of a glassy alloy is related to the ease by which melt can be cooled with the avoidance of crystal formation. The thermal stability and glass forming tendency play an important role in determining the utility of chalcogenide alloys as recording material [19-23]. The knowledge of the thermal stability and glass forming tendency in $Ge_{25}Se_{75-x}Sb_x$ glasses is, therefore, a subject of great interest.

2. EXPERIMENTAL DETAILS

Amorphous glassy alloys of $Ge_{25}Se_{75-x}Sb_x$ with $x = 6$, 9 12 and 15 were prepared by melt quenching technique. The highly pure materials (99.999 % pure) were weighed according to their atomic percentages and sealed in quartz ampoules under a vacuum of 10^{-6} Torr using turbo pump. The sealed ampoules were then placed in a Microprocessor Controlled Programmable Muffle Furnace with rocking mechanism. The temperature of the furnace was increases at three stems. Initially at 773 K for 4 hours, then 973 K for 4 hours, and finally at 1273 K for 6 hours. The rocked motion accomplishes a complete mixing of the materials in the ampoule. Rapid quenching in ice-water bath was used to obtain the bulk amorphous material. By breaking the ampoule, ingots of the sample were taken out and then using ceramic tools the amorphous material was crushed in to a fine powder. Thin films of $Ge_{25}Se_{75-x}Sb_x$ glasses were prepared on Si (100) wafer for energy dispersive X-ray spectroscopy (EDAX) by using Edward Coating Unit E-306. The surface morphology of as-prepared samples was examined by means of JEOL JSM-6360LV, Japan, scanning electron microscopy (SEM). A Regaku X-ray diffractometer Ultima IV was employed for studying the structure of the material. The first order phase transformation in $Ge_{25}Se_{75-x}Sb_x$ glas-ses were investigated by using Differential Scanning Calorimeter (Model–DSC plus, Rheometric Scientific Company, U.K). The instrument was calibrated with indium, lead and tin standards. Each sample was heated at a constant heating rate of 5, 10, 15 and 20 K/min and the changes in heat flow with respect to temperature were measured. The glass transition temperature and the crystallization temperature were determined using the microprocessor of thermal analyzer.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

Fig. 1 shows the energy dispersive X-ray spectroscopy (EDAX) of $Ge_{25}Se_{63}Sb_{12}$ thin films deposited on Si (100) substrate. The EDAX spectrum shows the peaks of Ge, Se, and Sb, thereby, confirming the presence of these elements in the samples. Thin films have been deposited on silicon wafer substrate and the silicon in the EDAX spectra shows very high intensity as compared to Ge, Se and Sb. Therefore, the peaks corresponding to Ge, Se and Sb are not much significant as compared to silicon peak, but the presence of all the elements have been observed as per our alloy composition. It is also observed that the composition obtained from EDAX analysis is almost same as that of starting composition of the as-prepared alloys.
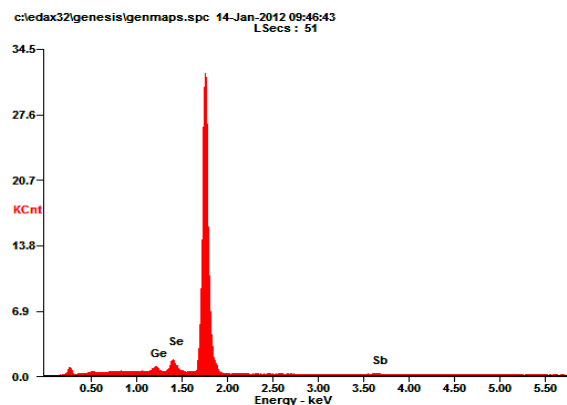

Fig. 1 – EDAX of $Ge_{25}Se_{63}Sb_{12}$ thin films deposited on Si (100) wafer

The surface morphology of $Ge_{25}Se_{60}Sb_{15}$ powder was examined by means of JEOL JSM-6360LV, Japan, scanning electron microscopy (SEM), shown in Fig. 2, which confirms the amorphous state of the samples.
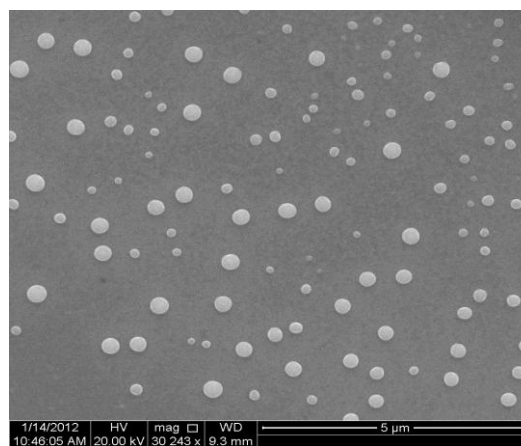

Fig. 2 – SEM of as-prepared $Ge_{25}Se_{60}Sb_{15}$ glasses

A Regaku X-ray diffractometer Ultima IV was employed for studying the structure of the as-prepared and crystallized samples (collected from the DSC pans after completing the scan).

Copper target was used as the X-ray source with $\lambda = 1.54178$ Å (Cu Kα_1). The scanning angle was in the range of 10°-90°. A scan speed of 2°/min and a chart speed of 1 cm/min were maintained. The X-ray diffraction traces of all samples were taken at room temperature and found to show similar trends and hence only one of them is shown in Fig. 3a and b.

The absence of sharp structural peak confirms the amorphous state of the samples while the presence of the sharp peaks confirms the crystalline nature of the samples.

3.2 Glass Transition (T_g) and Crystallization (T_c) Temperature and Enthalpy Released

Fig. 3 represents the DSC thermograms of $Ge_{25}Se_{69}Sb_6$ glass recorded at different heating rates 5, 10, 15 and 20 K/min. (Similar trends has also been observed by other glassy systems bur are not shown here).
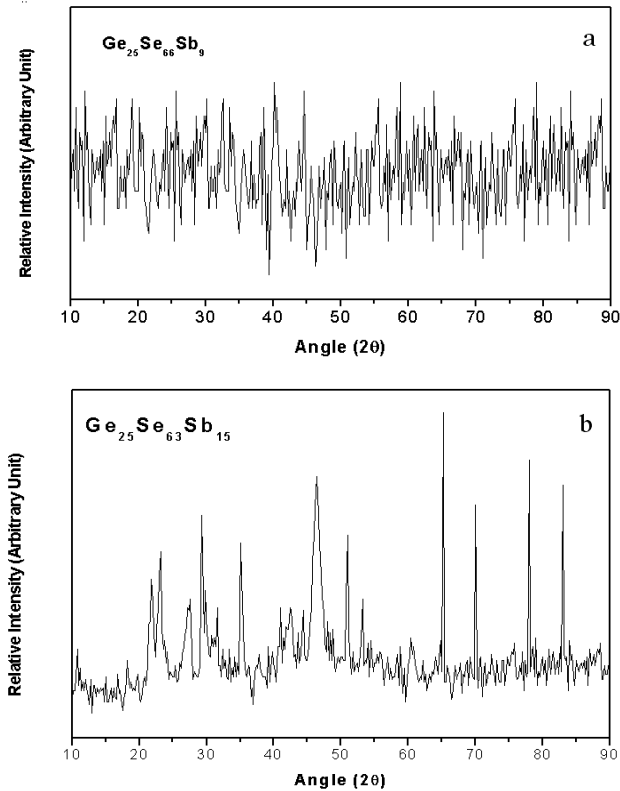
Fig. 3 – X-ray pattern of $Ge_{25}Se_{66}Sb_9$ sample (a) and X-ray pattern of crystallized $Ge_{25}Se_{60}Sb_{15}$ sample (b)

Fig. 4 – DSC plot of $Ge_{25}Se_{69}Sb_6$ glasses at different heating rates 5, 10, 15 and 20.

Two characteristic phenomena are evident in these DSC thermograms: (1) endothermic-like phenomenon indicating the glass transition region and (2) an exothermic phenomenon that manifest the crystallization process. The first order phase transformation in these glasses is characterized by measuring the glass transition (T_g) and crystallization temperature (T_c) with Sb contents and also the heating rates. The values of glass transition (T_g) and crystallization temperature (T_c) with Sb contents at the heating rate of 20 K/min are given in Table 1. It is clear from this table that T_g increases with increasing Sb contents in the Ge-Se system. The increase in T_g could be attributed either to the increase in effective molecular weight with increasing Sb content or to the increase in concentration of long polymeric chains of Ge-Se.

The T_g of a multi-component glass is known to be dependent on several independent parameters such as band gap, co-ordination numbers, bond energy, effective molecular weight, the type and fraction of various structural units formed [24-26]. In our study T_g increases with increasing Sb concentration. Theoretically, T_g is defined as the temperature at which the relaxation time τ becomes equal to the relaxation time of observation τ_{obs}. At the same time, T_g varies inversely [27] as the relaxation time. With increasing Sb concentration, τ_{obs} decreases and hence the glass transition temperature increases.

Both ($T_c - T_g$) and T_c represent the thermal stability of the glass. The values of ($T_c - T_g$) for different compositions are given in Table 1. It is clear from this table that ($T_c - T_g$) is highest for the composition of 6 % of Sb. Hence the glass with 6 % of Sb is most stable glass.

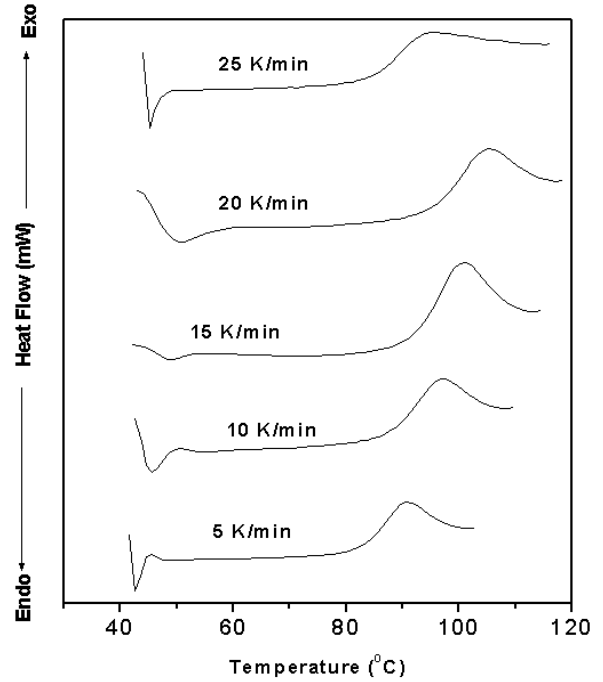The crystallization enthalpy ΔH_c was evaluated for all composition using the formula

$$\Delta H_c = kA / m, \tag{1}$$

where $k = 1.5$ is the constant of the instrument, A is the area of crystallization peak and m is the mass of sample.

The enthalpy released is found to be less for $Ge_{25}Se_{69}Sb_6$ glass which further confirms its maximum stability of this glass.

3.3 Activation Energy of Crystallization (ΔE_c)

The interpretation of the experimental crystallization data is given on the basis of Kissinger's, Matusita's and modified Ozawa's equations for non-isothermal crystallization. The activation energy (ΔE_c) for crystallization can therefore be calculated by using Kissinger's equation [10-11],

$$\ln (\beta / T_c^2) = -\Delta E_c / RT_c + D \text{ [4]}$$

The plot of $\ln (\beta / T_c^2)$ versus $1000 / T_c$ for $Ge_{25}Se_{66}Sb_9$ chalcogenide glasses are shown in Fig. 5, which come to be straight lines (similar trends has also been observed for other glasses and are not shown hear). The value of ΔE_c may be calculated from the slope of each curve and is given in Table 1.

The activation energy of crystallization increases with increasing Sb content in Ge-Se system, indicating that the rate of crystallization is faster as the Sb content increases. The increase in activation energy of crystallization may be interpreted in terms of increased hoping conduction in impurity induced states [28]. At higher concentration, alloying effect observed which could change the mobility gap and various other parameters of the original materials. The activation energy of crystallization is an indication of the speed of rate of crystallization.

Table 1 – Compositional dependence of crystallization parameters T_c, T_g, $(T_c - T_g)$, crystallization enthalpy (ΔH_c) and activation energy of crystallization (ΔE_c) of $Ge_{25}Se_{75-x}Sb_x$ from non-isothermal DSC experiments at a heating rate of 20 K/min

Sample	T_g (K)	T_c (K)	$(T_c - T_g)$ (K)	(ΔH_c) (J/mg)	ΔE_c (kJ/mole)
$Ge_{25}Se_{69}Sb_6$	323.25	389.19	65.94	1986.38	85.024
$Ge_{25}Se_{66}Sb_9$	327.34	384.16	56.82	2564.75	92.956
$Ge_{25}Se_{63}Sb_{12}$	331.21	379.46	48.25	3248.46	102.426
$Ge_{25}Se_{60}Sb_{15}$	336.44	372.13	35.69	4456.24	105.752
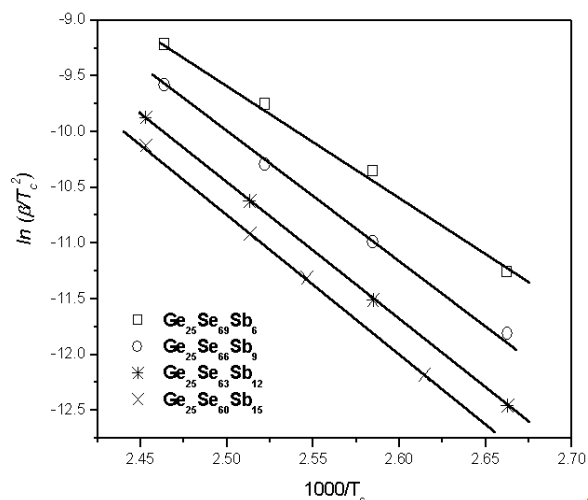
Fig. 5 – Plot of $\ln(\beta / T_c^2)$ as a function of $1000 / T_c$ (K) for $Ga_{15}Se_{85-x}Ag_x$ glass

4. CONCLUSIONS

Non-isothermal DSC measurements were performed to study the first order phase transformation in $Ge_{25}Se_{75-x}Sb_x$ chalcogenide glasses. It indicates that glass transition and crystallization temperatures depend on the heating rate and on Sb concentration. 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. The temperature difference $(T_c - T_g)$ and T_c is highest for the samples with 6 % of Sb. Hence, $Ge_{25}Se_{69}Sb_6$ glass is most stable. The enthalpy released is found to be less for $Ge_{25}Se_{69}Sb_6$ glass which further confirms its maximum stability. The activation energy of crystallization (ΔE_c) increases with increasing Sb contents in Ge-Se system, which indicates that the speed of rate of crystallization is faster with increasing Sb concentration in the present system.

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