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Thermal Conductivity, Thermal Diffusivity and Specific Heat of $Se_{98}In_{2-x}Sn_x$ ($x = 0, 0.5, 1, 1.5$) Semiconducting Glasses

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ABSTRACT

Measurements of thermal conductivity (λ) and thermal diffusivity (χ) of $Se_{98}In_{2-x}Sn_x$ ($x = 0, 0.5, 1, 1.5$) semiconducting glasses have been presented in this paper. The measured values of both λ and χ have been used to determine the specific heat per unit volume (ρC_p) of these glasses and in the composition range of investigation. Both λ and χ are found to increase systematically with the addition of Sn. This compositional dependence behavior of λ and χ is attributed to the replacements of the original structural units by Se-Sn units. These new structural units increase the cohesive energy of the system and account for the observed increase in λ and χ . The type of bond, iono-covalent, which Sn makes with Se as it is incorporated in Se-In-Sn glass, is in support of our results.

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الموصلية الحرارية. الانتشارية الحرارية والحرارة النوعية لأشباه

الموصلات الزجاجية $Se_{98}In_{2-x}Sn_x$ ($x=0, 0.5, 1, 1.5$)

ملخص

تعرض هذه الورقة قياس الموصلية الحرارية والانتشارية الحرارية لأشباه الموصلات الزجاجية $Se_{98}In_{2-x}Sn_x$ ($x=0, 0.5, 1, 1.5$) استخدمت قيم الموصلية الحرارية الانتشارية الحرارية التي تم قياسها للعينات سابقة الذكر في إيجاد الحرارة النوعية لكل وحدة حجم. تظهر النتائج أن زيادة كمية القصدير في العينة تؤدي إلى حدوث زيادة منتظمة في الموصلية الحرارية والانتشارية الحرارية. ويعزى السبب في ذلك إلى استبدال بعض وحدات البناء الأساسية بوحدات بناء جديدة ($Se - Sn$) والتي تعمل على زيادة طاقة تماسك العينة. حيث تبين أن نوع الرابطة ($Se-Sn$) تساهمية - أيونية وهو ما يؤيد النتائج التي توصلنا إليها.

1. Introduction

Semiconducting chalcogenide glasses are of particular interest due to their wide range of applications as solid state devices both in scientific and technological fields. Selenium based glasses exhibit a unique property of reversible transformation. This property makes these materials very useful in optical memory, X-ray imaging and photonics [1,2]. Se-In glass has got several advantages over pure and amorphous Se [3] and several attempts have already been made to utilize it in solar cells [4,5]. From a technological point of view, these glasses should be thermally stable with time and temperature during use. However, thermal instability leading to crystallization is found to be one of the drawbacks of these alloys. Researches [6,7] have been made in the transformation domain of chalcogenide glasses in attempts to improve thermal stability of binary glasses through the addition of a third element. The effect of the additives on the properties of binary glasses is, therefore, of great importance.

Although, many workers [6-12] have investigated the crystallization kinetics and thermal stability of binary and ternary chalcogenide glasses, using differential scanning calorimeter, but simultaneous measurements of thermal conductivity λ and thermal diffusivity χ of chalcogenide glasses have rarely [13,14] been carried out. However, the availability of a transient plane source (TPS) technique, which was developed by Gustafsson [15] as an improvement over the transient hot strip (THS) method, allows for an accurate experimental investigation of thermal conductivity and thermal diffusivity of materials. In the present work TPS technique was used to study the compositional dependence of λ , χ , and specific heat per unit volume ρC_p of $Se_{98}In_{2-x}Sn_x$ ($x=0, 0.5, 1, 1.5$) glasses.

2. Transient Plane Source Theory

The TPS method consists of an electrically conducting pattern (figure 1) in the form of a bifilar spiral, which also serves as a sensor of the temperature increase in the sample. Assuming the conducting pattern to be in the y-z plane of a coordinate system, placed in an infinite solid material, the rise in temperature at a point y-z at time, (t), due to an output power through the spiral per unit area Q is given by [16]

$$\Delta T(y, z, \tau) = \frac{I}{4\pi^{3/2}a\lambda} \int_0^\tau \frac{d\sigma}{\sigma^2} \int_A dy' dz' Q(y', z', t - \frac{\sigma^2 a^2}{\chi}) \exp\left[\frac{-(y-y')^2 - (z-z')^2}{4\sigma^2 a^2}\right] \quad (1)$$

Where $\chi(t-t') - \sigma^2 a^2$, $\theta = a^2/\chi$, and $\tau = [t/\theta]^{1/2}$, a is the radius of the hot disc (source and the sensor) which gives a measurement of the overall size of the resistive pattern, τ is known as the characteristic time, σ is a constant parameter, λ is the thermal conductivity in units of W/mK, and χ is the thermal diffusivity of the material in units of m^2/s . The temperature increase $\Delta T(y, z, \tau)$ because of the flow of current through the sensor gives rise to a change in the electrical resistance $\Delta R(t)$ which is given as

$$\Delta R(t) = \alpha R_0 \overline{\Delta T(\tau)}, \quad (2)$$

where R_0 is the resistance of the TPS element before the transient recording has been initiated, α is the temperature coefficient of the resistance (TCR), and $\overline{\Delta T(\tau)}$ is the properly determined mean value of the time-dependent temperature increase of the TPS element. $\overline{\Delta T(\tau)}$ is calculated by averaging the increase in temperature of TPS element over the sampling time, because the concentric ring sources in TPS element have different radii and are placed at different temperatures during transient recording. During the transient event, $\overline{\Delta T(\tau)}$ can be considered to be a function of time only. In general, it depends on many parameter, such as: the output power in TPS element, the design parameters [15] of the resistive pattern, and the thermal conductivity and thermal diffusivity of surroundings.

It is, however, possible to write down an exact solution [15] for the hot disc if it is assumed that the disc contains a number, m , of concentric rings as sources. From the ring source solution [16] one immediately gets:

$$\Delta T(\tau) = \frac{P_0}{\pi^{3/2}a\lambda} \overline{D_s(\tau)}, \quad (3)$$

where

$$D_s(\tau) = (m(m+1))^{-2} \int_0^\tau \frac{d\sigma}{\sigma^2} \left(\sum_{l=1}^m l \left(\sum_{k=1}^m k \exp\left(-\frac{(l^2+k^2)}{4\sigma^2 m^2}\right) L_0\left(\frac{lk}{2\sigma^2 m^2}\right) \right) \right) \quad (4)$$

In equation (4) P_o is the total output power, L_0 is the modified Bessel function and l, k are the dimensions of the resistive pattern. To record the potential difference variations, which are normally of the order of a few millivolts during the transient recording, a simple bridge arrangement, as shown in figure 2, was used. If it is assumed that the resistance increase will cause a potential difference $\Delta U(t)$, measured by the voltmeter in the bridge, the analysis of the bridge indicates that

$$\Delta E(t) = \frac{R_s}{R_s + R_o} I_o \Delta R(t) = \frac{R_s}{R_s + R_o} \frac{I_o \alpha R_o P_o}{\pi^{3/2} a \lambda} D_s(\tau) \quad (5)$$

$$\Delta E(t) = \Delta U(t) (1 - C \Delta U(t))^{-1} \quad (6)$$

where ΔE is the potential during which the bridge is working slightly off balance, and C is given by:

$$C = \frac{1}{R_s I_o \left(1 + \frac{\gamma R_p}{\gamma(R_s + R_o) + R_p} \right)} \quad (7)$$

The definition of various resistance's is found in figure 2. R_p is the lead resistance, R_s is a standard resistance with current rating that is much higher than I_o , which is the initial heating current through the arm of the bridge containing the TPS element, and γ is the ratio of the resistance's in two ratio arms of the bridge circuit, which is taken to be 100 in the present case.

3. Experimental

High purity (99.999%) of Selenium, Indium and Tin in appropriate atomic percent proportions was weighed in a quartz glass ampoule (length 7cm and internal diameter 10mm). The contents of the ampoule were sealed in a vacuum of 10^{-6} torr and heated in a furnace where temperature was raised at a rate of 3-4K per minute up to 1170K and kept around that temperature for 9h. During heating, the ampoules were frequently rocked to ensure homogeneity of the samples. The molten samples were then rapidly quenched in ice cooled water. For TPS measurements, the samples were made in the form of pellets of 12mm diameter and 1mm thickness. The surface of these pellets were so smooth to ensure perfect thermal contact between the samples and the heating element, as the TPS sensor is sandwiched between two identical pellets, of each composition, in the sample holder (figure 3). The change in voltage was recorded with a digital voltmeter, which was online to the personal computer. The power output to the sample was adjusted according to the nature of the sample material and was, in most cases, in the range of 6×10^{-6} - 16×10^{-6} W m⁻².

The measurements reported in the present paper were performed with a TPS element. It is made of a 10 μ m thick nickel foil (having a resistance of about 3.26 Ω and a TCR around 4.6x 10⁻³K⁻¹) with an insulating layer made of 50- μ m thick kapton, on each side of the metal pattern. Evaluation of these measurements was carried out in a way that was outlined by Gustafsson [15]. In experiments with insulating layers of such a thickness, it is necessary to ignore the voltage recorded during the first few seconds because of the influence of the insulating layers. However, owing to 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 seconds of recorded potential difference values and still obtain very good result. Furthermore, it should be noted that the temperature difference across the insulating layer could, after a short initial transient, be considered constant.

4. Results and Discussion

Simultaneous measurements of thermal conductivity and thermal diffusivity of pellets of $Se_{98}In_{2-x}Sn_x$ ($x = 0, 0.5, 1$ and 1.5) glasses, compacted under a load of 5 tons, were carried out at room temperature using TPS technique. For the sake of accuracy three measurements were conducted for each sample under identical conditions and the experimental data points were taken as the average of the three measurements. The measured values of thermal conductivity and thermal diffusivity were given in table 1. The obtained values were used to calculate the specific heat per unit volume of the glasses under investigation and are listed in the same table. In order to show the variation of thermal conductivity λ , thermal diffusivity χ and specific heat per unit volume ρ_{cp} with the composition of Sn, the results were plotted in figures 3-6, respectively. From figures 4 and 5 it can be observed that both thermal conductivity and thermal diffusivity slightly increased with the increase of tin atoms in Se-In-Sn glass and could be explained by considering the structural changes due to the addition of tin atoms. Sn is added at the expense of In and since Sn has a coordination number of 4 so it has to satisfy its coordination requirements by making bonds with Se. This leads to the formation $SnSe_4$ tetrahedral units dissolved in a matrix composed of Se chains. The replacement of some of the original Se-Se and Se-In structural units by Se-Sn units which have higher bond energy 95.9kcal/mol results in an increase of the cohesive energy of the system and accounts for the observed increase of thermal conductivity and thermal diffusivity. Furthermore, according to Tanaka [17] in the glassy compounds containing heavy elements, the physical properties of such glasses are influenced substantially by metallic characters. Indeed X-ray k-absorption edge studies as carried out by Kumar et al.[18] indicated that the type of bond existing in Se rich glasses containing heavy elements, like Sb and Sn, is not covalent but metallic or ionic-covalent..

Specific heat per unit volume ρ_{cp} values as obtained from the experimentally measured values of thermal conductivity and thermal diffusivity, are listed in table 1, for different compositions of Sn. Figure 6 shows the variation of specific heat per unit volume with Sn contents in Se-In-Sn glass. From the figure it is seen that the variation in specific heat is very small and can be treated as constant for all practical purposes. The so obtained values of specific heat per unit volume as derived from TPS technique are in good agreement with the Dulong-Pettits law at room temperature.

The slightly lower values of specific heat at higher composition of Sn are due to the non-availability of a large number of degrees of freedom in the alloy, which could absorb heat energy. The degrees of freedom available for absorbing heat energy will be less and lesser as Sn is added, because of the overall increase in thermal stability of the system.

5. Conclusion

The addition of heavy elements such as Sn to Se-In semiconducting glasses increases their cohesive energy and accounts for the observed increase in their thermal conductivity and thermal diffusivity. This is accompanied by a decrease in the specific heat of the samples due to reduction in the number of degrees of freedoms, which are responsible for the absorption of heat energy.

Acknowledgements

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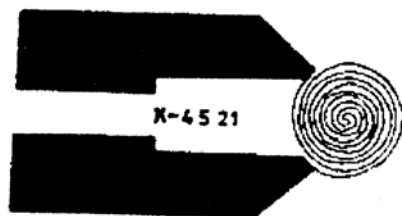


Figure 1. Schematic diagram of TPS sensor.

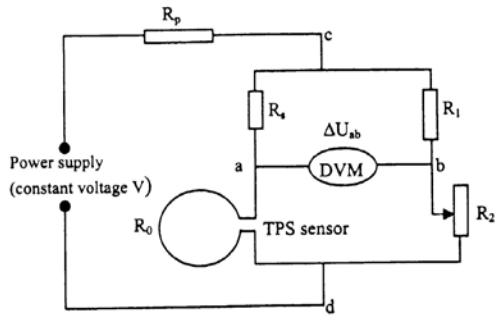


Figure 2. Schematic diagram of the electrical circuit used for simultaneous measurement of thermal conductivity and thermal diffusivity.

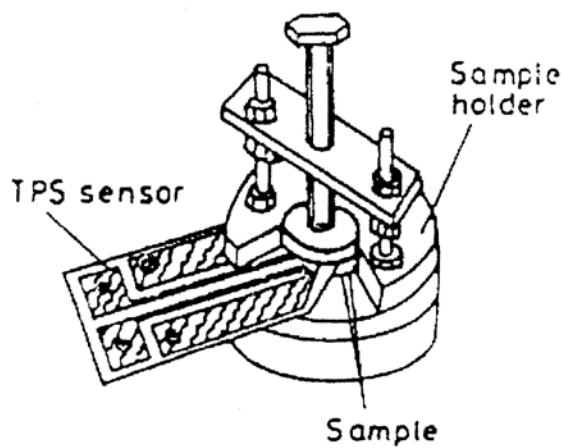


Figure 3. Sample holder diagram with TPS sensor

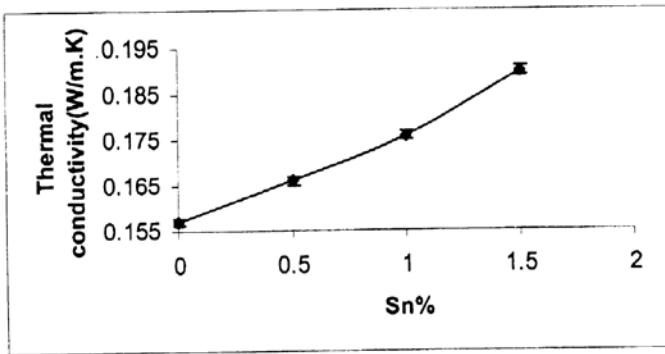


Figure 4. Thermal conductivity against Sn contents

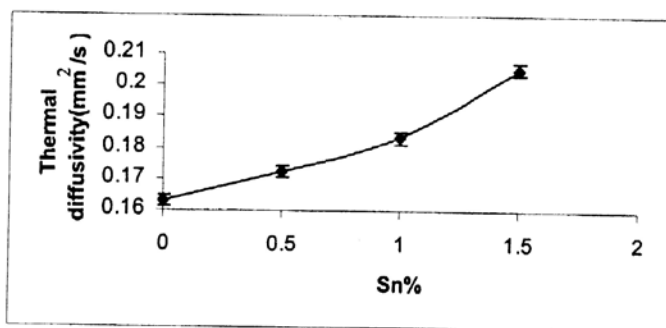


Figure 5. Thermal diffusivity against Sn contents

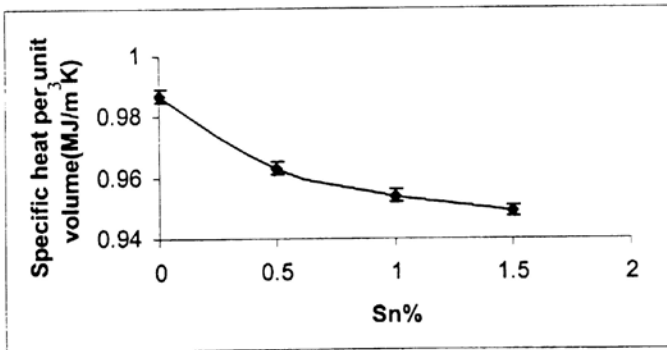


Figure 6. Specific heat per unit volume against Sn contents

Table 1

Thermal conductivity (λ), Thermal diffusivity (χ) and specific heat per unit volume (ρ_{cp}) of the $\text{Se}_{98}\text{In}_{2-x}\text{Sn}_x$ ($x = 0, 0.5, 1$ and 1.5) chalcogenide glasses

Composition	Thermal conductivity λ (W/ m-K)	Thermal diffusivity χ ($\text{mm}^2 \text{s}^{-1}$)	Specific heat per Unit volume ρ_{cp} ($\text{MJ}/\text{m}^3 \text{K}$)
$\text{Se}_{98}\text{In}_2$			
Exp.I	0.158	0.163	0.986
Exp.II	0.155	0.165	0.988
Exp.III	0.157	0.162	0.988
Av.	$0.157 \pm 9.12 \times 10^{-4}$	$0.163 \pm 9.12 \times 10^{-4}$	$0.987 \pm 7.07 \times 10^{-4}$
$\text{Se}_{98}\text{In}_{1.5}\text{Sn}_{0.5}$			
Exp.I	0.166	0.170	0.963
Exp.II	0.168	0.172	0.961
Exp.III	0.163	0.174	0.964
Av.	$0.166 \pm 14.7 \times 10^{-4}$	$0.172 \pm 11.5 \times 10^{-4}$	$0.963 \pm 9.12 \times 10^{-4}$
$\text{Se}_{98}\text{In}_1\text{Sn}_1$			
Exp.I	0.176	0.183	0.954
Exp.II	0.174	0.181	0.954
Exp.III	0.179	0.185	0.955
Av.	$0.176 \pm 14.7 \times 10^{-4}$	$0.183 \pm 11.5 \times 10^{-4}$	$0.954 \pm 4.08 \times 10^{-4}$
$\text{Se}_{98}\text{In}_{0.5}\text{Sn}_{1.5}$			
Exp.I	0.190	0.204	0.950
Exp.II	0.192	0.205	0.948
Exp.III	0.189	0.206	0.950
Av.	$0.190 \pm 9.12 \times 10^{-4}$	$0.205 \pm 5.77 \times 10^{-4}$	$0.949 \pm 7.07 \times 10^{-4}$

Answer to the comments of Referee (2)

Comment No. 3

Answer: The present paper is written in accordance to a previous research paper published by the author, Reference [13] in the list of references. A copy of the said paper published by the author is also enclosed. I would like to comment that the paper mentioned by the referee, Ref (11), is published by Dr.N.S.Saxena, who was my supervisor for the Ph.D, where we developed together the technique used, besides to that the paper in Ref (11) was received by the journal in August 7, 2001, while paper in Ref (13) was received by Bull .Mater .Sci in July 2001.

The spelling mistakes are corrected throughout the text.

Answer to Quires:

1-Experimental Errors have been calculated and are listed in Table (1) and also mentioned as error bars on the figures from 4-6.

2-Constant variable **changed to** constant parameter.

3-Definition of ΔE has been introduced in the text. Besides to that the thermal conductivity is included in equation (4) and is related to the thermal diffusivity through equation (1).

4- Θ is the characteristic time not τ and this has been modified in the text.

5-It is not always possible to add Sn up-to 10% to Se-In glasses. In fact the addition of heavy elements to Se based glasses is controlled by the phase diagram of the resulting ternary glass, otherwise crystallinity is formed in the sample and hence it is not pure semi-conductor.

6-The Glassy nature of the samples under investigation has been carried out by the author using DSC technique, has also been send for publication in a separate research paper.

