Thermal diffusivity measurements on In-Se-Tl bulk glasses by Photo-thermal deflection technique: Composition dependence and topological thresholds

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Abstract

The thermal diffusivity (α) of $In_{10}Se_{90-x}Tl_x$ bulk glasses ($7 \leq x \leq 15$) has been measured using photo thermal deflection (PTD) technique. It is found that the thermal diffusivity is comparatively high for $In_{10}Se_{90-x}Tl_x$ glasses, which is consistent with the threshold type of electrical switching exhibited by these samples. Further, the thermal diffusivity of $In_{10}Se_{90-x}Tl_x$ glasses is found to increase with the incorporation of the thallium initially (up to $x \leq 13$), which is consistent with the metallicity of the additive. This increase in α results in a maximum at the composition x=13; beyond x=13, a decrease is seen in α. This behavior seems to follow the change in network connectivity and rigidity. Also, the maximum observed in the composition dependence of thermal diffusivity at the average coordination <r>=2.46 (x=13) is attributed to the rigidity percolation threshold.

Keywords: Chalcogenides; Thallium addition; Thermal diffusivity

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1. Introduction

In most chalcogenide glass systems, many of the physical properties exhibit specific features like extremum, kink, change of slope, etc., at two network topological thresholds known as rigidity percolation threshold and chemical threshold [1-5]. Correlation of the features observed at specific compositions help us in identifying these two thresholds and also to understand the nature of the amorphous state as well as glassy state. Semiconducting chalcogenide glasses are finding extensive applications as electronic and optoelectronic device materials [6]. Specifically, the threshold and memory switching behavior and the infrared transmission properties of these glasses are used in memory devices and fiber optics

[7, 8]. Because of this there has been a great deal of interest in understanding the composition dependent variations of physical properties in these glasses. The determination of thermal parameters is an important method for characterization and analysis of chalcogenide glasses for various applications. Photo thermal deflection technique or the mirage technique being non-destructive and non-contact in nature is one such powerful and highly sensitive technique for measuring the thermal diffusivity of solid samples [9-13]. Thermal diffusivity α, is defined as $\alpha=k/\rho C$, where k is the thermal conductivity, ρ is the mass density and C is the specific heat capacity of the material. Physically, the inverse of α is a measure of the time required to establish thermal equilibrium in a given material, and it is unique for each material. The phenomenon of electrical switching in glassy chalcogenides has gained a lot of interest in modern times due to various technological applications. Usually, chalcogenide glasses which have high α values exhibit threshold type electrical switching and those with low α show memory behavior [14]. Thus, the α measurements have become important for characterizing switching glasses, for device modeling and design. Furthermore, the thermal diffusivity is fully dependent upon the effects of compositional and micro structural variables as well as processing conditions of the glassy material [15]. The present work deals with the thermal diffusivity measurements on $In_{10}Se_{90-x}Tl_x$ glasses $(7 \leq x \leq 15)$, using Photo-thermal deflection technique [6,16].

2. Experimental details

2.1 Sample preparation

Bulk $In_{10}Se_{90-x}Tl_x$ $(7 \leq x \leq 15)$ glasses have been prepared by vacuum sealed melt quenching method. High purity (99.99%) In, Se and Tl in appropriate atomic percent proportions are weighed using an electronic balance and are sealed in quartz ampoules (length ~ 5cm and inner diameter ~8 mm) under the vacuum of 10^{-5} Torr in order to avoid the reaction of glasses with oxygen at higher temperature. The sealed quartz ampoule containing sample is loaded in a horizontal rotary furnace and heated up to 850ºC at the rate of 100-120^{0}C/ hr and rotated at 10 rpm continuously for about 36 hrs to ensure a high degree of homogeneity of the melt. Quenching has been done subsequently in ice water + NaoH mixture. The ingots of the samples are taken out by breaking the quartz ampoules. The amorphous nature of the quenched sample is confirmed by the absence of sharp peak in the X-ray diffraction pattern.

2.2 Photo-thermal deflection spectroscopy technique

Photo-thermal deflection measurements have been undertaken using a custom built setup, in which intensity modulated Ar-ion laser (10mW @ 514nm) has been used as the pump beam and a He-Ne laser (5mW @ 632nm) as the probe beam. A flat sample piece of ~ 0.40 mm thickness is kept immersed at the bottom of a quartz cuvette. Carbon tetrachloride (CCl_4) is used as the coupling fluid because of its low values of thermal conductivity ($k=0.09 Wm^{-1}K^{-1}$), specific heat capacity ($C_p=0.85 Jg^{-1}K^{-1}$) and thermal diffusivity ($\alpha = 7.31 \times 10^{-4}$ cm^2/sec). It absorbs mainly below 250nm and has a very high rate of change of refractive index with temperature ($(dn/dT) = 6.12 \times 10^{-4} K^{-1}$) compared to many other liquids [17, 18]. The sample is placed horizontally at the bottom of a quartz cuvette. The pump beam is incident normal to the surface of the sample and a mechanical chopper is used to intensity modulate the pump laser beam. The probe laser beam skimming the surface of the sample is monitored with a position sensitive detector. The details of the PTD setup used in the present study and the calibration methods employed are as reported by Pulok et. al., [19].

The exposure to an intensity modulated light causes the excitation and the subsequent non-radiative recombination in the sample that are periodic and leads to the generation of a thermal waves in the sample [20], which are propagated to the surrounding liquid medium (CCl_4), setting up a temperature gradient in it. This temperature gradient causes a refractive index variation in the liquid medium above the surface of the sample [21, 22]. This refractive index variation causes a deflection in a probe laser beam (5mW @ 632nm) skimming the surface of the sample, which is detected by a position-sensitive quadrant detector and a lock-in amplifier. The penetration depth of the thermal waves into the sample is inversely proportional to the chopping frequencies. Hence the measurement of thermal parameter is usually done at lower chopping frequencies [23]. In the present experiment, the amplitude of PDS signal is measured in the frequency range of 0-200Hz. The entire experimental set-up is arranged on a vibration-free table to protect from the ambient vibrations.

3. Results

The variation of the PDS signal amplitude as a function of the chopping frequency of the pump-beam is shown in fig. 1 for a representative $In_{10}Se_{83}Tl_7$ glass, which shows that the signal decreases as a function of frequency. The modulation of intensity at higher frequencies reduces the time for optical interaction and the carrier generation in the material, which in-turn reduces the phonon contribution and noise contribution from various background sources leading to suppress the signal strength, and consequently accurate measurements are not possible in the high frequency region. Fig. 2 shows the plot of the log of the PDS signal amplitude against the square root of the chopping frequencies for selected experimental samples, here curves are almost straight line. The thermal diffusivity (α) of $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses determined from the slope of the straight lines using the relation $\alpha = \pi (l / \text{slope})^2$ cm^2/s, where l is the thickness of the sample. The errors in the measured values of α are ±2-3% and the source of error may be uncertainities in the determination of sample thickness. The variation of α of $In_{10}Se_{90-x}Tl_x$ glasses ($7 \leq x \leq 15$) with composition/average coordination number is shown in fig.3. The composition dependence of electrical OFF state resistance of $In_{10}Se_{90-x}Tl_x$ glasses is shown in fig.4, which shows that at lower thallium content the resistance is higher compared with that at higher thallium content.

4. Discussions

4.1 The composition dependence of thermal diffusivity

Chalcogenide glasses exhibit interesting variations in its thermal diffusivity (α) with composition [24-26]. It is known that the metallicity of the additive atoms is a key factor which determine the composition dependence of α. Usually, when more metallic elements are added, it is found that the α value increases, due to the increase in the number of phonon frequency modes. On the other hand, the addition of non-metallic components such as halogens, leads to a decrease in α [14, 19]. The present study indicates that the thermal diffusivity of $In_{10}Se_{90-x}Tl_x$ glasses lie in the range 0.024-0.086cm^2/s, where as that of $In_{10}Se_{90}$ base glass is 0.0017 cm^2/s. The higher thermal diffusivity values of $In_{10}Se_{90-x}Tl_x$ glasses can be attributed to the higher metallicity of thallium compared to selenium atoms. In

addition to the metallicity factor, network topological effects such as rigidity percolation, chemical ordering, etc., have been found to influence the composition dependence of thermal diffusivity of chalcogenide glasses. In many glassy systems, it has been observed that α increases with the addition of higher coordinated atoms which increases the network connectivity and structural rigidity [27, 28]. A maximum in the value of α has been observed at the rigidity percolation threshold in many systems [20, 28-32], the material undergoes a transition from a floppy polymeric glass to a rigid amorphous solid [4, 33]. Further addition of Tl(x>13), favors the formation of Tl-Tl bond reducing the Se-Se and In-In bond concentration and resulting a slight decrease in α value. That is, the bond length of Se-Se, In-In and Tl-Tl, are 232pm, 325pm and 340pm, respectively. The bond length of Se-Se is smaller than Tl-Tl and In-In. The effective molecular weight of glasses decreases as the bond lengths increase and hence the density of localized states decreases [34]. This decrease in the density of localizes states increases the porosity and produces more disordered structure [18], which is responsible for the decrease in the α value.

The average coordination number <r>, is an important parameter in determining the composition dependence of various physical properties of chalcogenide glasses. Using the coordination numbers 4, 2 and 4, for In, Se and Tl atoms respectively, then the average coordination number <r> of $In_{10}Se_{90-x}Tl_x$ glasses lies in the range 2.34 to 2.5 for the composition studied. According to Phillips' Constraint Theory [33] and Percolation Model [4], the rigidity percolation at which a percolation transition takes place from a polymeric glass to a rigid network or amorphous solid is expected to occur in the InSeTl system at <r> = 2.40. It is also suggested that the rigidity percolation threshold may be shifted towards higher values of <r> in certain glassy system [35]. The maximum value of α at x=13 (<r>=2.46) of the InSeTl system can be attributed to the mechanical stiffening of rigidity and the corresponding threshold in the internal stress. The number of zero frequency modes would be minimum at <r>=2.46 (36). At this composition, the network offers minimum resistance to the propagating thermal waves and consequently thermal diffusivity has a maximum value. Beyond the rigidity threshold, additional vibrational modes characteristic of a rigid elastic network become available and scattering of thermal waves by these modes leads to a reduction in the value of α [29].

5. Conclusions

The thermal diffusivity of bulk $In_{10}Se_{90-x}Tl_x$ glasses has been measured using photo thermal deflection technique. The thermal diffusivity, α, of $In_{10}Se_{90-x}Tl_x$ glasses lie in the range 0.024-0.086cm^2/s. The comparatively higher thermal diffusivity values of $In_{10}Se_{90-x}Tl_x$ glasses are consistent with the threshold type of electrical switching exhibited by these samples. The maximum seen in thermal diffusivity at the composition x=13 indicates that the glassy network is homogeneous and stress free and the scattering of the thermal waves is minimal. Correlation of the variation in OFF state resistance with that of α is in agreement with the variation in threshold switching voltages observed earlier. These observations are consistent with the concepts of rigidity percolation in covalent networks.

References:

[1] J. C. Phillips, Phys. Rev., B **31** (1985) 8157.

[2] J. C. Phillips, M. F. Thorpe, Solid State Commun., **53** (1985) 699.

[3] S. Asokan, G. Parthasarathy, E. S. R. Gopal, Phil. Mag. B **57** (1988) 49.

[4] M. F. Thorpe, J. Non-Cryst. Solids, **57** (1983) 355.

[5] K. Tanaka, Phys. Rev. B **39** (1989) 1270.

[6] D. Adler, Sci. Arner., **236** (1977) 36.

[7] J. A. Savage, P. J. Webber, A. M. PiH, IR Phys. **20** (1980) 313.

[8] R. Zallen, The Physics of Amorphous Solids, Wiley, New York, 1983.

[9] W. B. Jackson, N. M. Arner, A. C. Baccara, D. Fournier, App. Cpt. **20** (1981) 1333.

[10] G. Suber, M. Bertolotti, C. Sibilia, A. Ferrari, F. Genel Ricciqn diello. J. Thermal Anal., **32** (1978) 1039.

[11] B. C. Li, R. Gupta, J. Appl. Phys., **89** (2001) 859.

[12] K. Tanaka, T. Gotoh, N. Yoshida, S. Nonomura, J. Appl. Phys., **91** (2002) 125.

[13] L.C. Aamodt, J.C. Murphy, J. Appl. Phys., **54** (2) (1983) 581.

[14] Srirang Manohar, S. Murugavel, S. Asokan, Solid State Commun., **135** (2005) 323.

[15] A.C. Bento, H. Vargas, M.M.F. Aguiar, L.C.M. Miranda, Phys. Chem., Glasses **28** (1987) 127.

[16] J. Z. Liu, P. C. Taylor, J. Non-Cryst. Solids, **114** (1989) 25.

[17] Winefordner J D (Edit.) Photothermal Spectroscopy method for chemical analysis, Wiley, New York, 1996.

[18] R.C. Weast 58th ed. CRC Hand book of chemistry and Physics, CRC, Boca Roton. F.L 1978.

[19] Pulok Pattanayak, N. Manikandan, M. Paulraj, S. Asokan, 2007, J. Phys. Condens. Matter, **19** (2007) 036224.

[20] J. Philip, K. N. Madhusoodanan, Phys. Rev. B **38** (1988) 4127.

[21] S. R. Elliot, Physics of Amorphous Materials, London: Longmann, 1990, p 61.

[22] N. F. Mott, Phil. Mag., **19** (1969) 835.

[23] D. Founier, C. Boccara, A. Skumanich, N. M. Amer, J. Appl. Phys., **59** (1986) 787.

[24] K. N. Madhusoodhanan, J. Philip, S. Asokan, G. Parthasarathy, E. S. R. Gopal, J. Non-Cryst. Solids **109** (1989) 255.

[25] K. Nandakumar, J. Philip, J. Non-Cryst. Solids **144** (1992) 247.

[26] T. Velinov, M. Gateshki, D. Arsova, F. Vateva, Phys. Rev. B **55** (1997) 11014.

[27] K. N. Madhusoodhanan, J. Philip, G. Parthasarathy, S. Asokan, E. S. R. Gopal, Philos. Mag. B **58** (1988) 123.

[28] K. N. Madhusoodhanan, J. Philip, S. Asokan, E. S. R. Gopal, J. Mater. Sci. Lett. **7** (1988) 1333.

[29] Sheenu Thomas, J. Philip, J. Phys. Condens. Matter, **12** (2000) 4767.

[30] P. Kumar, K. Singh, Chalcogenide Lett., **4** (2007) 127.

[31] J. C. de Lima, N. Cella, L. C. M. Miranda, C. Chying An, A. H. Franzan, N. F. Leite, Phys. Rev., B **46** (1992) 14186.

[32] N. Manikandan, M. Paulraj, S. Asokan, J. Non-Cryst. Solids, **335** (2009) 58.

[33] J. C. Philips, J. Non-Cryst. Solids, **34** (1979) 153.

[34] N. F. Mott, E. A. Davis, Electronic Processes in Non- Crystalline Materials, Clarendon, Oxford, 1971.

[35] H. fritzsche, Fundamental Physics of Amorphous Semiconductors, ed. F. Yonezawa Springer, New York, 1981, p1.

[36] P. Agarawal, S. Goal, J.S.P. Rai, A. Kumar, Status Solidi(a) **127** (1991) 363.

FIGURE CAPTIONS.

FIGURE 1. The variation of PDS signal as a function of frequency for a representative $In_{10}Se_{83}Tl_7$ glass.

FIGURE 2. The variation of the logarithm of the PDS signal as a function of square root of frequency for the five sets of $In_{10}Se_{90-x}Tl_x$ glasses. a) $In_{10}Se_{83}Tl_7$, b) $In_{10}Se_{81}Tl_9$, c) $In_{10}Se_{79}Tl_{11}$, d) $In_{10}Se_{77}Tl_{13}$ and e) $In_{10}Se_{75}Tl_{15}$. Straight lines are least square fit to the data points.

FIGURE 3. Composition dependence of thermal diffusivity of $In_{10}Se_{90-x}Tl_x$ $(7 \leq x \leq 15)$ glasses.

FIGURE 4. The variation of OFF state resistance (R) of the $In_{10}Se_{90-x}Tl_x$ $(7 \leq x \leq 15)$ glasses with Tl composition.

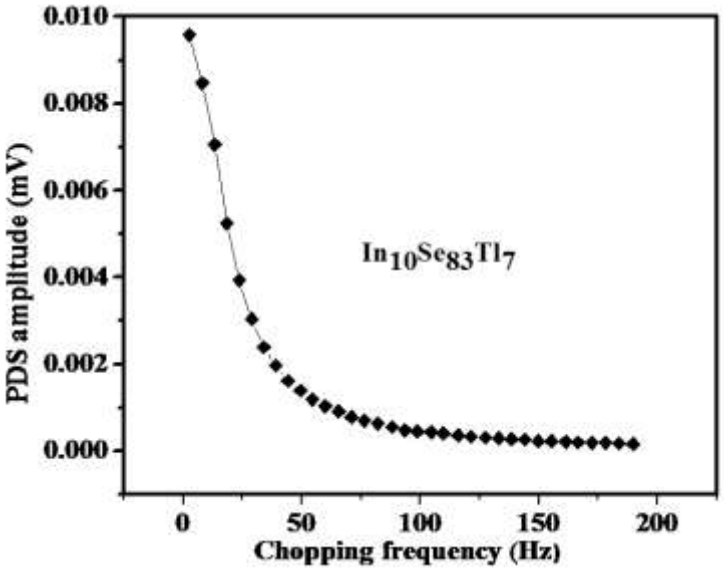


Figure 1

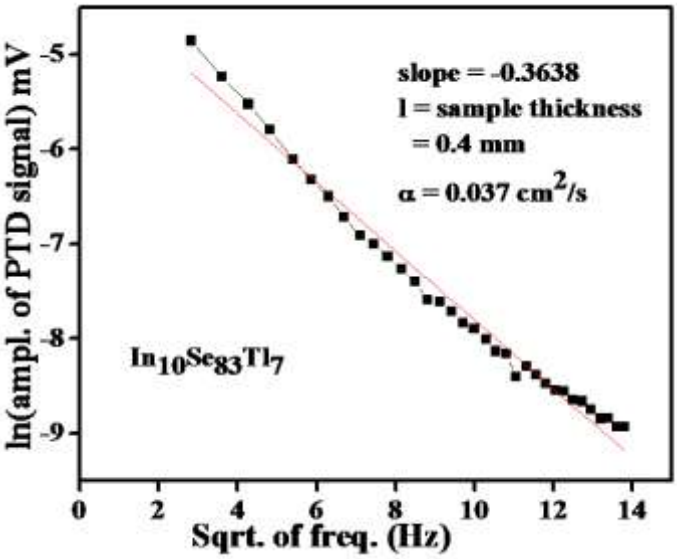
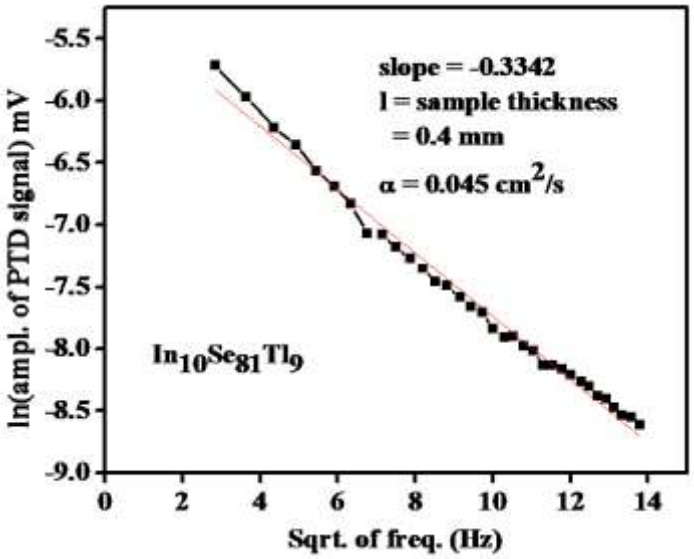


Figure 2(a)



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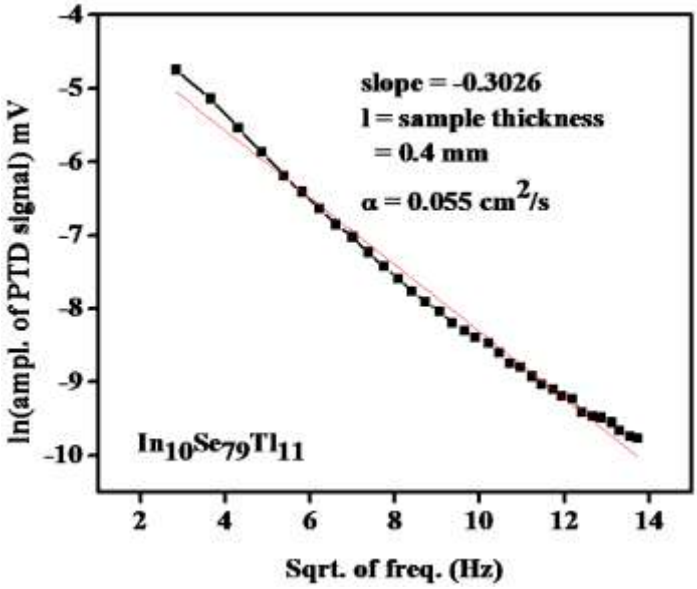

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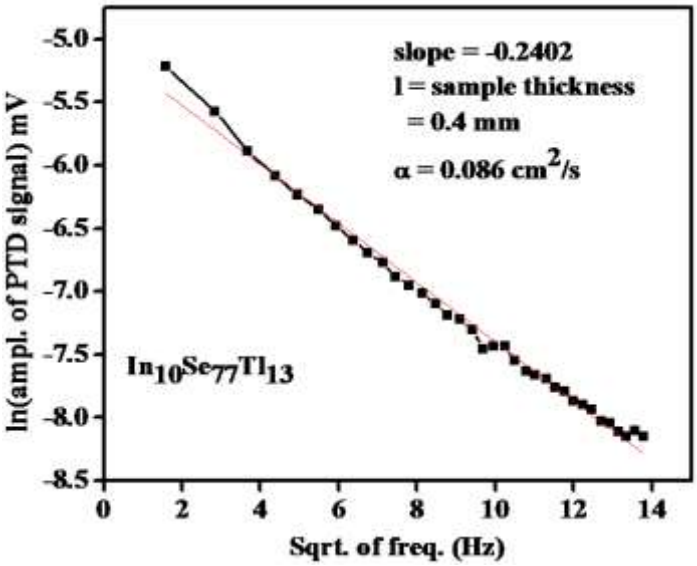

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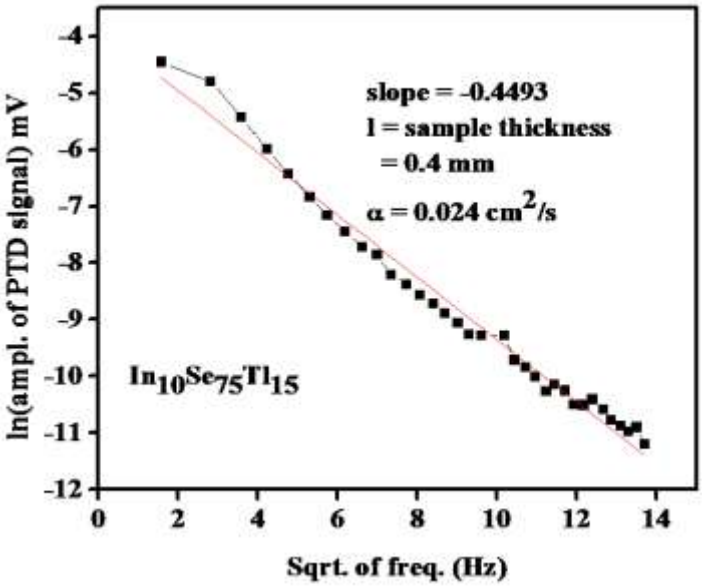

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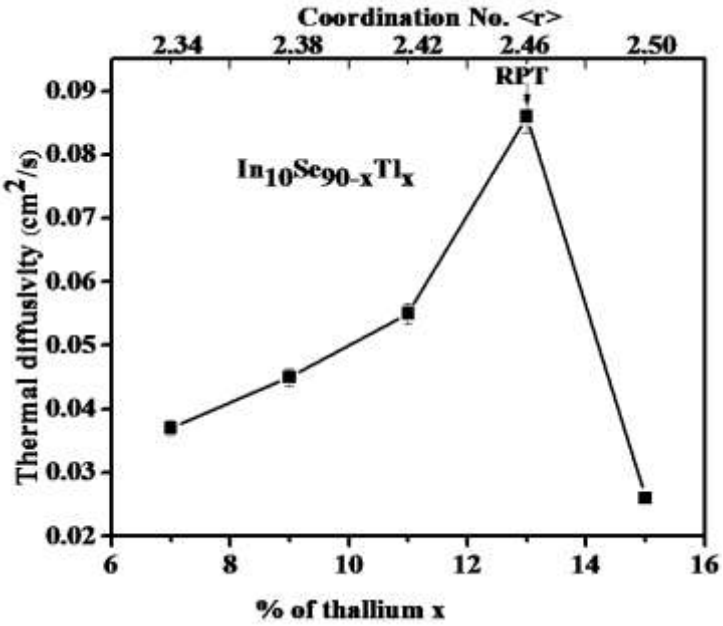

Figure 3

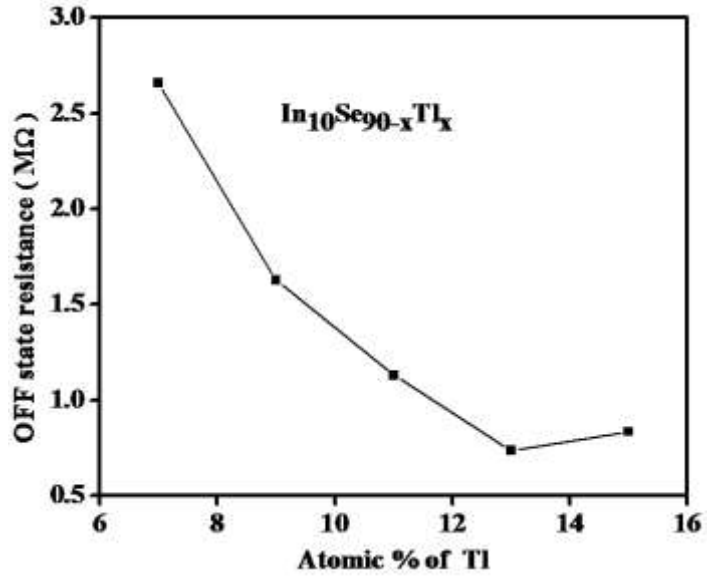

Figure 4