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Study of thermal stability in $Se_{90}Sb_{10-x}Ag_x$ glassy alloys

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Alloys of $Se_{100-x}Sb_{10-x}Ag_x$ (x=2, 4 &8) glassy system have been obtained by quenching technique. Kinetic parameters, which represent thermal stability, have been determined from differential scanning calorimetric technique. The rate of crystallization decreases with Ag concentration and is lowest for glassy $Se_{90}Sb_2Ag_8$ alloy. Thermal stability (T_c-T_g), Hruby criterion H_r, Saad Poulain '*S*' have been found to increase with Ag concentration and are maximum for $Se_{90}Sb_2Ag_8$. Thus, one can conclude that the rate of crystallization is related to the thermal stability. The reduced glass transition temperature for $Se_{90}Sb_{10-x}Ag_x$ is found to be 2/3, which shows that these glassy alloys are suitable for phase change optical memories.

Keywords: Chalcogenide glasses, Differential scanning calorimetry

1 Introduction

Semiconducting chalcogenide glasses are interesting materials in the field of disordered solids due to their wide range of applications in optoelectronics as optical waveguide[1], infrared optical fibers[2], and inexpensive solar cells[3] and in optical recording systems[4]. Since the discovery[5] of switching and optical memory effects in these materials, amorphous Se has become a material of considerable commercial importance in device technology. However, it has limited applications due to certain shortcomings as low crystallization temperature (T_c), low photosensitivity, lesser durability and more ageing effects. To overcome these difficulties, certain additives like[6,7] Ge, Sb, Te are used to overcome these problems. Calorimetric studies on Se – Sb binary glasses have been reported in literature[8,9]. The dielectric study on Se – Sb alloys, has also been reported by our group[10].

Recently, Ag doped chalcogenide glasses have become attractive materials for fundamental research[11-26] due to their current and potential applications in optics and optoelectronics such as photo doping, optical imaging, photolithography and phase change optical recording. In the present work we report thermal properties of Se-Sb-Ag glasses using differential scanning calorimetry.

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For the use of glasses for optical recording, recording materials must be stable in the amorphous state at low temperature and should have a short crystallization time. Therefore, it is important to know the rate of crystallization of these glasses which, in turn, depends on the thermal stability. With an object to evaluate the level of stability of the vitreous alloys, different quantitative methods have been suggested in the literature[27-33]. These methods have been used in the present study.

Generally, chalcogenide glasses exhibit single glass transition and single crystallization temperatures, but in the present study the glassy alloys of $Se_{90}Sb_{10-x}Ag_x$ (x = 2, 4 and 8) are found to have double glass transition and crystallization temperatures. Therefore, crystallization kinetics of these glassy alloys is studied in detail for both the phases present in these alloys.

2 Experimental Procedure

Quenching technique has been used to prepare glassy alloys of $Se_{90}Sb_{10-x}Ag_x$ (x = 2, 4 and 8). The exact proportions of high purity (99.999%) elements are weighed as per the atomic percentages used and the mixture is sealed in evacuated (10^{-5} torr) quartz ampoules (length 5 cm and internal diameter 8 mm). Each ampoule is kept inside the furnace at 800 °C temperature (where the temperature was raised at a rate of 3 – 4 °C min). During heating, all the ampoules were constantly rocked for 10 h for

obtaining homogeneous glassy alloys. Quenching is done in ice cooled water.

Fine powder of the glassy alloys is prepared for DSC studies. 10 to 20 mg of the powder is heated at constant heating rate and the changes in heat flow with respect to an empty reference pan are measured. DSC plus instrument (Rheometric Scientific Company, U.K.) is used to obtain non-isothermal scans at four different heating rates (5, 10, 15 and 20 °C/ min).

3 Theoretical Basis

3.1 Thermal stability

Various quantitative methods have been suggested to evaluate the level of stability of the glassy alloys. Most of these methods[27,30,31] are based on the characteristic temperatures such as the glass transition temperature (T_g), the on-set crystallization temperature (T_o), the peak crystallization temperature (T_c) and the melting temperature (T_m). Some of them[32,33,37] are based on reaction rate constant (K). These thermal parameters are easily and accurately obtained by DSC technique. Dietzel[27] introduced the first stability criterion, $\Delta T = T_c - T_g$. Hurby[30] developed the H_r criterion, $H_r = \Delta T / (T_m - T_c)$. Saad and Poulain[31] obtained another criterion, $S = \Delta T (T_c - T_o)/T_g$.

Thermal stability will be calculated for all the glassy alloys used in the present study. This will be useful to select a particular composition to have the best thermal stability for a particular glassy system.

3.2 Reduced glass transition temperature

The ease of glass formation can be determined by calculating the reduced glass transition temperature[38,39] $T_{rg} = T_g / T_m$. The values of this parameter are important for utilizing a particular glass for phase change application in optical memories. The best suitable glasses obey the two-third rule[40] which states that:

$$T_{rg} = T_g / T_m = 2/3$$

4 Results and Discussion

4.1 Thermal stability of glassy $Se_{90}Sb_{10-x}Ag_x$ (x = 2, 4 and 8)

Figures 1 and 2 show typical DSC thermograms for glassy $Se_{90}Sb_{10-x}Ag_x$ (x = 2, 4 and 8) at heating rate 15 K/min. Similar thermograms were obtained for other heating rates also (not shown here). These figures indicate that two phases occur simultaneously during glass transition region and crystallization region in glassy $Se_{90}Sb_{10-x}Ag_x$ (x = 2, 4 and 8) alloys.

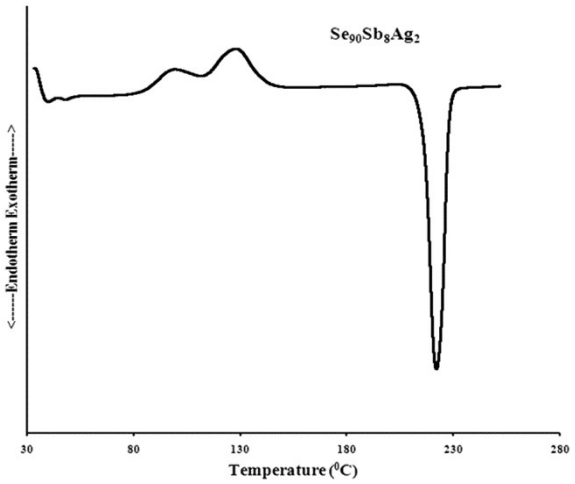

Fig. 1 — DSC thermogram for glassy $Se_{90}Sb_8Ag_2$ alloy for heating rate (15 °C/min).

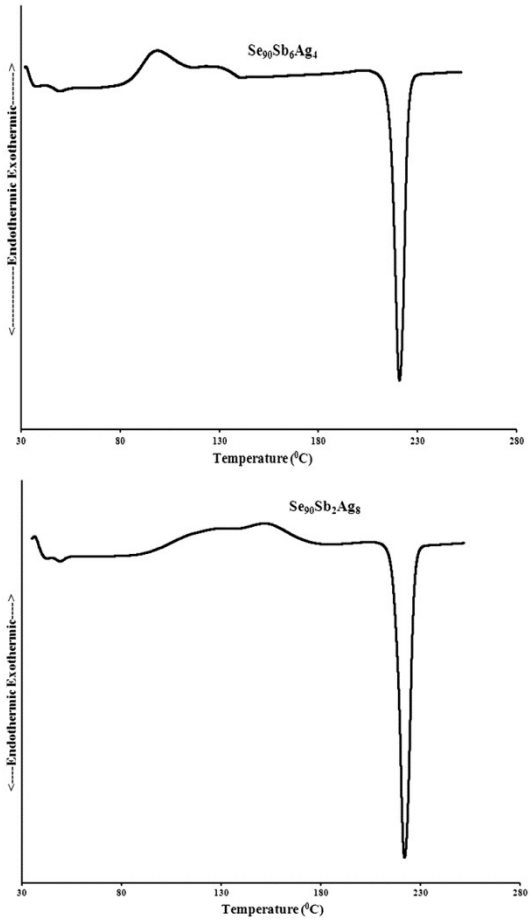

Fig. 2 — DSC thermogram for glassy $Se_{90}Sb_6Ag_4$ and $Se_{90}Sb_2Ag_8$ alloy for heating rate (15 °C/min).

Tables 1 and 2 show the crystallization temperature T_c at various heating rates for phase one and two in all the glasses studied. Values of difference of glass transition temperature (T_g) and crystallization

Table 1 — Crystallization temperature T_{c1} at different heating rates.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5^0C/min	363.04	360.75	401.23
10^0C/min	366.98	367.33	414.41
15^0C/min	372.46	371.66	402.73
20^0C/min	373.92	374.13	404.70

Table 2 — Crystallization temperature T_{c2} at different heating rates.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	388.51	391.28	---
10 °C/min	393.52	396.45	---
15 °C/min	401.09	397	424.62
20 °C/min	397.75	397.93	431.37

Table 3 — Values of $T_{c1} - T_{g1}$ for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	53.35	51.22	94.22
10 °C/min	56.89	55.18	99.58
15 °C/min	58.4	60.86	88.09
20 °C/min	60.84	59.43	92.88

Table 4 — Values of $T_{c2} - T_{g2}$ for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	72.02	71.93	–
10 °C/min	75.53	77.65	–
15 °C/min	77.95	72.42	101.20
20 °C/min	73.56	75.50	106.97

temperature (T_c) are given in Tables 3 and 4 for both the phases. Figures 3 and 4 show the variation of ($T_c - T_g$) with concentration of Ag for both phases. It is clear that ($T_c - T_g$) increases with Ag concentration. This indicates that thermal stability is higher at higher concentration of Ag.

The thermal stability parameter is also defined in the literature[31] by the following expression:

$$S = (T_c - T_o)(T_c - T_g) / T_g \quad \ldots (1)$$

Here, T_o represents the onset crystallization temperature, i.e., the temperature where crystallization peak starts. The values of S are given in Tables 5 and 6 for various glassy alloys at all the heating rate for both phases. Figures 5 and 6 show variation of S with concentration of Ag. From Figs 5 and 6 it is clear that values of S increases with concentration of Ag.

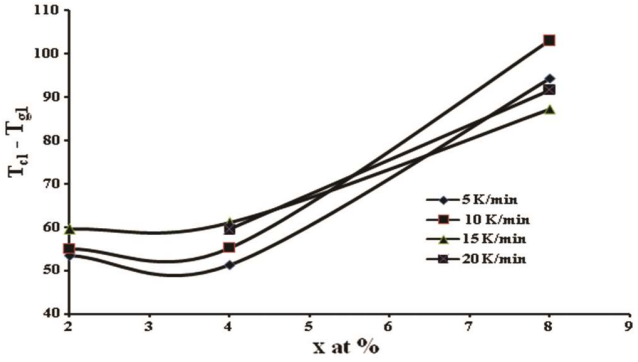

Fig. 3 — $T_{c1} - T_{g1}$ versus atomic percentage of Ag in glassy $Se_{90}Sb_{10-x}Ag_x$.

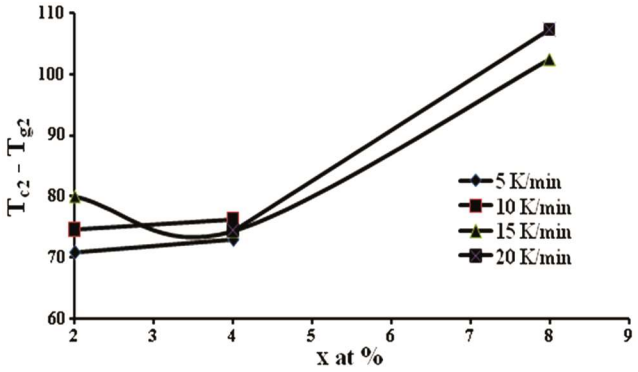

Fig. 4 — $T_{c2} - T_{g2}$ versus atomic percentage of Ag in glassy $Se_{90}Sb_{10-x}Ag_x$.

Table 5 — Values of S_1 for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	2.59	3.02	14.34
10 °C/min	3.21	3.59	16.34
15 °C/min	3.43	3.85	12.48
20 °C/min	3.48	3.61	13.19

Table 6 — Values of S_2 for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	3.11	0.29	–
10 °C/min	3.32	2.54	–
15^0C/min	3.40	1.12	4.26
20 °C/min	2.29	1.85	5.23

4.2 Evaluation of rate constant at peak crystallization temperature (K_p)

The rate constant K_p at the peak crystallization temperature (T_c) for a constant heating rate is given in Tables 7 and 8. The Gao-Wang model[41] has been used to calculate the value of the rate constant K_p at peak the crystallization temperature (T_c) for a constant heating rate:

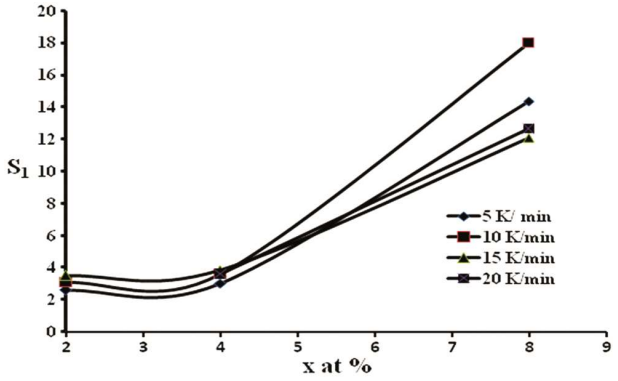

Fig. 5 — S_1 versus atomic percentage of Ag in glassy $Se_{90}Sb_{10-x}Ag_x$.

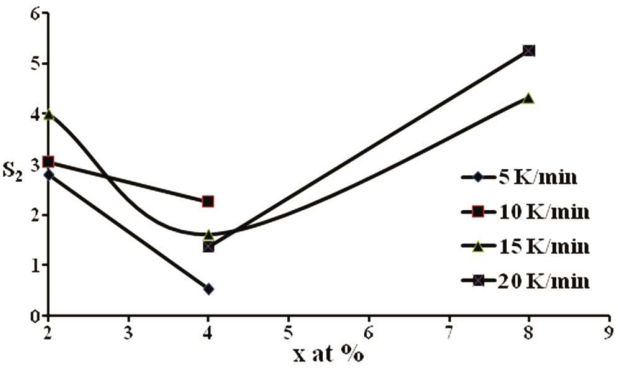

Fig. 6 — S_2 versus atomic percentage of Ag in glassy $Se_{90}Sb_{10-x}Ag_x$.

Table 7 — Heating rate dependence of rate constant K_{p1} $(min)^{-1}$ for first phase for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	0.59	0.52	0.24
10 °C/min	1.16	0.99	0.45
15 °C/min	1.69	1.46	0.71
20 °C/min	2.24	1.92	0.93

Table 8 — Heating rate dependence of rate constant K_{p2} $(min)^{-1}$ for second phase for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	0.69	0.65	----
10 °C/min	1.34	1.25	-----
15 °C/min	1.96	1.91	-----
20 °C/min	2.65	2.48	-----

$K_p = (E_c)/RT_c^2$ … (2) It is clear from this table that K_p decreases with the increase of Ag concentration and is the lowest for the highest concentration of Ag used in the present study.

Some other thermal stability criterion has been calculated which shows that in this series maximum stability occurs at 8 at% of Ag.

Table 9 — Values for H_{r1} for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	0.41	0.39	1.02
10 °C/min	0.45	0.44	1.18
15 °C/min	0.48	0.49	0.96
20 °C/min	0.83	0.49	1.04

Table 10 — Values for H_{r2} for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	0.69	0.70	-----
10 °C/min	0.76	0.81	-----
15 °C/min	0.81	0.73	1.44
20 °C/min	0.74	0.80	1.67

4.3 Evaluation of H_r criterion for glassy alloy (H_r)

Various quantitative methods have been suggested to evaluate the level of stability of the glassy alloys. Most of these methods[27,30,31] are based on the characteristic temperatures such as the glass transition temperature (T_g), the on-set crystallization temperature (T_o), the peak crystallization temperature (T_c) and the melting temperature (T_m). Hurby[30] developed the H_r criterion:

$$H_R = \frac{\Delta T}{T_m - T_c} \quad \ldots (3)$$

The values of Hurby number are given in Tables 9 and 10. Figure 7 shows the variation of H_r number with the % of Ag. From Fig. 7 we can see that value of Hurby number increases with increase in Ag concentration. The thermal stability ($T_c - T_g$), S factor, Hurby criterion H_r also increase with increasing concentration of Ag. Thus it is clear that thermal stability increases with Ag concentration and is maximum for the glassy alloy $Se_{90}Sb_2Ag_8$. The rate of crystallization is found to be decreases with increasing concentration of Ag. Thus one can conclude that the rate of crystallization is related with the thermal stability.

4.4 Reduced glass transition temperature (T_{rg})

The ease of glass formation can be determined by calculating the reduced glass transition temperature[38,39] T_{rg}. The values of this parameter are important for utilizing a particular glass for phase change application in optical memories. The best suitable glass obeys the two-third rule[40] which states that:

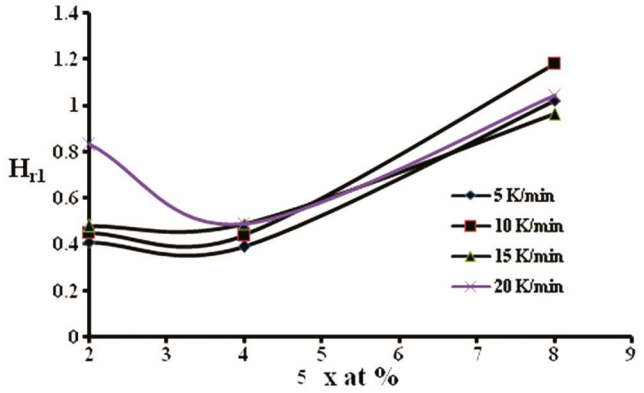

Fig. 7 — H_{r1} versus atomic percentage of Ag in glassy $Se_{90}Sb_{10-x}Ag_x$.

Table 11 — Values for T_{rg1} for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	0.62	0.63	0.62
10 °C/min	0.63	0.63	0.63
15 °C/min	0.63	0.63	0.63
20 °C/min	---	0.63	0.63

Table 12 — Values for T_{rg2} for various glassy alloys of $Se_{90}Sb_{10-x}Ag_x$.

Heating rate	$Se_{90}Sb_8Ag_2$	$Se_{90}Sb_6Ag_4$	$Se_{90}Sb_2Ag_8$
5 °C/min	0.64	0.65	0.65
10 °C/min	0.65	0.65	0.65
15 °C/min	0.65	0.65	0.65
20 °C/min	---	0.65	0.65

$$T_{rg} = = 2 / 3 \quad \ldots (4)$$

The value of T_{rg1} and T_{rg2} are given in Tables 11 and 12.

From the Tables 11 and 12 it is clear that glassy alloy $Se_{90}Sb_{10-x}Ag_x$ obey the two third rule as the value of T_{rg} for all glasses is approximately 0.66.

5 Conclusions

DSC measurements have been performed for glassy alloys of $Se_{90}Sb_{10-x}Ag_x$. DSC scans of these alloys show double peaks at glass transition region as well as in crystallization region. The values of $(T_c - T_g)$ increases with the increase of Ag concentration and is highest for the sample with 8 at % of Ag in the present study. The stability factor S is also highest for the same sample which confirms maximum stability of $Se_{90}Sb_2Ag_8$ glasses.

The rate of crystallization is found to be lowest for glassy $Se_{90}Sb_2Ag_8$ alloy. Thermal stability $(T_c - T_g)$, Hruby criterion H_r, Saad Poulain S has been found maximum for $Se_{90}Sb_2Ag_8$. Thus one can conclude that the rate of crystallization is related with the thermal stability. The reduced glass transition temperature values for $Se_{90}Sb_{10-x}Ag_x$ have been found 2/3 which shows suitability of these glassy alloys for phase change optical memories.

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