

Kinetic studies of bulk $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4$ and 5) semiconducting glasses by DSC technique

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Abstract Bulk samples of $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ glassy alloys are obtained by melt quenching technique. Differential scanning calorimetry (DSC) technique (under non-isothermal conditions) has been applied to determine the thermal properties of Se-rich glassy alloys at different heating rates. Results of glass transition temperature, enthalpy released, fragility and specific heat of $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4$ and 5) chalcogenide glasses have been reported and discussed. The glass transition temperature (T_g), activation energy of glass transition and fragility are found to increase with increase in Sn content. The glass transition temperature (by Gibbs–Dimarzio equation) also has been calculated. Both values of T_g (experimental as well as theoretical) are found to be in good agreement at a heating rate of 10 K min^{-1} . It has been observed that the value of specific heat (C_p) below glass transition and difference in the value of C_p before and after glass transition (ΔC_p) is highly compositional dependent. The enthalpy release is related to the metastability of the glasses, and the least stable glasses are supposed to have maximum ΔH_c .

Keywords Glass transition · Specific heat capacity · Enthalpy

Introduction

Chalcogenide glasses are made up of group VI elements (S, Se and Te) of periodic table. These glasses behave as semiconducting materials. During past year, an increasing interest has been observed towards these glasses because of their potential applications in solid state electronics and optical devices such as phase change optical recording, optical imaging, memory switching, non-linear optics and photo lithography [1–7]. Se-rich alloys are used in digital X-ray imaging and TV pick-up tubes. Amorphous Se having twofold coordination consists of randomly mixed long polymeric Se_n chain. When Te is introduced in Se, it results in changes in van der Waals bonds or interchain secondary bonds due to its large size and more electrons in its orbit. The binary chalcogenide glasses (Se-Te) have aging effect, lower crystallization temperature and lower thermal stability [8–10]. To overcome these difficulties, the third element is added as a chemical modifier to enhance the physical, thermal and optical properties [11]. By adding Sn, glass forming region becomes small but there is high transmittance in IR-region due to reduced optical band gap [12]. As Sn is introduced into Se–Te alloy, the coordination number of the system increases resulting in cross-linking of chains of atoms. This results in increase in glass transition temperature (T_g) with Sn content [13]. The present work reports the effect of Sn incorporation on thermal and physical properties of Se–Te glassy alloy. The comparison between experimental and theoretical values of glass transition temperature (T_g) has been reported. Also specific heat capacity of every sample is calculated. Specific heat is a very sensitive way in which atoms or molecules are dynamically bound in a solid. Thus, measurement of such parameter will lead to an effective test for characterizing material as glassy substance [14]. A sudden change in

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specific heat at the glass transition temperature is characteristic of the all chalcogenide glasses. There is jump of the specific heat close to the glass transition temperature following Dulong and the Petit law $C_p = 3R$. Some of the researchers [15–17] had given their attention towards specific heat of glassy alloys. The change in specific heat before and after glass transition is of diversified in nature. A lot of experimental work is required in this direction. Apart from that, in present study, the enthalpy release is related to the metastability of the glasses, and the least stable glasses are supposed to have maximum ΔH_c .

Experimental details

For the preparation of Se–Te–Sn glasses, high purity elements (99.999%) in appropriate atomic percentage were weighed into quartz ampoules. The ampoules, sealed under high vacuum conditions (10^{-5} Torr), were suspended in a vertical furnace at 900 °C for 8 h at heating rate of 3–4 °C/min. These ampoules are shaken vigorously after regular interval of time for homogeneous mixing. The melt was rapidly quenched in ice-water mixture. The quenched samples were removed from the ampoule by dissolving the ampoule in a mixture of HF + H₂O₂ for about 48 h. Amorphous nature of the samples was ensured by the absence of any sharp peaks in the X-ray diffractograms. The prepared solid solution in powder form has been used for thermal analysis using differential scanning calorimetry (DSC). About 10 mg each composition was first sealed in a standard aluminium pan, and the calorimetric thermograms were obtained with Mettler Toledo Stare System in the temperature range 25–500 °C at single heating rates (10 K min⁻¹) under nitrogen atmosphere. Calorimetric measurements were made under non-isothermal conditions.

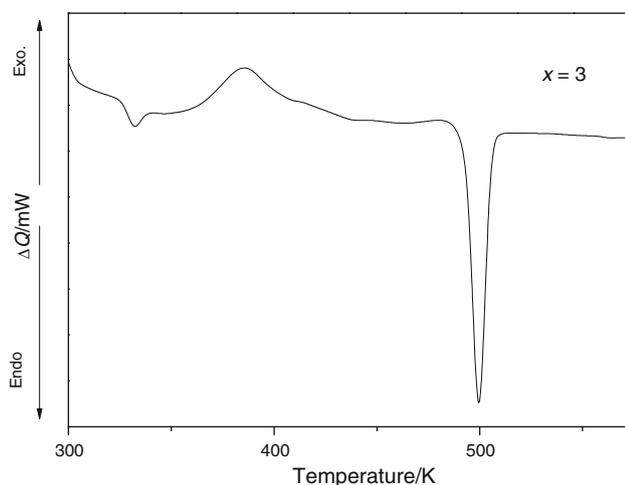


Fig. 1 Plot of DSC curves for Se₉₂Te₅Sn₃ alloy at 10 K min⁻¹

DSC thermograms of Se₉₂Te₅Sn₃ at 10 °C/min are shown in Fig. 1.

Results and discussion

Glass transition temperature

For the characterization of glassy materials, glass transition temperature (T_g) is the most important parameter. It depends upon connectivity and rigidity of vitreous network. By adding an element in Se with coordination number greater than 2, it will result in increase of T_g . The glass transition temperature can be calculated by Gibbs–Di Marzio equation. They have developed a second-order phase transition model and given an empirical relationship between glass transition temperature and density of cross-linking agents inserted inside a system of molecular chains. In a recent study by Sreeram et al. [18], a modified Gibbs–Di Marzio equation presented in the form:

$$T_g = \frac{T_0}{1 - \beta(\langle r \rangle - 2)} \quad (1)$$

In Eq. 1, the term $(\langle r \rangle - 2)$ stresses the role of cross linking. T_0 is the glass transition temperature of linear polymer and β is a system parameter having value between 0 and 1. For constant β , the relationship demonstrated by Micoulaut et al. [19] is as follows:

$$\beta^{-1} = \sum_{i=1}^{M-1} (r_i - 2) \ln \left[\frac{r_i}{2} \right] \quad (2)$$

In our composition, $\beta = 0.72$ and $T_0 = 333$ K [20]. The calculated values of T_g are given in Table 1.

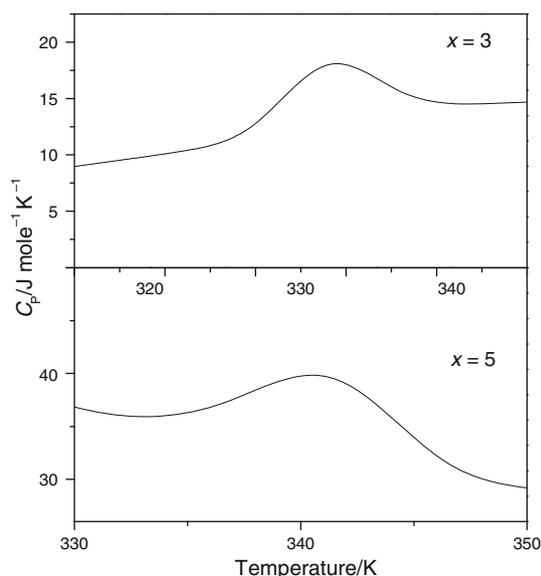
Experimentally differential scanning calorimetric (DSC) curves are recorded for Se₉₂Te_{8-x}Sn_x ($x = 0, 1, 2, 3, 4$ and 5) glassy alloys at a heating rate of 10 °C/min. Well-defined endothermic peaks are observed at glass transition temperature (T_g) as shown in Fig. 1 ($x = 3$ at 10 K min⁻¹ heating rate). It has been observed that glass transition temperature increase with heating rate as well as with Sn concentration (Table 1). Activation energy of glass transition (E_g) is calculated by Kissinger's method and reported in Table 1. The same trend of E_g has already reported in Sn containing glassy system [21].

Specific heat capacity

The variation of specific heat (C_p) of Se₉₂Te_{8-x}Sn_x ($x = 0, 1, 2, 3, 4$ and 5) with temperature is shown in Fig. 2. It has been observed that C_p shows a peak at T_g , i.e. T_g is normally defined as the temperature onset of the step-wise increase in heat capacity during heating of the glassy materials. Also, it is seen that when Sn is introduced in the

Table 1 The values of E_g (by Kissinger), fragility (F), specific heat capacity (C_p), excess heat capacity (ΔC_p), enthalpy released during crystallization (ΔH_c), T_g (theoretical), and T_g (experimental)

x	$E_g/\text{kJ mole}^{-1}$	F	$C_p/\text{J mole}^{-1} \text{K}^{-1}$	$\Delta C_p/\text{J mole}^{-1} \text{K}^{-1}$	$\Delta H_c/\text{J mg}^{-1}$	$T_g/\text{K Theoretical}$	$T_g/\text{K Exp.}$
0	101.23 ± 16	16.47	39.54	7.23	0.11	333	322.43
1	118.69 ± 33	19.13	25.74	6.72	0.035	337.86	324.44
2	132 ± 25	21.29	21.23	2.45	0.038	342.87	326.2
3	142.42 ± 26	22.81	18.86	2.32	0.019	348.03	327.2
4	167.74 ± 16	26.81	9.21	1.07	0.017	353.35	330.71
5	180.94 ± 17	28.13	40.72	2.96	0.12	358.83	334.47

**Fig. 2** Plot of C_p versus temperature (T) for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 3$ and 5) alloy

glassy material containing Se–Te, C_p decreases except at $x = 5$ at.%. The decrease in C_p may be due to breakdown of the thermodynamic equilibrium of the system or it may be due to the non-availability of the larger number of degrees of freedom in the alloy which could absorb heat energy [22]. It can be noted that for $x = 5$ at.%, the K_{gl} (glass forming ability) and the enthalpy released are minimum and maximum, respectively. This gives support regarding the decrease of thermal stability as Sn is doped it to Se–Te binary alloy.

Figure 2 shows typical C_p versus T plot obtained for $\text{Se}_{92}\text{Te}_5\text{Sn}_3$ glass at 10 K min^{-1} heating rate. It has been observed that below T_g , the C_p values agree with the classical limit of Dulong and Petit for the vibrational heat capacity of solids ($C_p = 3R$). The increase in C_p at glass transition temperature is due to the addition of translational and rotational modes made available by the breakage of bonds forming the glass network. The sudden jump at C_p can be attributed to the anharmonic contributions to the

specific heat [23]. The overshoot in the value of C_p at the upper end of “ C_p jump” is due to relaxation effects. The observed peak at C_p may be due to the fact that the relaxation time at this temperature becomes of same order as the time scale of the experiment because time scale is highly dependent both on temperature as well as instantaneous structure [24]. Excess heat capacity (specific heat capacity jump) at T_g can be calculated from the following relation:

$$\Delta C_p = (C_{pl} - C_{pg})_{T=T_g}, \quad (3)$$

where C_{pl} and C_{pg} are the heat capacity of liquid and glassy states across the glass transition (at $T = T_g$). ΔC_p reflects the amount of configurational change occurring in the network during glass to liquid transition. When Sn is introduced in Se–Te alloy, ΔC_p decreases up to $x = 4$ at.% and then increases for $x = 5$ at.%.

The decrease in ΔC_p may be due to the fact that with increasing Sn content the concentration of defect states increases. It leads to a decrease in structural relaxation time and hence decreases in ΔC_p . It may be due to the decrease in mean atomic mass because Te ($127.6 \text{ g mole}^{-1}$) is replaced by Sn ($116.7 \text{ g mole}^{-1}$) in our composition, so less specific heat is required for structural rearrangement. All these factors are responsible to decrease in C_p and ΔC_p , and increase of thermal stability. The different behaviour at $x = 5$ at.% may be due to formation of voids in the network, which requires more heat for structural rearrangement, results in increase in C_p and ΔC_p . For $x = 5$, glass forming ability is also small. This increase may be due to availability of the larger number of degrees of freedom in the alloy which could absorb the heat energy. The observed values of C_p and ΔC_p are shown in Table 1 and plotted in Fig. 3.

Fragility

Fragile glasses are substances with non-directional interatomic or intermolecular bonds. Strong glasses are those which show resistance to structural degradation and usually

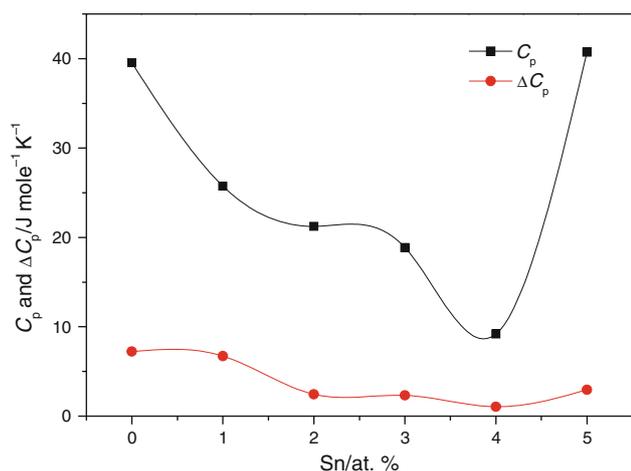


Fig. 3 Plot of C_p and ΔC_p versus Sn (at.%) for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) alloy

associated with a small ΔC_p . Fragility quantifies the anomalous non-Arrhenius transport behaviour of glassy materials near the ergodicity breaking glass transition region. Fragility (F) is calculated using the following relation [25]

$$F = \frac{E_g}{T_g \ln 10}, \quad (4)$$

where E_g is activation energy of glass transition and T_g is glass transition temperature. The value of $F \approx 16$ defined as the strong glass-forming liquids [26], while a high value of $F \approx 200$ represents the fragile glass-forming liquid [27]. In our investigated system, the values of F vary from ≈ 16 to 28 means strong glass forming liquid. Glass-forming liquids are classified based on the dependence of their viscosities; liquids that exhibit an Arrhenius temperature dependence on viscosity are defined as strong glass-forming liquids and those exhibit a non-Arrhenius

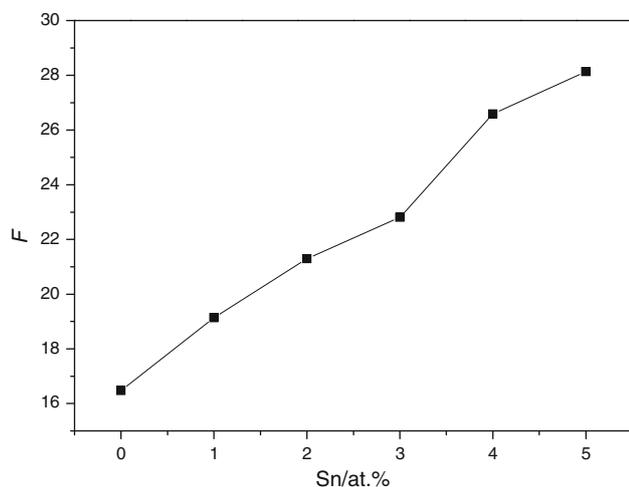


Fig. 4 Plot of F versus Sn (at.%) at heating rate 10 K min^{-1}

behaviour (described by a Vogel Tammann Fulcher equation) are declared as fragile glass-forming liquids. Fragility increases with the addition of Sn. The increase of F with increasing Sn concentration means that the glasses become more fragile and their tendency to structural arrangement increases with increasing non-directional interatomic bonds. The plots of F (fragility) with Sn concentration are shown in Fig. 4.

Enthalpy

The dependence of T_g in chalcogenide glasses is interpreted in terms of thermal relaxation phenomena. In such kinetic interpretation, the enthalpy at a particular temperature and time of the glassy system relaxes towards an equilibrium value. The enthalpy at a particular temperature and time $H(T, t)$ of the glassy system after an instantaneous isobaric change in temperature relaxes isothermally towards a new equilibrium value $H_c(T)$ according to formula [28]:

$$\left[\frac{\delta H}{\delta t} \right]_T = - \frac{(H - H_c)}{\tau}, \quad (5)$$

where τ is known as structural relaxation time.

The knowledge of the relaxation enthalpy is necessary to understand the structure and properties of glassy alloys. The enthalpy ΔH_c released during crystallization process is associated with the stability of glasses, i.e. glasses with the lowest value of $T_c - T_g$ will have maximum value of ΔH_c . The crystallization enthalpy (ΔH_c) was calculated using the relation, $\Delta H_c = kA/M$, where A is the area of the crystallization exothermic and k is the calibration constant of the instrument which is equal to 1.5. The value of k was deduced by measuring the total area of the complete melting endotherm of high purity tin and indium and using the well-known enthalpy of melting of these standard

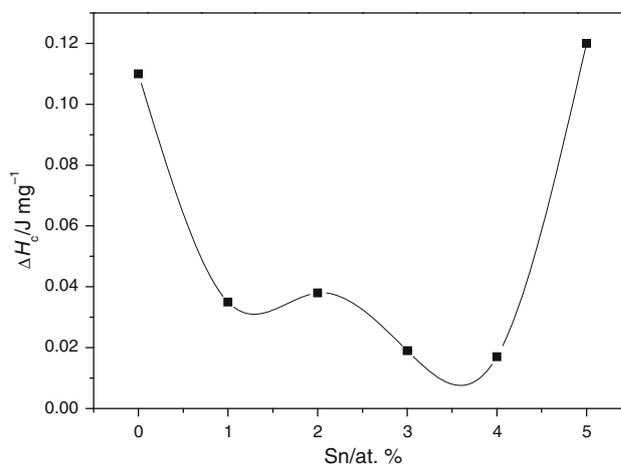


Fig. 5 Plot of ΔH_c versus Sn (at.%) at heating rate 10 K min^{-1}

materials. M is the mass of the sample in milligram. The values of ΔH_c for the $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4$ and 5) glassy samples at heating rate of 10 K min^{-1} is shown in Table 1. In our investigated composition $x = 4$ at.% have minimum enthalpy and maximum thermal stability. For $x = 0$ and 5 at.%, $T_c - T_g$ is minimum and hence maximum enthalpy. Apart from that small K_{gl} (glass forming ability) also supports maximum enthalpy. The plots of ΔH_c with Sn concentration are shown in Fig. 5.

Conclusions

A study of non-isothermal crystallization for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4$ and 5) performed by differential scanning calorimetry (DSC) shows a well-defined glass transition temperature followed by a crystallization peaks. The glass transition temperature calculated theoretically as well as experimentally is in good match. The fragility, specific heat capacity and change in heat capacity at glass transition (specific heat jump) are evaluated. The fragility found to increase with Sn concentration, while specific heat decreases from $x = 0$ to 4 and increases at $x = 5$. Another parameter ΔH_c (enthalpy release during crystallization) has also been calculated. The factors that determine thermal stability of glasses, i.e. the temperature difference $T_c - T_g$ and the enthalpy released ΔH_c , indicate that $x = 5$ at.% of Sn have small glass forming ability and reduced thermal stability.

References

- Wagner T, Frumar M, Suskova V. Photoenhanced dissolution and lateral diffusion of Ag in amorphous As-S layers. *J Non-Cryst Solids*. 1991;128:197–207.
- Ramesh K, Asokan S, Sangunni KS, Gopal ESR. Glass formation in germanium telluride glasses containing metallic additives. *J Phys Chem Solids*. 2000;61:95–101.
- Frumar M, Cernosek Z, Jedelsky J, Frumarova B, Wagner T. Photoinduced changes of structure and properties of amorphous binary and ternary chalcogenides. *J Optoelectron Adv Mater*. 2001;3:177–88.
- Elliot SR. *Physics of amorphous materials*. 2nd ed. London: Longman; 1991.
- Asobe M. Non-linear optical properties of chalcogenide glass fibres and their application to all-optical switching. *Opt Fiber Technol*. 1997;3:142–8.
- Fugimori S, Yagi S, Yamzaki H, Funakosky N. Crystallization process of Sb-Te alloy films for optical storage. *J Appl Phys*. 1988;64:1000–4.
- Katsuyama T, Satoh S, Atsumura HM. Scattering loss characteristics of selenide-based chalcogenide glass optical fibre. *J Appl Phys*. 1992;71:4132–6.
- Srivastva S, Mehta N, Singh CP, Shukla RK, Kumar A. Dielectric parameters in $\text{Se}_{70}\text{Te}_{30}$ and $\text{Se}_{70}\text{Te}_{28}\text{Zn}_2$ chalcogenide glasses. *Physica B*. 2008;403:2910–6.
- Kozicky MN, Mitkova M. Mass transport in chalcogenide electrolyte films—materials and applications. *J Non-Cryst Solids*. 2006;352:567–77.
- Vashneya AK, Mauro DJ. Microhardness, indentation toughness, elasticity, plasticity, and brittleness of Ge-Sb-Se chalcogenide glasses. *J Non-Cryst Solids*. 2007;353:1291–7.
- Singh AK, Mehta N, Singh K. Electrical properties of Se-Zn-In chalcogenide glasses. *Eur J Appl Phys*. 2009. doi:10.1051/epjap/2009047.
- Chander R, Thangaraj R. Thermal and optical analysis of Te-substituted Sn-Sb-Se chalcogenide semiconductors. *Appl Phys A*. 2010;99:181–7.
- Kaur G, Thangaraj R, Komatsu T. Crystallization kinetics of bulk amorphous Se-Te-Sn system. *J Mater Sci*. 2001;36:4530–3.
- Saraswat S, Kushwaha SSS. Specific heat studies in a-Se and a- $\text{Se}_{90}\text{M}_{10}$ ($M = \text{In, Sb, Te}$) alloys. *J Therm Anal Calorim*. 2009; 96:923–7.
- Kasap SO, Wagner T, Maeda K. Heat capacity and the structure of chalcogenide glasses by modulated temperature differential scanning calorimetry (MDSC). *Jpn J Appl Phys*. 1996;35:1116–9.
- Avagadro A, Aldrovandi S, Carini G, Siri A. Specific heat and thermal conductivity of ionic conductors and chalcogenide glasses at low temperature. *Philos Mag*. 1989;59:33–42.
- Pradeep P, Saxena NS, Kumar A. Heat capacities and relaxation effects of Se-Te-Cd glasses. *J Phys Chem Solids*. 1997;58:385–9.
- Sreeram AN, Swiler DR, Varshneya AK. Gibbs-DiMarzio equation to describe the glass transition temperature trends in multicomponent glasses. *J Non-Cryst Solids*. 1991;127:287–94.
- Micoulaut M, Naumis GG. Glass transition temperature variation, cross-linking and structure in network glasses: a stochastic approach. *Europhys Lett*. 1999;47:568–74.
- Imran MMA, Bhandari D, Saxena NS. Kinetic study of bulk $\text{Ge}_{22}\text{Se}_{78-x}\text{Bi}_x$ ($0, 4$ and 8) semiconducting glasses. *J Therm Anal Calorim*. 2001;65:257–74.
- Deepika, Rathore KS, Saxena NS. A kinetic analysis of non-isothermal glass-crystal transformation in $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$ ($0 \leq x \leq 0.5$) glasses. *J Phys Condens Matter*. 2009. doi:10.1088/0953-8984/21/33/335102.
- Sharma A, Barman PB. Effect of Bi incorporation on the glass transition kinetics of $\text{Se}_{85}\text{Te}_{15}$ glassy alloy. *J Therm Anal Calorim*. 2009;96:413–7.
- Mahadevan S, Giridhar A, Singh AK. Calorimetric measurements on As-Sb-Se glasses. *J Non-Cryst Solids*. 1986;88:11–34.
- Tiwari RS, Mehta N, Shukla RK, Aggarwal P, Kumar A. Specific heat studies in glassy $\text{Se}_{78}\text{Ge}_{22}$ and $\text{Se}_{68}\text{Ge}_{22}\text{M}_{10}$ ($M = \text{Cd, In, Pb}$) alloy. *Indian J Pure Appl Phys*. 2005;43:363–7.
- Ngai KL, Rendell RW, Pye LD, LaCourse WC, Stevens HJ. *The physics of non-crystalline solids*. London: Taylor and Francis; 1992. p. 309–42.
- Vilgis TA. Strong and fragile glasses: a powerful classification and its consequences. *Phys Rev B*. 1993;47:2882–5.
- Bohmer R, Angell CA, Richert R, Blumen A, editors. *Disorder effects on relaxational processes*. Berlin: Springer; 1994.
- Saiter JM. Physical ageing in chalcogenide glasses. *J Optoelectron Adv Mater*. 2001;3:685–94.