

THERMO-PHYSICAL PROPERTIES OF Se-Te-Sb VITREOUS CHALCOGENIDE SEMICONDUCTORS

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Measurements of thermo-physical properties such as effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) of $\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x$ (at $x = 2, 4, 6, 8$ and 10) chalcogenide glasses have been made with the help of Transient Plane Source (TPS) technique at room temperature. We have calculated phonon mean free path (τ) and thermal effusivity (e) of $\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x$ (at $x = 2, 4, 6, 8$ and 10) chalcogenide glasses from the measured values of effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e). In the present study the variation of thermo-physical properties i.e. effective thermal conductivity (λ_e), effective thermal diffusivity (χ_e), phonon mean free path (τ) and thermal effusivity (e) has been plotted as the function of average co-ordination number $\langle r \rangle$ which decides the stability of these glasses at different Sb at wt%. The measured values of the effective thermal conductivity (λ_e), and of the effective thermal diffusivity (χ_e) show maxima because the chain length is maximum, hence phonon mean free path is maximum at $\langle r \rangle = 2.06$. Thermal effusivity (e) shows its minimum at $\langle r \rangle = 2.06$ because of non availability of large number of degree of freedom to exchange the thermal energy with surroundings.

(Received October 4, 2007; accepted October 9, 2007)

Keywords: Chalcogenide glasses, Thermal conductivity, Thermal diffusivity, Thermal effusivity

1. Introduction

Systematic studies on the variation of different thermo-physical properties of chalcogenide glasses with average co-ordination number have gained considerable interest among solid state physicist. In these materials, the inter-atomic forces are predominantly covalent. Chalcogenide glasses prepared by melt quenching, in general, are p-type semiconductor [1]. This is attributed to following two reasons. (i) The number of electron excited above the conduction band mobility edge is smaller than the number of holes excited below the valence band mobility edge. (ii) The lifetime of free holes excited from positive defect state is higher than the lifetime of free electrons excited from negative defect state. Chalcogenide glasses exhibit attractive electrical and optical properties which makes them useful for several potential applications. Specifically, the threshold and memory switching behaviour and infrared transmission [2] of many of these glasses makes them potential material for use in memory device and optical data storage [3]. There are analytical applications of chalcogenide glasses as chemical sensors in environmental monitoring and process control [4] and as a Semiconductor-based Field-effect Platform for bio-chemical and physical sensor [5]. Especially Selenium alloys exhibit a unique property of reversible transformation which makes these systems very useful for optical memory, X-ray imaging and photonics [6]. Binary Se-Te alloys are found useful in practical application. From technology point of view these glasses should be stable with time and temperature. The addition of Sb as third element in Se-Te

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alloy improves the stability as well as conductivity. Thermal conductivity and diffusivity of chalcogenide glasses has been widely studied in the past years. This interest was stimulated by the fact that thermal diffusivity and conductivity are very sensitive to the structure of the solids. In fact, thermal conductivity in nonmetals is connected to the vibrations of the atoms in the network around their equilibrium positions and structural changes are expected to influence the heat diffusion process. In this paper we present the results got on effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) performed with the help of Transient plane source (TPS) technique introduced by Gustafsson [7]. With the help of these measured values of effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) we have calculated the thermal effusivity (e) and the phonon mean free path (τ), which play a very important role in the understanding of the stability and thermo-physical behaviour of $\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x$ chalcogenide glasses (at $x = 2, 4, 6, 8$ and 10).

2. Material preparation

High purity (99.999%) Se, Te and Sb in appropriate atomic percentages were weighed into a quartz glass ampoule (length of 5 cm and internal diameter of 8 mm). The contents of the ampoule (5 g) were sealed into a vacuum of 10^{-5} Torr and heated in a furnace where temperature was raised at a rate of 3–4 K per min up to 925 K and kept around that temperature for 10 h. To ensure the homogeneity, the ampoules were rocked frequently. Molten samples were then rapidly quenched in ice cooled water. Samples obtained by quenching were in the form of glasses. The glassy nature has been confirmed through X-ray diffraction. These bulk glasses were then crushed to fine powders by grinding process. Pellets of thickness, 1 mm and diameter, 12 mm were prepared by a pressure machine at a pressure of 5 tons.

3. Experimental

The measurements reported in the paper were performed with a TPS element which is made of 10 μm thick nickel foil with an insulating layer made of 50 μm thick kapton on each side of metal pattern. Evaluation of these measurements was performed in a way that was outlined by Gustafsson [7]. In experiments with insulating layers of such thickness, it is necessary to ignore the voltage recorded during first few seconds because of influence of insulating layers. However owing the size of the heated area of the TPS element, the characteristic time of the experiment is so long that it is possible to ignore a few second of recorded potential difference values and still get very good result. An important aspect of the design of any TPS element is that the pattern should be such that a large part of the hot area as possible should be covered by the electrically conducting pattern, as long as there is insulating between the different parts of the pattern. This is particularly important when insulating layers are covering the conduction pattern and the surface(s) of the sample. It should be noted that the temperature difference across the insulating layer can be considered constant after a short initial transient. The samples are in the form of pellets of 12 mm diameter and 1 mm thickness and the surface of the pellets are smooth so as to ensure perfect thermal contact between the sample and the heating elements, as the TPS sensor is sandwiched between the two pellets of sample material in the sample holders. The change in voltage was recorded with digital voltmeter, which was connected to the sample was adjusted according to the nature of the sample material and was in most case, in the range of $6\text{-}16 \times 10^{-6}$ W/m².

4. Results and discussion

The idea of using the average co-ordination number $\langle r \rangle$ to interpret the compositional dependence on thermo-physical properties, allows the importance of the topological structure to be

put in the evidence. It is well known that the coordination number of covalently bonded atoms in glass is given by the $8-N$ rule, where N is the number of the outer-shell electrons [8, 9]. For a multi-component, chain-forming chalcogenide glass system, the degree of crosslinking is often described by the concept of the average coordination number ($\langle r \rangle$), which is defined simply as the atom-averaged covalent coordination of the constituents [10]. The degree of crosslinking has a profound effect on the thermal and mechanical properties of chalcogenide glasses, because increasing the crosslinking makes the atoms become more tightly bound [11]. In the present paper, $\langle r \rangle$ is used to discuss its influence on the thermo-physical properties in $\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x$ (at $x = 2, 4, 6, 8$ and 10) chalcogenide glass systems. Average co-ordination number has been calculated as

$$\langle r \rangle = [(x) Z_{\text{Sb}} + (15) Z_{\text{Te}} + (85-x) Z_{\text{Se}}] / 100 \quad (1)$$

Where from literature $Z_{\text{Sb}} = 3.5$, $Z_{\text{Te}} = 2$ and $Z_{\text{Se}} = 2$ are co-ordination number of Sb, Te and Se separately and X is the atomic weight percentages of the elements Sb respectively in the glassy network. The composition falls in the range of $2.03 \leq \langle r \rangle \leq 2.15$. The amorphous nature of the as prepared sample was confirmed by X-ray diffraction using Philips Mode PV 1840 diffractometer with an iron $K\alpha$ radiation source ($\lambda = 1.937355 \text{ \AA}$).

4.1 Variation of phonon mean free path (τ) with effective thermal conductivity (λ_e)

Effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) of the samples of $\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x$ (at $x = 2, 4, 6, 8$ and 10) chalcogenide glasses has been measured by TPS technique at room temperature. Effective thermal conductivity (λ_e) in glassy semiconductor is dominant by transport of heat by the vibrational (phonon) modes of the network. Primarily, molecular vibration and defects in the structure limits the mean free path (τ) of the propagating phonon modes. In general, electronic contribution to thermal resistance is rather small due to the low concentration of electrons in the medium. In chalcogenide glasses, electrical conduction is primarily p-type due to the presence of charged defect state. The observed compositional dependence of phonon mean free path (τ) has been correlated with the increase of weak bond density in the structure of the compositions investigated with increasing Sb content at expense of Se content. Increase in thermal conductivity has been correlated with decrease in mobility. Phonon mean free path is given as.

$$\tau = \frac{3\rho \cdot \chi_e}{V} \quad (2)$$

Where χ_e is effective thermal diffusivity, ρ is density of the material and V is velocity of sound which is $\approx 2000 \text{ m/s}$ in most chalcogenide glasses [12]. The variation of effective thermal conductivity and phonon mean free path is shown in Fig. 1.

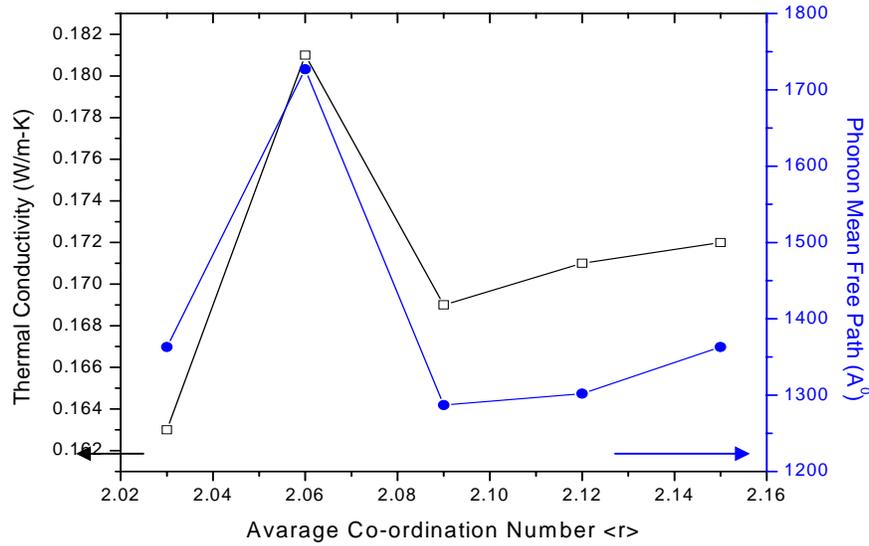


Fig. 1. Variation of the effective thermal conductivity (λ_e) and phonon mean free path (τ), respectively, as a function of average co-ordination number $\langle r \rangle$.

It is well known that in the alloys with selenium there is a marked tendency to form a polymerized network and the homopolar bonds are qualitatively suppressed [13]. The structure of a Se-Te system prepared by quenching is regarded as a mixture of Se_8 member rings, Se_6Te_2 mixed rings and Se-Te chain. A strong covalent bond exists between the atoms where as Van der Waals forces between the chains [14]. Initially there are Se-Se bonds with a small amount of Te-Te bonds. For lower concentration of Sb the system contains $\text{SbSe}_{4/2}$ tetrahedral units dissolved in a matrix composed of Se-Se chains, with the increase of Sb content Se-Se bonds now will be replaced by Se-Sb bonds because of cross-linking. As $\langle r \rangle$ increases from $\langle r \rangle = 2.03$ to $\langle r \rangle = 2.06$, effective thermal conductivity (λ_e) as well as phonon mean free path (τ) increases drastically and shows their maximum at $\langle r \rangle = 2.06$. Formation of Se-Sb heteropolar bonds are dominant in the system and is maximum at $\langle r \rangle = 2.06$. Further addition of Sb in the system favors the formation of Sb-Sb bonds due to which chain length decreases, hence phonon mean free path (τ) and effective thermal conductivity (λ_e) rapidly decreases at $\langle r \rangle = 2.09$. At higher values i.e. $\langle r \rangle = 2.12$ or more, the thermal conductivity and phonon mean free path remains nearly constant.

4.2 Variation of effective thermal diffusivity (χ_e) with thermal effusivity (e)

We know that the diffusion is the process in which net action of matter (particle or molecule), heat, momentum or light whose end is to minimize concentration gradient. The purpose of diffusion therefore is to minimize Gibbs free energy. This is a spontaneous process more familiarly known as a passive form of transport rather than active. The power dissipation in optoelectronics and microelectronic devices is an important mechanism limiting the device performance. The room temperature value of thermal diffusivity will help to optimize the power dissipation in such device [15]. Thermal effusivity (e) is also an important thermo-physical property, which characterizes the thermal impedance of matter i.e. its ability to exchange thermal energy with surrounding [16]. Importance of thermal effusivity (e) lies not only on the aforementioned thermal exchange characteristic but, also its utility in making complete thermal characterization through combination with other thermo-physical properties. Thermal effusivity (e) is given by the equation:

$$e = (\lambda_e \cdot \rho \cdot C)^{1/2} \quad (3)$$

where (λ_e) effective thermal conductivity, ρ density of material, and C is specific heat of the material. The variation of effective thermal diffusivity (χ_e) and thermal effusivity (e) with Sb content as a function of co-ordination number is shown in Fig. 2.

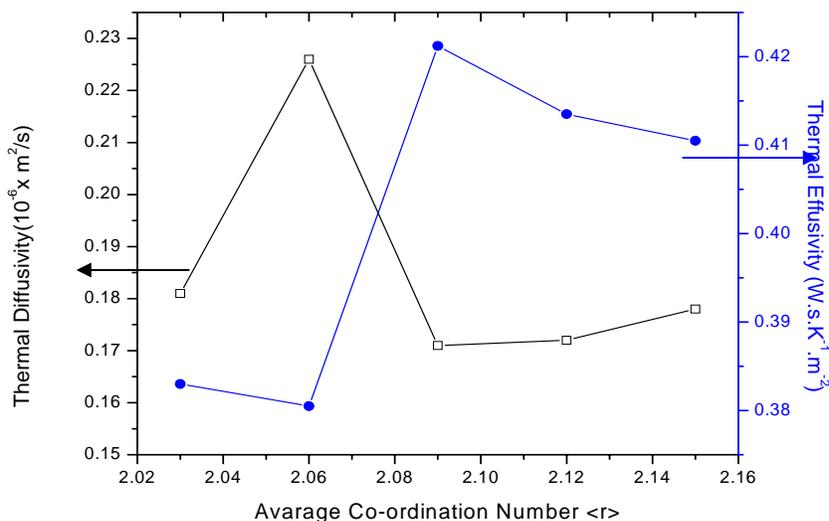


Fig 2. Variation of the effective thermal diffusivity (χ_e), and thermal effusivity (e), respectively, as a function of the average co-ordination number $\langle r \rangle$.

The thermal effusivity (e) shows a clear minimum, while effective thermal diffusivity (χ_e) shows a maximum at $\langle r \rangle = 2.06$, which corresponds to the critical composition of the series. As we introduce Sb in Se-Te matrix the free energy varies with the Sb content because of formation of different types of bonds in the system. Initially there is Se-Se bonds with lower bond energy (205.8 KJ/mol) A small amount of Te-Te bonds exists also. These pairs have very low bonding energy. For lower concentration of Sb the system contains $\text{SbSe}_{4/2}$ tetrahedral units dissolved in a matrix composed of Se-Se chains. With the increase of Sb content the glassy matrix becomes heavily cross-linked and the steric hindrance increases. Se-Se bonds of lower energy will be now replaced in the system by Se-Sb bonds of high energy (214.2 KJ/mol) and these bonds will reach a maximum at $\langle r \rangle = 2.06$ because of cross-linking of two factors: the effective thermal diffusivity show a maximum and the thermal effusivity exhibits a minimum because of non availability of large number of degree of freedom for heat transport at this $\langle r \rangle$. Specific heat also shows its minimum at $\langle r \rangle = 2.06$, which is also confirmed through the trend observed for heat release in the crystallization region of the glass in crystallization kinetics [17]. It is the non availability of large number of degree of freedom in the alloy which could absorb the heat energy. It means the system releases the least heat at $\langle r \rangle = 2.06$; hence the thermal effusivity (e) shows a minimum at this $\langle r \rangle$. Now as Sb content increases the specific heat increases because of the formation of Sb-Sb bonds of low energy (176.4 KJ/mol) at $\langle r \rangle = 2.09$, and the effective thermal diffusivity shows its minimum and thermal effusivity its maximum. Further addition of Sb corresponds to higher values of $\langle r \rangle \leq 2.12$. In these cases the effective thermal diffusivity slightly increases and the thermal effusivity decreases, which is possible because of availability of new degrees of freedom Thus, the thermal energy exchange with surrounding medium increases.

5. Conclusions

From the above study we concluded that the effective thermal conductivity (λ_e) and phonon mean free path (τ), increases as $\langle r \rangle$ increases and is maximum at $\langle r \rangle = 2.06$ because the chain length is maximum. So the phonon mean free path and the effective thermal diffusivity (χ_e) are maximum, the glassy matrix becomes heavily crosslinked and the steric hindrance increases. The maximum is reached at $\langle r \rangle = 2.06$ and the bond energy is also maximum here. The thermal effusivity (e) is minimum at $\langle r \rangle = 2.06$ because of non-availability of degree of freedom to exchange energy with the surrounding medium. As Sb content increases further, the effective thermal diffusivity (χ_e) decreases, the thermal effusivity (e) increases and is maximum at $\langle r \rangle = 2.09$ where the effective thermal diffusivity (χ_e) exhibits a minimum and at higher values of $\langle r \rangle$ the thermal effusivity (e) decreases and finally becomes constant and the effective thermal diffusivity (χ_e) increases and becomes almost constant as the thermal effusivity (e). Finally, we conclude that the composition corresponding to $\langle r \rangle = 2.06$ is a critical composition at which the effective thermal conductivity (λ_e), the effective thermal diffusivity (χ_e), the phonon mean free path (τ) reach their maxima and the thermal effusivity (e) is minimum.

Acknowledgements

Authors Dr. Kedar Singh and Mr. Pushpendra Kumar are thankful to CSIR (Project) and UGC (Rajeev Gandhi National Fellowship) for providing financial assistance, respectively. We are also thankful to Prof. N.S. Saxena Department of Physics, University of Rajasthan, Jaipur for help in various ways.

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