

The effect of Sb content on glass-forming ability, the thermal stability, and crystallization of Ge–Se chalcogenide glass

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Abstract The glass formation and devitrification of intermediate alloys in the Sb–Ge–Se system were studied by differential scanning calorimetry. A comparison of various simple quantitative methods to assess the level of stability of the glassy materials in the above mentioned system is presented. All of these methods are based on characteristic temperatures, such as the glass transition temperature, T_g , the onset temperature of crystallization, T_{in} , the temperature corresponding to the maximum crystallization rate, T_p , or the melting temperature, T_m . In this case, k_{gl} may be more suitable for estimating the glass thermal stability in above composition range than ΩT . In this work the parameter $K_r(T)$ is added to the stability criteria. The thermal stability of some ternary compounds of the Sb–Ge–Se type has been evaluated experimentally and correlated with the activation energies of crystallization by this kinetic criterion and compared with those evaluated by other criteria. All the results of criteria and kinetic parameter $K_r(T)$ confirm that the thermal stability decrease with increasing Sb content in the glassy system. The crystallization results are analyzed and both the activation energy of crystallization process and the crystallization mechanism are characterized. Finally, identification of the crystalline phases was made by recording the X-ray diffraction pattern of the transformed material. This pattern shows the existence of microcrystallites of two phases, the first is germanium Selenide $GeSe_2$ and the second is Sb_2Se_3

in amorphous matrix for annealed of $Sb_{2.5}Ge_{22.5}Se_{75}$ and $Sb_{10}Ge_{15}Se_{75}$ glass.

Keywords Sb–Ge–Se · Thermal stability · Crystallization kinetics · XRD

Introduction

The glassy alloys of chalcogen elements were an initial object of study because of their interesting semiconducting properties [1, 2] and more recent importance in optical recording [3]. Chalcogenide materials are becoming more and more popular due to their applications as infrared optical fibers, reversible phase change optical recording, etc. [4]. Infrared transmitting glasses based on Ge–Sb–Se are technologically important because they are good transmitters of radiation in the 2–16 μm wavelength region. The applications include fabrication of optical components like IR lenses, windows and filters used in thermal imaging systems. They are less sensitive to the presence of impurities. The Sb–Ge–Se films result sensitive for the UV exhibit mechanical, optical, and structural changes [5, 6]. Crystallization studies upon heating can be performed by two basic methods: isothermal and non-isothermal transformation [7, 8]. An understanding of the glass forming tendency and crystallization kinetics in these chalcogenide materials is very important to develop them for applications based on the amorphous to crystallization phase change and vice versa. A differential scanning calorimetry analysis is generally used to study the crystallization kinetics. In this study, the thermal stability of $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$), glasses has been discussed based on characteristic temperatures such as the glass transition temperature, T_g , the crystallization temperature,

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T_p , and the melting temperature, T_m . These thermal parameters are easily and accurately obtained by differential scanning calorimetry (DSC) during the heating processes of glassy alloy. The first thorough study on the glass thermal stability of various compounds was done by Sakka and Mackenzie [9], using the ratio T_g/T_m . Dietzel [10] introduced the glass criterion, $\Delta T = T_{in} - T_g$ (T_{in} is the onset temperature of crystallization), which is often an important parameter to evaluate the glass forming ability of the glasses. By the use of the characteristic temperatures, Hruby [11] developed the H_r criterion, $H_r = \Delta T / (T_m - T_p)$. Saad and Poulain [12] obtained two criteria, weighted thermal stability H' and S criterion, $H = \Delta T / T_g$, $S = (T_p - T_{in}) \Delta T / T_g$, respectively. The glass-formation factor of the materials is given by $k_{gl} = (T_{in} - T_g) / (T_m - T_g)$, and it is more suitable for estimating the glass thermal stability in above composition range than ΩT . The higher values of criterion parameters reflect the greater thermal stability of the glass.

On the other hand, in term of the formal theory of transformation kinetics, the kinetic parameter or the reaction rate constant has a temperature dependency according to the relation

$$K(T) = K_0 \exp(-E_c/RT) \quad (1)$$

where E_c is the effective activation energy for crystal growth and R is the gas constant. In addition, a kinetic parameter, $K(T)$, with an Arrhenian temperature dependence, is introduced to the stability criteria. Surinach et al. [13] and Hu and Jiang [14] introduced two criterion $K(T_g) = K_0 \exp(-E_c/RT_g)$ and $K(T_p) = K_0 \exp(-E_c/RT_p)$. In order to evaluate the thermal stability of glassy materials. Thus, the values of these two criterion indicate the tendency of glass to devitrify on heating. The larger their values are the greater tendency to devitrify.

The H_r parameter itself is a stability factor based on characteristic temperatures. Here, a stability criterion is defined as [14]

$$K_r(T) = K_0 \exp\left(\frac{-H_r E_c}{RT}\right) \quad (2)$$

where T is any temperature between T_g and T_p . The theoretical background for the definition of the parameter $K_r(T)$ would be based on the analysis of the relation between the parameters $K(T)$ and $K_r(T)$. Differentiating Eqs. 1 and 2 with respect to temperature and rewrite each parameters, results in

$$\frac{\Delta K_r}{K_r \Delta T} = \frac{H_r E_c}{RT^2} \frac{\Delta K}{K \Delta T} = \frac{E_c}{RT^2}$$

It should be noted that the above-mentioned variation of the parameter $K_r(T)$ is H_r times the variation in parameter

$K(T)$, which could justify the accuracy of the parameter. Just like the $K(T)$ criteria, the smaller the values of $K_r(T)$ are the greater thermal stability of the glass. The obvious advantage of this method is that it can evaluate the glass stability over a broad temperature range other than at only one temperature such as T_g or T_p .

Experimental

Bulk chalcogenide $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$) glasses were made from their components of 99.999% high purity. The proper amount for each material was weighed, and then the weighed materials were introduced into cleaned silica tubes. To avoid the oxidation of the samples the tubes were evacuated to 10^{-4} Pa. The ampoules were put into a furnace at around 900 K for 24 h. The ampoule was inverted at regular intervals of time to ensure homogeneous mixing of the constituents, and then the ampoule was quenched in a water bath to avoid crystallization. Both the homogeneity and the compositional contents of the prepared samples were checked using the energy dispersive analysis of X-rays (EDAX). It was found that the percentage ratios of the constituent elements are $Ge_{24.8 \pm 0.15}Se_{74.2 \pm 0.7}$, $Sb_{2.4 \pm 0.06}Ge_{22.4 \pm 0.25}Se_{74.3 \pm 0.7}$, $Sb_{4.9 \pm 0.55}Ge_{19.8 \pm 0.12}Se_{74.4 \pm 0.5}$, $Sb_{7.3 \pm 0.08}Ge_{17.4 \pm 0.1}Se_{74.7 \pm 0.8}$ and $Sb_{9.8 \pm 0.05}Ge_{14.8 \pm 0.11}Se_{74.3 \pm 0.5}$ according to the measurement performed using electron microprobe analysis. The glassy nature of the material was confirmed through a diffractometric X-ray scan, in a Philips diffractometer 1710, using Cu as target and Ni as filter ($\lambda = 1.542 \text{ \AA}$), showing an absence of the peaks, which are characteristic of crystalline phases.

The calorimetric measurements were carried out using differential scanning calorimeter Shimadzu 50 with an accuracy of ± 0.1 K. 20 mg powdered samples, crimped into aluminum pans and scanned at continuous heating rates ($\beta = 5, 10, 20, 30, 40 \text{ K min}^{-1}$). The value of the glass transition, T_g , the crystallization extrapolated onset, T_{in} and the crystallization peak, T_p , temperature were determined with accuracy ± 1 K by using the microprocessor of the thermal analyzer.

Results and discussion

Glass forming tendency in ternary $Sb_xGe_{25-x}Se_{75}$ glassy alloys

Figure 1 shows the DSC traces for $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$) glasses at heating rate $\beta = 10 \text{ K/min}$. The characteristic features of this curve of the considered glass show the appearance of a small single endothermic peak, this peak is attributed to the glass transition temperature, which

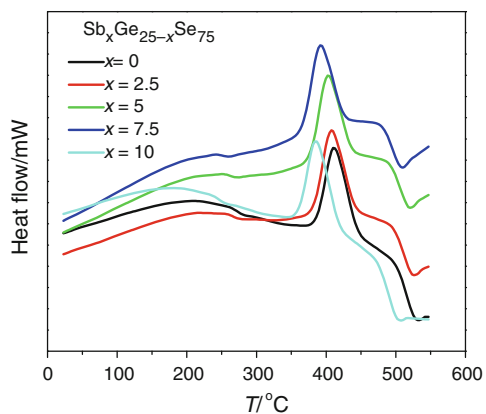


Fig. 1 Typical DSC trace of $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$) glass at heating rate, $\beta = 10$ K/min

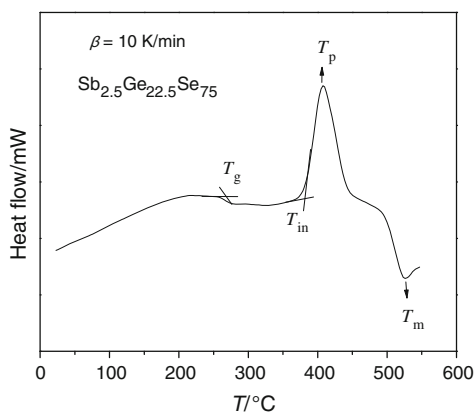


Fig. 2 shows the DSC curve of amorphous $Sb_{2.5}Ge_{22.5}Se_{75}$ chalcogenide glass recorded at heating rate $\beta = 10$ K/min

represents the strength or rigidity of the glass structure. Also, there is an exothermic peak originating from the amorphous-crystalline transformation. The exothermic peak has two characteristic points: the first point is the onset temperature of crystallization (T_{in}) and the second is the peak temperature of crystallization (T_p). This figure also shows the characteristic melting temperatures T_m .

Figure 2 shows the DSC thermograms of amorphous $Sb_{2.5}Ge_{22.5}Se_{75}$ chalcogenide glass recorded at heating rate $\beta = 10$ K/min. This figure shows that, the glass transition temperature, T_g , the crystallization temperature, T_p , and the melting temperature, T_m .

The characteristic temperatures T_g , T_{in} , T_p , and T_m from DSC scans as a function of Sb content at heating rate $\beta = 10$ K/min are given Table 1. The glass forming ability of the mentioned glasses studied can be estimated by using these characteristic temperatures. The deduced values of k_{gl} , as a function of Sb content at heating rate $\beta = 10$ K/min are given in Table 1. The decrease in k_{gl} with

Table 1 The values of thermal parameters of glass transition temperature T_g , onset temperature of crystallization T_{in} , crystallization temperature T_p and melting temperature T_m of $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$) alloys with different heating rates β

Alloy	β	$T_g/^\circ C$	$T_{in}/^\circ C$	$T_p/^\circ C$	$T_m/^\circ C$	K_{gl}	H_r	H'	$S/^\circ C$
Ge₂₅Se₇₅									
	5	248	396	408	531				
	10	261	407	419	541	1.08	1.18	0.56	6.67
	20	273	419	430	553				
	30	280	424	437	563				
	40	283	429	444	572				
Sb_{2.5}Ge_{22.5}Se₇₅									
	5	249	382	394	516				
	10	261	393	404	526	0.98	1.07	0.5	5.53
	20	274	405	414	538				
	30	279	410	420	548				
	40	284	415	425	557				
Sb₅Ge₂₀Se₇₅									
	5	253	374	386	507				
	10	264	385	396	517	0.92	1.01	0.46	5.06
	20	277	397	406	529				
	30	282	402	412	539				
	40	287	407	417	548				
Sb_{7.5}Ge_{17.5}Se₇₅									
	5	256	366	378	502				
	10	266	377	388	512	0.82	0.9	0.42	4.73
	20	278	389	398	524				
	30	284	394	404	534				
	40	288	399	409	543				
Sb₁₀Ge₁₅Se₇₅									
	5	259	360	370	498				
	10	268	371	381	508	0.75	0.81	0.38	3.79
	20	279	383	392	520				
	30	285	388	398	530				
	40	289	393	404	539				

The characteristic parameters K_{gl} , H_r , H' , and S at $\beta = 10$ °C/min according to the text. Temperature were determined with accuracy ± 1 K by using the microprocessor of the thermal analyzer

increasing Sb content reveals that the glass-forming ability decreases with increasing Sb content. This effect implies a greater crystallization tendency in glasses containing larger concentration of Sb. The existing stability criterion parameters based on these characteristic temperatures, H_r , H' , and S as a function of Sb content at different heating Table 1. It is found the values of these criteria decrease with increasing antimony content. Bearing in mind that the values of these parameters increase with increasing stability, it is possible to suggest that the higher the antimony content of the glass, the lower is its glass thermal stability [15–17].

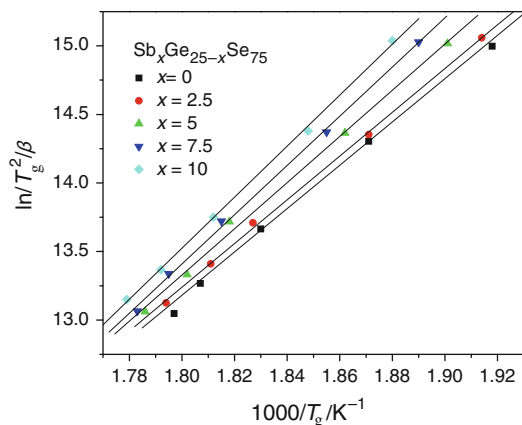


Fig. 3 Plot of $\ln[T_g^2/\beta]$ versus $1000/T_g$ of the analyzed materials

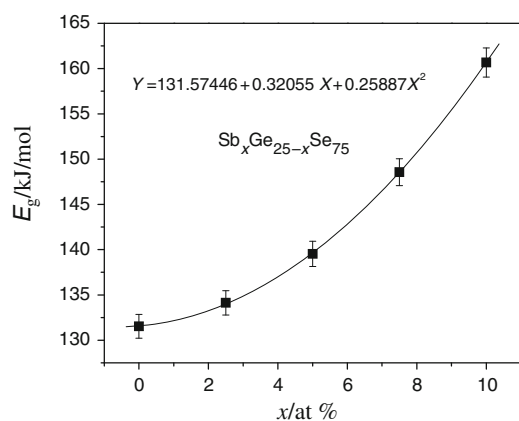


Fig. 4 Activation energy of transition E_g as a function of Sb content in $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$) glassy system

Determination the activation energy of glass transition, E_g of the investigated glass was obtained using the Kissinger formula, which is originally derived for the crystallization process and suggested to valid for glass transition [18]. This formula has the following form

$$\ln(T_g^2/\beta) = E_g/RT_g + \text{const.} \quad (3)$$

where R is the universal gas constant. A straight line between $\ln(T_g^2/\beta)$ and $1/T_g$, for different composition whose slopes yield a values of E_g (see Fig. 3), where the subscript g denotes magnitude values corresponding to the glass transition temperature. The effect of Sb content on the activation energy of glass transition E_g $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$) is shown in Fig. 4, from which one can observe the increase in E_g with Sb content. The increasing in the value of T_g with Sb content (as shown in Table 1) can be explained to some extent with the help of chemically ordered network model CONM wherein the formation of heteropolar bonds is favored over the formation of homopolar bonds. In the Sb–Ge–Se system, the various bonds involved are Se–Sb (51.45 kcal/mol), Ge–Se (49.4 kcal/mol) and Se–Se (44 kJ/mol). When the atomic

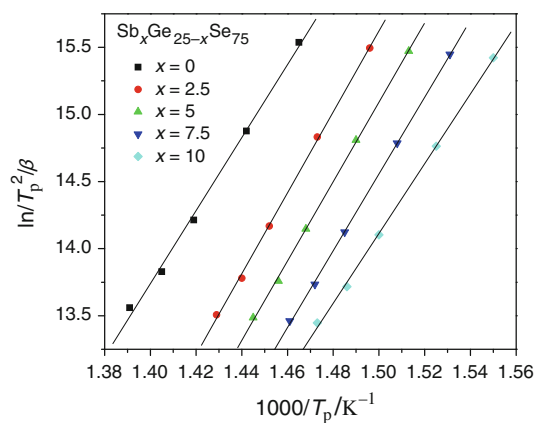


Fig. 5 Experimental plot of $\ln[T_p^2/\beta]$ versus $1000/T_p$ and straight regression lines for the different glassy alloys (β in $^\circ\text{C/s}$)

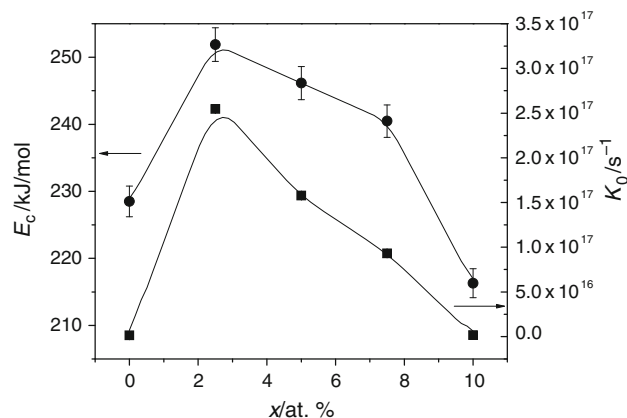


Fig. 6 The activation energy of crystallization, E_c , and frequency factor, K_0 of the analyzed alloys obtained from the straight regression lines fitted to values of $\ln[T_p^2/\beta]$ versus $1000/T_p$

percentage of Sb is increased in Sb–Ge–Se glass system, Sb is expected to combine preferably with Se because the bond energy of Se–Sb is greater than that of Ge–Se. This explains the increase in T_g with the increase in Sb content due to the formation of large number of heteropolar Sb–Se bonds and decrease in homopolar Se–Se and Ge–Ge bonds [19].

For the evaluation of activation energy for crystallization (E_c) by using the variation of T_p with β , Vázquez et al. [20] developed a Kissinger method for non-isothermal analysis of devitrification as follows:

$$\ln[T_p^2/\beta] = E_c/RT_p + \ln(E_c/RK_0) \quad (4)$$

Figure 5 represents the evolution of $\ln[T_p^2/\beta]$ versus $1/T_p$ for the different compositions. The plots were found to be straight lines. The activation energy, E_c , and frequency factor, K_0 , are then evaluated by least squares fitting method. Figure 6 shows the values for both E_c and K_0 as a function of Sb content. After knowing the values of E and

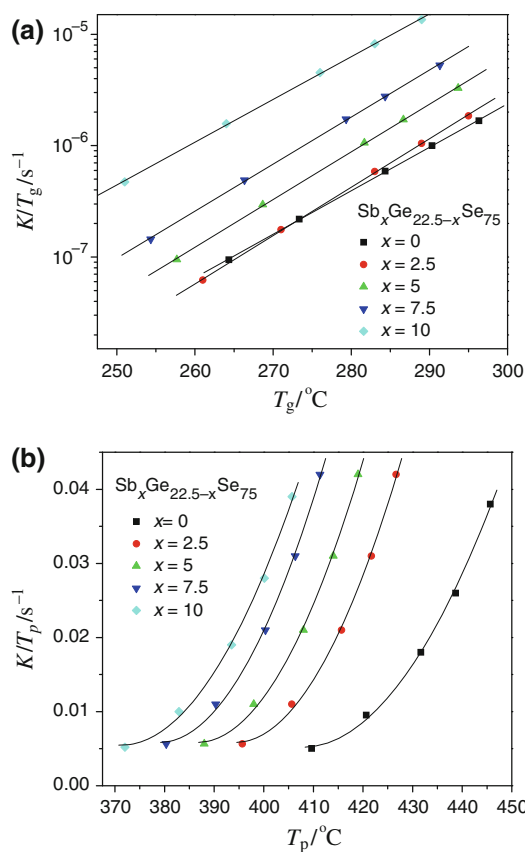


Fig. 7 Kinetics parameters: **a** $K(T_g)$ and **b** $K(T_p)$ versus characteristic temperature

K_0 , the kinetic parameters $K(T)$ and $K_r(T)$ of studied alloys were calculated by using the relationship (1) and (2), respectively. These calculations were carried out in order to compare the stability sequence of the studied materials from the quoted parameters with the corresponding sequence deduced from stability criteria based on characteristic temperatures. The values of $K(T_g)$ and $K(T_p)$ as a function of T_g and T_p for different compositions are shown in Fig. 7a and b. According to the literature [15–17], the smaller the values of $K(T_g)$ and $K(T_p)$ criteria, the better should be the glass-forming ability of the material. So the data for both $K(T_g)$ and $K(T_p)$ indicate that the thermal stability decrease with increasing Sb content. In addition, by using Eq. 2, the data of $K_r(T_g)$ and $K_r(T_p)$ were also calculated as a function of Sb content as shown in Fig. 8a and b, which confirm that the orders of stability decrease with increasing Sb content in $Sb_xGe_{25-x}Se_{75}$ ($0 \leq x \leq 10$). In comparison, Vázquez et al. [15] studied on the thermal stability in terms of characteristic temperature and kinetic parameters, which mentioned above in $Sb_xAs_{52-x}Se_{48}$ (with $x = 12, 16,$ and 20 at.%) glassy system. They found that the thermal

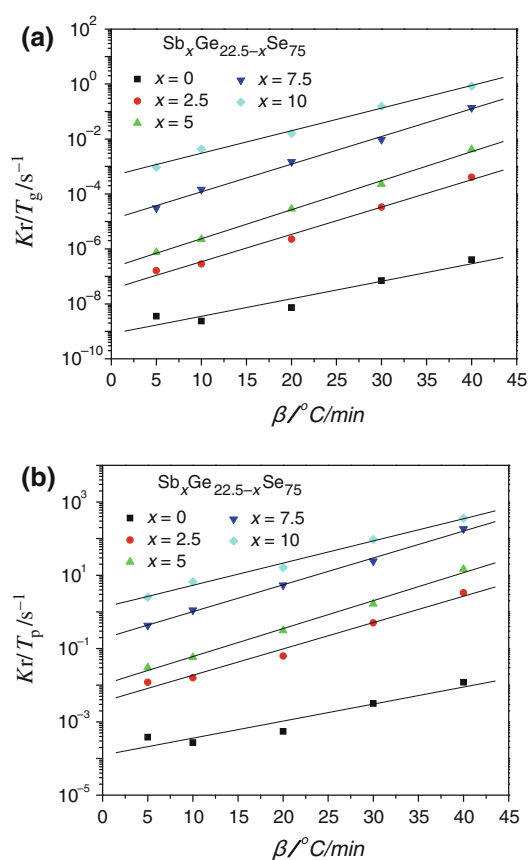


Fig. 8 Kinetics parameters: **a** $K_r(T_g)$ and **b** $K_r(T_p)$ versus heating rate β as a function of Sb content

stability of these glasses decreases with the increase of Sb content in agreement with the present work.

Crystallization rate and kinetic exponent

The theoretical basis for interpreting DSC results is provided by the formal theory of transformation kinetics as developed by Johnson and Mehl [21] and Avrami [22, 23]. The fraction, χ , crystallized at a given temperature, T , is given by $\chi = A_T/A$, where A is the total area of the exothermic between the temperature, T_i , where crystallization is just beginning and the temperature, T_f , where the crystallization is completed, A_T is the area between T_i and T , as shown in Fig. 9. The graphical representation of the volume fraction crystallized, shows the typical sigmoid curve as a function of temperature (see Fig. 10), in crystallization reactions, as it appears in the literature [24–26].

The ratio between the ordinates of the DSC curve and the total area of the peak gives the corresponding crystallization rates, which makes it possible to build the curves of the exothermal peaks represented in Fig. 11. It may be

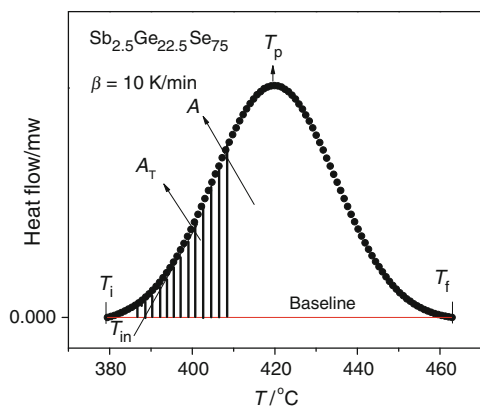


Fig. 9 DSC traces for $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ glass at heating rate $10\text{ }^\circ\text{C/s}$, the lined area AT shows between T_i and T_f of the peak. T_i , T_f , and T according to the text

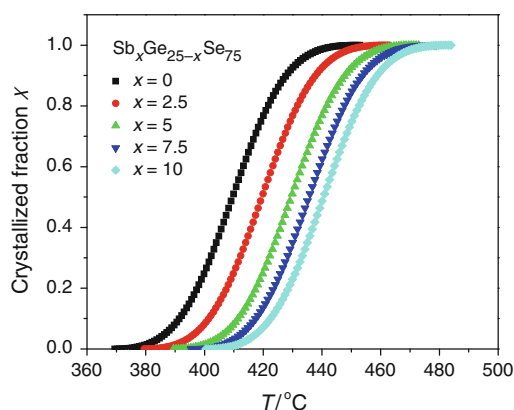


Fig. 10 Crystallized fraction as a function of temperature for $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ glassy system at different heating rates

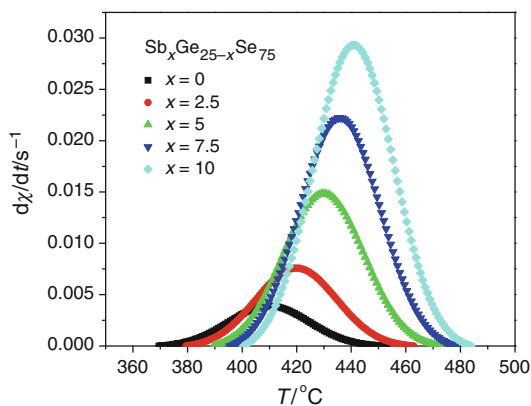


Fig. 11 Crystallization rate versus temperature of the exothermal peaks for $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ glassy system at different heating rates

observed that, the $(d\chi/dt)_p$ values increases as well as the heating rate, a property that has been widely discussed in the literature [27]. From the experimental values of the

$(d\chi/dt)_p$ one can calculate the kinetic exponent n by using the following equation

$$(d\chi/dt)_p = n(0.37\beta E_c)/(RT_p^2) \quad (5)$$

The n values for $\text{Sb}_x\text{Ge}_{25-x}\text{Se}_{75}$ glasses are calculated and listed in Table 2.

Finally, the experimental data, T_p , and $(d\chi/dt)_p$, shown in Table 1 and Table 2, respectively, and the above mentioned value of the activation energies of crystallization process for the crystallization peaks, make it possible to determine, through relationship (5), the kinetic exponent, n , for each of the experimental heating rates for the peaks for different composition, whose values are also given in Table 2, which one can observe the increase in $\langle n \rangle$ with Sb content. In comparison with another chalcogenide system, Shamshad and et al. [a] calculated the kinetic exponent, n for $\text{Se}_{80}\text{Te}_{20-x}\text{Pb}_x$ (with $x = 0, 2, 6$ and 10 at.%) glassy system. They found value of n increases with the increase of Pb content at expense of Te. These results are in good agreement with the present work.

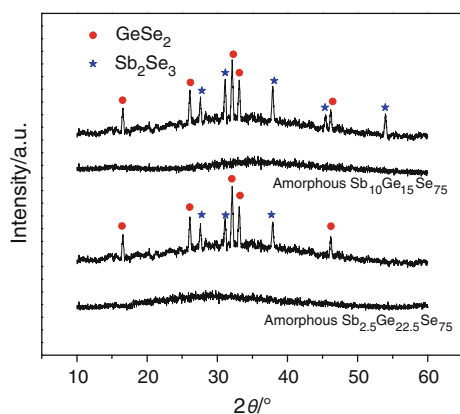
The kinetic exponent was deduced based on the mechanism of crystallization [28]. Mahadevan et al. [28] have shown that n may be 4, 3, 2, or which are related to different glass-crystal transformation mechanisms: $n = 4$, volume nucleation, three-dimensional growth; $n = 3$, volume nucleation, two-dimensional growth, $n = 2$, volume nucleation, one-dimensional growth; $n = 1$, surface nucleation, one-dimensional growth from surface to the inside. Therefore, bearing in mind the above obtained mean value, $\langle n \rangle = 2$ for the crystallization peaks, means volume nucleation, one-dimensional growth.

Identification of the crystalline phases

To identify the possible phases that crystallize during the thermal treatment applied to the samples, the X-ray diffraction patterns of $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ glasses annealed at 665 K for 2 h and also $\text{Sb}_{10}\text{Ge}_{15}\text{Se}_{75}$ glass annealed at 640 K for 2 h. For this purpose, Fig. 12 shows the most relevant portions of the diffractometer tracings for the as-quenched glasses and for the materials submitted to the thermal process. The diffractogram of the transformed material of $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ and $\text{Sb}_{10}\text{Ge}_{15}\text{Se}_{75}$ after the crystallization process suggests the presence of microcrystallites of two phases shown in Fig. 12. According to the JCPDS files, the first phase is germanium Selenide GeSe_2 (card No. 15-0404), which crystallizes in the orthorhombic crystal system with lattice parameters $a = 4.375 \pm 0.04$ nm, $b = 3.825 \pm 0.04$ nm and $c = 10.8 \pm 0.1$ nm. The second phase is antimony Selenide Sb_2Se_3 (card No. 15-0861), which crystallizes in the orthorhombic crystal

Table 2 Maximum crystallization rate $d\chi/dt$, kinetic exponent n , and average kinetic exponent $\langle n \rangle$ for $\text{Sb}_x\text{Ge}_{25-x}\text{Se}_{75}$ ($0 \leq x \leq 10$) alloys with different heating rates β

x $\beta/^\circ\text{C min}^{-1}$	0		2.5		5		7.5		10	
	$d\chi/dt$	n	$d\chi/dt$	n	$d\chi/dt$	n	$d\chi/dt$	n	$d\chi/dt$	n
5	3.15	1.73	3.88	1.86	4.2	2.01	4.57	2.19	4.78	2.48
10	6.14	1.75	7.58	1.87	8.19	2.02	8.91	2.2	9.32	2.5
20	12.1	1.77	14.92	1.89	16.13	2.05	17.54	2.23	18.35	2.54
30	18.05	1.8	22.26	1.92	24.06	2.07	26.17	2.26	27.37	2.58
40	23.81	1.81	29.36	1.92	31.74	2.08	34.52	2.27	36.11	2.59
$\langle n \rangle$		1.77 ± 0.033		1.89 ± 0.028		2.05 ± 0.032		2.23 ± 0.035		2.54 ± 0.048

**Fig. 12** XRD patterns of amorphous and crystallized for both $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ and $\text{Sb}_{10}\text{Ge}_{15}\text{Se}_{75}$ glass samples

system with lattice parameters $a = 11.633 \pm 0.1$ nm, $b = 11.78 \pm 0.1$ nm, and $c = 3.985 \pm 0.04$ nm.

Conclusions

The glass-forming ability of some alloys in $\text{Sb}_x\text{Ge}_{25-x}\text{Se}_{75}$ ($0 \leq x \leq 10$) system has been evaluated by using various thermal stability criteria, based on characteristic temperatures. It is found the values of these criteria decrease with increasing antimony content. Bearing in mind that the values of these parameters increase with increasing stability, it is possible to suggest that the higher the antimony content of the alloy, the lower is its glass thermal stability. The deduced values of k_{gl} , for the different compositions reveal that the glass-forming ability decreases with increasing Sb content. This effect implies a greater crystallization tendency in glasses containing larger concentration of Sb. Moreover, in this work, the $K_r(T)$ criterion has been considered for the evaluation of glass stability from DSC data. It includes both the kinetic parameters and the critical temperatures. Therefore, it is reasonable to think that the obtained data from the quoted criterion agree satisfactorily with the values, which result from the existing criteria based on characteristic

temperatures and $K(T)$ criteria. A high value of $K_r(T)$ means poor stability of the glass. The values of $K(T_g)$, $K(T_p)$ and $K_r(T)$ increase with increasing with increase Sb content, it means that the thermal stability decrease with increasing Sb content in $\text{Sb}_x\text{Ge}_{25-x}\text{Se}_{75}$ system. The kinetic exponent, n has been obtained by using the volume fraction crystallized corresponding to the maximum crystallization rate. By this method, the kinetic exponent are calculated in a set of exotherms taken at different heating rates, and the corresponding mean for each composition. Bearing in mind the above obtained mean value, $\langle n \rangle$ increase with increasing the Sb content. Finally, identification of the crystalline phases was made by recording the X-ray diffraction pattern of the transformed material. This pattern shows the existence of microcrystallites of two phases, the first is germanium selenide GeSe_2 and the second is Sb_2Se_3 in amorphous matrix for annealed of $\text{Sb}_{2.5}\text{Ge}_{22.5}\text{Se}_{75}$ and $\text{Sb}_{10}\text{Ge}_{15}\text{Se}_{75}$ glass.

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