

A Study of Thermal Stability And Crystallization Kinetics of SbSeGe Glassy Alloys

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Abstract. Alloys of $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) have been prepared using melt quenching technique. Differential thermal analysis has been used to determine the three characteristic temperatures, glass transition (T_g), glass crystallization (T_c) and melting temperature (T_m), at four heating rates 5, 10, 15 and 20 K/min. The thermal stability and ease of glass formation have been evaluated in terms of Hruby parameter and reduced glass transition temperature respectively. The activation energy for glass crystallization (E_c) has been calculated using Kissinger's method and Marseglia theory. The composition dependence of T_g and E_c has also been discussed.

1. Introduction

Extensive studies have been performed on chalcogenide glasses due to their excellent physical properties and they are potential candidates for many technological applications like waveguides, thermal imaging etc [1, 2]. Study of glass transition and crystallization behavior in chalcogenide glasses is of particular interest because they are connected with important phenomena like switching [3], reversible optical recording [4], etc. Information about thermal stability and crystallization kinetics can be obtained using non-isothermal methods. Chalcogenide glasses exhibiting no exothermic crystallization reaction above the glass transition temperature (T_g) show a threshold switching type [5]. On the other hand, glasses exhibiting an exothermic crystallization reaction above T_g exhibit a memory type of switching. Memory switches come from the boundaries of the glass-forming regions, where glasses are stable and have a tendency to crystallize when heated or cooled slowly [5].

In the present paper, thermal stability and crystallization kinetics of $Sb_{10}Se_{65-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) glassy alloys has been reported. *Ge* acts as a network modifier and has been added to the system at the cost of *Se*. Differential Thermal Analysis has been used to determine the three temperatures viz. glass transition (T_g), glass crystallization (T_c) and melting temperature (T_m). Thermal stability has been discussed in terms of Hruby parameter [6] and reduced glass transition temperature [7]. Crystallization kinetics has been studied using two approaches namely, Kissinger [8] and Marseglia theory [9]. The results obtained from different methods have been compared and discussed.



2. Experimental

Bulk samples of $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) were prepared using melt quench technique. The detailed experimental procedure for sample preparation is given elsewhere [10]. The composition of the bulk samples was analyzed using a scanning electron microscope (SEM) (Zeiss EVO 40 EP with EDAX attachment operated at 20 kV). The amorphous state of the alloys was confirmed by the absence of sharp peaks in the X-ray diffraction peaks (X'Pert PRO) [10]. The thermal behavior of the samples was investigated using DTA (EXSTAR TG/DTA 6300). DTA runs were taken at four different heating rates 5, 10, 15, and 20 K/min. For each run, approximately 10 mg of the sample was taken in alumina pans in an atmosphere of dry nitrogen at a flow rate of 200 mL min⁻¹ under non-isothermal conditions. The analyzer was calibrated prior to the measurements using the known latent heats of high purity elements zinc, indium and lead. The temperature precision of microprocessor of thermal analyzer was ± 0.1 K [11].

3. Results and Discussion

DTA traces for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) samples have been given in [11]. Three characteristic peaks corresponding to glass transition (T_g), glass crystallization (T_c) and melting (T_m) were obtained. T_g , T_c and T_m values for heating rate (α) 15K/min have been given in Table 1. T_g increases with increase in concentration of Ge upto $x = 25$ and decreases at $x = 27$. This is due to the fact that with Ge addition to $Sb_{10}Se_{90}$ weak $Se-Se$ bonds are being replaced with tetrahedral $Ge(Se_{1/2})_4$ units which contain strong $Ge-Se$ bonds, in addition to Sb_2Se_3 structural units. At $x = 25$, system becomes completely rigid with the formation of $Ge(Se_{1/2})_4$ and Sb_2Se_3 units only. At $x = 27$, homopolar $Ge-Ge$ bonds are formed in addition to $Ge(Se_{1/2})_4$ and Sb_2Se_3 units thereby decreasing T_g [12]. T_c and T_m also show a similar trend with Ge addition to $x = 0$ (Table 1).

Table 1. Values of T_g , T_c and T_m for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) glassy alloys at heating rate 15K/min

Sample	T_g (K)	T_c (K)	T_m (K)
$x = 0$	340.93	421.11	497.51
$x = 19$	519.08	659.53	778.12
$x = 21$	524.20	671.00	789.62
$x = 23$	529.83	679.62	790.49
$x = 25$	538.18	688.57	795.74
$x = 27$	536.36	682.27	793.74

3.1. Thermal stability and glass forming ability

There is no absolute criterion to parameterize the glass formation. Two parameters extensively used for quantitative characterization have been evaluated. The first criterion is Hruby parameter (K_{gl}) which indicates the glass forming ability and is expressed as [6],

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c}$$

where $(T_c - T_g)$ represents the nucleation process and $(T_m - T_c)$ represents the growth process. The difference between $T_c - T_g$ increases with Ge content showing a maximum at $x = 25$ at% and then decreases for $x = 27$ at% (Table 2). Thus, K_{gl} is maximum for $Sb_{10}Se_{65}Ge_{25}$ indicating maximum thermal stability and hence, glass forming ability.

Second criterion is reduced glass transition temperature ($T_{rg} = T_g/T_m$) [7] which indicates ease of glass formation. The value of T_{rg} remains almost constant and is equal to 2/3. That is why it is also called 'two-third rule'. The values of T_{rg} are found to be of order of 2/3 (Table 2) indicating good glass forming ability of all the compositions.

Table 2 Values of K_{gl} , T_{rg} and E_c for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) glassy alloys.

Sample	K_{gl}	T_{rg}	E_c [8] (KJ/mol)	E_c [9] (KJ/mol)
$x = 0$	1.049	0.6853	72.55	75.99
$x = 19$	1.184	0.6671	127.31	132.73
$x = 21$	1.238	0.6639	131.48	136.99
$x = 23$	1.351	0.6703	134.02	139.59
$x = 25$	1.403	0.6763	136.90	142.55
$x = 27$	1.309	0.6757	135.70	141.29

3.2. Theoretical aspect of calculating E_c

The activation energies in a crystallization process involve activation energy for nucleation, growth and whole crystallization process. It has been pointed out that in non 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 [13]. The activation energy of crystallization has been evaluated using two approaches.

In the first approach, E_c has been calculated using Kissinger's equation [8],

$$\ln\left(\frac{\alpha}{T_c^2}\right) - \frac{E_c}{RT_c} + \text{constant}$$

where R is universal gas constant. The activation energy is calculated from the slopes of Figure 1 and found to be maximum for $x = 25$ at. %.

In the second approach E_c has been calculated using Marseglia's theory [9],

$$\ln\left(\frac{T_c}{\alpha}\right) - \frac{E_c}{RT_c} + \text{constant}$$

The slope of $\ln(T_c/\alpha)$ vs. $1000/T_c$ in Figure 2 gives the activation energy. The slope increases with increase with Ge addition upto $x = 25$ and decreases with further Ge addition.

The values of E_c calculated from the two methods are in good agreement with each other (Table 2). Variation in the values of E_c is due to different approximations used in two approaches. The variation in E_c values with Ge at. % can be interpreted in terms of bond energies. The bond energy of a heteropolar bond is [14],

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2$$

where E_{A-A} and E_{B-B} are the homopolar bond energies and χ_A and χ_B are corresponding electronegativities. According to chemical bond approach [15], atoms combine more favorably with the atoms of different kind than with the same kind. Bonds are formed in order of decreasing bond energies thereby favoring chemical order. $Sb_{10}Se_{90}$ system contains only Sb-Se and Se-Se bonds with energies 43.96 kcal/mol and 44 kcal/mol respectively [16]. With the addition of Ge , stronger $Ge-Se$

bonds having energy 49.92 kcal/mol start replacing *Se-Se* bonds increasing the cohesive energy of the system [16]. At $x = 25$, the system has a complete 3-dimensional structure with *Sb-Se* and *Ge-Se* heteropolar bonds only, and hence maximum cohesive energy. An increase in cohesive energy increases bonding strength of the system thereby, increasing T_c and hence, E_c . The maximum value of E_c at $x = 25$ indicates that atoms in their glassy state require more energy to jump to the crystalline phase. Thus, $x = 25$ is the most stable composition. At $x = 27$, homopolar bonds having energy 37.60 kcal/mol are formed leading to a decrease in cohesive energy [16]. A decrease in cohesive energy decreases T_c and hence, E_c at $x = 27$.

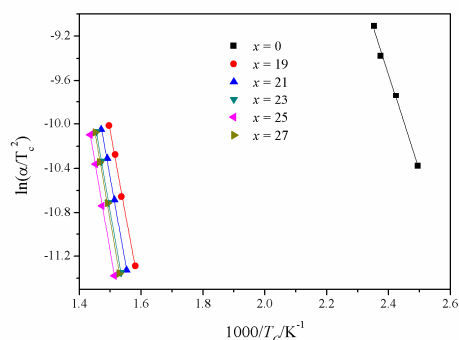


Figure 1. Variation of $\ln(\alpha/T_c^2)$ with $1000/T_c$ for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) glassy alloys.

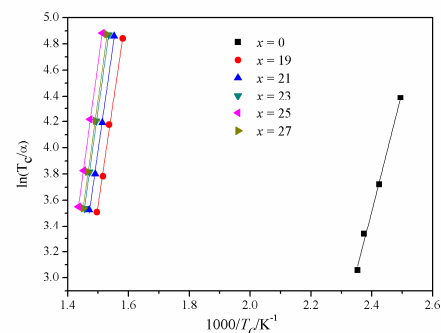


Figure 2. Variation of $\ln(T_c/\alpha)$ vs. $1000/T_c$ for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) glassy alloys.

4. Conclusion

The effect of *Ge* addition on the thermal stability and activation energy of $Sb_{10}Se_{90-x}Ge_x$ glassy alloys has been investigated. The glass transition temperature shows a maximum at $x = 25$. From the heating rate dependence of T_c the activation energy for the crystallization has been calculated using Kissinger's approach and Marzaglia's theory. E_c , increases with increase in *Ge* content upto $x = 25$ and then decreases for $x = 27$. The addition of *Ge* leads to the formation of *Ge-Se* bonds at the expense of the *Se-Se* bonds leading to a 3D structure at $x = 25$. Hruby parameter and T_{rg} also suggest that $Sb_{10}Se_{25}Ge_{25}$ is thermally most stable composition.

5. References

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