Thermal stability and glass transition kinetics in GeTeSb glasses by using non-isothermal measurement

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In this paper we have analysed the thermal properties of three different compositions of chalcogenide glasses $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5). The samples have been prepared using the melt quenching technique and the characterisation is done using X-ray diffraction. The compositional dependence on properties were studied using Differential Scanning Calorimetry (DSC) analysis using non-isothermal measurement. The glassy sample crystallized by two transition temperatures T_{g1} and T_{g2}.The dependence of glass transition temperature on heating rate has been studied by Lasocka empirical relation and the Kissinger equation. As a result, the apparent activation energy for glass transition has been determined. Thermal stability has also been determined from the temperature difference between the onset crystallization and glass transition temperature.

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Keywords: Chalcogenide glasses, Differential scanning calorimetry, Glass transition temperature, Activation energy

1. Introduction

As of late, chalcogenide materials are broadly examined for their potential applications both in active additionally to detached solid-state gadgets and optical devices[1-6].It has been found that the chalcogenide is of special interest, due to its device applications such as optical fibers [7], reversible phase change optical recording [8], memory switching [9], X-ray imaging [10], xerography [11], electrographic applications such as photoreceptors in photocopying and laser printing [12-14].Various studies has been done on impurities effect on optical, electrical and thermal properties of GeTeSb chalcogenide glasses. The glass-forming region is reduced and very close to eutectic and peritectic compositions [15]. This range of compositions exhibit double glass transition and double stage crystallisation during annealing. These phenomena have been widely studied in previous work [16-18]. The addition of Antimony to GeTe glasses causes a marked change in their thermal properties. The present research is centered on the study of the Sb integration's effectiveness on varied thermal parameters GeTe binary system using differential scanning calorimetry**.** The dependence of T_g on the heating rate α has been studied using two approaches, the empirical relation suggested by Lasocka and the Kissinger equation**.** The activation energy of glass transition E_{g1} and E_{g2}have been determined using Kissinger models. Thermal stability has also been determined from the temperature difference between the onset crystallization and glass transition temperature.

2. Experimental

Glassy powders ofthe $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) were prepared by the melt quenching technique, high purity (99.999%) elements were weighed according to their atomic percentage, and were sealed in a quartz ampoule in a vacuum (10^{-5}torr). The sealed ampoules were placed

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inside a furnace and the temperature of the furnace was raised from room temperature to 1000°C at a rate of 4°C/min, the ampoules were rocked frequently for 10h to make the melt homogeneous, each ampoule is then quenched in icy water to obtain the composition in the glass state. The glassy nature of the sample was confirmed by X-ray diffraction measurements which shown in Figure 1.

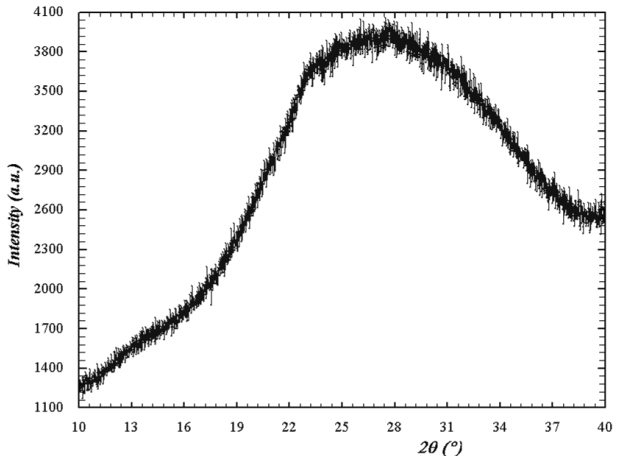

Fig.1.XRD pattern $Ge_{14.5}Te_{84.5}Sb_{01}$ glassy alloy.

3. Results and discussions

3.1. Non-isothermal crystallization kinetics

For DSC studies, we have taken 10 mg of each sample of $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) glassy alloys. The differential scanning calorimetry curves of glassy alloys $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) glasses were recorded at heating rate 10˚C/min is shown in figure 2.The DSC curves contains two region in which they are divided into two peaks. The first region represents glass transitions T_{g1} as well as T_{g2} while the second one shows two crystallization peaks.

The obtained values of glass transition temperature T_{g1} and T_{g2} with different compositions and heating rates at 3, 5, 7 and 10 K/min are given in table 1 while in table 2, the peak glass transition temperatureT_{gp1} and $T_{gp2}$with different compositions are represented.

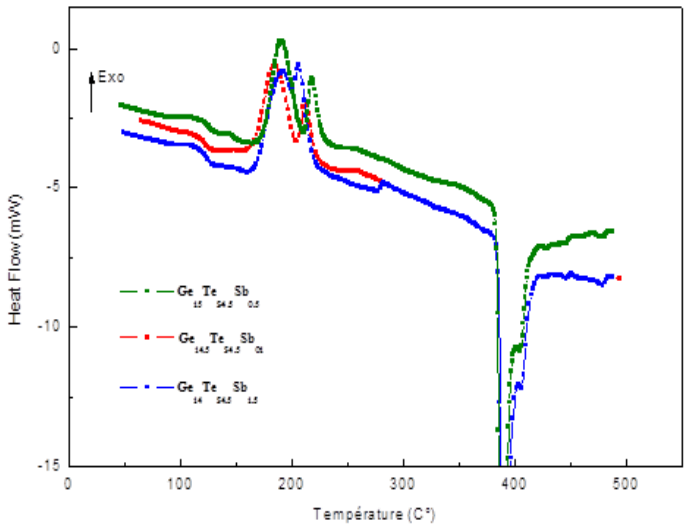

Fig.2.DSC curves for $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) glassy alloys at heating rate of 10°C/min.

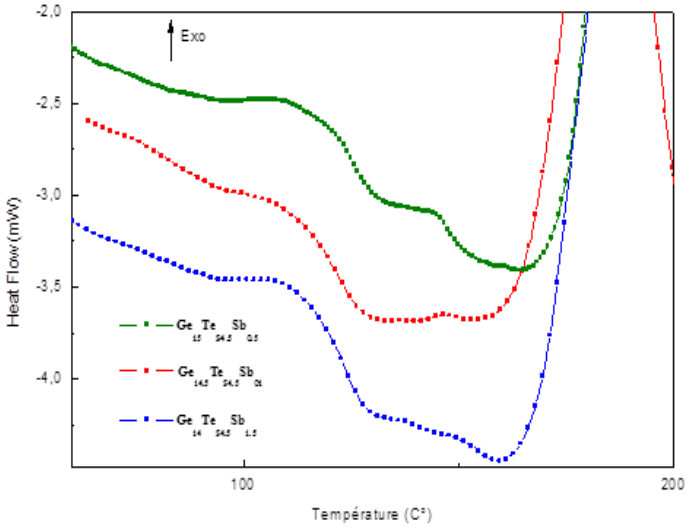

Fig.3. Glass transition region for $Ge_{15}Te_{85-x}Sb_x$ *(x=0.5, 1, 1.5) glassy alloys at heating rate of 10°C/min.*

Table 1.The values of glass transition temperature T_g *at different heating rates 3, 5, 7, 10°C/min for* $Ge_{15}Te_{85-x}Sb_x$ *(x=0.5, 1, 1.5)glassy alloys.*

Heating rate (°C/min)	$Ge_{15}Te_{84.5}Sb_{0.5}$		$Ge_{14.5}Te_{84.5}Sb_{01}$		$Ge_{14}Te_{84.5}Sb_{1.5}$	
	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
03	90	105	79	110	72	121
05	111	120	101	128	93	138
07	120	138.7	110.6	144.8	102	149
10	126	145	117	150	113	158

Table 2.The values of glass transition temperature T_{gp} *at different heating rates 3, 5, 7, 10°C/min for* $Ge_{15}Te_{85-x}Sb_x$ *(x=0.5, 1, 1.5)glassy alloys.*

Heating rate (°C/min)	$Ge_{15}Te_{84.5}Sb_{0.5}$		$Ge_{14.5}Te_{84.5}Sb_{01}$		$Ge_{14}Te_{84.5}Sb_{1.5}$	
	T_{g1P} (°C)	T_{g2P} (°C)	T_{g1P} (°C)	T_{g2P} (°C)	T_{g1P} (°C)	T_{g2P} (°C)
03	101	111	92	117	84	130
05	116	127	110	137	102	146
07	123	13	119	151	108	155
10	135	152	126	158	120	164

From the tables (1,2) we can notice that the glass transition temperature increases with increasing the Sb content. The glass transition Temperature is known to depend on several independent parameters such as the average coordination number [19,20].

3.2. Glass transition région

The dependence of T_g on the heating rate α has been studied using two approaches, the first approach is the empirical relation suggested by Lasocka [21] in the form:

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

where A and B are constants for a given glass composition, the value of A indicates the glass transition temperature for the heating rate of 1°C/min, while B is proportional to the time taken by the system to reduce its glass transition temperature T_g , when its heating rate is lowered from 10 to 1 K/min [22], the value of A and B can be obtained from the slop of straight line of the plot T_g versus lnα .Figure4 show the plot of T_g versus lnα for different composition$Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) glassy systems. The values A and B are given inTable3.

The second approach is the evaluation of activation energy of the glass transition using the Kissinger equation [23] relating, the peak temperature T_{gp} with heating rate α is written as:

$$\ln\left(\alpha / T_{gp}^{\,2}\right) = -E_g / RT_{gp} + \text{constant} \quad (2)$$

Where E_g is the activation energy of the glass transition, T_{gp} is the peak glass transition temperature, α is the heating rate and R is the universal gas constant. The activation energy of the glass transition $E_g$is calculated from the slopes of the plots between ln(α / T_{gp}^2) and 1000/T_{gp} in Fig. 5, the values of the activation energy of glass transition are listed in Table 4. From Table 4 the value of E_g decreases with increasing Sb.

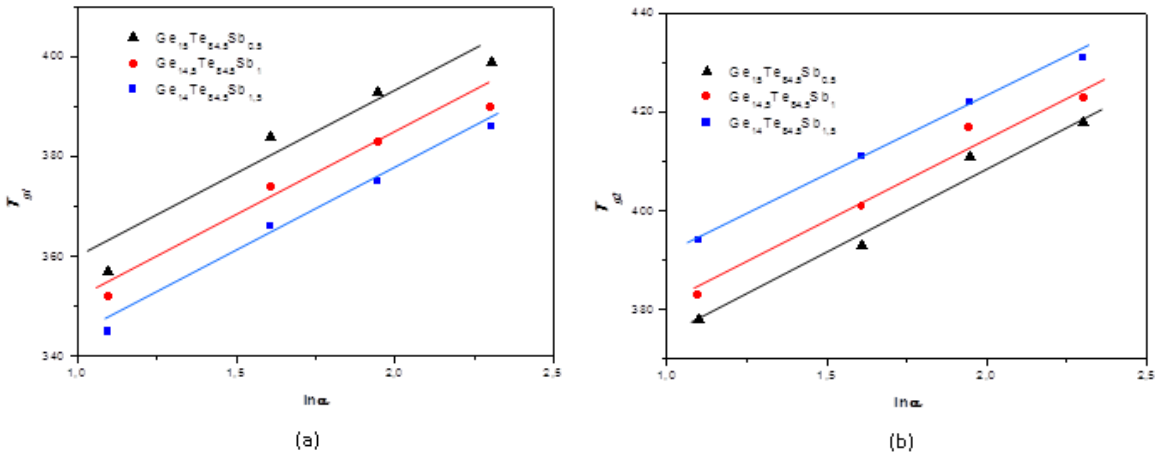

Fig.4.Plots of Lasocka (a) T_{g1}versus ln(α), (b) T_{g2} versus ln(α).

Table 3.Values of Lasocka's parameters A and B of $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5)glasses.

Composition	A_{Tg1}(K)	A_{Tg2}(K)	B_{Tg1} (min)	B_{Tg2}(min)
$Ge_{15}Te_{84.5}Sb_{0.5}$	322,26 ± 11.50	339.44 ± 6.90	35.06 ± 6.41	34.82 ± 3.84
$Ge_{14.5}Te_{84.5}Sb_1$	319.59 ± 7.43	345.84 ± 6.70	31.71 ± 4.13	34.59 ± 3.73
$Ge_{14}Te_{84.5}Sb_{1.5}$	309.28 ± 4.19	360.53 ± 2.39	33.76 ± 2.34	31.03 ± 1.33

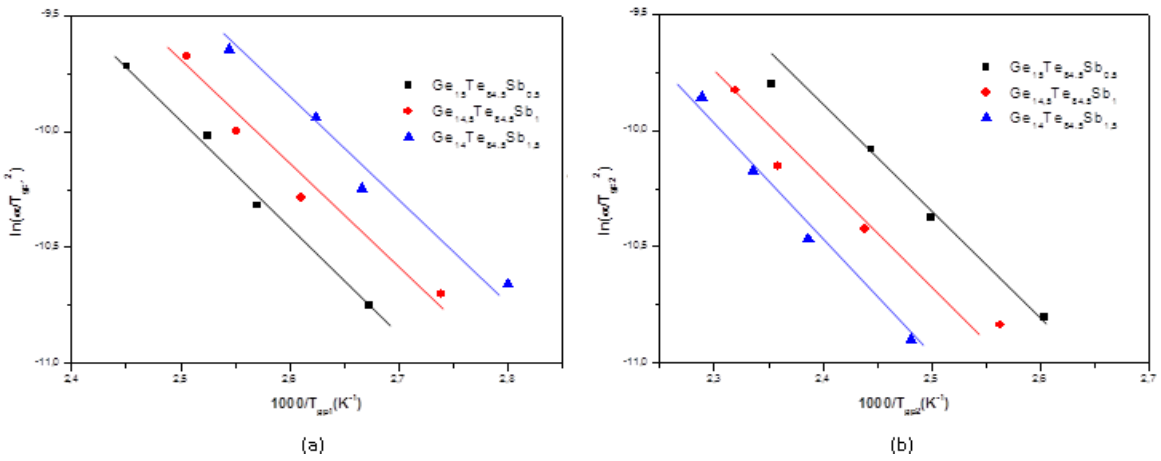

Fig.5. Kissinger Plots(a) $ln(\alpha/T_{gp1}^2)$ versus $1000/T_{gp1}$, (b) $ln(\alpha/T_{gp2}^2)$ versus $1000/T_{gp2}$.

Table 4. Values of activation energy of glass transition E_{g1} and E_{g2} for $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) glasses as obtained from Kissinger relation.

Composition	E_{g1}(KJ/mol)	E_{g1}(eV)	E_{g2}(KJ/mol)	E_{g2}(eV)
$Ge_{15}Te_{84.5}Sb_{0.5}$	39.08 ± 2.29	0.41± 0.02	33.70 ± 2.29	0.35 ± 0.02
$Ge_{14.5}Te_{84.5}Sb_1$	35.17 ± 4.56	0.37± 0.05	32.22 ± 4.25	0.33 ± 0.04
$Ge_{14}Te_{84.5}Sb_{1.5}$	33.16 ± 3.45	0.34± 0.04	31.46 ± 2.82	0.46 ± 0.03

The dependence of T_g on the heating rate could be interpreted in terms of thermal relaxation phenomena. Theoretically, T_g is defined as the temperature at which the relaxation time τ becomes equal to an experimental time of observation τ_{obs}. At the same time, T_g varies inversely with the relaxation time [4]. With the increase of the heating rate, τ_{obs} decreases and, hence, T_g increases. The increasing value of activation energy E_{g1} for glass transition can be explained using the heat of atomization, which increases on the addition of Sb. The increase in E_g indicates that the probability of the system toward devitrification decreases on Sb alloying

3.3. Thermal stability

In non-isothermal study, the temperature difference between the onset temperature of crystallization T_c and the glass transition temperature T_g is important indicator of the thermal stability [25] as well Thermal stability and glass-forming ability of alloys depend upon the stoichiometric component of elements. Figure 6 shows the variation of $T_c - T_g$ with percentage composition of Sb in the $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) glasses. It is also noted from figure 6 (a) that the thermal stability is at a maximum when the Sb content reaches 1.5 at. % for $Ge_{15}Te_{85-x}Sb_x$ and highest for$Ge_{15}Te_{84.5}Sb_{0.5}$is shown in figure 6 (b).

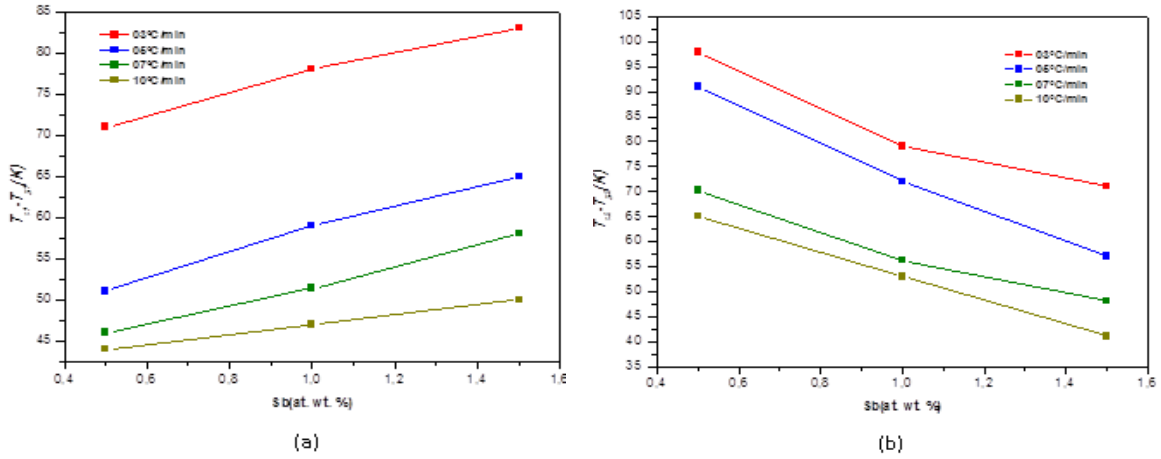

Fig.6.(a) Variation of T_{c1}– T_{g1} with atomic weight percentage of Sb;(b) Variation of T_{c2} – T_{g2} with atomic weight percentage of Sb.

4. Conclusion

A study of glass transition kinetics of phase transformation of $Ge_{15}Te_{85-x}Sb_x$ (x=0.5, 1, 1.5) chalcogenide glasses has been performed by DSC. DSC curves show two glass transition peaks and two crystallization peaks indicating good homogeneity of glass. Glass transition temperature T_{g1} and T_{g2} increase with heating rate. Activation energy of glass transition E_g has been evaluated using Kissinger relation.

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