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THERMAL TRANSPORT IN $Se_{81}Te_{15}Sb_4$ CHALCOGENIDE GLASS

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Measurement of effective thermal conductivity (λ_e) effective thermal diffusivity (χ_e) of $Se_{81}Te_{15}Sb_4$ thin pellets prepared under a load of 5 tons is carried out in the temperature range 25 °C to 85 °C using the transient planar source (TPS) technique. In the heating process the modification of λ_e and χ_e isobserved . Both quantities are found toreqach a maximum at 65 °C, which lies in the vicinity of the glass transition temperature. During the cooling process λ_e and χ_e remain the same at all temperatures. Such behaviour proves the thermal hysteresis in the sample, which can be explained on the basis of the structural changes in the material.

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1. Introduction

The chalcogenide glasses have recently attracted the attention because of their use in various solid state devices. The structural studies of these materials are very important for better understanding of the transport mechanisms in them. The studies of chalcogenide glasses are also attractive due to their importance in preparing corrosion resistive and electronic memories materials [1-3]. Moreover, they are interesting as core materials for optical fibers for light transmission, especially when short wavelength transmission and good flexibility are required [4-6].The selenium has wide commercial applications and its device applications like switching memory, xerography, X-ray imaging, photonic and non-linear applications etc. made it attractive. It also exhibits unique properties of reversible transformation [7,8]. However, pure selenium has disadvantages because of its short life time, low sensitivity and thermal instability [9].Binary Se-Te alloys are found to be useful in practical applications from the technological point of view, these glasses being stable with time and temperature. The addition of Sb as third element in Se-Te alloy improves the stability as well as the photoconductivity [10].

The common view regarding selenium is that it exist in two structural forms : long helical chains and eight membered rings with strong covalent bonds existing between the atoms within the molecular unit and weaker force, perhaps the van-der- Waals type binding together neighboring units [11] . It is well known that thermal relaxation occurs in these glasses[12], when a glassy substance suffers instantaneous changes in temperature (during the quenching process) relaxes from the state of higher enthalpy towards an equilibrium state of lower enthalpy. This type of thermal relaxation depends on the annealing temperature and time and may be quite fast near the glass transition temperature. There were investigated [13,14] the glass transition phenomenon, crystallization kinetics and were carried out simultaneous measurement of effective thermal conductivity and effective thermal diffusivity of $Se_{85-x}Te_{15}Sb_x$ (x= 2, 4, 6, 8 and 10) chalcogenide glasses. In order to make the chalcogenide glasses useful in the above mentioned applications it is very important to investigate their thermal transport properties. The investigation of effective thermal conductivity and effective thermal diffusivity with temperature will provide us with the understanding of the mechanism of degradation in these glasses. So far no serious efforts have been made to measure temperature dependence of thermal transport properties such as the effective thermal conductivity and effective thermal diffusivity of these materials. It has been shown that $Se_{81}Te_{15}Sb_4$ glass has better thermal stability than other glasses of this type. Therefore, we have chosen $Se_{81}Te_{15}Sb_4$ chalcogenide glass for the investigation of the temperature dependence of thermal transport properties. The study of thermal transport such as thermal conductivity and thermal diffusivity of materials is important from many points of view. A different feature of the thermal conductivity and thermal diffusivity is that , it can be used as a tool in the study of imperfections, dislocations and voids as the carrier mean free path is affected by lattice defects[15]. In the present work an attempt has been made to study the variation of effective thermal conductivity **(λ_e)** and effective thermal diffusivity **(χ_e)** of $Se_{81}Te_{15}Sb_4$ chalcogenide glass in a temperature range from 25 ^oC to 85 ^oC during heating and cooling process. The technique used for the measurement **λ_e** and **χ_e** is transient planar source (TPS), which has been developed by S.E. Gustaffson [16] as an important over the transient hot strip (THS) method . The transient planar source theory is given in the reference[14].

2. Material preparation and Experimental Technique:

In the present research work the quenching method has been adopted to prepare the $Se_{81}Te_{15}Sb_4$ chalcogenide glass. The desired amount of the Se, Te and Sb of high purity (99.999 %) were weighted using an electronic balance. The high pure material having the desired composition ratio of the elements were selected into quartz ampoule (length 5 cm and internal diameter 8 mm) in vacuum of 10^{-6} Torr and heated in a furnace where the temperature was raised at rate of 3-4 ^oC/min up to 900 ^oC and kept at this temperature for 9-10 hours, to ensure the homogeneity of the sample. The molten sample was rapidly quenched in ice cooled water. Sample obtained by quenching was in the form of glass. Glassy nature of the material has been confirmed through X-ray diffraction. This bulk glass was than crushed to fine powders by mortal and pestle method. The sample with the shape of pellet of thickness 1 mm and diameter 12 mm is obtained by a pressure machine at a load of 5 tons. The surface of these pellets is smooth so as to ensure a perfect thermal contact between the sample and heating elements, as the **TPS** sensor as shown Fig.1 sensor is sandwiches between two pellets of sample materials in the sample holder as shown Fig.2. The schematic diagram of the electric circuit used for the simultaneous measurements of effective thermal conductivity (λ_e) and effective thermal diffusivity (**χ_e** **)** is shown in Fig. 3.The entire arrangement of the sample holder with the sample is placed in an electrical furnace, which is maintained at constant temperature within $\pm$ 1 ^oC. Several runs of the experiment are performed at each recorded temperature to ensure the reproducibility of these results. Also, to reach thermal equilibrium, the samples are maintained at particular temperature for at least two hours before the experimental data are recorded. The change in the voltage was followed with a digital voltmeter, which was connected online to the personal computer . The power output to the sample was adjusted according to the nature of the sample material.

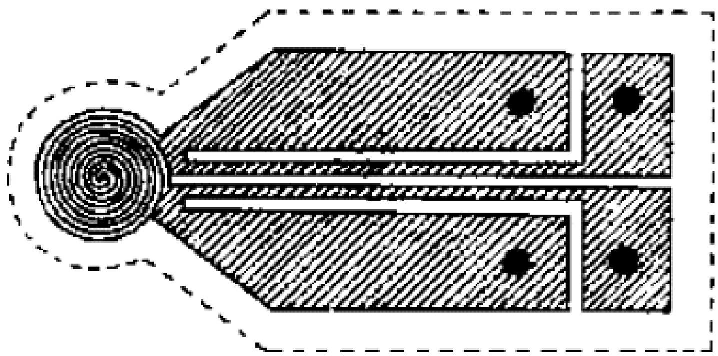

Fig. 1. Schematic diagram of TPS sensor.

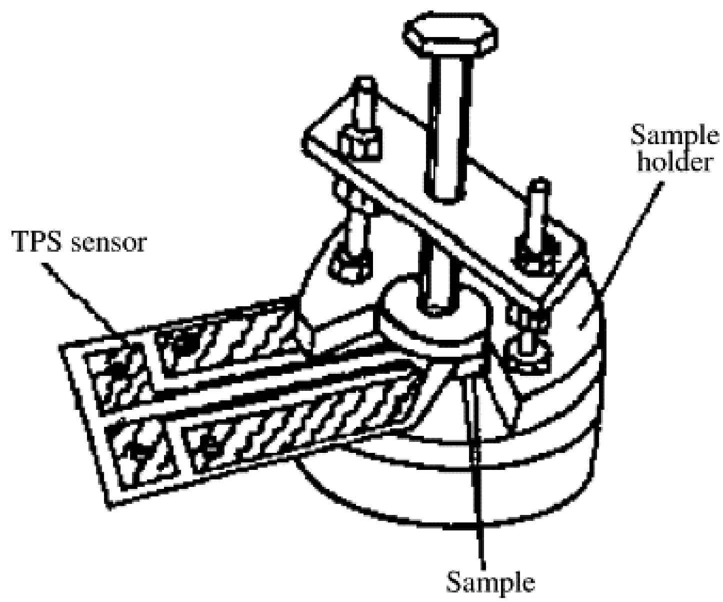

Fig. 2. Sample holder diagram with TPS sensor.

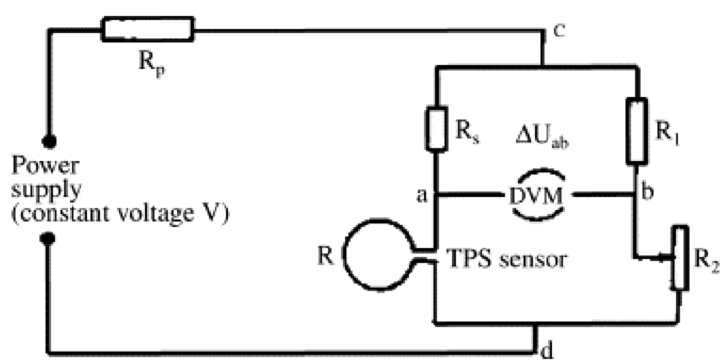

Fig. 3. Schematic diagram of electrical circuit used for simultaneous measurement of effective thermal conductivity and effective thermal diffusive

3. Results and discussion

Simultaneous measurements of the effective thermal conductivity (λ_e) and effective thermal diffusivity (**χ_e**) of the pellets of Se_{81} Te_{15} Sb_4 chalcogenide glass, compacted under the load of 5 tons, were carried out in the temperature range from 25 ^oC - 85 ^{o} C using the transient planar source (TPS) technique. In order to show the variation of the effective thermal conductivity and effective thermal diffusivity with temperature (heating and cooling) the results have been plotted in Fig. 4 - 5. One observes from the Figs. 4 - 5 that during the heating process the effective thermal conductivity and effective thermal diffusivity vary with temperature and reach a maximum at 65 ^oC. This maximum for both quantities (λ_e and χ_e) is obtained in the vicinity of glass transition temperature (T_g). For cooling process the effective thermal conductivity and effective thermal diffusivity remain constant with temperatures. The structure of Se-Te system proposed by melt quenching is regarded as a mixture of selenium 8-member rings, Se_6Te_2 chains and Se-Te polymeric chains. A strong Se_6Te_2 covalent bond [17] exists between atoms in the ring, where, as in between the chains, only the van der -Waals forces are dominants. An addition of Sb in this case is at the cost of Se. The number of Se_8 rings decreases while the number of Se-Te polymeric and Se-Te mixed rings increases i.e. interchange bonds are heavily cross linked in the glassy region [13]. T_g decreases with the increase of the ring concentration and increases with the decrease of the ring concentration. Therefore, the glass transition temperature (T_g) of $S_{81}Te_{15}Sb_4$ chalcogenide glass increases and a higher configuration entropy than in Se-Te glass is obtained.

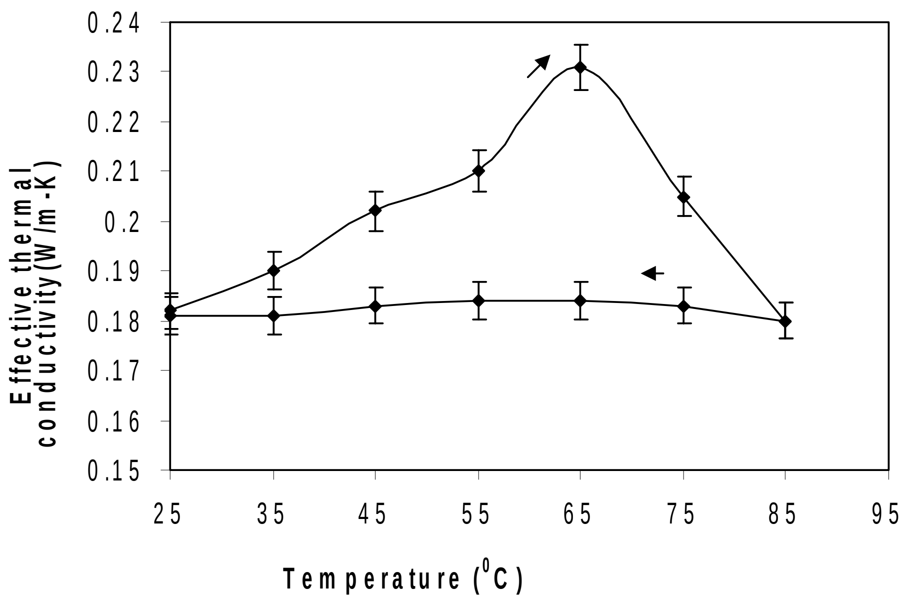

Fig.4 Effective thermal conductivity with different temperature of $Se_{81}Te_{15}Sb_4$ Chalcogenide glass.

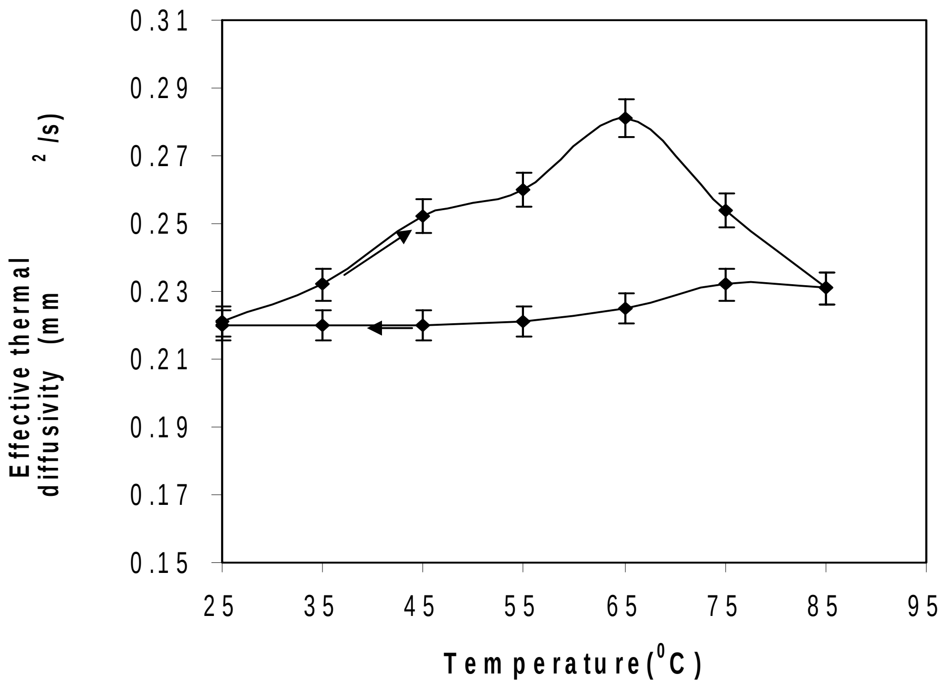

Fig.5 Effective thermal diffusivity with different temperature of $Se_{81}Te_{15}Sb_4$ chalcogenide glass.

At normal heating rates amorphous materials generally crystallize just above the glass transition temperature, the glass transition temperature can be taken as the lower limit for the crystallization. The crystallization below the glass transition is extremely slow due to high activation energy for atom movement. The glass transition temperature is therefore a good parameter of first-order estimation of the archival life stability of phase change materials [18].

The effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) measurement shown in Figs.[4,5], for both heating and cooling process. Both quantities can be explained on the basis of density of state model in amorphous solids proposed by Mott and Davis [19]. According to this model, the localized states near the mobility edges depends on the degree of the disorder and defects presents in amorphous network. Unsaturated bonds coexist with with some saturated bonds [20]. These unsaturated bonds are responsible for the formation of some defecs in the materials, which produces localized states in amorphous solids.

During the heating processes the amount of heat absorbed by the glassy system in transition region in proportion to $\Delta Q = T\Delta S$ (where ΔS is the entropy difference between two metastable states in certain temperature region). In the initial period of heating a few Van der-Waals bonds are broken as in λ_e and χ_e graphic profile. Further, the increase in the temperature of the breaking of the interchange unsaturated bonds takes place. The breaking of interchange unsaturated bonds are maximum at the glass transition temperature (T_g = 65 ^oC), which is the reason we found a maximum effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) in $S_{81}Te_{15}Sb_4$ chalcogenide glassy system. Thus, the glassy system has been structurally relaxed in the vicinity of the glass transition temperature (at 65 ^oC), due to the availability of the large number of degrees of freedom in the glassy region, and the absorbed heat energy will be maximum. Furthermore, the increase of temperature beyond the vicinity of glass transition temperature (T_g), reduces the effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) due to non-availability of large number of degrees of freedom in the glassy region, which could be absorbed less amount of heat energy.

On other hand, during the cooling process no such type of behaviour is observed in the effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e). In the entire cooling process the value of the effective thermal conductivity (λ_e) and the effective thermal diffusivity (χ_e) have been found constant (i.e. no structural changes were observed). Therefore, the effective thermal conductivity (λ_e) and the effective thermal diffusivity (χ_e) do not change during the cooling process.Such type of materials shows hysteresis during one thermal cycle and the hysteresis is maximum at the vicinity of glass transition temperature due to structural relaxation.

4. Conclusions

It can be concluded from the above study on $Se_{81}Te_{15}Sb_4$ chalcogenide glass, that in heating process λ_e and χ_e are varied with temperature due to structural changes in the material. In the cooling process λ_e and χ_e are constant due to the fact that the structure of the material does not change.

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