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

S Sharda\textsuperscript{1}, P Sharma\textsuperscript{2} and V Sharma\textsuperscript{2}

\textsuperscript{1} Faculty of Physical Sciences, Shree Guru Gobind Singh Tricentenary University, Gurugram, Haryana, India
\textsuperscript{2} Department of Physics & Materials Sciences, Jaypee University of Information Technology Waknaghat, HP, India

E-mail: sunandasharda@gmail.com

Abstract. Alloys of $\text{Sb}_{10}\text{Se}_{65-x}\text{Ge}_x$ ($x = 0, 19, 21, 23, 25, 27$) 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 $\text{Sb}_{10}\text{Se}_{65-x}\text{Ge}_x$ ($x = 0, 19, 21, 23, 25, 27$) 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 \textit{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 (\(\alpha\)) 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 \(Sb\)(Se\(^2\))\(^3\) structural units. At \(x = 25\), system becomes completely rigid with the formation of \(Ge(Se\)\(^{1/2}\))\(^4\) and \(Sb\)(Se\(^2\))\(^3\) units only. At \(x = 27\), homopolar Ge-Ge bonds are formed in addition to \(Ge(Se\)\(^{1/2}\))\(^4\) and \(Sb\)(Se\(^2\))\(^3\) units thereby decreasing \(T_g\) \[12\]. \(T_c\) and \(T_m\) also show a similar trend with \(Ge\) addition to \(x = 0\) (Table 1).

| 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.

| Sample \( x \) | \( K_{gl} \) | \( T_{rg} \) | \( E_c \) [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 up to \( x = 25 \) 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 \( \chi_A \) and \( \chi_B \) 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 dominate.
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 \( \ln \left( \frac{\alpha}{T_c^2} \right) \) 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 \( \ln \left( \frac{T_c}{\alpha} \right) \) 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 Marseglia’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
[1] Han Z, Lin P, Singh V, Kimerling L, Hu J, Richardson K, Agarwal A, and Tan D T H 2016 Appl. Phys. Lett. 108 141106
[2] Cha D H, Kim Hye-Jeong, Hwang Y, Jeong J C, and Kim J 2012 Appl. Opt. 51 5649
[3] Lee M J, Lee D, Cho S H, Hur J H, Lee S M, Seo D H, Kim D S, Yang M S, Lee S, Hwang E, Uddin M R, Kim H, Chung U I, Park Y and Yoo I K 2013 Nat. Commun. 4 2629
[4] Borisenko K B, Shamhugam J, Williams B A O, Ewart P, Gholipour B, Hewak D W, Hussain R, Jävörfi T, Siligardi G and Kirkland A I 2015 Sci Rep. 5 8770
[5] Kumar H, Mehta N and Singh K 2009 Phys. Scr. 80 065602
[6] Hruby A 1972 J. Phys. B 22 1187
[7] Kauzmann W 1948 Chem. Rev. 43 219
[8] Kissinger H E 1957 Anal. Chem. 29 1702
[9] Marseglia E A 1980 J. Non-Cryst. Solids 41 31
[10] Sharda S, Sharma N, Sharma P and Sharma V 2012 Mater. Chem. Phys. 134 158
[11] Sharda S, Sharma N, Sharma P and Sharma V 2014 J. Therm. Anal. Calorim. 115 361
[12] Sharda S, Sharma N, Sharma P and Sharma V 2013 J. Non-Cryst. Solids. 362 136
[13] Saxena M 2004 Bull. Mater. Sci. 27 543
[14] Pauling L 1976 The nature of chemical bond (Cornell University; New York)
[15] Bicerano J and Ovshinsky S R 1985 J Non-Cryst Solids 75 169
[16] Sharda S, Sharma N, Sharma P and Sharma V 2011 Defects and Diffusion Forum 319–317 45