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A study of crystallization rate constant of Se-In-Sb chalcogenide glasses

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Abstract

$Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) chalcogenide glasses are prepared in bulk form using melt quenching technique. DSC runs of these samples have been taken at six different heating rates (5, 10, 15, 20, 25, 30 K/min). The variation in glass transition temperature T_g with Sb concentration and average coordination number <z> at different heating rates has been studied. The activation energy (E_c) and rate constant (K) of crystallization have been evaluated using Augis - Benett's model. The variation of rate constant (K) with temperature and composition is studied. Besides these, the dependence of E_c with Sb concentration has also been studied. We have observed Meyer–Neldel rule between pre-exponential factor K_0 and activation energy of crystallization E_c in the present case.

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Keywords: Chalcogenide glasses, DSC, Crystallization rate constant, M-N rule

1. Introduction

An understanding of the kinetics of crystallization in glasses is important for the manufacturing of glass-ceramics and in preventing devitrification. Nucleation and crystallization rates are sometimes measured directly in the microscope [1] but this method could not be applied to glasses in which nucleation and crystallization occurred in times below 1h [2] Differential scanning calorimetry (DSC) is valuable for the quantitative study of crystallization in different glassy systems. This study of crystallization kinetics has been widely discussed in the literature [3–5], and thus many authors applied the Johnson–Mehl– Avrami (JMA) [6-8] equation to the non-isothermal crystallization process [9-10].

Many activated phenomena, including solid-state diffusion in crystals and polymers, dielectric relaxation, conduction and thermally stimulated processes in polymers, and electronic conduction in amorphous semiconductors obey the compensation law or Meyer– Neldel rule [11]. It appears to be a fundamental property of many families of activated processes following an Arrhenius dependence on temperature.

$$\chi = \chi_0 \exp(-\Delta E / KT) \qquad (1)$$

Here χ is the absolute rate of a thermally activated process, χ_0 the pre-exponential factor. It is frequently found that, when ΔE is varied with a family of processes (for example, related chemical reaction), then pre-exponential factor, χ_0 obeys the following empirical relation:

$$\chi_0 = \chi_{00} \exp(-\Delta E / E_{MN}) \qquad (2)$$

where χ_{00} and E_{MN} are positive constants. E_{MN} is known as Meyer–Neldel energy for the process in question. Since then, the origin of this relation is referred to as the Meyer–Neldel relation or MN rule and the physical interpretation of χ_{00} and E_{MN} has been the subject of speculations. The discussion of whether there is one universal explanation for the MNR in different systems is not yet settled [12].

2. Experimental details

Glassy alloys $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) were prepared by the conventional melt-quenching technique. High-purity (99.999%) Se, Sb and In in appropriate atomic weight proportions were placed in a quartz ampoule and sealed under a vacuum of 10^{-5} Torr. The ampoules were then heated at 900^0C for about 15 h with continuous rotation to facilitate homogenization of the sample. The molten samples were rapidly quenched in ice-cooled water to obtain the glassy state. The ingot so produced was then grind gently using a pestle and mortar to obtain a powder form. The glassy nature of the samples was ascertained by X-ray diffraction (XRD). Fig.1 shows the diffractograms of the $Se_{90}In_8Sb_2$ compositions. Absence of any sharp peak confirms that all samples are amorphous.

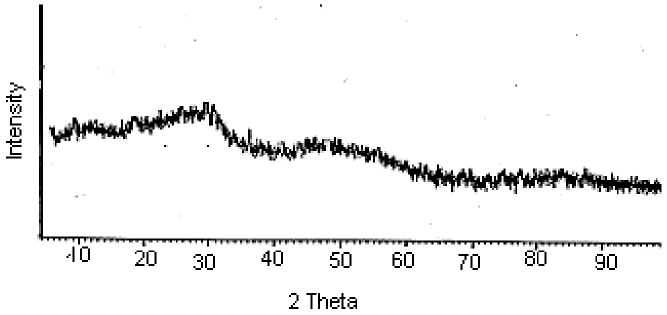

Fig.1: XRD pattern of $Se_{90}In_8Sb_2$ chalcogenide glass at room temperature in powder form

The thermal behavior of the samples was investigated by DSC using a Rigaku DSC 8230 instrument. Runs were taken at six different heating rates, i.e. 5, 10, 15, 20, 25 and 30 K/min on accurately weighed samples in aluminum pans under non-isothermal conditions. The accuracy of heat flow measurement is ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer is ±0.1K. The temperature range covered in DSC was from room temperature to 250^0C. Fig. 2 shows DSC thermograms of all samples, i.e. $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10), at a heating rate of 10 K/min.

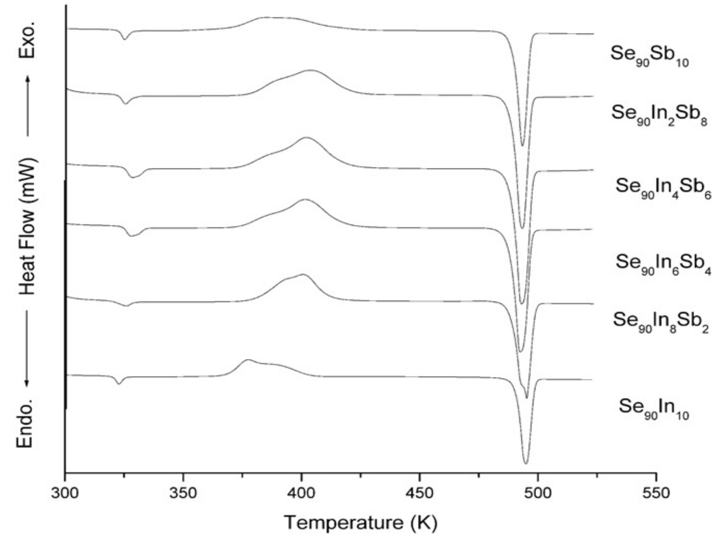

Fig. 2: DSC traces of $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) chalcogenide glass at a heating rate of 10 K/min heating rate.

3. Result and discussion

The glass transition temperature represents the strength or rigidity of the glassy structure of the alloy. The glass transition region has been studied in terms of variation of glass transition temperature with composition and heating rate. The variation in T_g with composition and average coordination number at different heating rates for $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) is shown in Fig. 3.

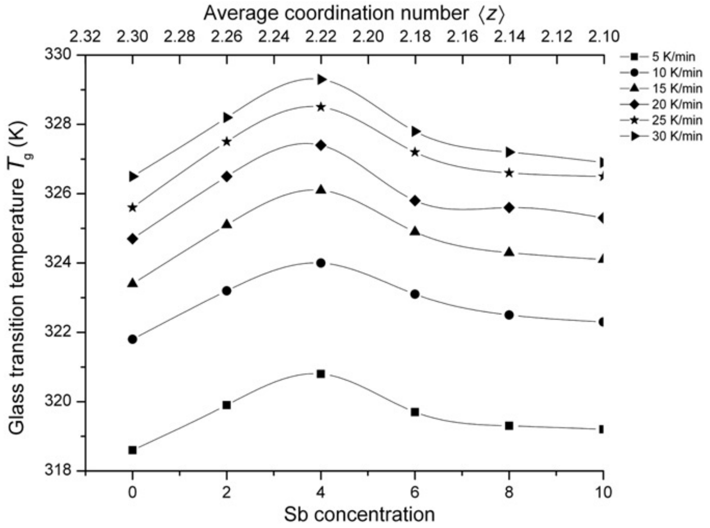

Fig. 3: Variation in glass transition temperature T_g with Sb concentration and average coordination number <z> at different heating rates.

In the case of $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) glasses, the average coordination number could only be determined if the 8–N rule for the coordination number of In (z=5) is assumed to exist. Using this rule, values of average coordination number <z> have been calculated and are plotted with the glass transition temperature (T_g)

on parallel x-axes, as shown in Figure 2. The glass transition temperature is highest for coordination number 2.22, which corresponds to 4 atomic weight % of Sb. However, if approximate use of the 8–N rule for In is not made, the average coordination number does not vary with Sb composition as $(z)_{Sb}=3$ and $(z)_{In}=3$.

The non-isothermal crystallization data are usually interpreted in terms of Johnson – Mehl - Avrami (JMA) theoretical model in which the crystallization fraction χ can be described as a function of time according to the following equation:

$$\chi=1-\exp[-(Kt)^{n}] \quad (3)$$

where n is the Avrami exponent and K is defined as the effective overall reaction rate.

In general, crystallization rate constant K increases exponentially with temperature indicating that the crystallization is a thermally activated process. Mathematically, it can be expressed as

$$K=K_0\exp(-E_c / RT) \quad (4)$$

where E_c is the activation energy of crystallization, K_0 is the pre exponential factor and R is the universal gas constant. The pre-exponential factor (K_0) known as the frequency factor, which gives the number of attempts per second made by the nuclei to overcome the energy barrier, reflecting the information about the number of nucleation sites, has also been calculated.

In eq. (2)), E_c and K_0 are assumed to be practically independent of temperature (at least in the temperature interval accessible in the calorimetric measurements). The values of E_c and the pre-exponential factor K_0 can be obtained by Augis & Bennett's[13] equation, is given by

$$\ln(\alpha/T_c)=-E_c/RT_c+\ln K_0 \quad (5)$$

This method has an extra advantage that the intercept of ln (α/T_c) versus $1/T_c$ gives the pre-exponential factor K_0. The variation of activation energy of crystallization with Sb concentration is shown in Fig.4 and the calculated values of pre-exponential factor are tabulated in Table 1.

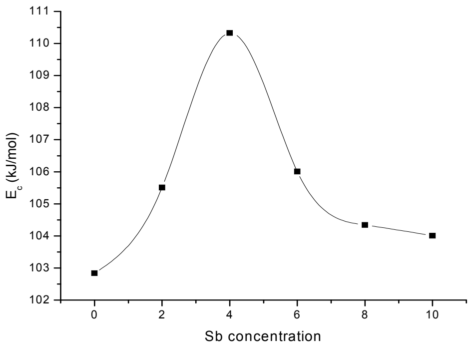

Fig. 4 Plot of activation energy E_c versus Sb concentration

There is a tendency for Se-containing glasses to form polymerized networks and homopolar bonds are qualitatively suppressed [14]. The activation energy (E_c) increases up to 4 at% of Sb. With further addition of Sb, chains as well as ring structures are affected and a decrease in E_c is observed. At lower percentages of Sb, the system contains $SbSe_{4/2}$ tetrahedral units dissolved in a matrix composed of Se chains. With increase of Sb content, the glassy matrix becomes heavily cross-linked and steric hindrance increases. The Se–Se bonds (bond energy 205.8 kJ/mol) will be replaced by Sb–Se bonds, which have higher bond energy (214.2 kJ/mol). Hence, the cohesive energy of the system increases with increasing Sb content, resulting in an increase in the activation energy. The E_c is a maximum at 4 at% Sb, the critical composition at which the system becomes a chemically ordered alloy containing high-energy Sb–Se heteropolar bonds. Further addition of Sb favors the formation of Sb–Sb bonds (bond energy 176.4 kJ/mol), reducing the Sb–Se bond concentration and, thus, the cohesive energy, resulting in a decrease in E_c.

Table1: Calculated value of the pre exponential factor (K_0) for different glassy alloys.

Sample	$Se_{90}In_{10}$	$Se_{90}In_8Sb_2$	$Se_{90}In_6Sb_4$	$Se_{90}In_4Sb_6$	$Se_{90}In_2Sb_8$	$Se_{90}Sb_{10}$
Pre exponential factor K_0 (sec^{-1})	1.10 x 10^{13}	1.51 x 10^{13}	2.98 x 10^{13}	1.68 x 10^{13}	1.34 x 10^{13}	1.24 x 10^{13}

In order to evaluate the stability in glasses, different workers have defined some stability criterion based on Arrhenius temperature dependence of rate constant. Hu et al [15] developed K (T_c) criterion

$$K(T_c) = K_0 \exp(-E_c/RT_c) \qquad (6)$$

The plot of ln K vs Sb concentration at different heating rates is shown in Fig 5(a). The value of ln K is minimum for 4 at weight % of Sb for all the heating rates. The value of ln K increases with the heating rate as shown in Fig. 5(b). High values of ln K or K means poor stability of glass which shows that the $Se_{90}In_6Sb_4$ glassy system is more thermally stable among the $Se_{90}In_{10-x}Sb_x$(x=0,2,4,6,8,10) glassy systems.

This is also confirmed from the values of the thermal stability parameter S [16] as reported in earlier paper [17]. Thus the stability result based on the Arrhenius dependence of the rate constant K agrees with S criterion. Hence one can conclude that the rate of crystallization is related to thermal stability in the present glasses.

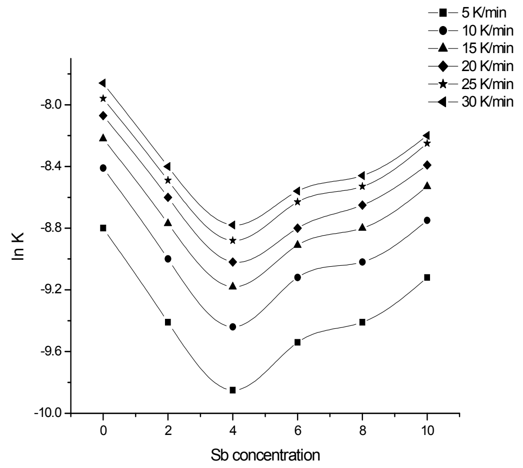

Fig. 5(a): Plot of ln K versus Sb concentration at different heating rates

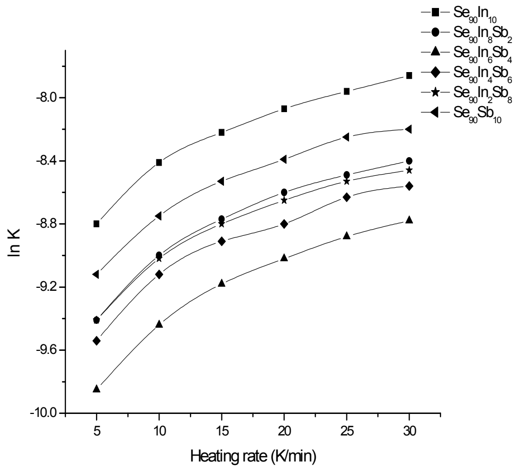

Fig. 5(b): Plot of ln K versus heating rate different Sb concentration

Fig. 6 shows the plots of ln K_0 vs. E_c for glassy $Se_{90}In_{10-x}Sb_x$ systems. It is clear from Fig.6 that K_0 is not a constant but depends on E_c. Curve fitting is done by least square method and the square of coefficient of correlation (R^2=0.9834) of the ln K_0 vs. E_c plot.

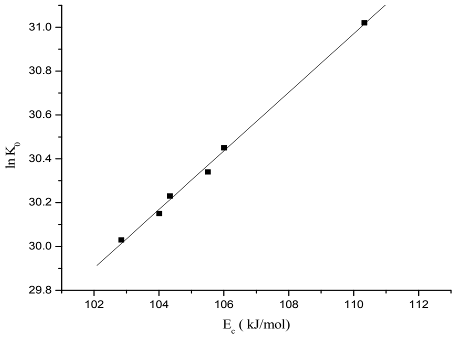

Fig. 6: The plots of ln K_0 vs. E_c for glassy $Se_{90}In_{10-x}Sb_x$ systems

The straight line with good correlation coefficient indicating that K_0 varies exponentially with E_c following the relation: $\ln K_0 = \ln K_{00} + E_c / kT_0$ and confirms the validity of MN Rule in glassy $Se_{90}In_{10-x}Sb_x$ systems for non-isothermal crystallization.

4. Conclusion

Chalcogenide glasses of glassy $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) systems have been prepared by quenching technique. The glass transition temperature is highest for coordination number 2.22, which corresponds to 4 atomic weight % of Sb. The activation energy of crystallization increases as the Sb concentration increases up to 4 atomic weight percentages and further addition of Sb reduces it.

Temperature dependence of crystallization rate constant K (T) has been studied for various glassy alloys. It has been found that K (T) is thermally activated. The activation energy, however, depends on the composition. The activation energy and pre-exponential factor satisfies the MN rule for all the glassy systems. This shows that the MN rule, which is generally observed for thermally stimulated processes in polymers and electronic conduction in amorphous semiconductors; also observed for the crystallization in chalcogenide glasses.

References

[1] Praveen K. Jain, Deepika, K. S. Rathore, N. S. Saxena, Chalcogenide Letters 5, 126(2008)

[2] J. Vazquez, D. Garcia-G. Barreda, P. L. Lopez-Alemany, P. Villares, R. Jimenez-Garay, J.of Non-Cryst.Solids **345**, 142 (2004).

[3] A. A. Soliman, M.B. El-Den, Chalcogenide Letters **4**, 35 (2007)

[4] Anis Ahmad, Samshad A. Khan, K. Sinhal, M. Zulfequar, and M. Husain, Eur. Phys. J. Appl. Phys. **38**, 211 (2007)

[5] M. Abdel-Satar, M. A. Abdel-Rahim and A. El-Korashy, International Journal of Pure and Applied Physics, **3**, 59 (2007)

[6] M. Avarami, J. Phys. Chem **7**, 212 (1939).

[7] M. Avarami, J. Phys. Chem **8**, 212 (1940)

[8] W.A. Johnson and R.F. Mehl, Trans.Am.Inst.Miner.Eng.**135**, 419 (1939).

[9] N. Mehta, A. Kumar, Journal of Optoelectronics and Advanced Materials, **7**, 1473 (2005)

[10]. M Abu El-Oyoun, J. Phys. D: Appl. Phys. **33**, 2211 (2000)

[11] W. Meyer, H. Neldel, Z Tech Phys **18**, 588 (1937)

[12] N. Mehta, A. Kumar, J Mater Sci. **42**, 490 (2007)

[13] J. A. Augis, J. E. Bennett, J. Thermal Anal. **13**, 283 (1978)

[14 M.K. Rabinal, N. Ramesh Rao and P.C. Mathur, J. Mater. Sci. **26**, 3433(1991)

[15] L. Hu and Z. Jiang. *J. Chin. Ceram. Soc.* **18,** 315 (1990).

[16] M. Saad and M. Poulin, Mater. Sci. Forum **11**, 19 (1987)

[17] P. K. Jain, Deepika, N. S. Saxena, Philosophical Magazine **89(**7), 641 (2009)