Journal of Ovonic Research Vol. 5, No. 2, April 2009, p. 43 - 50

CRYSTALLIZATION KINETICS OF GeSe CHALCOGENIDE GLASS WITH ANTIMONY

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Alloys of $Ge_{2.5-x}$ $Se_{7.5}Sb_x$ glass system with ($0.5\leq x \leq 2$), obtained with rapid quenching, have been thermally characterized with calorimetric measurements**.** The crystallization kinetics of $Ge_{2.5-x}$ $Se_{7.5}Sb_x$ chalcogenide glasses are discussed under non- isothermal conditions by differential thermal analysis (DTA). The glass transition temperature (T_g), the temperature at which crystallization begins (T_0) the temperature corresponding to the maximum crystallization temperature (T_c) and the melting temperature (T_m) are determined. Studies of the crystallization kinetics using the non-isothermal single scan technique shows that the nuclei are already present and the growth occurs in two or three dimensions. The Hruby number (HR) which is a strong indicator of glass forming tendency (GFT), thermal stability parameter (S) representing resistance to devitrification are studied.

(Received April 12, 2009; accepted April 28, 2009)

Keywords: GeSe:Sb, Chalcogenide, Kinetics, DTA, Glass forming tenedency

1. Introduction

The importance of $Ge_{2.5-x}$ $Se_{7.5}Sb_x$ glasses with ($0.5\leq x \leq 2$) is due to their interesting optical properties for their potential use as optical fibers, where they show high transparency to infrared radiation in the 2-16µm range [1]. Physical properties of $Ge_{2.5-x}$ $Se_{7.5}Sb_x$ with ($0.5\leq x \leq 2$), as chalcogenide semiconducting glasses, are strongly dependent on their composition [2, 3]. Therefore, it is important to study their physical properties. Consequently, the glass forming region was found to extend from about 5 to 35 at% Germanium 5 to 40at% Antimony, the rest being Selenium [4].

The kinetic of first- order phase transformation, such as crystallization, is important in physics, chemistry, ceramic and material science. Thermal analysis methods, including differential thermal analysis (DTA) are particularly important, since they are easy to be carried out and are quite sensitive [5]. In DTA 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 is recorded as a function of time while non isothermal method, the sample is heated at fixed rate and the heat evolved is recorded as a function of temperature or time. While isothermal experimental analysis techniques are more definite but non-isothermal thermo-analytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed, makes these experiments attractive. Non-isothermal experiments can be used to extend the temperature range of measurements rather than the isothermal experiments. Many phase transformations occur too rapidly to be measured under isothermal conditions because of transitions inherently associated with the experimental apparatus. Industrial processes often depend on the kinetic behavior of systems undergoing phase transformation under non-isothermal conditions. In this respect, a definitive measurement of non-isothermal transformation kinetic is desirable.

The phase transformation in chalcogenide glasses is studied by non- isothermal technique [6], because of their usage in numerous applications in semiconductor technology and their resent importance in optical recording system. The effect of metal addition on physical properties of vitreous chalcogenide semiconductors has been studied by many workers [7-10]

The present work is concerned with the study of the crystallization kinetics and evaluation of the activation energies of $Ge_{2.5-x}Se_{7.5}$ Sb_x glasses with x= (0.5, 1, 1.5, 1.8, and 2) by using the non-isothermal method. Moreover studying the effect of Sb content on the thermal stability and GFT in $Ge_{2.5-x}Se_{7.5}$ Sb_x . For this purpose, the Hruby number (H_R), thermal stability parameter (S) and reduced glass transition temperature (T_{rg}) are evaluated for the present glassy alloys.

2. Experimental

Five different composition of chalcogenide glass system $Se_{7.5}$ $Ge_{2.5-x}$ Sb_x (0.5≤ x ≤2x) were prepared by direct synthesis from selenium (4N), germanium and antimony (5N) purity. In all, a total weight of elements of 5g was placed in silica tube and sealed under vacuum of the order of 10^{-5} Torr. Each sample was kept inside a rocking oscillatory furnace whose temperature was raised up step by step to the melting point of each element (Se, Sb and Ge) at rate of $100^oC/h$ and was kept at this value for 2h then maintained at 1000^oC for 15hours. Then, there is the samples were quenched in ice water to form the bulk samples. Differential thermal analysis (DTA) was performed by a Shimadzue DTA-50 instrument with selected heating rates $2{,}10^oC/min$ in thestarted from room temperature-to800^oC. The temperature precision of the equipment is ±0.1K. The sample with masses of ≈15 mg encapsulated in conventional platinum sample pans in an atmosphere of dry nitrogen at a flow rate of 30 ml/min. The instrument was calibrated prior the measurement by using high purity metal standards (In, pb, and Zn) with known latent heat. The values of the glass transition temperature (T_g) the onset temperature of crystallization (T_o), the peak temperature of crystallization (T_c) and the melting temperature T_m were determined by using the microprocessor of the apparatus.

3. Results and discussion

Fig. (1) Shows typical DTA trace out of freshly prepared $Ge25_{-x}Se_{7.5}$ Sb_x glasses taken at a constant heating rate of 10^0 C/min. In this figure the endothermic peak due to the glass transition (T_g) is observed for all the glassy samples at temperatures ranging from (180^0 C/min to 240^0 C/min) . Above T_g an exothermic peak T_c occurs in the range from 200 to 480^0 C/min. The figure shows also that the glasses are characterized by melting point T_m lying respectively in the ranges(580-800^0 C/min).

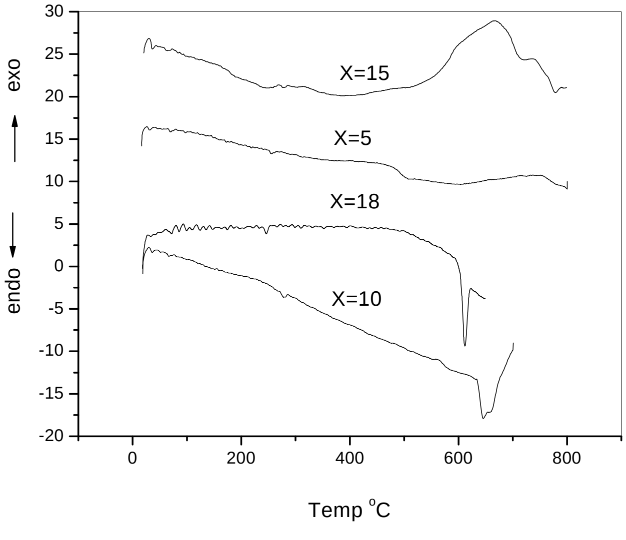

Fig. 1. DTA themograms obtained at heating rate 10 ^oC/min

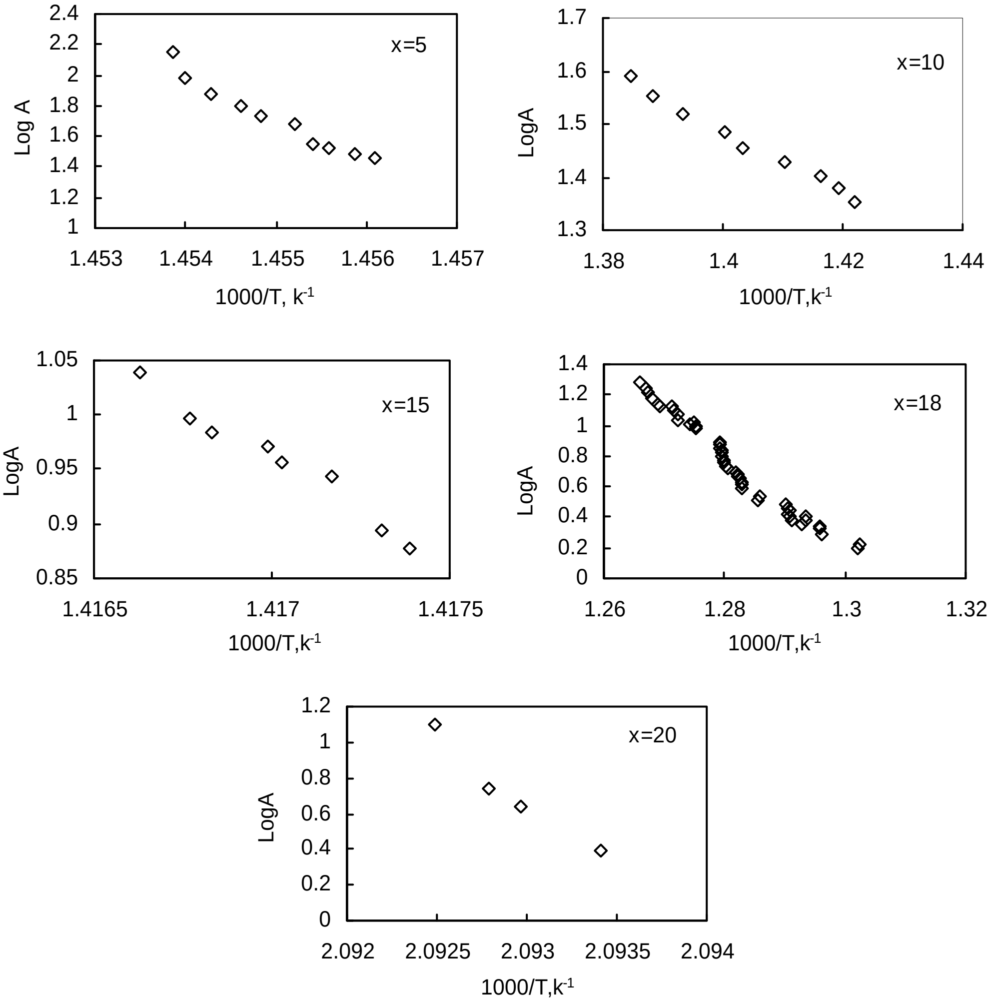

Fig. 2. Plot of log (g(α)) versus 1/T. for investigated samples

The transition temperatures for 10 ^0C/min heating rate are listed in table {1}

Table 1. Transition temperatures as a function of composition

Composition	10 ^oC/min T_g (K)	10 ^oC/min T_o (K)	10 ^oC/min T_c (K)	10 ^oC/min T_m (K)
Sb5	518.24	627.44	739.6	714.78
Sb10	533	808.85	839.56	634.08
Sb15	487.8	824.87	929.6	778.92
Sb18	536.1			611.07
Sb20	430.28	469.42	493.51	581

The kinetics of crystallization process of $Ge_{2.5-x}Se_{7.5}Sb_x$ glasses is studied through determination of the kinetics parameter (n) which reflects the reaction order or Avrami index and the activation energy E of the process. Non- isothermal single scan technique is applied to study the thermally activated phenomena for the investigated system. To do this, a constant slow scan rate (φ= dT/dt = 2 ^{0}C/min) was maintained. The avrami equation for solid to solid transformation can be used to describe the kinetics of isothermal crystallization [11]:

$$\alpha = 1-\exp(kt^n) \qquad \{1\}$$

where n is the avrami exponent, α is the degree of crystallization at time t ($\alpha = A_T/A$) where A is the total area of the exotherm and A_T is the area under the exothermic peak at any temp. T and A_T is the area under the exothermic peak at any temp T. and K is the thermally activated constant rate. The temperature dependence follows the Arrhenius relation.

$$K = K_0 \exp(-E/RT) \qquad \{2\}$$

Where K_0 is the frequency factor(considered to be constant with respect to temperature), and R is the gas constant. E is the apparent activation energy including the activation energy for nucleation and for growth. Eq.(1) is often used for deducing relationship describing non-isothermal crystallization process. From eqs.(1,2) we have

$$\ln[-\ln(1-\alpha)] = n(\ln K_0) - E/KT + n(\ln t) \qquad \{3\}$$

At constant t value, a plot of $\ln[-\ln(1-\alpha)]$ against 1/T can be used to obtain E.

Recent studies show that a simple DSC (DTA) model using single scan technique can be employed to study thermal crystallization in amorphous chalcogenide semiconductors [7,12]. In this model, the assumption is made that the extent of crystallization is proportional to the relevant area under the DTA peak. Under this assumption a plot of log [g(α)] versus 1/T yields a straight line, when an appropriate mathematical description of the reaction process is used. This description is given by:

$$\mathrm{Log}[g(\alpha)] = \log[EK_0^{1/n} / \varphi R] - E/nRT \qquad \{4\}$$

The calculations of the function g(α) was carried out by Stava and Skavara for the different reaction kinetic equations[13,14]. From the function log g(α)=f(1/T), it can be deduced that, all the reaction kinetic equations give the best fit to the increasing part of DTA peak and is obtained for function A_2 where ($A_2 = -\ln(1-\alpha)]^{1/2}$. A_2 indicates that random nuclei during crystallization processes of Ge-Se-Sb glasses.

Fig.(2) shows the plot of Log[g(α)] vs. 1/T for the investigated samples.

A plot of $\ln[-\ln(1-\alpha)]$ vs 1/T fig.(3) should yield a straight line whose slope is E/R. The value of E is correlated with effective activation energy E/n, obtained from the slope of log[g(α)] vs 1/T, to estimate the value of n, which reflects the nucleation rate and the growth morphology.

Table 2. calculated Kinetic Parameters

composition	E kJ/mol	n
Sb5	114.73	1.6
Sb10	114.48	3.16
Sb15	648.4	1.6
Sb18	248.9	3.57
Sb20	289	3.8

Table 3. The reduced glass transition temperature (Trg), Hruby numbers (Hr), and the thermal stability(S)

Coposition	Trg(Tg/Tm)	Hruby umber Hr=(Tp-Tg)/(Tm-Tp)	Stability parameters S=(Tp-To)(Tp-g)/Tg
Sb5	0.53	0.88	47.9
Sb10	0.59	4.53	17.66
Sb15	0.48	5.27	94.85
Sb18	0.62		
Sb20	0.55	0.221	3.54

Tables{2} gives the values of E and n. From the table it is clear that the crystallization energy decreases with increasing Sb content, which means that the addition of Sb assists crystallization.

4. Theoretical basis

Several criteria are found in many papers [15-20] evaluating the GFT and thermal stability of the amorphous materials.

Various quantitative methods are suggested to evaluate the level of stability of the glassy alloys. Most of these methods [15-17] are based on the characteristic temperatures such as the glass transition temperature (T_g), the on-set crystallization temperature (T_c), the peak crystallization temperature (T_p) and the melting temperature T_m. Some of them [18-20] are based on reaction rate constant K. The thermal parameters are easily and accurately obtained by DTA technique.

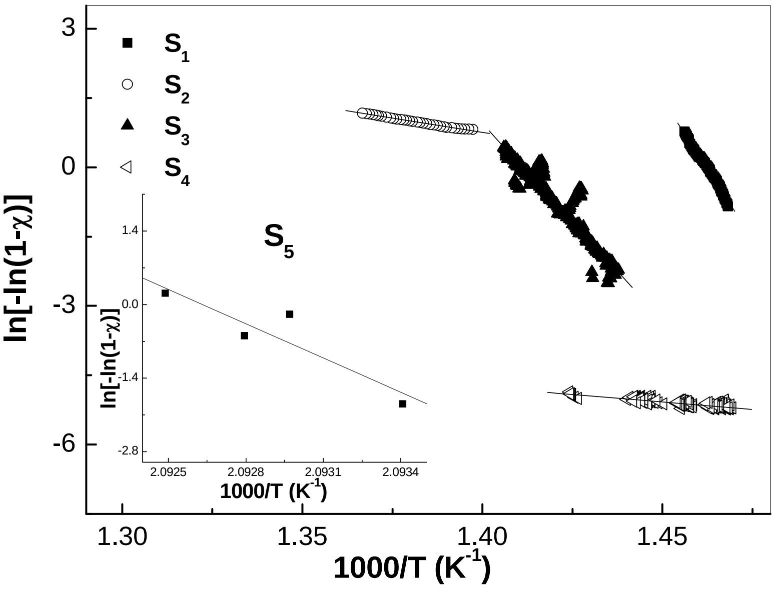

Fig. 3. Plot of ln(-ln(1-α)) versus 1/T for the investigated samples.

Dietzel [15] introduced the first stability criterion, $\Delta T=T_p-T_g$. using the characteristic temperatures. Hruby [16] proposes the criterion $H_R = \Delta T/(T_m-T_P)$. The criterion of Saad and Poulain [17] reflects the resistance to devitrification after formation of the glass. In eq.(4) the term $(Tc-T_0)$ delays the nucleation process. The values of S are given in Table 3 for various glassy alloys. The peak crystallization temperature (T_c) is another important factor, which is a strong indicator of the thermal stability. The composition dependence of S and T_c are shown in Fig. 4.

From these figures it is clear that S and T_c increases up to 4 at% Sb content and with further addition of Sb both parameters decrease (see Fig.4).

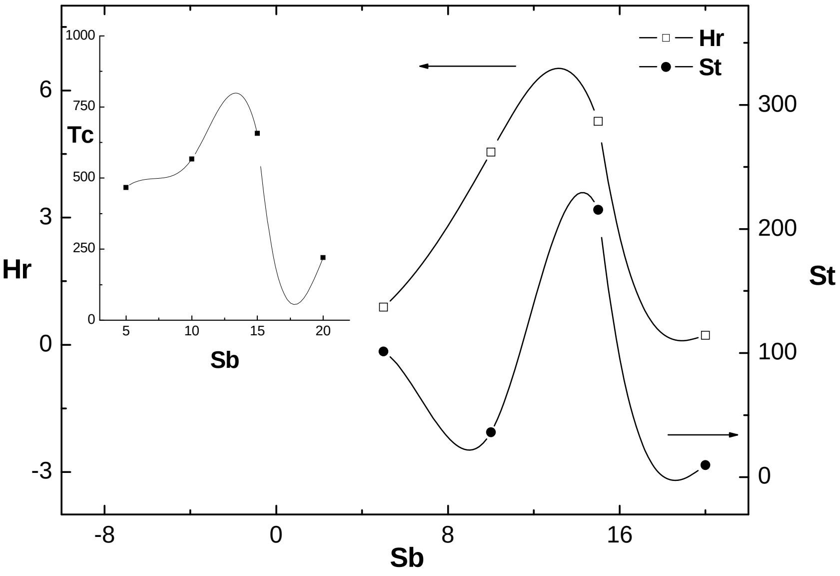

Fig. 4. Composition dependence of thermal stability parameters (s),Hruby number (Hr), and crystallization temperature

The ease of glass formation can be determined by calculating the reduced glass transition temperature Trg = (Tg/Tm)[21,22]. The values so obtained obey the ″two-thirds rule″, which states that

$$T_{rg}=T_g/T_m=2/3 \qquad \{5\}$$

The single endothermic glass transition peaks at T_g and single exothermic crystallization peak at T_p indicates the homogeneity of these glasses. The thermal stability parameter is [17]:

$$S = (T_c+T_0)(T_c-T_g)/T_g \qquad \{6\}$$

It reflects the resistance to devitrification after formation of the glass. In eq.(6) the term (T_p- T_c) is related to the rate of devitrification transformation of the glassy phases. On the other hand, for high values of the term (T_p-T_g) the nucleation process is delayed. The values of S are given in Table3 for various glassy alloys. The peak crystallization temperature (Tp) is another important factor, which is a strong indicator for the thermal stability. The composition dependence of S and Tp are shown in fig. (4).

The easiness of glass formation can be determined by calculating the reduced glass transition temperature Trg = (Tg/Tm)[21,22]. The values so obtained obey the ″two-thirds rule″, which states that

$$T_{rg}=T_g/T_m=2/3 \qquad \{7\}$$

The ratios (Tg/Tm) for various glassy alloys are given in Table 3. It is evident from this tables that the "two-third rule" holds fairly well in the present Ge-Se-Sb glass system. The values of (T_g/T_m) are found to be nearly equal to 0.66 for different Sb concentration at the heating rate. The Hruby number (Hr), which is a strong indicator of GFT, is defined as the ratio of Tc-Tg and Tm-Tc and is given by [16]:

$$H_R=(T_p-T_g)/(T_m-T_p) \qquad \{8\}$$

Higher values of (Tc-T_g) delay the nucleation process and the small values of Tm-Tc retards the growth process. The values of HR are given in Table 3. For various glasses, the composition dependence of HR is shown in Fig. 5. From this figure it is clear that GFT is maximum for 14 at% of Sb. Similar trend is observed in thermal stability parameters S and crystallization temperature Tp. This shows that the peak values of HR, S and Tp are for 14-15 at% of Sb. This composition can be considered as a critical composition (average coordination number ~ 2.4) at which the system becomes a chemical ordered alloy.

5. Conclusion

1-The study of crystallization kinetics of glasses in $Se_{7.5}\,Ge_{2.5-x}\,Sb_x$ with

$0 \leq x \leq 20$ using E, n show that these glasses follow three dimensional growth in the crystallization process. Furthermore, glasses rich in Sb show lower thermal stability and higher crystallization ability depending on the Sb content.

2- The values of the order of crystallization, n for all stages of crystallization of the examined compositions lie in the range 1.6-3.8.

3- The kinetic results indicate that, nuclei are already present in the quenched materials and crystallization mechanism is a random process in three dimensions.

4- Some kinetic and thermodynamic parameters (S, H_R and T_{rg}) for glassy

Ge Se Sb alloys are studied by non-isothermal DSC technique, and reveals.

that both thermal stability and Gft are highest for 14 at % of S. This composition can be considered as a critical composition (average coordination number ~ 2.4).

5-The value of n is evaluated from the slopes of the straight lines and fit of these relation give an average value of n as shown in table(2). For GeSe Sb chalcogenide glasses, no specific heat treatment is performed to the DTA scans to nucleate the sample. Therefore, n is considered to be equal to (m+1) for the glasses. The calculated values of n are not an integer, which means that the crystallization process of GeSe Sb chalcogenide glass occurs with different mechanisms and the predominant one is the process in which n=4 for x=10, 18 and 20 however n=2 for x= 5 and 15. Therefore, the value of the corresponding m is equal to 3 for 10, 18, and 20 and m=1 for 5 and 15. Therefore, it is somewhat reasonable to suggest that GeSeSb crystallization process occurs by bulk crystallization in three dimensions and one dimension, respectively.

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